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Ph. D. Dissertation

EXERGY COST ASSESSMENT OF WATER RESOURCES: PHYSICAL HIDRONOMICS

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CERTIFIE:

that the Ph.D. Dissertation "Exergy cost assessment of water resources: Physical Hydronomics" has been developed under their supervision by the Ph.D. candidate Amaya Martínez Gracia.

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Exergy cost assessment of water resources: Physical Hydronomics

Amaya Martínez Gracia

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Abstract

Human development and its sustainability unconditionally rely on water. Water as a resource is essential for all daily human activities and it can be nowadays considered as a resource even more valuable than oil.

The Georgescu-Roegen's statements about the connexion between the Economy and the Thermodynamics, together with the Eco-integrator approach introduced by Naredo after analyzing the water cost definitions given in the European Water Framework Directive (WFD), and the theory of the thermoeconomic cost proposed by Valero, are the outline backgrounds of the work presented in this study.

Assuming that the physical laws are called to be the objective and universal tools to assess water costs, Physical Hydronomics (PH) has been developed as the accounting tool for the WFD application. PH is defined as the specific application of the Thermodynamics to physically characterize the degradation and correction of water bodies. The Second Law of Thermodynamics, through the exergy loss calculation, is the basic working tool in this study. The final objective of PH is to use those calculated physical costs as a guide to allocate the environmental and resource costs proposed by the WFD by 2015.

In this dissertation, the general framework, the foundations, and the accounting principles of PH are developed. Firstly, WFD was carefully studied an interpreted from a Thermodynamics perspective. The different water costs defined in the Directive were translated into exergy concepts and the study hypothesis was established. The diverse river statuses proposed by the Directive were defined in exergy terms by means of their quantity and quality characterization. Secondly, from the quantity and quality measurements in the river (they give the exergy value to water bodies), the exergy profiles of the river at different statuses (those defined by the WFD) are obtained. Then, the environmental cost of water is obtained (in energy units) as the exergy needed to cover the gap between the current state of the river and the objective state defined by

the applicable legislation to fulfil the European requirements. To do it, the thermodynamic efficiency of water treatment technologies was introduced in the analysis. In the last step, the water costs, calculated in energy units, are converted in economic units by introducing the energy price.

Moreover, Physical Hydronomics presents an important advantage in relation to other approaches: costs can be allocated according to the degradation (exergy costs) provoked by the different water users in the water bodies. The Polluter Pays Principle stated by the WFD can be therefore implemented. In addition to that, PH overcomes the proposal by defining the Degrader Pays Principle, which joins the quantitative and qualitative water degradation of water within the analysis.

To illustrate the application of the PH methodology, two case studies were developed: the Muga and the Foix watersheds, both located in the Inland Basins of Catalonia, but with quite different characteristics features. The results show that similar results to conventional Measurements Plans to fulfil the WFD objectives are obtained. However, the cost allocation can be performed within this methodology attending to an objective measurement, the water degradation due to each water use.

The last part of this dissertation is devoted to a methodology different from the PH: the emergy approach. The WFD costs are defined according to the emergy basis and the hypothetical real price of water is obtained. In this case, there is not any projection to 2015, just an evaluation of the current situation of the Foix watershed, which is the river basin selected to show the methodology.

A mis abuelas

Por vuestro tesón, vuestro amor
y vuestra generosidad infinita.

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Tras el trabajo desarrollado, los titubeos iniciales, la enorme oportunidad que se presentó al centrar mi trabajo en el mundo del agua, las miles de vueltas a cada uno de los capítulos y los intensos momentos vividos, es tiempo ahora de realizar esta pequeña reflexión. Quisiera resumir en unos pocos párrafos las aportaciones, transmisiones, sensaciones compartidas y enriquecimiento que he recibido de muchas personas a lo largo de estos años.

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Seguiré trabajando en los círculos disjuntos. Pero de cualquier forma, tal vez no esté tan mal que unos cuantos se queden así, concéntricos, revoltosamente organizados.

INDEX

CONTENTS

Chapter 1. Motivation and justification

Chapter 1

Motivation and justification

The requirements of the European Water Framework Directive (WFD) regarding the environmental cost of water can be understood as the origin of this dissertation. The necessity of an objective methodology able to connect the Physical reality of water bodies with Economics gave sense to the development of Physical Hydronomics (PH), the thermodynamics-based approach to assess water costs, developed and presented in this work.

The WFD as a water management reference is a legal text that arose from a series of different European Union Environmental Action Programs and it integrates different partial Directives aimed at water management. It added a new point regarding the protection of water environments and resources, using an integrated approach to the natural environment and socio-economic issues. Like all other European Directives, the WFD has to be transferred to the state and regional legislations and instruments are required for its application and to comply with the terms imposed by the WFD itself. In Spain, the WFD has been incorporated into the Revised Water Law (*Real Decreto Legislativo 1/2001- de 20de julio, por el que se aprueba el texto refundido de la Ley de Aguas.*) and into the Instruction of Hydrological Planning (*Orden ARM/2656/2008 de 10 de septiembre, por la que se aprueba la instrucción de planificación hidrológica.*).

The WFD has provided the authorities responsible for water policy with the necessary instruments to fulfil its imposed environmental objectives. The drawing up of the document IMPRESS (impacts and pressures report) in each area, which defines the bodies of water, pressures, impacts and possible risks of incompliance with the objectives, forms a solid base for the preparation of river basin plans. On the other hand, economic analysis required by the WFD contributes to the knowledge of the costs of water services and economic uses.

Of particular interest is the concept of *hydrographical demarcation* as the new area of planning and management. This concept has already formed part of water management history in Spain, unlike some other European states. The concept of *hydrographical basin*, linked to continental waters but without associating to transition or coastal waters, has been the base for Spanish legislation on water.

Another novelty brought by the WFD as an integrated management tool is the principle of sustainability. Along with the environmental applications, it also involves plans for public participation that increase management transparency. In economic analysis, the *Full Cost Recovery (FCR) Principle* is an essential element for favouring the economic efficiency in water use.

Finally, river basin water plans are the result of the management measures derived from the numerous tools documentated by the WFD. These plans are compulsory for each demarcation, and must be drawn up by the corresponding authorities. Additionally, river basin water plans must be accompanied by plans to follow up the agreed measures and measurement programs that control, from a scientific-technical perspective, the evolution of water quality resulting from the different management actions developed to fulfil the WFD's objectives.

This is the framework where this dissertation was developed. The necessity of comprehensive and objective methodological tools to succeed in the WFD implementation, make us to consider the exergy as a proper physical magnitude to contribute in this task.

The methodology proposed in this phD can significantly help to fulfil many of the mentioned requirements. It allows the inclusion of quantitative and qualitative features within the same analysis and uses objective parameters coming from Thermodynamics for defining and allocating the water costs.

1.1. Water: life and conflicts source

Water is the most plentiful natural resource on the planet: over two-thirds of the Earth is covered by water. It regulates the temperature of the planet and cycles essential nutrients through the land and air. Water is the basic building block for all life on Earth. The water cycle is understood as the flow of water through the atmosphere, biosphere, lithosphere, and hydrosphere. Thus, water is both the most abundant natural resource on Earth and a fundamental element of life whose preciousness requires diligent management.

All living organisms require water for their survival. Furthermore, every living organism is made primarily of water. Plants are between 80-90% water, fish are around 80%, and humans 60-70%. All chemical reactions in living cells require water and it is through water that information is passed between cells. Production of food, as well as living organisms, would not exist without water; human development and its sustainability, therefore, unconditionally rely on it.

The guidance philosophies for the management of water supplies varied during the last twentieth Century. Until 1950, water management was governed by the goal of moving water to where it was most needed, particularly for irrigation of agricultural lands. The belief that pollutants would disperse in the water, provoked that rivers and lakes were used to carry away wastes from municipal and industrial uses. At present, the focus of water management has shifted to considerations of municipal, agricultural, and industrial supplies, water quality, and the protection of aquatic ecosystems.

A quote from Mikhail Gorbachev, former leader of the Soviet Union summarizes the previous reflections. It is from the Oct/Nov. 2000 issue of Civilization Magazine (Linder et Al, 2007).

"Water, not unlike religion and ideology, has the power to move millions of people. Since the very birth of human civilization, people have moved to settle close to water. People move when there is too little of it; people move when there is too much of it. People move on it. People write and sing and dance and dream about it. People fight over it. And everybody, everywhere and every day, needs it. We need water for drinking, for cooking, for washing, for food, for industry, for energy, for transport, for rituals, for fun, for life. And it is not only we humans who need it; all life is dependent upon water for its very survival."

The situation made clear the need of creating a realistic market for water. If water price increases, water would be effectively treated as a finite and precious resource, reflecting all costs associated with its use. Then, maybe individuals would adapt, innovate, and find creative ways to trade and conserve it. When prices do not reflect scarcity, it can result in waste, inefficiency, and environmental degradation.

It is therefore clear that water is becoming a very valuable good: water as a resource is nowadays comparable to oil; it is essential to all daily human activities. Water scarcity has triggered desperation in countries that already have little access to water, let alone reliable water supplies. This desperation usually cannot be resolved by negotiations. If governments or rebels want water badly enough, they resort to force to obtain it. Water has very rarely been the main ingredient in international conflicts, but it is often factored into the problem due to its economic importance (Gleick, 2008). Then, with the risk of water shortages around the world becoming more and more repeated, water is the fuel of certain conflicts in many regions around the world. “Water Wars” are becoming inevitable in the world's future as the misuse of water resources continues among countries that share the same water source. The rapid population increase has greatly affected the amount of water readily available to many people.

In particular, conflicts can be caused by water which includes military, industrial, agricultural, domestic and political uses. They arise over who has the power to control water and therefore control the economy and population. Conflicts can also be a result of pollution affecting the quality of the water supply. This lack of water quality can cause a conflict to arise regarding the distribution of water.

The increase of urbanization has increased the demand for water. With the problem of uneven water distribution future conflicts can occur. As societies become more developed they tend to use more resources such as water (Klare, 2001).

Many regions around the world deal with shortages of water. However, some areas deal more with conflicts over inadequate water supplies and disputes over shared water supplies. In regions where countries compete for access to water, the relations between the countries are likely to be unstable. Severe water scarcity is strongest in the Middle East and Northern Africa. The need for water in these regions is essential for food production used in irrigation farming.

1.2. The necessity of resource assessment.

As one of the three traditional primary inputs (land, labour, and capital), land has been traditionally used as an inclusive term of the natural environment, covering entities such as oceans, atmosphere or solar energy. Virtually all resource allocation takes place on land. Misallocation of land inevitably entails misallocation of numerous valuable functions. At the outset, *land* in economics covered the physical universe outside of humans. Everything that owes its usefulness to human inputs was classified under *capital*, and those things that owe nothing to it were classified as *land*. The reason that it was called *land* had to do with the major concerns of predominantly agricultural societies (Hubacek, 2006).

However, the subsequent history of the concept of land in Economics shows an increasingly narrow perception of the contribution of the natural world to human well-being. By the early 20th century interest in land was restricted to only those attributes that gave immediate economic value. With the environmental crises and increased environmental awareness in the late 20th century, various aspects of land, such as support of biodiversity or sources of non-renewable resources, have found their way back into the economic discourse. The role of land and natural resources, its conceptualization, and its measurement in economic theory has therefore changed considerably over time.

For a considerable period there has been much talk about the need to integrate the natural environment into traditional Economics as a mean of modifying natural resource consumption patterns which are affecting the delicate balance of the Earth. The idea of evaluating natural resources under the term *natural capital* as well as the services of ecosystems (minerals plants and animals of the biosphere seen as producers of oxygen, filters of water, erosion inhibitors or other service providers) was considered. The concept of natural capital is an approximation of ecosystem evaluation, as opposed to the traditional vision of all non-human life as a passive natural resource and also to the idea of *ecological health*. Such capital is complementary to other forms of capital included in the production process and various authors have dealt with the relation between these forms of capital (Hubacek, 2006).

In consequence, natural capital can be defined as the aggregation of all environmental assets, and is used by society for three broadly defined purposes: environmental services, resource uptake, and waste disposal (Dunlap, 1993; England, 1998). The natural capital can be assessed from different points of view. One of them, and perhaps the most commonly known is the economic point of view.

Georgescu-Roegen (1971) designed nature as "the silent companion of man" to point that nature works as a fund, performing a diversity of functions such as the maintenance of soil fertility, climate control, or natural beauty.

The economic process needs not only environmental services but also material and energy flows of low entropy. These flows can be classified as *renewable* and *non-renewable* resources. Because most resources used by humans are, to a great extent, a result of ecosystem processes, it is assumed that aggregated natural resources will behave as renewable resources.

At the other end of the economic process, the disposal of high entropy residuals is unavoidable, both in the production process and during consumption. Nature receives what society no longer wants, and its assimilation capacity is subject to critical loads and bounded degradation rates.

Pollution, understood as the outflow of the production process, and natural resources, defined as the inflows to production, are, from an ecological point of view, disturbances that can be grouped into natural capital depletion. Natural capital is the provider and absorber of flows, not the flows themselves (Rodrigues et al., 2005). Environmental amenities are used without being consumed, but human action does interfere with ecosystems' ability to deliver them (Kraev, 2002).

In traditional economic analysis, natural capital would be classified as *Earth* and not as *capital*, since this term has been always associated with human activities. Nevertheless, it has been argued that it should be treated as capital since it can be improved or degraded by its use and it also allows its productive capacity to be evaluated. Many policy makers and economists believe that natural capital should have a role in the Economics. Some indicators such as inflation or Gross Domestic Products (GDP) could be modified in some way.

In this regard one of the greatest criticisms of the current mercantilist economic model is the approximation of natural capital resources: analyses from the conventional economic or environmentalist point of view undervalue natural capital, in the sense that it is treated as a production factor: exchangeable for labour and technology (human capital). From the ecological economists perspective human capital is complementary to natural capital as opposed to exchangeable for it, since human capital is one way or another directly derived from natural capital. It rejects classical economics vision of rising energy consumption in a given system being directly related to well being - through empirical studies on the Jevons Paradox, or theoretical refutations of orthodox neoliberal hypothesis of dematerialisation of the Economy. It concentrates on the management of biodiversity and on creativity (or natural capital and individual capital), in the terminology occasionally adopted to describe them economically. These issues will be further developed in Chapter 3.

The key underlying problem is always the accurate economic valuation of natural resources. Environmental economics uses evaluation methods which are more or less debatable and, from ecological economics, alternatives are developed for the indirect measurement of sustainability such as the ecological rucksack or the total materials requirement, ecological footprint or space requirements.

1.2.1. Difficulties to assess Environmental Costs

From the previous ideas, it is easy to conclude that *environmental costs* are quite difficult to evaluate, at least with the current analysis tools traditionally used by water management policies. It is well known that standard economics has tried to internalize certain environmental aspects that in fact were considered as “externalities” of the system, giving rise to a lot of literature about environmental valuations. Some attempts have been made to measure the value of water and ecosystem services using different approaches. For instance, the hedonic methodology generally traced to Rosen (1974), assumes a relationship between residential home or land owner utility functions and ambient water quality within their local watersheds (see for instance Steinnes (1992)). Other approach is based on indirect methods (e.g. travel cost method), which seeks to recover estimates of individuals' willingness to pay for environmental quality (such as river quality) by observing their behaviour in related markets (Loomis et al., 2000). The contingent valuation method uses surveys to ask respondents about their monetary values for non-market goods (see the study of Bonnieux (2003) for its application to water resources).

Although ambitious, these methods have provoked numerous critics, as they have serious reliability problems, since they are based on subjective opinions. Generally, economic reasoning through monetary costs cannot tackle the assessment of environmental costs in a rigorous and comprehensive way. Cost of products and services are calculated by adding the resources required to produce them. But resources are, in turn, the products of a previous process that consumed new resources, and so on. Nevertheless, moving back to Nature, it is very difficult to know the fair price of the free resources and services that are continuously taken from it. Usually the standard practice is to estimate the cost of natural resources using the information of the imperfect prices that they would be associated within the market in a given institutional framework. In this way, the chain of the objectivity of cost is broken since this is formed by price policies that are not based on Physics. In other words, converting physical effects into monetary costs based on the technical input–output coefficients is only justifiable when no alternative and more rigorous methods are available.

Fortunately it is possible to resort to other disciplines different from neoclassical Economics, for which the natural environment is not something far removed from it, but it is a part of the system. Certainly, both thermodynamics and ecology rely on the nature of the system itself as well as on its interaction with the surrounding environment.

The key issue is not to substitute traditional methods through new ones, but to open the old closed schemes and give way to other approaches, which are open, multidimensional and multidisciplinary, and able to give a better solution to current management demands.
Some notable examples have tried to quantify the embodied energy linked to ecosystem functions through physical based approaches such as Gascó and Naredo (1994), Costanza (1981), Odum (1983) or Faber et al. (2006).

The arising question is whether or not natural capital can be evaluated in a physical unit as a way of Nature to be taken into account. Some authors as Naredo and Valero (1999) have searched for the answer in Thermodynamics, particularly in the Second Law. As Naredo (Naredo and Valero, 1999) analyzes, standard economy is only concerned with what being directly useful to man, is also acquirable, valuable and produce-able. For this reason, most of the natural resources, remain outside the object of analysis of the economic system. The price-fixing mechanisms, rarely take into account the concrete physical characteristics which make them valuable. But natural capital has at least two physical features which make minerals or fresh water for example unusual: a particular composition which differentiates them from the surrounding environment, and a distribution which places them in a specific concentration. These intrinsic properties can be in fact evaluated from a thermodynamic point of view in terms of exergy (Valero, 2001).

The application of the exergy analysis in the evaluation of natural fluxes and resources on Earth (Exergoecology- Valero, 1998) could become a future rigorous tool for natural resources accounting. The consumption of natural resources implies destruction of organized systems and dispersion, which is in fact generation of entropy (or exergy destruction). This is why the exergy analysis can perfectly describe the depletion of natural capital and specifically, the degradation of water bodies.

Already in the nineteenth century, the recognized economist Cournot (1861, reedited by Vrin, 2002) stated that "*one should be very little versed in economical sciences and be unaware of the need for measurements we have, for not seeing that the 'living force' (today called exergy or thermodynamic available energy) should become the measuring standard*".

1.3. Global and local water degradation

There exists different scales were water degradation can be studied. When the attention is focused in global resources, quantity-related parameters are usually collected in world records. As the system boundaries are reducing, more detailed data are needed.

The global perspective is focussed on getting a water resources inventory of the available resources. However, the local approach tries to develop local degradation studies, including their effects on the environment and the required Measures Planning for its restoration.

In the way of becoming able to correctly asses the environmental cost of natural resources and, in particular, of water, there is an urgent need to improve our practical and theoretical understanding of land and water degradation processes. In particular, the physical, chemical and biological deterioration of soils and water bodies. The work presented here search to help bridging the gap between water as natural resource and water as an economic good.

Identifying water degradation is the starting point to look for corrective actions and behaviours to be implemented. Such degradation can be analyzed in a global or in a local perspective. It will mainly depend on the chosen boundaries and on the available data. Last legislation tendencies face the problem with a global perspective, but acting at local level, i.e., surface waters, coastal waters, transitional waters are analyzed in river basins and aquifers.

1.4. Water and energy: a very close relationship

Because of the interconnection between water and energy, it is vital to manage them together, rather than in isolation. The energy savings from water conservation and the water savings from energy efficiency are inextricably linked, and these linkages should be considered when determining the best course of action from an economic, social or environmental perspective.

A nation's water and energy resources are inextricably entwined. Energy is needed to pump, treat, transport, heat, cool, and recycle water. On the flip side, the force of falling water turns the turbines that generate hydroelectric electricity, and most thermal power plants are dependent on water for cooling (CEC, 2005). The systems of manmade storage, treatment and conveyance structures require large amounts of energy to deliver quality water.

At the first step, water is diverted, collected, or extracted from a source. Then, its transport and eventual water treatment facilities are previous to its distribution to end users. What happens during end use primarily depends on the type of use. Wastewater from urban uses is collected, treated, and discharged back to the environment, where it becomes a source for someone else.

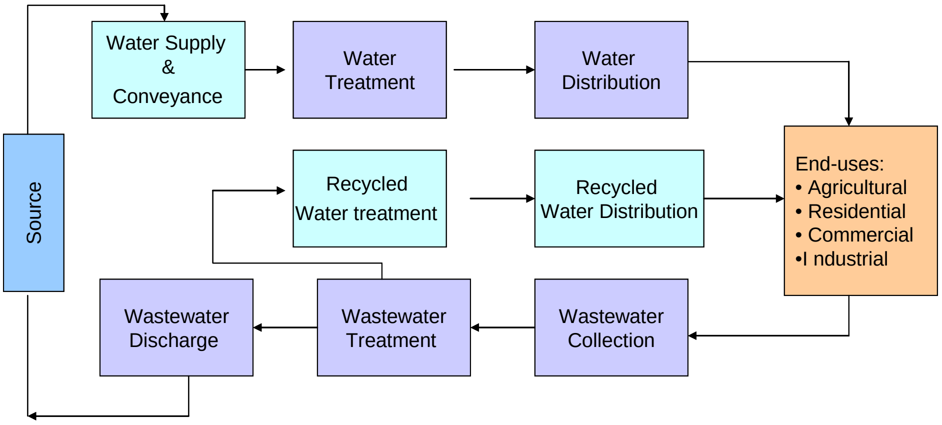


Figure 1.1. Water use cycle (Source: CEC, 2005)

The dynamic give-and-take relationship between water and energy resources is present along the whole water cycle (Figure 1.1).

Each element of the water use cycle has unique energy intensities, with a considerable variability in both the range of intensities for each segment and the components of the water use cycle.

For the water supply and conveyance, the energy intensity is determined primarily by the volume of water that is transported, the distance, and the changes in topography along its route. In water treatments, a key factor is the intended end user and its water quality requirement. Some sources of water need very little treatment, so their energy intensity is low, but some others need much more treatment (e.g., brackish groundwater or seawater desalination). Regarding water distribution, some fresh water distribution systems are gravity fed, but most require some pumping. The primary driver of increased energy for water distribution is urban growth.

Wastewater collection also demands energy. Some wastewater collection systems use gravity to bring the wastewater to a treatment plant. Nevertheless, most of them need energy to lift or transfer the wastewater. The same happens for the wastewater discharge. In the wastewater treatment, energy consumption is compulsory, though some require more than others depending on the quality of the waste stream, the level of treatment required, and the treatment technologies used.

Finally, the energy needed for the recycled water and distribution depends upon the level of wastewater treatment in existing facilities. The effluent may be recyclable without requiring additional treatment to displace potable water sources used for non-potable applications. More energy is needed if additional treatment is required.

The ranges of energy intensities for the mentioned water-related processes are presented in Table 1.1

Water-Use Cycle Segments	**Low**	**High**
Water Supply and Conveyance	0.00	3.70
Water Treatment	0.03	4.23
Water Distribution	0.18	0.32
Wastewater Collection and Treatment	0.29	1.22
Wastewater Discharge	0.00	0.11
Recycled Water Treatment and Distribution	0.11	0.32

Table 1.1. Range of energy intensity of the water use cycle. Units: kWh/m^3. (Source: adapted from CEC, 2005)

Energy efficiency in the water and wastewater industry saves money in operations and maintenance costs, reduces capital costs of new supply, improves solvency and operations capacity of water utilities, improves service coverage, reduces emissions and improves water quality, among a host of other related benefits. In order to support larger efforts to reduce energy use in water and wastewater systems, larger-scale energy and water management should be entrusted to the local level for implementation. The term 'watergy' efficiency has been coined by the Alliance to Save Energy (2007) to describe the combined water and energy efficiencies which are available to municipalities and water users.

The most widely recognized aspect of the water-energy relationship is hydropower production. Hydroelectricity supplies over 20% of the world's electricity needs. Countries like Norway, Iceland, Canada and Austria produce well over 70% of their electricity supplies through hydroelectricity (EIA, 2008). Figures on this issue will be presented in Chapters 2 and 4. Involvement of the energy utility provides the needed support for implementing energy efficiency measures and ensuring that efforts to reduce energy and water waste are sustainable as a business practice. Energy efficiency in any water utility never has a beginning or an end. To sustain its energy savings, a water utility must continue to monitor its energy use and set goals for improvement.

In the study presented in this work, the energy needed to restore the quantity and quality in the rivers is a key issue. In this sense, energy efficiency in the proposed water utilities and the minimization of energy resources consumption are crucial.

1.5. The opportunity presented by the European Water Framework Directive.

The European Council Water Framework Directive came into force on 22 December 2000, establishing a new, integrated approach to the protection, improvement and sustainable use of Europe's rivers, lakes, estuaries, coastal waters and groundwater. This legal text introduces, among numerous novelties, two significant changes related to the way the water environment must be managed across the European Community: the types of environmental objectives to be considered and a river basin management planning system

On the one hand, previous European water legislation sets objectives to protect particular uses of the water environment from the effects of pollution and to protect the water environment itself from especially dangerous chemical substances. These types of objectives are taken forward in the Directive's provisions for Protected Areas and Priority Substances respectively. The Directive also introduces new, broader ecological objectives, designed to protect and, where necessary, restore the structure and function of aquatic ecosystems themselves, and thereby safeguard the sustainable use of water resources. Future success in managing Europe's water environment will be mainly judged by the achievement of these ecological goals. Theses objective states for the waters will appear later on in this dissertation (Chapter 5) and will be named as *good ecological state* (GES) and *high state (HS).*

On the other hand, a river basin management planning system is the key mechanism for ensuring the integrated management of: groundwater, rivers, canals, lakes, reservoirs, estuaries and other brackish waters, coastal waters, and the water needs of terrestrial ecosystems that depend on groundwater, such as wetlands. The planning system is called to provide the decision-making framework within which costs and benefits can be properly taken into account when setting environmental objectives, and to set out cost-effective combinations of measures to achieve the objectives that could be designed and implemented. It will also provide new opportunities for anyone to become actively involved in shaping the management of river basin districts – neighbouring river catchments, together with their associated stretches of coastal waters.

This second aspect concerning hydrological aspects, presents a new approach in the treatment of hydrological units, as it defines them according to the Directive's objectives. In order to regulate the exploitation of water resources and to prevent the deterioration of its quality by protecting and improving aquatic environments related to it, the Directive establishes deadlines and promotes a sustainable use of the resource. For this reason, the first task of the Directive obliges Community Member States to identify and characterise water bodies as the basic hydrological units. They are the basis of the analysis of the characteristics of river basins, which become the territorial units for management. The purpose of this initial work consists in making an accurate description of the status of the surface water and groundwater, which can be revised every six years. This description requires specific information and monitoring programmes, and it is the basis for regulating the water use, which will be defined by the River Basin Water Plans.

In addition to the two mentioned features, from the point of view of hydrological description, two premises in the understanding and application of the WFD should be also pointed out: Firstly, water is the element being managed. Its availability, always taking into account the quality/quantity pairing, is related to special local features of the water cycle, on the natural side, and to current exploitation of the resource, relating to human action. Secondly, the GES of aquatic systems is the main objective of the Directive. It supports a sustainable water use because it can be understood as an indicator of the correct exploitation of water resources, respecting its natural dynamics.

Water bodies in a River Basin District are differentiated according to the mentioned categories (rivers, lakes, wetlands, coastal water, groundwater), and classified under different characteristic-based types (morphometric, environmental, climatic and geographical, etc). In strong pressurized areas, highly-modified water masses appear, but they do not need to reach the GES because it is neither economically nor socially viable, or the impact of their recovery leads to even worse environmental impact. There, the objective is the Good Ecological Potential (GEP), which accounts for their maximum possible quality.

1.5.1. Water uses and their sustainability

In spite of the promotion of the sustainable use of water, and based on the protection of water resources, the idea of sustainability is a very diverse one, due to its application in several spheres related to the Environment. The definition of a sustainable exploitation of water given by the Australian Department of the Environment and Heritage (DEH, 2004) is that use which, measured in a planning time context, involves acceptable pressure and protects the economic, social and environmental values that depend on it. This definition emphasises that sustainable use must be based on an extraction system and not on a predefined volume. A system is understood as a set of management measures defined for a river basin and for specific periods in which permitted extraction volumes must be conditioned by the pace of recharge and the pressures generated on the environment; it allows that in exceptional, clearly specified circumstances, extraction volumes should change with regard to those fixed in the established planning period.

So, achieving an acceptable level of pressure involves recognising that a level of impact is actually acceptable and must be agreed by consensus. This *consensus*, term cited in the WFD as *public participation*, will normally have to include environmental, economic and social aspects, and also give time for the environment to adapt to a new balance. That is, it involves the integrated management of the water cycle, both of human needs and of the associated ecosystems, but adapted to the overall response of the system (specifically the river basin) depending on the new information and generated needs. In the case of the Directive, the status of the water bodies will become the indicator to assess the acceptability of the pressure exercised on the environment.

Any water use gives rise to a reduction in existing resources along the time, whatever it was a river flow or an aquifer. Exploitation that involves an unacceptable reduction in flow or volume stored therefore falls outside the definition of sustainable use. For this reason, if levels below the appropriate ones are reached because of extreme seasonal or year-on-year hydrological variations, it must be defined whether this pressure is acceptable (in order to maintain supply) and whether amendments to the management plans must be adopted. In other words, *sustainable management* involves a degree of flexibility in the determination of the extraction systems, controlled by equity between generations and a balance between environmental aspects and social and economic values (UN-WWAP, 2006). Drawing up river basin plans and periodically updating them is the basis of the regulation of exploitation systems.

This definition of sustainability recognises that water resources have multiple values – all of them legitimate – from those associated with the maintenance of ecosystems to those generated by supplying human demand, as well as their social, cultural or landscape nature, among others. From them, ecological-type values deserve special consideration, as inappropriate exploitation involves the risk of irreversible impacts.

A summary of the specific contents of the WFD can be found in Annex A of this dissertation.

1.5.2. Recent water history in Spain

The economic and environmental analysis of water issues in Spain has always been an important research question. Spain is a relatively large country in the European Union (EU), with a land surface of 505 958 km^2 (islands included) and an average precipitation around 340,000 hm^3/year (684 mm), with a substantial spatial and temporal rainfall variation. The water scarcity is especially acute in the south-eastern watersheds, triggered by aquifer overexploitation.

Looking at the last few years in Spain, the management of water resources involved in the application of the *Spanish National Hydrological Plan* (SNHP) has generated intense social involvement and, derived from it, matters concerning water have been the subject of discussion and debate. In this period, the need for water management based on respect for the environment and on the sustainable use of these resources has been taking on overwhelming importance. These values currently make up the cores of water policy explicitly declared by the Spanish government.

The fact of recognising that nature is probably the most important water user provides a different view of water use. The Water Act of 1985, updated in 2001, recognises the importance of the water cycle in the dynamic of natural systems and refers to its protection. However, despite this legal definition, the establishment of a sustainable view of water management was not reflected in the Spanish National Hydrological Plan (SNHP) of 2001, which resulted in intense social and academic mobilisation leading to its repeal in 2004. This action against the Plan, which began in the area around the Ebro River, has been the subject of consideration at European level because of the intention to manage a natural resource – water – which is indispensable for human development and the preservation of the natural environment, in an objective way, involving participation.

The SNHP, intended to be the fundamental norm shaping the framework for water management and water quality in Spain, consisted of two main parts: (1) a new water transfer of 1,050 cubic hectometres per year from the basin of the river Ebro to other river basins in the north, south-east, and south of Spain; and (2) of a block of 889 public water works affecting all the Spanish river basins which is listed in Appendix 2 of the Law. Obviously, the main project was the large water transfer to the *Levante* and south-eastern regions in order to solve the critical problems of overuse, degradation and scarcity of water resources, consequence of decades of water resource mismanagement (Albiac et al, 2003).

Many organisms and institutions claimed against the article 13 of the Law, authorising the transfer Plan. As an example, the World Wide Fund for Nature (WWF) asserts that the Ebro transfer would have a negative effect on the areas supplying the water, which already have a much lower socio-economic level than the areas which would receive the water. This organism affirmed that the Spanish government's analysis hided this reality under three basic errors: not taking into account the river basin perspective; offering superficial data for the autonomous communities rather than looking more closely at a local level; and using misleading socio-economic indicators (WWF, 2004).

Aragón and *Catalonia*, two regions of the basin from which water was to be transferred, strongly opposed the Plan. While Aragón opposed it from the very beginning, *Catalonia* voted in favour of it in 2001, but later on, in 2003, joined Aragón against the Plan after the regional political party in power was defeated. They argued that the SNHP was conventional, supply-oriented and could not be justified on economic, environmental or social grounds. Furthermore, the water transfer was considered to be unnecessary if proper demand management practices were implemented in the water-importing regions. In terms of sustainability, numerous analyses indicated that the environmental and the economic principles were mostly ignored (AG, 2001).

Because funding from the European Commission was necessary for the construction of the infrastructure considered within the Plan, the Government of Aragon and several environmental groups complained formally to the European Commission on the magnitudes and distributions of the various negative impacts of the Plan (Tortajada, 2006). A Seminar was organised in 2003 by the European Community (EC) with the objective to promote dialogue between the Spanish and Aragonian Governments and the environmental groups. In the light of the discussions and the results of the different technical studies, and after considering that the Plan did not address properly economic and environmental concerns, there were several reports within the EC which did not recommend the financial support for the implementation of the SNHP. Nevertheless, before the European Commission could take a final decision, the 2004 elections in Spain resulted in the change of the ruling political party and the cancellation of the 2001 SNHP.

For the last years, two important factors are present in water policy: an important delay and the expensive cost of water for the agricultural sector. Irrigation users mean that they can not afford to pay the real cost of the provided water (Llamas, 2009).

A complete chronology of the Ebro transfer proposal can be found in Tortajada (2006), as a case study for the 2006 Human Development Report. Albiac et al. (2006) also make an interesting review of this chapter of the Spanish hydrological history.

Later on, the Law 11/2005 (*LEY 11/2005, de 22 de junio, por la que se modifica la Ley 10/2001, de 5 de julio, del Plan Hidrológico Nacional*) was enacted. This law proposed the Programme on *Actions for the Management and Use of Water* whose objective was to develop and implement appropriate water policies in full consideration of water quantity and quality issues.

The basis for what might be called reasonable water management (*new water culture*) in Spain can be seen in the texts written by Martínez (1997), Arrojo and Naredo (1997), Llamas et al. (2000), Prat and Munne, (2000), Arrojo (2004), Martínez and Jiménez (2003), Aguilera and Arrojo (2004) and Estevan and Naredo (2004), among many others, in which water is valued not only as a necessity for human use. Instead, its ecological, geodynamic, social and even aesthetic function is recognised and it is considered as a heritage that must be protected and preserved.

1.5.3. The Spanish water authorities and the WFD

The autonomous basin management organisations, called *Basin Confederations*, have existed in Spain since 1926 (first in Europe). For nearly a century, they have demonstrated their efficiency and even served as a model for the European Union in establishing the new river-basin management bodies in the Water Framework Directive, called *river basin districts*.

The creation of the basin confederations (the first being that of the Ebro) was initially a response to the principle of decentralisation. It seemed reasonable that the river basin should be the unit for water management. Over time this farsighted idea has become established as an unquestioned certainty in the governance of water resources.

The *basin confederations* (or *water agencies*, as the management bodies are called when the autonomous regions have exclusive powers over a particular river basin) have full executive autonomy to carry out their function: hydrological planning in their basin; management of resources and usage; demand management; execution of new hydraulic infrastructures; water policy; protection of waters in the public domain, etc.

The implementation of the WFD with the threefold aim of satisfying the demand for water, achieving a good ecological status of the bodies of water and taking measures against floods and droughts, has represented a boost for the Spanish basin confederations.

The management of water by water district as established by the WFD has not meant any significant change for the basin confederations because of the mentioned long experience.
The territorial based water management model organised on a pyramidal basis is the basis for achieving river basin management that cuts across administrative borders. The basin confederations combine the whole of this organisational framework related to water and thus adapt perfectly to core concepts behind the Integrated Water Resources Management (IWRM) and WFD, i.e. decentralisation and participation.

In Spain, the water authorities are entities under public law with their own legal personality, separate from the State. For administrative purposes they answer at present to the Ministry of the Environment and Rural and Marine Affairs.

Under article 21 of the Water Act, the functions of the basin organisations are as follows:

- To draw up the Water Basin Plan for their basin, including its monitoring and review.
- To manage and control the water in the public domain, including flowing surface water, the beds, banks and perimeters of the rivers and lakes, and groundwater.
- To manage and control water use in the general interest of the nation or that affecting more than one autonomous region.
- To plan, construct and exploit works undertaken using the organisation own funds, as well as those ordered by central Government.
- To comply with those functions derived from agreements with the autonomous regions, local corporations and other public or private bodies, or those with private entities.
- To perform these functions, basin organisations have been granted the following competences:
    - Granting authorisations and concessions referring to water in the public domain. Except for those relating to work and actions of general interest to the State, which correspond to the Ministry.
    - Inspection and monitoring of compliance with the conditions of authorisations and concessions relative to water in the public domain.
    - Organising forums and hydrological studies on flood risk and the control and quality of water.
    - Study, planning, construction, preservation and exploitation and improvement of water works included in their own plans, as well as those which they may be charged with.
    - Defining quality objectives and programmes for water, in accordance with hydrological planning.
    - Providing technical and advisory services.

In consequence, these already assigned attributions help significantly in the WFD implementation.

The WFD establishes the environmental quality objectives in rivers as one of the basic pillars for achieving a good ecological status by the year 2015. This represents a new challenge for the coordination of the environmental policies of autonomous regions and central government and the basin organisations. This coordination involves the power allocation.

In terms of participation in water management, another of the pillars of the European Union water policy, the basin confederations have, since their creation, included a significant degree of representation in their various bodies: the users assemblies, water withdrawal commission, exploitation boards, water council and governing board. Participation by water users in management may be considered a model as even the budget of each of the sub basins is participated in by the users themselves through the exploitation boards. The incorporation of civil society in general is progressing with active participation in drawing up the river basin plan and the creation of a committee of competent authorities. This active participation is a result of the more holistic approach to water management in the 21st century, when environmental factors are becoming increasingly important.

1.5.4. The Water Framework Directive (2000/60/EC) in Catalonia

The concept of Ecological Status, which is introduced by the regulatory text of the Water Framework Directive, appears as a key measurement item for analysis of the quality of water systems and their management, and includes consideration of their state of health (an expression of the structure and operation of ecosystems). This concept appears in Catalan legislation on water (Law 6/1999- *de 12 de julio, de Ordenación, Gestión y Tributación del Agua.*), and in the amended text of the legislation on water in Catalonia (Legislative Decree 3/2003 of 4 November).

In the case of Catalonia, the deployment of the regulations falls under the competence of the Catalan Water Agency. The calendar of the WFD in the CWA is shown in Table 1.2.

Date	**Descripcion**
December 2000	Publication and entry into force of the Water Framework Directive
December 2003	Implementation of the Directive in the Spanish legal system. Implementation of the WFD: (Article 24), Delineation of hydrographic areas and designation of the competent authorities (Article 3).
December 2004	Analysis of the characterisation of hydrographic boundary, study of the repercussions of human activities on the status of surface waters and groundwaters (analysis of pressures and impacts and the risk of non-compliance with the Directive objectives) and economic analysis of the costs of water-related services and the current percentage of costs recovered (Articles 5, 6 and 7) (IMPRESS document).
December 2006	Drawing up of the programme for monitoring and control of the environmental and chemical status of surface water and the chemical and qualitative status of groundwater (Article 6).
December 2006	Publication and public provision of the calendar, the consultation measures and the working programme for drawing up the Catalan River Basin District Management Plan (Article 14).
December 2007	Publication and public availability of a provisional outline of the important subjects dealt with in determining measures and drawing up the Catalan River Basin District Management Plan (Article 14).
December 2008	Publication and public availability of an outline of the draft of the Catalan River Basin District Management Plan (Article 14).
December 2009	Approval of the programme of measures to be contained in the work carried out (plans and programmes) and the management measures to be carried out in order to attain the objectives of the Directive, namely the good ecological status of water by the end of 2015 (Article 11). It should be remembered, as set down in the Water Framework Directive, that for the most appropriate measures to be defined a cost-effectiveness analysis must first be carried out.
December	Drawing up of the Catalan River Basin District Management Plan (new Hydrological Basin

2009	Plan) (Article 13).
December 2010	Member States must ensure that they apply a water-pricing policy that provides the necessary incentives for efficient water use and an appropriate tax contribution or policy that will lead to the full recovery of costs for water-related services. Costs will be broken down into domestic, industrial and agricultural, and financial, environmental and resource or opportunity costs will be taken into account (Article 9).
December 2012	The Member States must ensure they apply a combined approach involving the control and reduction of point and diffuse sources of pollution in line with best available techniques (Article 10). The programme of measures required to attain the good status of water will also be operational (Article 11).
December 2015	The Member States must attain the good status of their bodies of water: the highest ecological and chemical status for surface water (inland and coastal) and the highest chemical and quantitative status of groundwater, with the exception of bodies of water that have been declared heavily modified and those for which temporary exemption has been requested for a justified reason (Article 4).

Table 1.2. Schedule of the WFD in Catalonia (source: CWA).

Planning is a tool that must enable real conditions, in this case the aquatic environment, to be defined and objectives to be set, which must be met through the carrying out of a plan. These objectives are set for different long-term objectives (from 10 to 20 years in our case), and the plan is based on detailed studies of the current situation.

The current regulation is contained in the Edict of 16th March 1999, published in the *Official Gazette of the Catalan Government* (DOGC) of 25th May 1999, which makes public the text that includes the determinations of the regulatory text of the Hydrological Plan for the Internal Basins of Catalonia.

The current *Hydrological Plan for the Internal Basins of Catalonia*, approved by Royal Decree 1664/1998 (*RD 1664/1998, de 24 de Julio, por el que se aprueban los Planes Hidrológicos de Cuenca*), which approved the river basin hydrological plans (Official State Gazette - BOE- number 191, of 11th August 1998), is supported by technical bases. Describes the hydrological state in 1992 and foresees situations in 2002 and 2012 as a first and second horizon. The Hydrological Plan includes the Water Treatment Plan which, following the same philosophy, describes the quality of rivers at source (1990) and sets objectives for the end of the Plan.

Taking into account the WFD, it is considered the validity of the current Hydrological Plan and determines its updating and review according to Decree 3/2003, of 4th November, which approved the reworked text of the legislation on water in Catalonia, called The Catalan River Basin District Management Plan.

1.6. The need of this PhD thesis

WFD constitutes in this work a thinking framework from which a tool for water Governance is proposed. The Directive's text provides general guidelines, but its implementation is still quite open to water managers interpretation.

The final objective of the Directive is to provide each river basin with a water plan including all water resource management elements necessary for achieving the indicated objectives. Water planning is a way to improve and provide support to the appropriate management, facilitating decision-making processes. It must be understood as a systematic process in the description and control of water bodies, integrating various uses and sensitivities concerning the resources. Furthermore, it can be understood as an iterative process, in the sense that it must be flexible in order to incorporate new criteria and adapt itself to changing circumstances.

The planning process indicated by the Directive is added to other management processes currently taking place in each area, and this may be a source of conflicts. It understands that achieving certain environmental objectives will make it necessary to change attitudes and alter positions in relation to the use of water and with the preservation of its quality, with increased associated costs that are difficult to assume in the short or medium term. In this management process, the current situation is determined (with all its hydrological, ecological and socio-economic complexity) and, based on this, the objectives and programmes necessary to achieve it are defined. This cyclical process must be completed with information and consultation with the various agents (encouraging public participation to legitimise the made decisions), a precise monitoring programme and means of assessing the process during the period the plan is being applied.

A fundamental aspect of the WFD regards the water costs. According to Paragraph 1 in its 9th Article, *member states shall take account of ….the environmental and resource costs (*of water)…. However, these costs concepts are not wider developed within the Directive, what meant a relevant doubt from the beginning. The first document published by the EC in order to help with the Full Cost Recovery implementation, was the "Information sheet on Assessment of the Recovery of Costs for Water Services for the 2004 River Basin Characterisation Report (Art. 9)", devoted to provide support to the WFD implementation through practical advice, material and examples and elaborated by the designed as ECO1 (ECO1, 2003) group. Regarding the cost definitions, the glossary of terms of the produced document give the following definitions:

- *environmental costs* are defined as representing the costs of damage that water uses impose on the environment and ecosystems and those who use the environment (e.g. a reduction in the ecological quality of aquatic ecosystems or the salinisation and degradation of productive soils);
- r*esource costs* are defined as the costs of foregone opportunities which other uses suffer due to the depletion of the resource beyond its natural rate of recharge or recovery (e.g. linked to the over-abstraction of groundwater).

In spite of that effort, it was evident that the distinction between environmental and resource costs was not clear-cut. Then, in order to further clarify the concept of environmental and resource costs, a second European drafting group (ECO2) was set up in September 2003 to prepare a non-binding information sheet on the definition and assessment of environmental and resource costs in the context of the implementation of the WFD (ECO2, 2004). The concepts were wider worked and the summary of the report stated that

- *environmental costs* are defined as the environmental damage costs to the water environment and its users as a result of alternative competing water use, while
- *resource costs* are defined as the costs of an economically inefficient allocation of water, either in terms of water quantity or water quality, over time and across

> different water uses. The document also indicates that the calculation of resource costs can be based upon the estimation of environmental costs, but there may also be resource costs in the absence of environmental damage costs.

As a result, the general feeling is that the EC efforts to clarify the meaning of the 9th article of the Directive, current water economic analyses are not able to completely fulfil the WFD regarding the water cost. Although it seems to be finally admitted that the environmental and the resources costs are close to be the same (Escriu et al., 2007), there still exists a partially empty research line where some other sciences apart from Economics are called to play an important role when the considered assets are the finite water resources. Here is where exergy could help.

The exergoecology paradigm and its core fundamentals were developed by Valero and Naredo (1999) in their book "Desarrollo económico y deterioro ecológico" (Economical development and ecological degradation). They stated the basis for a general theory of the physical cost of economic processes, and provide some examples of the exergy replacement costs of minerals.

Following that research line, Valero directed two PhD thesis in the CIRCE institute of the University of Zaragoza , where further developed in the the exergoecology approach was carried out. The first one entitled *Exergy cost analysis of the mineral wealth on earth. Applicaton for the management of sustainability*, by Ranz (1999); the second one, *Exergy assessment of natural resources, minerals, water and fossil fuels*, was elaborated by Botero (2000). Ranz (1999) analyzed the most suitable reference environment for the minerals exergy assessment and calculated the chemical exergy of some mineral commodities, while Botero (2000) extended the exergy analysis to other natural resources and used the exergy cost to asses the mineral, fossil fuels and water value. More recently, a third PhD thesis, *Exergy evolution of the mineral capital on earth*, by Valero D. (2008), was focused on the analysis of the state of the mineral's exergy on earth and its degradation velocity, due to the human action. These studies, sustain the beginning of this work.

In this dissertation, an additional and comprehensive methodology to help in the WFD's implementation is presented. Exergoecology approach is applied to calculate the water costs defined by the European WFD. A new methodology, called Physical Hydronomics, is proposed and its procedures are developed, connecting Physics and Economics. The Environmental Cost defined within the PH, clearly includes the environmental and resource costs defined by the WFD.

The first milestone of PH was presented Valero and Uche (2007) in the workshop about *water cost and water accounting* celebrated in Barcelona in 2007, organized by the CWA, the Institute of Ecological Sciences and Tecnologies (Autonomous University of Barcelona) and the New Water Culture Foundation (FNCA). Preliminary results were introduced and some interesting opinions about the accurancy of this calculation method were shared. Most of the issues, regarding mainly with the PH completeness, have been solved along the following years and they are presented in this dissertation.

Firstly, WFD was carefully studied and interpreted from a Thermodynamics perspective. The different water costs defined in the Directive were translated into exergy concepts and the study hypotheses were established. The diverse river statuses proposed by the

Directive were defined in exergy terms by means of their quantity and quality characterization.

The dichotomy quantity-quality needs to be carefully observed in any water analysis. The quality of water is as important as its quantity. Traditionally, the flows statement has been the main worry in water management. The WFD gives quite precise indication to the quality objectives definition. However, not much is said about the required flows. The definition of those objectives flows is also a hidden task within the WFD implementation. Mainly based on the preference curves for some fishes species, lists of minimum flows are becoming public in Spain. However, important external interests are mixing on those flows determination.

The existing parallelism between the changing water features along the river and the degradation in the river watershed due to water uses gives the key issue to postulate that the water degradation calculated from these two perspectives should theoretically match up. Accordingly, the Polluter Pays Principle intensively promulgated by the WFD can be applied to allocate water costs.

The methodology also helps in the elaboration of the Measurements Plan of the watersheds, since the proposed water-restoration methodologies are a core part for the cost estimation.

Finally, it is important to mention that this PH approach could be considered as innovative, since the WFD interpretation and implementation has been traditionally led by biologists and economists. Biologists have covered the quality objectives field, while conventional economist have been tried to correctly interpret the FCR principle. Technicians only take part when the Plan of Measures has to be defined. Thus, the inclusion of thermal engineers in this “closed” world means a probably fruitful initiative.

This methodology has been tested in the IBC. Real rivers sampling data are obtained from CWA and surface waters simulation software is used to obtain the river exergy profiles. Many of the required input data have been provided by the CWA as well.

In the last part of the dissertation, a complementary study to define the environmental cost of water has been developed under a different perspective: the Emergy approach, a methodology based on systems evaluation that enlarge the boundary conditions.

This PhD was conceived as a tool to contribute to an adequate water management of water, a scarce and actually valuable natural resource. PH is not called to substitute any of the existing methodologies, but to complete the nowadays existing ones.

1.7. Structure of the dissertation

Eight chapters comprise this work. In detail, the structure of this dissertation is as follows:

In this first chapter, the context and motivation of the thesis are expounded. The European WFD is shown as the background for the environmental cost of water definition and Thermodynamics as a viable science to be applied for its definition.

In the second chapter, an extensive review of the water world is carried out: resources, uses, quality, technologies and regulation are the main topics forming this part. Many different bibliography sources have been included in this chapter. Firstly, a description of the Hydrosphere and the hydrological cycle (HC) are presented. Then, the influence of humans in the HC is described through the water resource distribution, water uses, scarcity and degradation. Afterwards, the parameters defining water quality are presented. Finally, the water demand management and the water supply technologies are introduced. All the summarized concepts and descriptions are used latterly on in the study.

When natural resources are used in households or in any production process, they are embodied in the final good or service produced. The price charged for the product contains an element of rent which implicitly reflects the value of the natural resource. Establishing this implicit element is at the heart of valuing the stock of the resource. In the case of water, however, which is often an open access resource, this implicit element is often zero. If water is being treated as an economic good more and more, it is therefore expected that in the future the resource rent for water would be positive and thus value of the water stocks would be included in the balance sheets of a nation. This reflection is the starting point for the Chapter 3, where, the difficulty of the economic assessment of the environmental services is raised. The different meaning of the value, cost and price concepts are given; a brief historical review of the economic perception of natural resources is presented and the current water resources management in Europe and in Spain are introduced.

The thermodynamic background of this dissertation is found in Chapter 4. Exergy, the property to measure water availability, is linked to natural resources assessment by Exergoecology, the application of the Second Law of Thermodynamics analysis through the exergy analysis in the assessment of natural fluxes and resources on the Earth. The exergy components are explained, and the more adequate reference environment for water bodies analysis is also analyzed here. In addition to that, a detailed study about the measurement and exergy content of organic matter dissolved in river is done, both from the classical exergy approach and from the eco-exergy approach proposed by Jorgensen.

Next step in Chapter 4 is the introduction of the Exergy Cost concept. Firstly, the minimum exergy cost is calculated as the exergy difference between two given exergy states. Secondly, the inherent irreversibility of the real processes is included and the real exergy cost can be defined. Finally, the value of the hydrological cycle is quantified through the exergy assessment of the renewable fresh world water resources, and the world water withdrawal. In order to make the results more understandable than only final numbers, the exergy required to restore the hydrological cycle is considered to be obtained from the sun. Then, the surface required solar technologies is calculated (to obtain that exergy from electricity utilities fed by solar irradiation).

The core section of the dissertation arises in Chapter 5, where the Physical Hydronomics methodology is defined and developed. Physical Hydronomics is the specific application of the Thermodynamics to physically characterize the degradation and correction of water bodies, i.e., the physical application to European Water Framework Directive. After obtaining the exergy profile of a river, the characterization of the exergy states of a river according to the WFD is done. The definition of WFD's cost in exergy terms is give: the integral replacement cost (IRC) comprises the service cost (SC), the environmental cost (EC) and the remaining resources cost (RRC) of water. The calculation procedure is explained and a simple example is presented to make easier its understanding. Because of the definition of the river exergy states in quantity and quality, the mathematical sign of the exergy cost can be sometimes negative, contrary to the initially expected results. Therefore, a detailed analysis of the water costs signs is summarized in Chapter 5.

Because of the importance of the surface water simulation models in the study, this chapter includes the comparison of alternative simulation softwares. At the end of the chapter, the important equivalence between the river degradation and the degradation due to water uses along the water course are tackled. The relationship between the IRC and the degradation provoked by uses is stated at this point. This is a crucial point to sign the praises of PH: the exergy analysis of the river and of the water uses within its basin allows to allocate the cost of water among the different water users.

The application of PH to real case studies is the aim of Chapter 6. Two Catalonian watersheds, located in the Internal Basins of Catalonia, the Muga and the Foix basins are studied. The methodological steps described in Chapter 5 are performed. The results are given in energy and economic terms and the corresponding analysis is presented.

The penultimate chapter of the dissertation, Chapter 7, is though as a complementary vision of problem regarding the estimation of the environmental costs of water. The Emergy approach is structured from the idea of translating any mass or energy flow into solar energy units. This methodology accredits long experience and good results in the ecosystem management field. It can be understood as a more global analysis, with quite different background from PH. However, results from both methodologies show certain interesting coincidences that reinforce the PH as a useful working tool.

To sum up, Chapter 8 gathers the synthesis of this dissertation, its contributions and the perspectives opened by this work. The definition of the dynamic PH methodology and its application to two real watersheds is the main contribution. However, many more limited studies are included, such as the reference environment definition, the analysis of other methodologies or the static evaluation of global water resources. The available research fields for keep going in the PH development are numerous.

A set of six annexes complete the work. Each of them is devoted to a specific subject that was considered important for the study completeness. Annex A provides additional information about the WFD basis. Annex B covers some chemical issues referred in Chapter 4 which were to general to be included in that chapter text. Annex C includes wider information about the available water simulation software and a detailed description of the simulator used in this dissertation (Qual2k). Annex D summarizes many of the external data used for the work: chemical, physical and technologies references in the IBC. Annex E is called to complete the information given in Chapter 7 regarding the Emergy approach. Finally, tables and maps from calculations are presented in Annex F, in order to complete the summary of results given in Chapter 6.

Chapter 2

Water world: resources, quality, uses and technologies

Seven different sections have been developed in this heterogeneous chapter. Its final aim is providing a global vision of the physical water context, but also some detail about water uses. Any of the presented section finds its sense along the following chapters, where Chapter 2 will be referred. They cover, therefore, the background water world information needed for this PhD thesis elaboration.

Points 2.1 and 2.2 provide details about world water resources and the hydrological cycle, including quantity and quality figures that are needed for the studies carried out in Chapter 4 and to establish, for example, the reference environment as seawater.

Next point, 2.3, covers the information regarding the water resource distribution and use, adding interesting information about the water stress and the water footprint indicators.

Since the water quality characterization is a key issue in this dissertation, section 2.4 is devoted to summarize the most important quality parameters commonly used to define the quality of water. The parameters used to measure the organic matter content in water are also included; they will be applied in Chapter 4, where a study to determine the organic exergy component is treated.

The water degradation (both in quantity and quality) provoked by humans is considered along the 2.5 point, and it is applied in Chapters 5 and 6. Municipal, industrial and agricultural water uses are characterized. These figures are very important for the environmental cost allocation among the water users, according to the polluter (degrader) pays principle mentioned in Chapter 1.

Finally, water demand management and supply technologies are tackled in the last part (sections 2.6 and 2.7), where the water supply enhancement and demand management strategies are reported.

2.1. Water as a natural resource

The two first sections of this chapter, 2.1 and 2.2, aim to a quantitative and qualitative description of the main water bodies comprising the Hydrosphere from a global perspective. Such description will find its completely meaning in the exergy assessment of the global fresh water resources carried out in Chapter 4.

Water is one of the most widely distributed substances on planet Earth; in different forms and amounts it is available everywhere, interacting with the atmosphere, biosphere and lithosphere. The world's water exists naturally in different forms and locations: in the air, on the surface, below the ground and in the oceans. Figure 2.1 shows that among the total water, only 2.5% is fresh water. This freshwater is divided into glaciers (68.7%), groundwater (30.1%), permafrost (0.8%) and the smallest amount, 0.4% is the surface and atmospheric water. The last group is constituted by freshwater lakes (67.4%), wetlands (8.5%), soil moisture (12.2%), atmosphere (9.5%), rivers (1.6%) and biological water (0.8%).

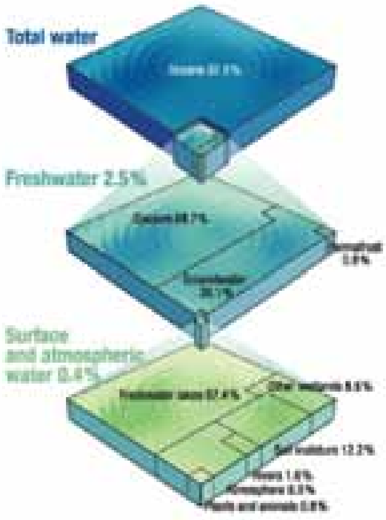


Figure 2.1. Global distribution of the world´s water. (Source: UN-WWAP, 2006)

It is clear that water and water resources occupy a special place among natural human life and in powering many of the natural processes shaping the Earth. It is the basis for the entire organic world, an integral part of the ecological system and often the most important element of the landscape for human beings. However, it should also be mentioned that many of the world's natural disasters and extremes are associated with water or the lack of it.

Of greatest significance is fresh water as this is the most important natural resource. Life is not possible without it, because it has no substitute. Mankind has always consumed fresh water and have used it for many other purposes; however, for most of historical time the human impact on water resources was insignificant or local in character. The properties of natural waters including their changing and cleaning during their movement through the hydrological cycle and their ability for self-purification allowed the fresh waters to retain their characteristic purity, quantity and quality over time.

2.2. Hydrosphere description and the hydrological cycle.

The Earth's Hydrosphere is one of the oldest mantles of this planet and it appeared between 3.5 and 4 billion years ago (Klige et al., 1998). It developed together with and in close relationship to the lithosphere, the atmosphere, and then with life itself. Up to the present the mechanisms of the origin of water on the Earth have not been completely explained (Kotwicki, 1991). However, the degasification theory seems to be the most likely explanation (Rubey, 1951; Vinogradov, 1959; Artyushkow, 1970; Condie, 1989). According to this theory the basic mass of the Hydrosphere formed as a result of the processes of melting and degassing the Earth's mantle and it was determined by geophysical processes operating at depth.

The Hydrosphere surrounding the Earth includes liquid, solid and gaseous forms of water, as indicated in the Figure 2.2º. The hydrological cycle transports this water about the Earth exchanging energy and moving materials as part of the process. The hydrosphere unity is determined by not only its continuity but also the constant water exchange between all its elements. It includes all mentioned types of natural waters – oceans, seas, rivers, lakes and glaciers, underground, atmospheric and biologically combined waters. All of them are interrelated and water moves from one situation to another as the hydrological cycle progresses. The lower limit of the hydrosphere is assumed to be at the level of Mokhorovic surface, and the upper limit practically coincides with the upper atmospheric limit (Blyutgen, 1972). Although a large volume of freshwater exists 'in storage', it is more relevant to evaluate the *renewable annual water flows*, taking into account where and how they move through the hydrological cycle.

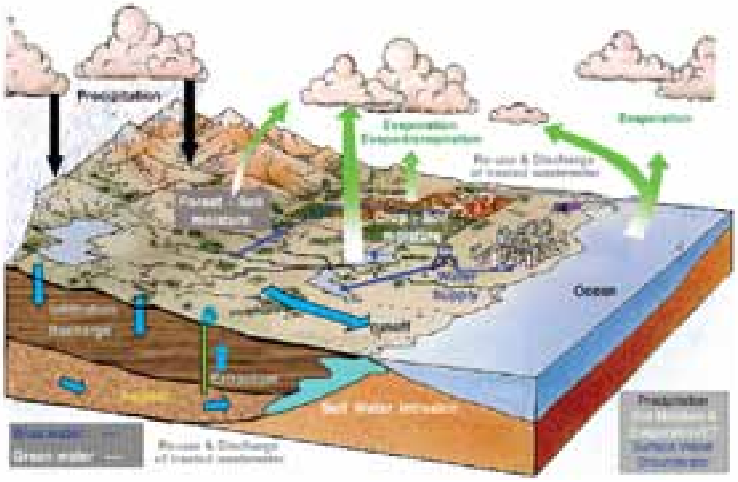


Figure 2.2. Schematic of the hydrologic cycle components in present-day setting. (Source: UN, 2006)

The schematic of the hydrological cycle in Figure 2.2 illustrates how elements can be grouped as part of a conceptual model that has emerged from the new discipline of ecohydrology, which stresses the important relationships and pathways shared among hydrological and ecological systems (Zalewski et al., 1997). This conceptual model takes into consideration the detail of the fluxes of all waters and their pathways while differentiating between two components: 'blue water' and 'green water'. Blue waters are directly associated with aquatic ecosystems and flow in surface water bodies and aquifers. Green water is what supplies terrestrial ecosystems and rain-fed crops from the soil moisture zone, and it is green water that evaporates from plants and water surfaces into the atmosphere as water vapour. This concept was developed by Falkenmark and Rockström (2004) who contend that the introduction of the concepts of "green water" and "blue water", to the extend that they simplify the discussion for non-technical policy-makers and planners, may help to focus attention and resources on the often neglected areas of rain-fed agriculture, grazing grassland, forest and wetland areas of terrestrial ecosystems and landscape management.

The total volume of the contemporary Hydrosphere, according to current data (Shiklomanow and Rodda, 2004) is 1,396 million km^3. As is was stated at the beginning of this chapter, fresh water in all its states makes up only 2.5% of the total (see Table 2.1).

Type of water	**Area of distribution (km^2 x 10^3)**	**Volume (km^3 x 10^3)**	**Water layer (m)**	**Fraction o total volume of hydrosphere (%)**	**Fraction of fresh water (%)**	**Averagere replacement time (yr)**	
World Ocean	361,300	1,338,000	3700	95.81%	—	2,889	b
Ground water (gravity and capillary)	134,800	23,400 a	174	1.68%		1,400	d
Predominantly fresh ground water	134,800	10,530	78	0.75%	29.23%	994	e
Soil moisture	82,000	16.5	0.2	0.00%	0.05%	1	c
Glaciers and permanent snow cover:	16,228	24,064	1,463	1.72%	66.79%	12,850	c
Antarctica	13,980	21,600	1,546	1.55%	59.95%	12,850	
Greenland	1,802	2,340	1,298	0.17%	6.49%	12,850	
Arctic Islands	226	83.5	369.0	0.01%	0.23%	12,850	
Mountainous regions	224	40.6	181.0	0.00%	0.11%	1,600	d
Ground ice of permafrost zone	21,000	300	14.0	0.02%	0.83%	10,000	d
Water in lakes:	2,059	176.4	85.7	0.01%		10	c
Fresh	1,236	91	73.6	0.01%	0.25%	10	
Salt	822	85.4	103.8	0.01%		10	
Swamp water	2,683	11.5	4.3	0.00%	0.03%	3	c
River stream water	148,800	2.1	0.0	0.00%	0.01%	0	c
Biological water	510,000	1.1	0.0	0.00%	0.00%	0	c
Water in air	510,000	12.9	0.0	0.00%	0.04%	0	c
Total volume of the hydrosphere	510,000	1,396,514	2,718	100%		3,023	
Fresh water	148,800	36,029.20	235	2.58%	100%	8,995	

(a) With no account of underground water of the Antarctic, approximately estimated at 2 million km^3, including predominantly fresh water of about 1 million km^3

(b) Average value from Suomi, 1992 and Shiklomanov and Rodda, 2004

(c) Average value from Buenfill, 2001 and Shiklomanov and Rodda, 2004

(d) Shiklomanov and Rodda, 2004

(e) Buenfill, 2001

Table 2.1. Hydrosphere content. (Source: Adapted from Shiklomanov and Rodda 2004, Buenfill 2001 and Suomi 1992)

The waters of the Hydrosphere are in constant, usually cyclic, motion under the effects of solar radiation, the energy released from the Earth's interior and gravitational forces.

In addition to free (gravitational) water, the Lithosphere contains a large amount of physically and chemically combined water. The average content of that water amounts to 3.5% of the rock weight, i.e. some $0.24 \cdot 10^{24}$ g (Derpgolts, 1971). Combined water does not participate actively in the hydrological cycle, at least at recognizable time-scales, and is not taken into account in this kind of studies.

Due to geological processes about 1 km^3 of water a year is released from the mantle through degasification and this rises gradually to the Earth's surface. As a result of convection in the mantle, part of this matter can emerge through breaks in ocean rift zones related to oceanic ridges (Monin, 1977). The global process of water exchange provides some stability in the distribution of waters between the land, the oceans and the atmosphere. This equilibrium is relative and can change in time, and these changes can lead to corresponding changes in hydrological and climatic conditions.

Water evaporating from the surface of reservoirs, soil and vegetation enters into the atmosphere as water vapour where it is dissipated upwards by turbulent diffusion and is transported by air currents from one place to another. With a temperature decrease, water vapour is condensed, transforming it to a liquid or solid. During rainfall from clouds, part of the water returns to the Earth's surface (inland cycle), and part of it returns to reservoirs in the form of runoff. Some precipitation can fall into the ocean, as was indicated in Figure 2.2.

In fact, about 90% of water evaporated from the surface of the oceans and seas falls back into the sea, short-circuiting the cycle. A smaller part of it, about 10%, participates in the major cycle, being transported by atmospheric circulation to the land where, as rainfall, it can be involved in a number of smaller versions of the complete hydrological cycle when surface and ground water and ice drainage reaches the World Ocean, closing the complete cycle. Part of the water is combined and decomposed by plants.

Solar heat evaporates water into the air from the Earth's surface. Land, lakes, rivers and oceans send up a steady stream of water vapour; this spreads over the surface of the planet before falling down again as precipitation. Precipitation falling on land is the main source of the formation of the waters found on land: rivers, lakes, groundwater, glaciers. A portion of atmospheric precipitation evaporates; some of it penetrates and charges groundwater, while the rest - as river flow - returns to the oceans where it evaporates: this process repeats again and again. A considerable portion of river flow does not reach the ocean, having evaporated in the endorheic regions, those areas with no natural surface runoff channels. On the other hand, some groundwater bypasses river systems altogether and goes directly to the ocean or evaporates. Quantitative indices of these different components of the global hydrological cycle are shown in the diagram (Figure 2.3). Every year the turnover of water on Earth involves 577,000 km^3 of water. This is water that evaporates from the oceanic surface (502,800 km^3) and from land (74,200 km^3). The same amount of water falls as atmospheric precipitation, 458,000 km^3 on the ocean and 119,000 km^3 on land. The difference between precipitation and evaporation from the land surface (119,000 - 74,200 = 44,800 km^3/year) represents the total runoff of the Earth's rivers (42,700 km^3/year) and direct groundwater runoff to the ocean (2,100 km^3/year). These are the principal sources of fresh water to support life necessities and man's economic activities water is in permanent motion, constantly changing from liquid to solid or gaseous phase, and back again.

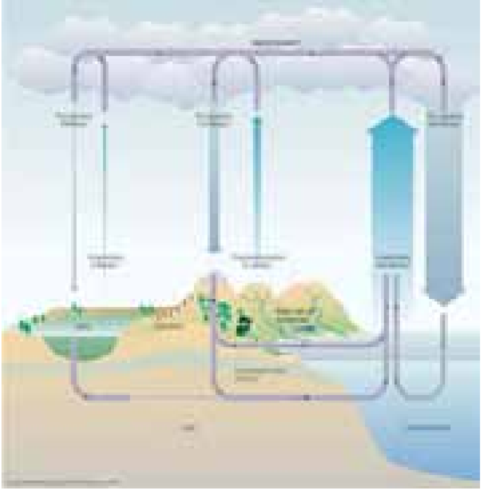


Figure 2.3. Global precipitation, evaporation, evapotranspiration and run-off (Source: UNEP, 2008)

In addition to that, other part of the water contained by the Earth is in chemical compounds, such as crystal hydrate, sorbate and many other forms which are found in porous depostis in the Earth's crust. This chemically combined water can be removed from the total water exchange for thousands of years. The crustal rocks lose water during the process of metamorphization and subduction under the effects of high pressure and high temperature. This water rises through rock pores and appears on the Earth's surface (Vinogradov, 1973).

The water cycle on Earth is usually treated as a closed system. However, there exists some water external exchanges that, although small in quantity, do happen. Solar energy and energy from space, together with cosmic dust, meteorites and meteors, arrive from space. The Earth in its turn gives back part of its energy to space and dissipates hydrogen and helium to it (Alpatjyev, 1983; Kulp, 1951). This exchange of matter and energy brings about 0.01 km3 of water per year (Derpgolts, 1971; Alpatjyev, 1969) from space to the Earth. At the same time part of the hydrosphere is lost due to the dissipation of light gases, and their escape beyond the limits of the Earth's gravitational field, amounting to about 0.1 km^3 per year (from 0.03 to 0.27 km^3) according to Yuri, 1959; Pavlov, 1977 and Alpatjyev, 1983.

The hydrologic cycle is usually depicted on a global scale. However, the hydrologic cycle operates at many scales, from the hydrologic cycle of the Earth to the hydrologic cycle of a person's back yard. Generally, to use the small amount of the Earth's water that is suitable for humans (that is, only about one-third of one percent), people who manage water resources are most interested in the hydrologic cycle of watersheds.

2.2.1. The world ocean.

The World Ocean holds by far the largest part of total volume of water on the planet. However, in recent years, studies have appeared (Wallace, 1996) that show volumes which differ from the data here by between 0.7% and 10%. Including the water stored in the bottom silts of the oceans causes the 10% difference.

World Ocean has accumulated 3.06•10^{25} J of heat (Stepanov, 1983). Every year it takes up almost twice as much solar energy as the land, and this factor determines its important role in the planetary heat exchange. The major portion of this energy is employed in evaporation over 500.000 km^3 per year of water, which ensures global water exchange.

Seawater composition will be an important parameter for the studies developed in this work. The average sewater composition is given in Table 2.2.

Substance	**Concentration, (mg/g)**
Cl^-	19.351
Na^+	10.784
Mg^{2+}	1.284
SO^{2-}_4	2.713
Ca^{2+}	0.412
K^+	0.399
HCO^-_3	0.107
Br^-	0.067
Sr^{2+}	0.008
CO^{2-}_3	0.048
$B(OH)^-_4$	0.003
F^-	0.013
$B(OH)_3$	0.009
Sum	**35.198**

Table 2.2. The composition of average seawater. (Source: adapted from Millero, 1996)

2.2.2. Glaciers and ice sheets

About three-quarters of the world's entire natural freshwater is contained within ice sheets and glaciers.

Glaciers are giant "water reservoirs" and "coolers" greatly influencing the climate and water regime of the Earth. Their state and the changes from this state over time are important indicators of global climatic and hydrological changes -past, present and future-. Cooling and warming and the advance and recession of glaciers result in the change of all the elements of the hydrological cycle: precipitation, runoff and evaporation, and the volume of water stored on land and in the ocean. During glaciation a large amount of water becomes locked up as snow and ice on the land. As a result the volume of runoff decreases, the world ocean level falls by tens of metres, uncovering extensive areas of continental shelves. With the decline of glaciation, river flow increases, the volume of water in the ocean becomes larger, the level rises and the land area diminishes. The main source of water in most glacier systems is snow and ice melt. Some water is also derived from geothermal melting and internal deformation (Paterson, 1994).

The total area of the present glaciation exceeds 16 million km^2 (what represents 3.23% of the Earth's surface - 510,065,284 km^2-). The mean ice thickness on this area is 1,700 m, and the maximum is more than 4,000 m (in Antarctica). The distribution of ice sheets and glaciers and the water stored in them is given in Table 2.3. According to Korzun (1974), to estimate the mean thickness of ice, data from the few measurements from ice drilling and seismic sounding are used. These data are applied by analogy to other glaciers taking into account their morphological features.

Two great ice masses, the Antarctic and Greenland ice sheets contain about 99%: most of the iced water is concentrated in Antarctica (almost 90%), while the remainder is found in Artic (about10%) and in mountain glaciers. The total water volume in the ice across the globe is estimated to exceed 24 million km^3. The accuracy of the assessment of that water storage in the Antarctica, for example, is about ± 3.0 million km^3 (Korzun, 1974).

Antarctica and Greenland are the only places where continental ice sheets currently exist. These regions contain vast quantities of fresh water. The volume of ice is so large that if the Greenland ice sheet melted, it would cause sea levels to rise some six meters all around the world. If the Antarctic ice sheet melted, sea levels would rise up to 65 meters (Shiklomanov and Rodda, 2004).

2.2.2.1. Antarctic ice sheet

Antarctica is Earth's southernmost continent, overlying the South Pole. It is situated in the southern hemisphere, almost entirely south of the Antarctic Circle, and is surrounded by the Southern Ocean. At 14.4 million km^2, it is the fifth-largest continent in area after Asia, Africa, North America, and South America. About 98% of Antarctica is covered by ice, which averages at least 1.6 kilometres in thickness.

Antarctica is the coldest place on Earth. At the 3-kilometer-high Vostok Station in Antarctica, scientists recorded Earth's lowest temperature: −89 °C (British Antarctic Survey, 2006). For comparison, this is 11 °C colder than subliming dry ice. Antarctica is a frozen desert with little precipitation; the South Pole itself receives less than 10 centimeters per year, on average. Temperatures reach a minimum of between −80 °C and −90 °C (in the interior in winter and reach a maximum of between 5 °C and 15 °C (near the coast in summer).

At the South Pole, the snow surface is 2,800 metres in altitude and the mean annual temperature is about –50ºC, but at the Soviet Vostok Station, 3,500 metres above sea level, the mean annual temperature is –58ºC. Along the coast of East or West Antarctica, where the climate is milder, mean annual temperatures range from –20ºC to –9ºC (Hemingway, 1974).

Region	**Area of glaciers (km^2)**	**Water volume (km^3)**	**Water volume (%)**
Artic			
Greenland	1,802,400	2,340,000	9.69%
Franz Josef Land	13,735	2,530	
Novaya Zemlya	24,420	9,200	
Severnaya Zemlya	17,470	4,620	
Arctic Islands	226,090	83,500	
Canadian Archipelago	148,825	48,400	
Spitzbergen (Western)	21,240	18,690	
Small Islands	400	60	
	2,254,580	**2,507,000**	**10.38%**
Europe			
Iceland	11,785	3,000	
Scandinavia	5,000	645	
Alpes	3,200	350	
Caucasus	1,430	95	
	21,415	**4,090**	**0.02%**
Asia			
Pamir-Altai	11,255	1,725	
Tien Shan	7,115	735	
Dzungarian Ala Tau, Sayan Mountains	1,635	140	
Eastern Siberia	400	30	
Kamchatka, Plateau of Koryak	1,510	80	
Hindu Kush	6,200	930	
Karakoram Pass	15,670	2,180	
Himalayas	33,150	4,990	
Tibet	32,150	4,820	
	109,085	**15,630**	**0.06%**
Noth America			
Alaska (Pacific Coast)	52,000	12,200	
Inner Alaska	15,000	1,800	
USA	510	60	
Mexico	12	2	
	67,522	**14,062**	**0.06%**
South America			
Venezuela, Colombia, Andes, Tierra del Fuego	7,100	2,700	
Patagonian Andes	17,900	4,050	
	25,000	**6,750**	**0.03%**
Oceania			
New Zeland	1,000	100	
New Guinea	15	7	
	1,015	**107**	**0.00%**
Africa			
Kenya, Mount Kilimanjaro, Ruwenzori	**23**	**3**	**0.00%**
Antarctica			
Antarctica	**13,980,000**	**21,600,000**	**89.45%**
TOTAL	**16,458,617**	**24,147,639**	

Table 2.3. Present-day glaciation of continents and islands of the Earth. (Source: Shiklomanov and Rodda, 2004)

2.2.2.2. Artic ice sheet

Greenland is the world's largest island, and is the largest dependent territory by area in the world. It also contains the world's largest national park.

Greenland ice sheet covers 81% of the total area of Greenland. The coastline of Greenland is 39,330 km long, about the same length as the Earth's circumference at the Equator. The highest point on Greenland is Gunnbjørn at 3,694 metres. However, the majority of Greenland is under 1,524 metres elevation.

Regarding the climatic change effects on this area, the annual mean temperature increased from -14.7ºC (1991) to -10.8ºC (2003), mean spring temperatures increased from -17.2º C to -13.6ºC, and fall temperatures show a similar trend from -13.8ºC to -10.3ºC for the 1991 to 2004 record. The largest increase of 6º C was observed for mean winter temperatures, ranging from -25.3ºC (1991) to -19.3ºC (2003) (Steffen, 2005).

The Greenland ice sheet is huge compared with all the other glaciers in the world, except that of Antarctica. Greenland (2,190,000 km^2) is mostly covered by ice (1,802,400 km^2), but isolated glaciers and small ice caps totalling 76,000 km^2 occur around the periphery. The mean altitude of the ice surface is 2,135 metres, and the bedrock surface is near sea level over most of the interior of Greenland, but the mountains occur around the periphery. Thus the ice sheet, in contrast to the Antarctic ice sheet is confined along most of its margin. The unconfined ice sheet does not reach the sea along a broad front anywhere, so that no large ice shelves occur.

The climate of Greenland, though cold, is not as extreme as that of Antarctica. The lowest mean annual temperatures, about –31ºC, occur on the north central part of the north dome, and temperatures at the crest of the south dome are about –20ºC (Enc.Brit., 1974).

In Table 2.4, the average composition of glaciers on Earth is shown. It was calculated by Brown (2002; cited by Valero D, 2008) after compiling the chemical composition of glacial runoff for the different regions of the world that appear in the Table 2.4.

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}
Average comp.	12.69	2.59	18.44	1.98	48.15	27.38	7.71

Table 2.4. Concentration of major ions in glacial runoff from different regions of the world (in mg/l). (Source: adapted from Valero D., 2008)

2.2.3. Underground ice

Permafrost is soil at or below the freezing point of water for two or more years. Ice is not always present, as may be in the case of nonporous bedrock, but it frequently occurs and it may be in amounts exceeding the potential hydraulic saturation of the ground material.

Areas of permafrost extend over northeast Europe and the north and north-eastern parts of Asia, including the Arctic islands; they cover northern Canada and the fringes of Greenland and Antarctica, as well as higher parts of South America. The total area of permafrost is about 21 million km^2, some 14% of the land area. In the Southern

Hemisphere (Antarctica, south America) permafrost covers about 1 million km^2. The depth of permafrost ranges from 400 to 650 m. Underground ice within this range is found as vein formations and strata. The water stored as underground ice can be estimated only approximately due to lack of data and few studies (Grave, 1968) but the most likely figure is 300 thousand km^3 (Shiklomanov and Rodda, 2004). In the permafrost areas 150-200 km^3 of water occurs in the form of river ice.

The annual snowfall over the Earth is about $1.7 \cdot 10^{13}$ tonnes, and this snow covers an area of between 100 and 126 million km^2 (around 22% of the Earth's surface). The distribution of snow varies considerably from year to year depending on climatic conditions.

2.2.4. Underground water

The volume of gravitational water contained in the pores, fissures and fractures of the water-saturated strata of the Earth's crust represents the natural storage of water underground. The geographical distribution of ground water is closely related to the geological structure of the Earth's crust. It also depends considerably on the climatic factors: precipitation, condensation and evaporation, and particularly on the infiltration. Since runoff also depends on these factors, there is a strong relationship between ground water and runoff: ground water draining to rivers is included in the volume of runoff, being its most stable contribution to the hydrograph, especially during dry periods and drought.

The reliable estimation of ground water storage is very difficult. The water content of water-bearing strata can be obtained approximately by multiplying the volume of water-bearing table by a water loss factor and effective porosity. The natural storage of ground water is determined down to the absolute depth of 2,000 m -the depth of the isobath which indicates approximately the distribution of the Earth's continental crust-.

Substance	Granite	Serpentinite	Shale
Cations or oxide			
SiO_2	39	31	5
Al	9	0.2	0
Fe	1.6	0.06	3.5
Ca	27	9.5	227
Mg	6.2	51	29
Na	9.5	4	12
K	1.4	2.2	2.7
Anions			
HCO_3	93	276	288
CO_3	0	0	0
SO_4	32	2.6	439
Cl	5.2	12	24
Fe	0	0	0
NO_3	7.5	6.8	0.9
PO_4	0	0	0

Table 2.5. Constituents of ground waters from different rock types. Concentrations in μg/g. (source: White et al., 1963)

The mean altitude of each continent was used for calculating the total volume of ground water stored in the Earth's crust (Shiklomanov and Rodda, 2004). The total storage of ground water to the 2,000 level in the Earth's crust was estimated to be 23.4 million km^3. Main constituents of groundwater are shown in Table 2.5.

2.2.5. Lakes and reservoirs

There are 145 large lakes across the globe with an area of more than one million km^2 and holding 168 thousand km^3 of water (see Table 2.6). This is 95% of the total volume of all the world's lakes, giving a total volume of lake water of 176.4 thousand km^3. Of this total 86 thousand km^3 is fresh water and 81 thousand km^3 is salty. The hydrology of about 40% of the world's large lakes has not been studied and their volumes are estimated approximately.

Continent	**Number of lakes**	**Total area ($km^2 \cdot 10^3$)**	**Water resources (km^3)**	
			Fresh	**Salt**
Europe	34	430	2,027	78,000
Asia	43	210	27,782	3,165
Africa	21	197	30,000	0
North América	30	393	25,623	19
South America	6	28	913	2
Australia and Oceania	11	42	154	174
TOTAL	**145**	**1,300**	**86,499**	**81,360**

Table 2.6. Water resources in the principal lakes of the Earth. (Source: Shiklomanov and Rodda, 2004)

2.2.6. Water stored in swamps

Swamps and bogs are widespread across the Earth with a total area of approximately 2.7 million km^2 or about 2% of the land area (that is, about 3 millions square kilometres). As it can be seen in Table 2.7, the swampiest continent is South America. The total volume of water in the world's swamps and bogs is estimated to be about 11,470 km^3. This value has been obtained on the assumption that the mean thickness of the peat bog is 4.5 m, their volume is 12,070 km^3, and that they are 95% water.

Continent	**Bog area ($km^2 \cdot 10^3$)**
Eurasia	925
Africa	341
North América	180
South America	1,232
Australia and Oceania	4
TOTAL	**2,682**

Table 2.7. Area of bog over the Earth. (Source: Shiklomanov and Rodda, 2004)

2.2.7. Water stored in channel networks

The Hydrosphere also includes the water stored in the river channel network (rivers and streams). The total volume of this water - 2,115 km^3 - was estimated by the Russian

State Hydrological Institute taking into account the volume of runoff and the lengths of the main rivers and their tributaries. Its figures are shown in Table 2.8. In spite of the very small volume of water in the river channels, it is this water which is continuously renewed and it is the most important for human use.

Continent	**Water volume in river channels (km^3)**
Europe	80
Asia	565
Africa	195
North América	250
South America	1,000
Australia and Oceania	25
TOTAL	**2,115**

Table 2.8. Water volume in river channels of the Earth. (source: Shiklomanov and Rodda, 2004)

There is a great variation in the concentrations of dissolved materials in stream and river water. Nonetheless, an extensive amount of available data allowed Livingstone (1963) to estimate the mean composition of world river water (see table Table 2.9).

Substance	**Concentration µg/g**
HCO^-_3	58.4
$SO\ ^{2-}{}_4$	11.2
Cl^-	7.8
NO^-_3	1
$Ca\ ^{2+}$	15
$Mg\ ^{2+}$	4.1
Na^+	6.3
K^+	2.3
Fe^{2+}	0.67
SiO_2	13.1
Sum	**120**

Table 2.9. Mean chemical contents of world river water (Source: Livingstone, 1963)

2.2.8. Water stored in soil

The soil moisture is an integral part of the Hydrosphere. This water occurs mainly in the top two metres of the soil. The total volume of soil moisture is estimated to be approximately 16,500 km^3 (Korzun, 1974). This figure assumes that soil moisture is 10% of the 2-m layer, and that the area of soil containing moisture covers 55% of the land area or 82 million km^2.

From the standpoint of food production and ecosystem maintenance, soil moisture is the most important parameter to net primary productivity (NPP) and to the structure, composition and density of vegetation patterns (WMO, 2004). Near-surface soil moisture content strongly influences whether precipitation and irrigation water either run off to surface water bodies or infiltrate into the soil column.

2.2.9. Water stored in living organisms, plants

Biological water, understood as the water included in living organisms such as plants and animals, is an active link in the hydrologic cycle. Part of the water that evaporates from the land and enters into the atmosphere is due to transpiration of soil moisture by vegetation. The processes of evaporation and transpiration (evapotranspiration) are closely linked to the water found in soil moisture; these processes act as driving forces on water transferred in the hydrological cycle. Movement through soil and vegetation is large and accounts for 62% of annual globally renewable freshwater. Alpatjyev (1969) gives the volume of living matter in the biosphere as $1.4 \bullet 10^{12}$ tonnes. The water content of living matter is about 80% (Derpgolts, 1971), i.e. 1,120 km^3.

2.2.10. Water stored in the Atmosphere

The water contained in the atmosphere, as water vapour, water drops and ice crystals, is an important part in the Hydrosphere, possibly the most active part. The total volume of moisture in the atmosphere, according to the different estimates (Korzun, 1974b; L'vovich, 1986; Wallace, 1996), varies from 12,900 km^3 to 14,000 km^3.

Evapotranspiration rates depend on many locally specific parameters and variables which are difficult to measure and require demanding analyses in order to calculate an acceptable level of accuracy. Other hydrological, cycle-related and meteorological data are also considered in the estimation of the rates. Today, however, local water management in basins or sub-basins can better calculate transpiration rates.

Evaporation from surface water bodies such as lakes, rivers, wetlands and reservoirs is also an important component of the hydrological cycle and integral to basin development and regional water management. In the case of artificially created reservoirs, it has been estimated by Rekacewicz (2002) that the global volumes evaporating since the end of the 1960s have exceeded the volume consumed to meet both domestic and industrial needs.

2.2.11. Average replacement time of water bodies

Of course water in the Hydrosphere is connected by the hydrological cycle; however the rates of movement and residence times are very different for water in its different states.

Biological waters included in plants and living organisms are renewed most rapidly – perhaps over a period of few hours. Plants transpire this water. Atmospheric water, which forms due to evaporation from any water surface, is renewed over a period of a year and is spent mainly for evaporation and partly on runoff. Water stored in swamps has a 5-year residence time.

Most lake water is renewed on average over a period of 17 years. However, different lakes have different renewal times. For example, for Lake Baikal this time is 380 years. All other types of natural waters (glaciers, groundwaters, ocean waters etc.) are renewed more slowly, possibly over periods of thousands and even tens of thousands of years. The largest period is for the ice in the tundra and in Antarctica, which may be renewed only over several hundreds of thousand of years (Kotlyakov, 1984). The average replacement time of water bodies is shown in Table 2.1. Several sources have been consulted in order to get the values. The highest replacement time is for glaciers and permanent show cover: 12,850 years (Suomi, 1992; Shiklomanov and Rodda, 2004). Ground ice of permafrost zone is supposed to be renovated every 10,000 years (Shiklomanov and Rodda, 2004). The shortest average replacement time, some few days, is for biological water and water in air (Buenfill, 2001a; Shiklomanov and Rodda, 2004).

The average replacement time for total water reserves, 3,022 years, represents the weighted average of all storage replacement times. Similarly, the replacement time of total fresh water reserves represents the weighted average of all fresh water replacement times, around 9,000 years. The difference is due to fact that the replacement time for oceans is shorter than for the biggest fresh water reservoirs, the glaciers.

Until this point, the first objective of the chapter has been covered. The global description of the water resources on Earth has been completed. It is time now to attend to the interrelationship of humankind and the water cycle.

2.3. How human influences the hydrological cycle

A new assessment proposal for water costs assessment is going to be defined in this dissertation. Carefully thinking on its context and applicability is then compulsory.

This 2.3 section is called to provide tools that help to set the later studied water bodies within the global world situation attending to the water uses. In this sense, it will be possible to compare the reality of a Mediterranean watershed to the world average, i.e., how comparable the considered local problems are in a global perspective.

Each component of the hydrologic cycle –precipitation, surface water runoff, groundwater recharge, and evaporation- changes the quality of a water body. For example, precipitation in the form of rain or snow can carry airborne pollutants to the Earth's surface; surface water runoff can cause erosion and transport sediments; infiltration and groundwater recharge can leach chemicals into aquifers; and evaporation can elevate concentrations of pollutants in bodies of water reducing the total volume of water. Each natural component of the hydrologic cycle can have a negative effect on water quality. Natural processes such as chemical reactions between rock and water, erosion and sedimentation caused by flowing water, and infiltration of surface water into groundwater aquifers can all create pollution. In some locations, water is naturally of such poor quality that plants and animals cannot survive.

Humans also have a tremendous effect on water quality. Fresh surface water and fresh groundwater are the only parts of the hydrologic cycle that can be used by them. Every year human influences grow and cause more and more changes to natural processes, including the hydrological cycle. These changes bring about alterations to the water balance and to water resources and their availability. Every person contributes to waste the environment through the consumption of resources such as food, clothing, housing, or fuel for transportation. The rapid growth of population, the development of industrial production and the rise of agriculture have resulted in the increased use of water. These circumstances are also contributing to the deterioration of our existing water quality and are creating significant challenges for water managers, industry, and fish and wild life agencies.

2.3.1. Distribution

The availability of water resources and their distribution in space and time has begun to be determined by human activity, in addition to the natural variation in climate. In many part of the world water resources are being degraded by pollution. The consequence is that the ever-increasing demand cannot readily be met by the available water resources in many areas and the availability of water has become a prime factor limiting the growth of the population and the development of the economy. Especially severe problems arise in arid regions where the population is growing rapidly and the limited resource is already used to a high degree.

Globally, water supplies are unevenly distributed. Some countries experience an abundant water supply, while other countries suffer from severe water shortages. In some areas, such as India and Africa, water withdrawals are so high that surface water supplies are shrinking and groundwater supplies are being depleted faster than they can be replenished. Climate change is also an increasing cause for concern for water managers, as glaciers that feed many of the world's rivers, recede at an alarming rate.

If the yearly runoff were evenly distributed in space and time, freshwater resources would be greatly sufficient to provide water for all. A quick calculation shows that water available for human consumption represents 15,000 litres per person and per day. However, this figure does not reflect reality, because freshwater resources are not evenly distributed. Rainfall and runoff are apportioned in both space and time in an irregular manner. Some regions receive enormous quantities of water, others receive almost none. Many regions get nearly 100% of their precipitation during a brief rainy season.

Therefore, renewable water potentially available for human consumption is evaluated at 10,000 to 12,000 km^3 per year. Out of this quantity, only 30 % was withdrawn in 2000, or around 4,000 km^3, and 15 %, or around 2,000 km^3, was consumed (i.e. evaporated) (Shiklomanov, 1997). At the global level, the water situation is not so alarming, but due to uneven distribution, some countries face water scarcity. In the future, total water withdrawal will grow by about 10-12% every ten years, and by 2025 it will reach approximately 5,100 km^3/year, a 1.38-fold increase (UNESCO, 2008). Water consumption will grow somewhat slower, with an increase of 1.26 times.

Human activities have also changed the character of ground water. Although there are some examples of artificial recharge of aquifers, more often the water table has been lowered to provide water for drinking. Every year up to 20 thousand km^3 of ground water is abstracted (Plotnikov, 1976), which results generally in the reduction of aquifer storage and the lowering of ground water levels, and in some cases in land subsidence.

The construction of reservoirs has led to the slowing down of the movement of river waters. Slowing the movement of water can influence its quality particularly by the accumulation of pollutants. Because the world ocean water is contaminated by oil products, this leads to the reduction of evaporation from the water surface by about 10% (Duvanin, 1981) and this contributes to the reduction in the rate of exchange of water between the ocean and the land surface.

The biggest problems are in Asia (36% of global water resources y 60% of World population) and Europe (with 8% of resources and 13% of the population). See Figure 2.4.

Figure 2.4. Water availability versus population. (Source: UN-WWAP, 2006)

2.3.2. Variability

Rainfall is distributed around the world geography and changes between seasons along the year. These rainfall variations have been associated with changes in sea surface temperature, in the monsoonal circulation, changes in large-scale circulation in the Southern hemisphere and continental land use, and with atmospheric phenomena.

Because of this reasons, a highly variable rainfall and high rates of evaporation used by vegetation or stored in lakes, wetlands and aquifers occur, leading to an enormous challenge to store and delivery water resources. Dams reduce the numbers and extent of floods and dry periods. Nevertheless, the conditions in the natural water flows are altered (affecting the river functions and impacting on aquatic ecosystems).

The coefficient of rainfall variation (CVR) is often used make comparisons of rainfall variability. For any country, the CVR is calculated as the rainfall standard deviation divided by the mean precipitations (Finlayson and McMahon, 1988). Extreme flows and high fluctuations are more common in countries with warm temperatures. Figure 2.5 summarizes the variability of annual rainfall per some representative countries versus the CVR coefficient.

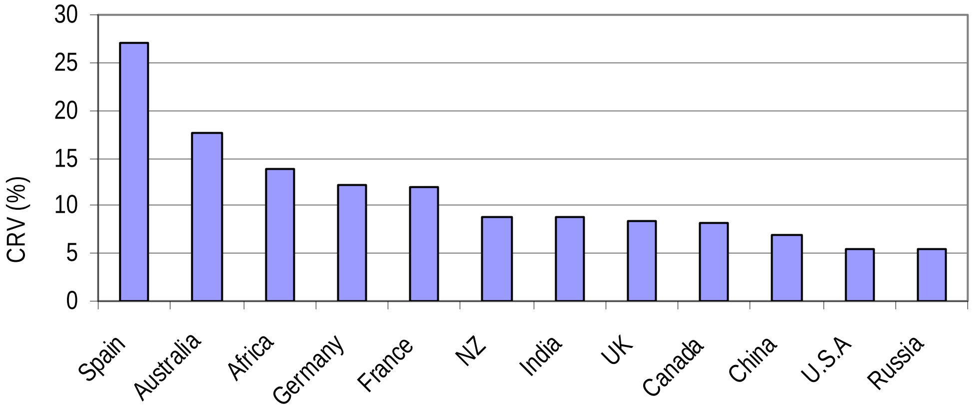


Figure 2.5. Variability of annual rainfall in different countries. (Source: adapted from Finlayson and McMahon, 1988; World Data Center of Meteorology, 2008)

It is important to highlight that Rainfall Variation Coefficient in Spain is higher than in the other studied countries. The main reason is the Spanish warm Mediterranean weather. Figure 2.6 represents the CVR of the Spanish Geography.

Figure 2.6. Rainfall variation coefficient in Spain (Source: Couchoud, 2003)

The high rainfall variability, together with high evapotranspiration rates and geographic separation of water resources and irrigation development, are important factors to account for in Spain. They all make the storage and delivery of water an enormous challenge.

Aquifers can be used with surface water reservoirs to secure water supplies. There could be complemented with subsurface storage which expands storage capacity, recharging aquifers during water excess periods with the aim of having a resource when necessary. Using aquifers as storages is becoming a good alternative considering the existing constraints of building new dams due to environmental concerns and general lack of suitable sites. Its infrastructure costs are generally cheaper, and water can be filtered, improving its quality. However, although the concept is not difficult, for using aquifers it is necessary to understand very well the hydrological and biological processes involved (NLWRA, 2001).

In addition to natural causes, many factors can simultaneously affect runoff within large river basins,, such as abstractions for irrigation and other agricultural purposes, as well as for industrial and municipal water supply. There can be soil drainage, deforestation, agrosilviculture, urbanization, opencast mining, and mine water pumping, stream bank straightening, and excavation of sand and gravel from river channels and other activities. There may be large scale diversions of flow from one basin to another and river flow control by reservoir operation.

Analysis of the different anthropogenic factors influencing the hydrological regime leads to conclusions about the need to consider the role of all factors related to water abstractions from water bodies, including the control of runoff. It is necessary to do so in order to estimate the human impact on water resources at the global scale. The factors causing a decrease in surface runoff and runoff from ground water are widely distributed. They are capable of exerting an especially pronounced effect on the state of water resources over large regions. In this connection the present section treats the changes in global use of fresh water for public water supply, industrial production and for agriculture, as well as water losses due to evaporation from reservoirs.

2.3.3. General water use.

Since antiquity, irrigation, drainage, and impoundment have been the three types of water control having a major impact on landscapes and water flows. Since the dawn of irrigated agriculture at least 5000 years ago, controlling water to grow crops has been the primary motivation for human alteration of freshwater supplies. Today, principal demands for fresh water are for irrigation, household and municipal water use, and industrial uses. Most supplies come from surface runoff, although mining of "fossil water from underground aquifers is an important source in some areas. The pattern of water withdrawal over the past 300 years shows the dramatic increases in this century.

While the world's population tripled in the 20th century, the use of renewable water resources has grown six-fold. Within the next fifty years, the world population will increase by another 40 to 50 % (Figure 2.7). This population growth -coupled with industrialization and urbanization- will result in an increasing demand for water and will have serious consequences on the environment.

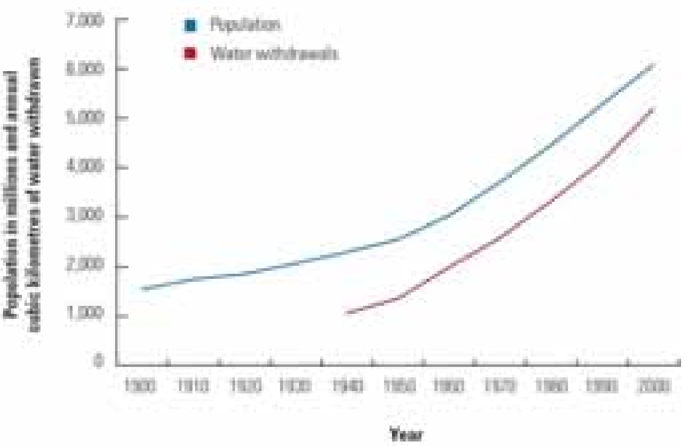


Figure 2.7. Historical tendency of population and hydrological resources withdrawals (Source: UN. 2008)

The natural capacity of water of movement through the hydrological cycle and its ability for self-purification gave birth to the illusion that water resources would always be pure and readily available: it was almost as if they were a gift from the natural environment. In these circumstances, historically, the tradition arose of a careless attitude towards the use of water and water resources; the cost of waste water treatment was kept to a minimum and little was spent on protection of water resources from pollution.

This situation has changed dramatically during recent decades. In many regions and in most countries, the results of long-term neglect and misuse of water resources have become obvious due to the increasing use of water resources and the transformation of land use in most river basins. For the first 50 years of the twentieth century the quantity of water used globally grew to 785 km^3 (157 km^3 for every 10 years), while from 1951 to 1960 the growth rate increased more than fourfold and it rose by 620 km^3/year (Shiklomanov, I.A. and Rodda, J.C., 2004).

This acceleration occurred principally because of the rapid expansion of irrigation, the growth of the volume of water used by industry and for the production of thermal power.

During recent decades the dramatic increase in water use due to the growth of the global economy has led to serious anthropogenic changes in the characteristics of the hydrology of rivers and lakes, particularly changes in the quantity and quality of their water. These changes, which have also affected ground water, have led to alterations in the water budgets of many river basins and changes in the available water resources.
At the present time, about 57% of total water withdrawal and 70% of global water consumption occurs in Asia where the major irrigated lands of the world are located. During the next few decades, according to UNESCO predictions, the most intensive growth in water withdrawal is expected to occur in Africa and South America -by 1.5-1.6 times- and the smallest in Europe and North America -1.2 times- (Figure 2.8).

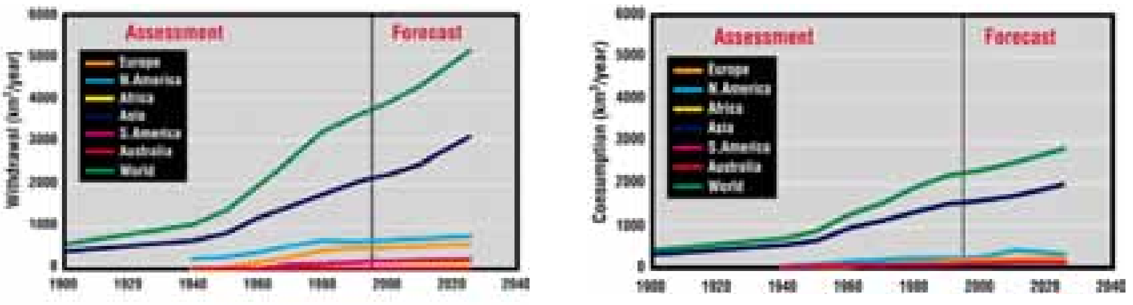


Figure 2.8. Water withdrawal and consumption by continents (Source: Unesco, 2008)

In addition to water consumption, water use by the humans also affects to its quality. Almost any human use means water quality degradation. Specific pollution due to use is detailed in section 2.5, use by use.

Waste water treatment is a duty in order to avoid infectious illnesses derived from that water pollution, specially keeping in mind that 1 l of waste water can pollute 8 l of potable water (Cech, 2003). The solution has to be based on effective sewage collection systems and water treatment plants. Before detailing the amount and degradation of water in each sector, the parameters defining water quality are going to be analyzed in section 2.4.

2.3.3.1. Consumptive and Non-Consumptive Water Use

Consumptive water use refers to water that is not returned to streams after use. For the most part, this is water that enters the atmospheric pool of water via evaporation (from reservoirs in arid areas) and from plant transpiration (especially from *thirsty* crops such as corn and soja). Irrigated agriculture is responsible for most consumptive water use, and decreases surface run-off. An extreme example is the Colorado River, which has most of its water diverted to irrigated agriculture, so that in a normal year, no water at all reaches the river's mouth.

Agriculture is responsible for 87 % of the total water used globally. In Asia it accounts for 86% of total annual water withdrawal, compared with 49% in North and Central America and 38% in Europe. Rice growing, in particular, is a heavy consumer of water: it takes some 5,000 litres of water to produce 1 kg of rice. Compared with other crops, rice production is less efficient in the way it uses water. Wheat, for example, consumes 4,000 m^3/ha, while rice consumes 7,650 m^3/ha.

A great deal of water use is non-consumptive, which means that the water is returned to surface runoff. Usually that water is contaminated however, whether used for agriculture, domestic consumption, or industry. The World Health Organization (WHO) estimates that more than 5 million people die each year from diseases caused by unsafe drinking water, and lack of sanitation and water for hygiene. This has economic effects as well: an outbreak of cholera in Latin America killed hundreds of people, and cost hundreds of millions of dollars.

2.3.4. Water stress, virtual water and water footprint

There are several indicators evaluating the basic human necessities per capita. The most known and used is the *water stress index*, established as 1,000 m^3/person/year. Water stress results from an imbalance between water use and water resources. The water stress indicator measures the proportion of water withdrawal with respect to total renewable resources (WWC, 2009). It is a criticality ratio (CR), which implies that water stress depends on the variability of resources.

Water stress causes deterioration of fresh water resources in terms of quantity (aquifer over-exploitation, dry rivers, etc.) and quality (eutrophication, organic matter pollution, saline intrusion, etc.) The value of this criticality ratio that indicates high water stress is based on expert judgment and experience (Alcamo et al., 2000). It ranges between 20% for basins with highly variable runoff and 60% for temperate zone basins. In the map shown in Figure 2.9, an overall value of 40% is taken to indicate high water stress. It can be seen that the situation is heterogeneous over the world. This ratio can not be reached by many African countries, in Middle East or in Asia.

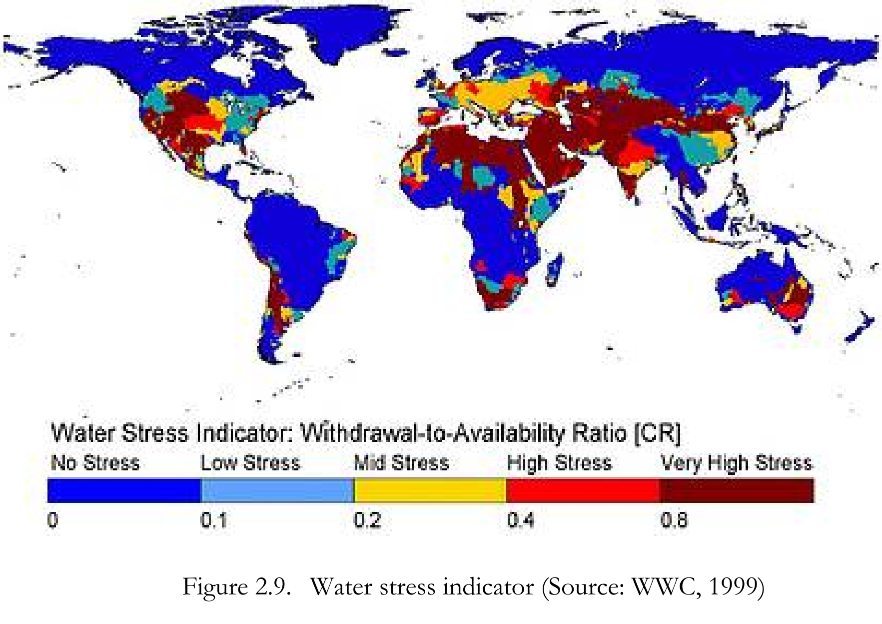


Figure 2.9. Water stress indicator (Source: WWC, 1999)

A 1997 UN assessment of freshwater resources found that one-third of the world's people experience moderate to high water stress. Moderate water stress levels are said to occur when water consumption exceeds renewable freshwater supply by 10 per cent. The problems are most severe in Africa and West Asia. In Asia, where water has always been regarded as an abundant resource, per capita availability declined by 40-60% between 1955 and 1990. Projections suggest that most Asian countries will have severe water problems by the year 2025. Most of Africa historically has been water-poor.

The role of *virtual water* deserves attention as well. The term *virtual water* was introduced by Tony Allan in the early 1990s (Allan, 1993). It is defined as the volume of water required to produce a commodity or service (Allan, 1999; Hoekstra, 1998). When there is a transfer of products or services from one place to another, there is little direct physical transfer of water (apart from the water content of the product, which is quite insignificant in terms of volume). There is however a significant transfer of virtual water.

For producing 1 kg of grain, around 1.5 m3 of water are required. For producing 1 kg of cheese, about 5000 l of water are needed and for 1 kg of beef we need in average 16000 kg of water (Chapagain and Hoekstra, 2003). According to a recent study by Williams et al. (2002), the production of a 32-megabyte computer chip of 2 grams requires 32 kg of water.

The virtual water trade balances for thirteen world regions can be identified in Figure 2.10, where the largest virtual water trade flows are also drawn. This information has been extracted from the *Value of Water Research Report Series No.12*, by IHE Delft (Hoekstra, 2003). There are a set of publications regarding these issues, containing high amount of information. Considering the period 1995-1999, the top-5 list of countries with net virtual water export is: United States, Canada, Thailand, Argentina, and India. The top-5 list of countries in terms of net virtual water import for the same period is: Sri Lanka, Japan, Netherlands, Republic of Korea, and China. Countries that are relatively close to each other in terms of geography and development level can have a rather different virtual water trade balance. While European countries such as the Netherlands, Belgium, Germany, Spain and Italy import virtual water in the form of crops, France exports a large amount of virtual water. In the Middle East we see that Syria has net export of virtual water related to crop trade, but Jordan and Israel have net import. In Southern Africa, Zimbabwe and Zambia had net export in the period 1995-1999, but South Africa had net import (Hoekstra, 2003). In terms of global trade, virtual water does not only raise awareness about water interdependencies, but it can also serve also as a means for improving water efficiency.

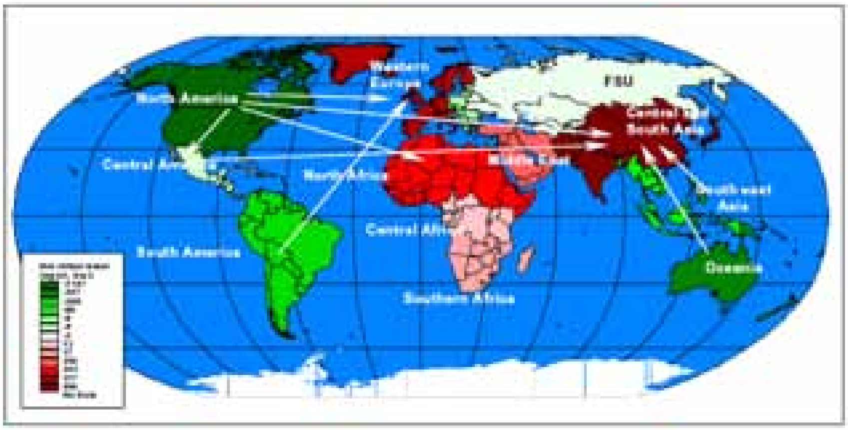


Figure 2.10. Virtual water trade balances of thirteen world regions over the period 1995-1999. The arrows show the largest net virtual water flows between regions (>100 Gm^3). (Source: Hoekstra, 2003)

In a further step, a broader indicator, the *water footprint*, links virtual water and world trade. Via the sum of domestic water use and virtual water, it can be considered how water used for the production of export commodities on the global market can contribute significantly to the changes in local and regional water systems

The *water footprint* of a country is defined as the volume of water needed for the production of goods and services consumed by the inhabitants of the country (Hoekstra and Chapagain, 2004). It can be calculated with either the top-down approach or bottom-up approach. In the top-down approach, the water footprint is calculated as the sum of water use in the country plus gross virtual water import into the country minus gross virtual water export. In the bottom-up approach, the individual water footprints of the inhabitants of a country are aggregated to get the total water footprint of a country. Individual water footprints are calculated by multiplying all consumed goods and services with their respective virtual water content.

Based on the top-down approach, the global average water footprint is found to be 1,240 m^3/yr/cap. There are large differences between countries. In the USA, the average water footprint is 2,500 m^3/cap/yr, while it is 700 m^3/cap/yr in China (Figure 2.11).

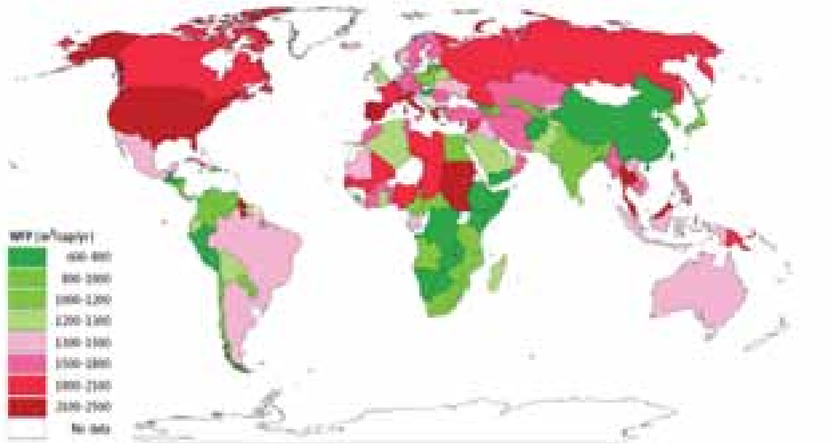


Figure 2.11. Average national water footprint per capital (m^3/capita/yr) in 2004. (source: Hoekstra and Ghapagain, 2007)

It has been noted, for example, that since Japan consumes large quantities of American cereals and soybeans, it might be suggested that this in turn leads to the mining of aquifers and further water use of rivers in North America. Figure 2.11 shows national water footprints around the world. Green means that the nation's water footprint is equal to or smaller than global average. Countries with red have a water footprint beyond the global average.

According to the report Alive Planet 2008 of WWF-Adena (WWF-Adena, 2008), Spain occupies the fifth position on world-wide scale as far as the denominated hydric track, a variable that analyzes the volume of fresh water used generally to produce the goods and services consumed by each citizen. Spain, in addition, comprises of the group of States of the Mediterranean (Portugal, Italy, Greece and Cyprus) that every time has a greater "brought about hydric stress" because the water begins to become a little good to the most important being the demand than the amount available, situation that will get worse as a result of the climatic change.

A thousand tons of water produces one ton of wheat, which has a market value of US $200. In contrast, the same amount of water used in industry yields an estimated US$14,000 of output -70 times as much- (Hunt, 2004). Those countries that can afford to import grain, therefore, often find that imports of virtual water –the substitution of food imports for irrigated agriculture production paid for by urban and commercial growth- are an attractive alternative to continued use of water in agriculture.

According to Hoekstra (2003), more than 200 international water systems exist in the world, and about 50 to 60% of the global population resides within them. It is clear them the huge importance of the security in the water systems: improving food self-sufficiency by a basin country may lead to a conflict with other nations sharing in an international water system. Importing *free virtual water*, may be seen as a mechanism to abate conflicts among basin countries. Tradeoffs between trading *real water* and *virtual water* should be examined before carrying out a large-scale transboundary water transfer scheme.

After examining general water issues on water, the *macro* vision of the situation has been drafted and it is time now to concrete some specific relevant aspects in this PhD thesis elaboration. In particular, the type of sources polluting the water bodies, and the parameters defining that water quality. The description, both in quantity and quality, of the point and diffuse pollution sources within a watershed will be a key point in the watersheds evaluation. Therefore, it is necessary to review first the most important used parameters to characterize the water quality.

2.4. Parameters defining water quality

As important as the amount of the water resource, is the quality of it. The concept describing non desirable elements in water is pollution, and a water body is considered to be polluted if it is unusable for a particular purpose. It can occur either naturally or through human activity.

In the past, the basic chemical and biochemical processes affecting water quality were the result of nature. Long before humans settled along the banks of rivers such as the Yangtze in China and the Nile in Egypt, sediment-laden floods carried metals and minerals that contributed to poor quality of water. Ancient floods of the Mississippi River filled adjacent oxbow lakes and marshes with organic materials such as decaying plants and animals. The aridity of the Colorado River watershed caused salt from alkaline soils to enter the river for thousands of years before human cultivation began. Groundwater in certain regions, or at great depths, contained dissolved minerals that rendered it unfit for human consumption. These natural processes greatly affected water quality around the world long before the negative influences of humans.

Unfortunately, humans have caused incredible levels of water pollution. The U.S. Environmental Protection Agency reported that 40 percent of the streams, lakes, and estuaries that were assessed (32% of all U.S. waters) were not clean enough for uses such as fishing and swimming. Leading pollutants in these impaired waters included sediments, bacteria, nutrients, and metals. Runoff from urban areas and agricultural lands were the primary sources of these pollutants.

The recent Directive 2008/105/EC of the European Parliament and of the council of 16 December 2008 defines some environmental water quality standards in accordance with the provisions and objectives of Directive 2000/60/EC, which establishing a framework for Community action (a strategy against pollution of water, which requires further specific measures for pollution control and environmental quality standards) in the field of water policy.

This Directive lays down Environmental Quality Standards (EQS) for priority substances and certain other pollutants as provided for in Article 16 of Directive 2000/60/EC, with the aim of achieving good surface water chemical status and in accordance with the provisions and objectives of Article 4 of that Directive.

Member States may designate mixing zones (article 4) adjacent to points of contaminants discharge (which permissible concentrations are listed in Part A of its Annex I), which will have to be included in river basin management plans produced in accordance with Directive 2000/60/EC.

On the basis of reports from Member States, including reports in accordance with Article 12 of Directive 2000/60/EC and in particular those on transboundary pollution, the Commission shall review the need to amend existing acts and the need for additional specific Communitywide measures, such as emission controls. A Member State shall not be in breach of its obligations under this Directive as a result of the exceedance of an EQS if it can demonstrate that the exceedance was due to a source of pollution outside its national jurisdiction.

Finally, the Commission shall consider inter alia the substances set out in its Annex III for possible identification as priority substances or priority hazardous substances. The Commission shall report the outcome of its review, accompanied with relevant proposals, to the European Parliament and to the Council by 13 January 2011.

2.4.1. Pollution Sources

In this section it is summed up where pollution comes from and how it is transported to waterbodies (such as rivers, lakes, or estuaries). Pollution sources are divided into two categories: point source and nonpoint sources.

A *point source* of pollution is generally defined as contamination discharged through a pipe or other discrete, identifiable location. Pollution from a point source is relatively easy to quantify, and impacts can be directly evaluated.

Nonpoint source pollution is generated from broad, diffuse sources that can be very difficult to identify and quantify. Such a pollution enters rivers, lakes and other water bodies through surface and groundwater movement, and even from the atmosphere through precipitation.

Point source and nonpoint source pollution are caused by human activities. It is important to separate these activities from natural water quality degradation, sometimes called "background pollution" or "natural contamination". Naturally degraded water quality, as explained before, can be caused by chemical reactions between water and metals and minerals, natural erosion, forest litter, natural migration of salts, and other normal processes of the hydrologic cycle. In Table 2.10, some examples of point and nonpoint sources are listed.

Point source pollution:	Nonpoint source pollution
Factories and wastewater treatment plants	Lawns, gardens and golf courses
Landfills	Agricultural practices
Abandoned mines	Street refuse
Underground and above-ground storage tanks	Contruction activities
	Dredging activities

Table 2.10. Point source and non-point source pollution. (Source: adapted from Cech, 2003)

2.4.2. Basic parameters in water quality

The monitoring of water quality of rivers dates back to around 1890 when some European rivers, such as the Thames and the Seine, highly contaminated due to domestic sewage, were monitored in terms of a few simple parameters of dissolved oxygen, pH, etc. With the rapid industrialization and development of the energy sectors and high-input agriculture, there has been an exponential rise in the number of water quality indicators, corresponding to the increasing diversity of pollutants (Meybeck and Helmer, 1989). These indicators, including the earliest monitored simple indicators, major irons, organic, and inorganic matters, and toxic pollutants, etc., cover a broad range of water quality. In order to comprehensively evaluate the water quality, a variety of evaluation methods such as the single index, fuzzy mathematics, principal factor analysis, specialist evaluation, gray correlation, radial basis function, artificial neural network, and comprehensive index evaluation, etc. have been established.

Common to all those models is the unavoidable subjectivity, of the weighting factor for each involved indicator, mathematical models or corresponding parameters. Due to the subjective weighted factors out of so-called specialist inquiry, contradictory evaluations may be resulted for the same water quality data with different specialist groups. For reasonable and consistent water resource exploitation and management, it is essential to pursue a unified objective assessment of water quality.

The main parameters found in water quality reports are:

- Temperature, pH, turbidity, hardness and dissolved oxygen
- Inorganic chemicals: metals and minerals
- Organic chemicals: natural organic chemicals, synthetic organic chemicals (including pesticides).
- Nutrients: nitrogen and phosphorus.
- Eutrophication and microorganisms

Significant pollution sources in river basins, such as large industrial plants, may be termed 'hot spots' and prioritized for clean-up within a river basin management plan.
It is important to consider not only the level or concentration of individual substances, but also their combined effect. It is very expensive to monitor water quality for the presence of numerous chemicals, each of which must be tested for separately. By

monitoring the populations of certain organisms, called indicator organisms (such as frogs, molluscs or certain insect species), it is possible to create a picture of how the water body is being affected over time. These ecotoxicological methods provide a more cost-effective way of assessing the impact of industrial discharges on ecosystems.

Measurements of chemical parameters are usually expressed in the physical unit of milligrams per litre (mg/l) or grams per cubic meter (g/m^3). The concentration of trace constituents is usually expressed as micrograms per litre (μg/l) or nanograms per litre (ng/l). The concentration can also be expressed as parts per million (ppm), which is a mass to mass ratio. The relationship between mg/l and ppm is given in Eq. 2.1:

Eq. 2.1. $$ppm = \frac{mg/l}{specific\_gravity\_of\_fluid}$$

For dilute systems, such as those encountered in natural waters and wastewater, in which one litre of sample weigh approximately one kilogram, the unit of mg/l or g/m^3 are interchangeable with ppm. The terms part per billion (ppb) and parts per trillion (ppt) are used interchangeably with μg/l and ng/l, respectively.

2.4.2.1. Temperature

Many physical, biological, and chemical characteristics of surface water are dependent on temperature. Excessive temperature changes can accelerate chemical processes and can be detrimental to aquatic plants and wildlife. Increased heat in water can reduce its ability to hold dissolved oxygen, while sudden temperature “shocks”, often caused by heated industrial water released into a lake or stream, can be deadly to many aquatic species. Removal of shade trees and shrubs along a shoreline can also affect the temperature of a water body, particularly during warmer seasons of the year. Fish respond to water temperature variations and often move to new locations when temperature changes vary by little more that 1 to 4ºC.

Water temperature is greatly affected by depth. Surface water is generally much colder at greater depths than shallow water, since it requires more time to absorb heat. Such temperature variations can cause lakes to “turn over” in the spring and fall, creating variable water quality characteristics. By contrast, groundwater at depths less than 91 meters generally maintains a constant temperature of approximately 10ºC, while surface water in lakes can range between a frozen state to 21-27ºC and higher during the summer.

2.4.2.2. pH

The hydrogen potential, pH, is defined as the negative logarithm of the hydrogen ions activity. For dilute solutions, however, it is convenient to substitute the activity of the hydrogen ions with the molarity (mol/l) of the hydrogen ions. As it is well known, the common pH scale extends from 0 (very acidic with a high concentration of positive hydrogen atoms, H^+) to 14 (very alkaline, or basic, with a very high concentration of negative hydroxyl ions, OH^-). A pH of 7.0 represents exact neutrality of water at 8ºC.

Raw water found in rivers and lakes generally has a pH between 4 and 9, while pure distilled water is at 7. Fish have a narrow range of pH preference that varies by species.

Water outside the normal pH range for particular species of fish can cause physical damage to skin, gills, and eyes, and in severe cases, can be fatal.

2.4.2.3. Turbidity

Turbidity is the relative measure of clarity and is the result of suspended matter in water that reduces the transmission of light. It can be caused by silt, very small organic particles, salt, plankton or decaying vegetation, whose presence results in a cloudy appearance of water.

Turbidity can create water quality problems because toxic chemicals can attach to suspended particles. In addition, drinking water treatment can be hindered if turbid surface water sources are used. Treatment for turbidity can remove some chemicals and waterborne diseases that bond to the fine suspended matter.

Turbidity in water is measured in NTU (Nephelometric Turbidity Units). A nephelometer, which electronically measures light scatter in waterm, can be used to determine turbidity. An alternative measurement can be done with the simple Secchi disk, with 20 centimeters in diameter and divided into alternating black and white quadrants to enhance visibility. It is tied to the end of a white nylon rope which is marked in black every tenth of a meter and in red every meter. Water with turbidity levels greater than 5 NTU is not safe for recreational use or human consumption. Levels less than 25 NTU cannot sustain aquatic life (EPA-US, 2004).

2.4.2.4. Sediment load and suspended solids

The sediments being carried by a river mainly consists on silt, clay, and some fine sand, but larger particles can be carried during flood events when water volumes and velocities are greater. The all are named as suspended load, and can be transported for hundreds or thousands of kilometres. As water velocity slows, sediments settle to the riverbed, on to the adjacent natural levees, or near the mouth of a river to form a delta.

Rivers also carry a dissolved load consisting of dissolved materials that remain in solution. Additional water flows will dilute these solutions but may not totally eliminate such dissolved materials unless water chemistry changes (Cech, 2003). Rivers that receive groundwater inflow generally have higher dissolved loads than rivers composed only of surface water runoff due to dissolved minerals available from underground formations.

The total amount of erosional material carried from a drainage basin is defined as sediment yield and it is generally measured in terms of weight per year. As far wastewater, it also contains a variety of solid materials varying from rags to colloidal material. In the characterization of wastewater, coarse materials are usually removed before the sample is analyzed for solids. Typically, about 60% of the suspended solids in a municipal wastewater are settleable. Total solids (TS) are obtained by evaporating a sample of wastewater to dryness and measuring the mass of residue. A filtration step (1.5 μm, 105 °C) is used to separate de total suspended solids (TSS) from the total dissolved solids (TDS). It is useful sometimes to apply the relation between TDS and conductivity for a water sample (APHA, 1985).

2.4.2.5. Hardness

Water hardness is the traditional measure of the capacity of water to react with soap, hardwater requiring considerably more soap to produce lather. It is not caused by a single substance but by a variety of dissolved polyvalent metallic ions, predominantly calcium and magnesium cations, although other cations, e.g. barium, iron, manganese, strontium and zinc, also contribute (WHO, 1996).

Hard water is sometimes described as an inability to create soap suds when washing. Because of calcium and magnesium which form a solid precipitate, hard water often creates a buildup of scale on hot water heaters, showers, and porcelain surfaces that can clog hot water pipes, water heaters, and boilers, but for the most part is purely an economic problem (Cech, 2003). Excessive hardness can be removed through softening processes such as filtering hard water through layers of salt. However, they are not recommended in cold water supplies.

Soft water can be difficult to use for washing since soap is not easily removed from skin or other surfaces. Surface water is softer than groundwater because it has less contact with soil minerals and originated more recently as rain.

mg $CaCO_3$/l	
0-75	soft
75-150	moderately hard
150-300	hard
>300	Very hard

Table 2.11. The degree of hardness can be described in milligrams per liter of calcium carbonate($CaCO_3$). (Source: Cech, 2003)

Hardness of water can be a factor in degenerative cardiovascular disease such as heart disease, hypertension, and stroke.

2.4.2.6. Inorganic Chemicals

Inorganic chemicals are substances in which two or more chemical elements other than carbon are combined, as well as some compounds containing carbon but lacking carbon-carbon bonds (e.g., carbonates, cyanides).

They may be classified by the elements or groups they contain (e.g., oxides, sulfates). The major classes of inorganic polymers are silicones, silanes, silicates, and borates. Coordination compounds (or complexes), an important subclass of inorganic compounds, consist of molecules with a central metal atom (usually a transition element) bonded to one or more nonmetallic ligands (inorganic, organic, or both) and are often intensely coloured. Here, metals and minerals and nonmetals are explained.

Metals

Metals are elements found naturally in the mineral ores of the Earth's crust. Some metals, such as calcium, zinc, and iron, can be healthful in proper quantities, but copper, lead, cadmium, mercury, arsenic, and chromium can be toxic.

Mining, excavation, and other construction activities can stir and expose these metals to the natural forces of the hydrologic cycle. Surface water runoff, groundwater infiltration, and ground water pumping can lead to natural chemical reactions that can be harmful to human and wildlife (WRI, 2001). Activities that disperse bottom sediments of lakes or streams can cause metals to remain in suspension for long periods of time.

Naturally occurring metals in drinking water are common. Copper is present in tap water if blue or green stains are present on porcelain fixtures such as sinks or bathtubs. Red or brown stains on porcelain indicate iron (rust), whereas black stains are probably caused by manganese. Production processes of factories can spill out heavy metals, such as lead, copper, and zinc, and can create serious problems for human health and the environment. Since the beginning of the Industrial Age, the production of these three metals has increased tremendously, with a tenfold increase between 1850 and 2000 (Valero D, 2008).

Minerals

Minerals are naturally occurring, crystalline materials that have a distinct inorganic chemical composition. Some minerals are used in their natural state (such as gold and diamonds), whereas others are refined to extract desired metals (iron, copper, and zinc). All surface water and groundwater contain minerals.

Minerals are consumed through food and water, and are needed by the human body to regulate chemical reactions of enzymes. Important minerals in the human diet include calcium, phosphorus, potassium, magnesium, sulphur, sodium, and chloride (Kundell and Hussein, 2009). Trace elements required by the body include iron, zinc, selenium, manganese, and chromium. Minerals may compete with each other in the body for adsorption. For example, a diet rich in manganese may decrease the amount of iron adsorbed by the body.

Salts

Surface water runoff and groundwater infiltration from precipitation and irrigation can cause salts to leach and contaminate surface and groundwater supplies. Salinity can be harmful to certain plants, aquatic species, and humans. High levels of salt in drinking water can lead to high blood pressure and other health concerns for humans. Saline soils can harm plants by pulling moisture out of roots and by reducing the uptake of water and fertilizer. However, plant tolerance for salt varies greatly by vegetation type (Cech, 2003).

As an example, the presence of salts in the Llobregat River is a major problem for the Catalonian Region in Spain. It is due to the presence of mines along the river course. A further example is the Colorado River Basin, located in a region of aridity and saline soils. Natural and human-caused surface runoff, from irrigation return flows, storm water runoff, and urban drainage, all compound the problem of high salinity levels in the Colorado River particularly in lower reaches of the river basin.

2.4.2.7. Organic content

Organic compounds are normally composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in some cases. The organic matter in wastewaters typically consists of proteins (40-60%), carbohydrates (25-50%), and oils and fats (8-12%). Urea, the major constituent of urine, is another important organic compound contributing to fresh wastewater. Because urea decomposes rapidly, it is seldom found in other than very fresh wastewater. Along with the proteins, carbohydrates, fats and oils, and urea, wastewater typically contains small quantities of a very large number of different synthetic organic molecules, with structures ranging from simple to extremely complex.

Natural organic chemicals

Organic chemicals contain carbon and can be classified as natural or synthetic, whereas natural organic chemicals occur in nature as the result of decomposition of plants and animals. Prehistoric forest, grasslands, and wetlands, provide complex carbon-based compounds found naturally in water and soil. These organic chemicals can develop into naturally occurring nitrates, nitrites, and ammonia. High levels can cause health problems in both animals and humans.

Synthetic organic chemicals

Synthetic organic chemicals (SOCs) are not found naturally and are generally developed in laboratories for mass production by industry. Synthetic organic chemicals can persist in the environment for long time periods because natural decomposing processes are unable to degrade these complex compounds. Many SOCs are carcinogens –substances or agents that stimulate the formation of cancer-. Petroleum-based industries are a major source of SOC's in water supplies (Cech, 2003). Synthetic organic chemicals include industrial solvents such as benzene, carbon tetrachloride, polychlorinated biphenyls, and pesticides:

- Benzene (C_6H_6): A carcinogen used as a commercial solvent in petroleum refining and coal processing.
- Carbon Tetrachloride (CCl_4): A carcinogen used in the manufacture of fire extinguishers, solvents, and cleaning agents.
- Polychlorinated Biphenyls (PCBs): A carcinogen formerly used in fluids of electrical transformers and capacitors in the electronics industry. Its use was discontinued in 1976 when it was found to cause ecological damage.
- Pesticides are generally synthetic organic chemicals used to eliminate unwanted pest. They include herbicides which kill plants and weeds, fungicides which kill fungus, nematacides which kill nematodes, and rodenticides which kill rodents such as rats and mice. Pesticides are used to increase crop yields, improve public health, and enhance the appearance of landscaped areas. Approximately 50% of pesticides are used for non-agricultural purposes such as golf courses, lawns, parks, schools, roadways, railways, utility rights-of-way, and public buildings. Pesticides are designed to remain in the application area to control target pest and then degrade into harmless products (Tilman et al., 2002). However, some degradation rates (measured as half-life) allow contaminants to reach groundwater or surface water sources before breaking down. The half-life of many common pesticides varies from 3 to 150 days.

2.4.2.8. Measuring of organic content

Over the years, a number of different analyses have been developed to determine the organic content of wastewaters. In general, the analyses may be classified into those used to measure aggregate organic matter comprising a number of organic constituents with similar characteristics that cannot be distinguished separately, and those analyses used to quantify individual organic compounds.

In general, the analyses used to measure aggregate organic material may be divided into those used to measure gross concentrations of organic matter greater than about 1.0 mg/l and those used to measure trace concentrations in the range of 10^{-12} to 1.0 mg/l. Laboratory methods commonly used today to measure gross amounts of organic matter in water include biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and total oxygen demand (TOD).

Trace organics in the range of 10^{-12} to 10^{-3} mg/l are determined using instrumental methods including gas chromatography and mass spectroscopy (Cech, 2003). Within the past 10 years, the sensitivity of the methods used for the detection of trace organic compounds has improved significantly, and detection of concentrations in the range of 10^{-9} mg/l is now almost a routine matter.

In this section, attention is devoted to the mentioned measurements of gross amounts of organic matter: TOC, COD, BOD and TOD, which can be used as raw data for the forthcoming exergy calculations.

2.4.2.9. Biochemical Oxygen Demand (BOD)

It is the most widely used parameter of organic pollution applied to both wastewater and surface water is the 5-day BOD (BOD_5). This determination involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter. Obtained results are used to determine the approximate quantity of oxygen that will be required to biologically stabilize the organic matter present, to determine the size of waste-treatment facilities, to measure the efficiency of some treatment processes, and to determine compliance with wastewater discharge permits.

If sufficient oxygen is available, the aerobic biological decomposition of an organic waste will continue until all the waste is consumed. Three more or less distinct activities occur. First, a portion of the waste is oxidized to end products to obtain energy for cell maintenance and the synthesis of new cell tissue.

Simultaneously, some of the waste is connected into new cell tissue using part of the energy released during oxidation. Finally, when the organic matter is used up, the new cells begin to consume their own cell tissue to obtain energy for cell maintenance. This third process is called endogenous respiration. Using the term COHNS (which represents the elements carbon, oxygen, hydrogen, nitrogen, and sulphur) to represent the organic waste and the term $C_5H_7NO_2$, first proposed by Hoover and Porges in 1952 (cited by Metcalf and Eddy, 2003) to represent cell tissue, the three processes are defined by the following generalized chemical reactions:

Oxidation:

Eq. 2.2. $$COHNS + O_2 + bact \rightarrow CO_2 + H_2O + NH_3 + end\_products + energy$$

Synthesis:

Eq. 2.3. $$COHNS + O_2 + bacteria + energy \rightarrow C_5H_7NO_2$$

Endogenous respiration:

Eq. 2.4. $$C_5H_7NO_2 + 5O_2 + bacteria \rightarrow 5CO_2 + H_2O + NH_3 + 5H_2O$$

If only the oxidation of the organic carbon that is present in the waste is considered, the ultimate BOD is the oxygen required to complete the three reactions given above. This oxygen demand is known as the ultimate carbonaceous or first-stage BOD, and is usually denoted as UBOD.

2.4.2.10. Chemical Oxygen Demand (COD)

The COD test is used to measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in an acid solution, as illustrated in 0, when the organic nitrogen is in the reduced state, oxidation number=-3, (Metcalf and Eddy, 2003).

$$C_nH_aO_bN_c + O_2 + dCr2O_7^{2-} + (8d + c)H^+ \rightarrow nCO_2 + \frac{a + 8d - 3c}{2}H_2O + cNH_4^+ + 2dCr^{3+}$$

$$where \qquad d = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3} - \frac{c}{2}$$

Although it would be expected that the value of the ultimate carbonaceous BOD would be as high as the COD, this is seldom the case. Some of the reasons for the observed differences are as follows:

- many organic substances which are difficult to oxidize biologically, such as lignin, can be oxidized chemically
- certain organic substances may be toxic to the microorganisms used in the BOD test
- high COD values may occur because of the presence of inorganic substances with which the dichromate can react.

From an operational standpoint, one of the main advantages of the COD test is that it can be completed in about two and a half hours, compared to five or more days for the BOD test. To reduce the time further, a rapid COD test that takes only about 15 minutes has been developed.

2.4.2.11. Total Organic Carbon (TOC)

The TOC test, done instrumentally, is used to determine the total organic carbon in an aqueous sample. The test methods utilize heat and oxygen, ultraviolet radiation, chemical oxidants, or some combination of these methods to convert organic carbon to carbon dioxide (a main oxidation product) which is measured with an infrared analyzer or by other means.

TOC is often used when levels of organic matter are low; it is a good parameter to measure and, actually, a more accurate indication of some of the pollutants that cause the majority of the problems to the BOD test. It is also gaining in favour because it takes only 5 to 10 minutes to complete. More recently, a continuous on-line TOC analyzer has been developed, in conjunction with the space program, which can be used to detect TOC concentrations in the ppb range. Such instruments are currently being used to detect the residual TOC in the treated effluent from microfiltration and reverse osmosis treatment (Visco et al., 2005).

Theoretical Oxygen Demand (ThO) complements these laboratory tests and it is determined from the chemical formula of the organic matter.

2.4.2.12. Total Oxygen Demand (TOD).

This method involves the oxidation of the sample to stable end products in a platinum-catalyzed combustion chamber. TOD is determined by measuring the oxygen content of the inert carrier gas, nitrogen. TOD measurements are becoming more popular because of their quickness in determining what is entering the waste water treatment plants and how the plant is responding. The results obtained generally will be equivalent to those obtained in the COD test.

2.4.2.13. Interrelationships between BOD, COD and TOC

The TOC of a wastewater can be used as a measure of its pollution characteristics, and in some cases it has been possible to relate TOC to BOD and COD values. If a valid relationship can be established between results obtained with the TOC test and the results of the BOD test for a given wastewater, use the TOC test for process control is recommended (Metcalf and Eddy, 2003).

Typical values for the ratio of BOD/COD for untreated municipal wastewater are in the range from 0.3 to 0.8 (Table 2.12). If the BOD/COD ratio for untreated wastewater is 0.5 or greater, the waste is considered to be easily treatable by biological means. If the ratio is below about 0.3, either the waste may have some toxic components or acclimated microorganisms may be required in its stabilization.

Type of wastewater	BOD/COD	BOD/TOC	COD/TOC
Untreated	0.3-0.8	1.2-2.0	2.909
After primary settling	0.4-0.6	0.8-1.2	2
Final effluent	0.1-0.3[a]	0.2-0.5[b]	1.75

Table 2.12. Relation among organic measurement parameters (Source: adapted from Metcalf and Eddy, 2003)

2.4.2.14. Dissolved oxygen

Oxygen comprises about 21% of the atmosphere but only a fraction of 1% of water. Where atmosphere and water meet, the great difference in proportions causes oxygen to become dissolved in water. Dissolved oxygen (DO) is comprised of microscopic bubbles of oxygen gas, O_2, in water and is critical for the support of aquatic plants and wildlife in lakes and streams. DO is produced by diffusion from the atmosphere, aeration of water as it passes over falls and rapids, and as a waste product of photosynthesis. It is affected by temperature, salinity, atmospheric pressure, and oxygen demand from aquatic plants and animals. It is measured in parts per million or milligrams per litre.

Most aquatic plants and animals need dissolved oxygen in water to survive. However, oxygen is only slightly soluble in water. The actual quantity of oxygen that can be present in solution is governed by the solubility of the gas, the partial pressure of the gas in the atmosphere, the temperature and the concentration of the impurities in the water (Metcalf and Eddy, 2003).

Species, such as trout, require medium to high levels of DO, while warm-water fish such as catfish or carp require lower concentrations. High levels of dissolved oxygen allow a variety of aquatic organisms to thrive. Ideally, dissolved oxygen levels should be near saturation levels in surface water to provide maximum levels for fish. Elevated levels of dissolved oxygen also make drinking water taste better but can be corrosive to water pipes.

2.4.3. Nutrients

Plants, animals, microorganisms, and even single-cell bacteria must extract substances from the environment for energy and growth. These substances are called nutrients and include nitrogen (N), phosphorus (P), magnesium (Mg), calcium (Ca), and iron (Fe). Nitrogen, phosphorus, and associated compounds are particularly important in the study of water quality.

2.4.3.1. Nitrogen

Nitrogen is important as plant nutrient for crop production, lawns, landscaping, golf courses, forest growth, and other vegetation. It is most abundant in its atmospheric form (N_2). Nitrogen gas comprises 78.1% of the Earth's atmosphere, by volume (Los Alamos, 2001)

Nitrate (NO_3^-) is created by bacterial action on ammonia (NH_3), by lightning, or through artificial processes that include extreme heat and pressure. Nitrate is found in soluble form in both surface and groundwater. It is not bound by soil particles, is consumed by plants, and converts into gaseous forms by microbial action. Nitrates can pollute groundwater aquifers by leaching through soils, or they can move laterally with surface water or subsurface flow to contaminate surface waters. In proper amounts, nitrates are very beneficial. However, excessive concentration in water can cause health problems if consumed by humans (Cech, 2003).

The Maximum Contaminant Level (MCL) established by the U.S. Environmental Protection Agency for nitrate is 45 ppm, which equals 10 ppm nitrate-nitrogen (NO_3-N). In Europe, the Council Directive 75/440/CEE, of 16 June 1975, concerning the quality required of surface fresh water specifies, in its attached 2, an imperative maximum value of 50 mg NO_3^-/l, and recommended values of 25 mg NO_3^-/l and 2 mg N Kjeldahl /l , respectively. N Kjeldahl include no NO_3^- contribution.

Nitrite (NO_2^-) is a salt formed by the action of bacteria on ammonia and organic nitrogen. Nitrite, also found in soluble form in water, is a n intermediate form created by bacterial action on ammonium (NH_4^+) or nitrate (NO_3^-). Ammonium is converted to the nitrite and nitrate forms rather quickly by nitrifying bacteria. These add oxygen to the ammonium ion and convert it to nitrate.

Ammonia toxicity is a problem for aquatic life, whereas nitrite toxicity is a problem for infants. Nitrites react directly with human blood and other warm-blooded animals to produce methemoglobin. Methemoglobin destroys the ability of red blood cells to carry oxygen and can cause a condition called methemoglobinemia, or "blue baby" syndrome in infants primarily under three months of age. Water with nitrite levels exceeding 1.0 mg/l should not be used for feeding infants. The drinking water standard for nitrates is 10 mg/l.

Nitrite toxicity in fish is greater in water with low DO levels because, as mentioned, nitrite reduces the ability of blood to carry oxygen. Nitrites can produce "brown blood disease" in fish and occur mostly in farm or commercial fish ponds when sediments are disturbed. Disturbance typically occurs during the spring and fall turnovers or through mechanical agitation to increase dissolved oxygen levels. Although fish tolerance for nitrite is low (often less than 0,15 mg/l), their tolerance for nitrate (NO_3^-) is high, typically grater than 1000 mg/l (CAST-US, 1996).

Ammonia (NH_3) and ammonium (NH_4^+) are commonly found in surface water, in the soil, and as a byproduct of decaying plant tissue and decomposition of animal waste. Ammonia and ammonium are rich in nitrogen and excellent fertilizers. Ammonia levels at 0,1 mg/l usually indicate polluted surface waters, whereas readings above 0,2 mg/l can be toxic for many aquatic species. (Cech, 2003). High levels of ammonia are often found downstream of wastewater treatment plants and near ponds that have large populations of water fowl, such as ducks and geese, which produce waste.

2.4.3.2. The Nitrogen Cycle

The nitrogen cycle (Figure 2.12) is driven by nitrogen, oxygen, and bacteria. It is the natural process of converting the reservoir of nitrogen gas from the atmosphere into usable forms of nutrients for plants and animals. The nitrogen cycle includes complex interactions with various forms of nitrogen, notably: atmospheric nitrogen (N_2), organic nitrogen (N), nitrite (NO_2^-), nitrate (NO_3^-), ammonia (NH_3) and annonium (NH_4^+). Each form of nitrogen affects plant utilization and can have negative impacts on water quality. The nitrogen cycle includes four main components: nitrogen fixation, mineralization, nitrification and denitrification (Figure 2.12).

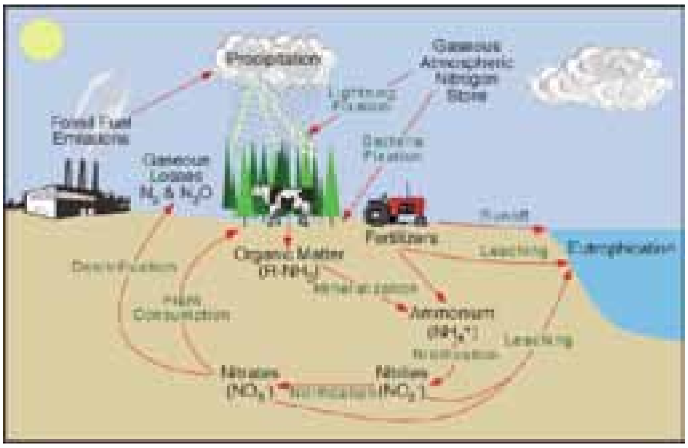


Figure 2.12. Nitrogen Cycle (source: Pidwirny, 2008)

Nitrogen Fixation

Animals, including humans, cannot utilize nitrogen gas from the atmosphere or from inorganic compounds. Instead, nitrogen must first be converted into an organic form (nitrogen combined with carbon), through a process called nitrogen fixation. This process requires substantial amounts of energy to break apart the nitrogen molecule, since it has a triple bond between the two nitrogen atoms, making the molecule almost inert. Nitrogen gas (N_2) will react with oxygen only in the presence of high temperatures and pressures, or through bacterial activity, to create organic nitrogen (N), nitrate (NO_3^-) or ammonia (NH_3). This process can be caused by atmospheric fixation by lightning, biological fixation by bacteria and algae, and industrial fixation caused by combustion reactions in power plants, chemical processes to make fertilizers, or inside internal combustion engines. Industrial fixation requires great pressure and temperatures.

Biological fixation accounts for about 70% of the total conversion of nitrogen into biologically useful forms of nitrate. The Rhizobium bacteria in root nodules of legume crops such as clover, alfalfa pinto beans, and soybeans, in surface water environments such as wetlands complexes, and in the soil can convert nitrogen gas in the atmosphere into biological matter. Approximately 20% of all nitrogen fixation –from nitrogen gas to ammonia- occurs through industrial processes. Atmospheric nitrogen fixation from discharge lightning accounts for less than 5% of total fixed nitrogen conversion from atmospheric nitrogen (N_2) to nitrate (NO_3^-). Agriculture may now be responsible for approximately 35% of all nitrogen fixation on Earth through the use of fertilizers produced by industrial fixation and biological fixation caused by the production of legume crops (Bezdicek and Kennedy, 1998). The average nitrogen fixation rates are shown in Table 2.13.

Type of Fixation	**Fixed N (10^6 metric tons/yr)**
Nonbiological	
Industrial	about 50
Combustion	about 20
Lightining	about 10
Total nonbiological	about 80
Biological	
Agricultural land	about 90
Forest and nonforest land	about 50
Sea	about 35
Total biological	about 175

Table 2.13. Nitrogen Fixation rates. (Source: Cech, 2003)

Mineralization

Mineralization, or decay, is the process of organic matter, such as dead plants and animal waste, decomposing in the presence of oxygen. The principal storehouse for nutrients found in the soil is within organic matter, such as decaying plants or animal waste. Organic matter can hold more than 96% of all soil nitrogen (Donahue, R. et al, 1983).

Nitrification

The process of organic nitrogen (N) changing into nitrate (NO_3^-) is called nitrification and it is a rapid anaerobic process that requires bacterial action. The common soil bacterium Nitrosomonas oxidizes ammonia (NH_3), or organic matter, into nitrite (NO_2^-). Nitrobacter, another common bacterium, relatively quickly oxidizes nitrite (NO_2^-) into nitrate (NO_3^-).

2.4.3.3. Phosphorus

In contrast to nitrogen, phosphorus does not exist in a gaseous state but occurs naturally as a salt in the mineral apatite. Apatite, $Ca_5(PO_4)_3(OH)0.33F0.33Cl0.33$, is found in igneous, metamorphic, and sedimentary rocks. Phosphorus is a common nutrient found in soil and water, and is quickly bound to soil particles or is consumed by plants. Phosphorus can originate from dissolved leach rate from rocks, from decomposing organisms, animal waste, manufacturing processes, effluent from wastewater treatment plants, and as artificial fertilizers. Much of the phosphorus found in sewage effluent is from synthetic detergents.

Phosphorus by itself does not have any notable health effects on humans. However, phosphorus levels above 1.0 mg/l may interfere with coagulation processes at water treatment plants. This can hinder the removal of microorganisms bound to sediments and other particles from drinking water (WHO, 1996).

Nonpoint source pollution of eroding sediments in runoff is the primary mechanism whereby phosphorus enters surface water. In many cases, point sources, such as wastewater treatment plants, are also very important contributors. Lake and reservoir sediments serve as phosphorous sinks and can cause excessive growth of algae and phytoplankton (Cech, 2003). Such growth often occurs when summer warming conditions of the normally cooler water at the bottom of a lake stimulate the release of phosphorus from the sediments at the bottom of the water body.

2.4.3.4. The Phosphorus Cycle

Processes of the hydrology cycle add phosphorus to the soil where it can be consumed by plants. Decaying plants and animal waste decompose and return phosphorus to organic form in the soil, where the phosphorus cycle continues.

The usual forms of phosphorus that are found in aqueous solutions include the orthophosphate, polyphosphate, and organic phosphate. The orthophosphates, for example, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, are available for biological metabolism without further breakdown. The polyphosphates include those molecules with two or more phosphorus atoms, oxygen atoms, and, in some cases, hydrogen atoms combined in a complex molecule; they undergo a quite slow hydrolysis in aqueous solution and revert to the orthophosphate forms. The organically bound phosphorus is usually of minor importance in most domestic wastes, but it can be an important constituent of industrial wastes and wastewater sludges (MSU, 2008). When plant materials and waste products decay through bacterial action, the phosphate is released and returned to the environment for reuse.

Much of the phosphate eventually is washed into the water from erosion and leaching. Again water plants and algae utilize the phosphate as a nutrient. Studies have shown that phosphate is the limiting agent in the growth of plants and algae (Cech, 2003). If not enough is present, the plants are slow growing or stunted. If too much phosphate is present excess growth may occur, particularly in algae.

A large percentage of the phosphate in water is precipitated from the water as iron phosphate which is insoluble. If the phosphate is in shallow sediments, it may be readily recycled back into the water for further reuse. In deeper sediments in water, it is available for use only as part of a general uplifting of rock formations for the cycle to repeat itself. Human influences on the phosphate cycle come mainly from the introduction and use of commercial synthetic fertilizers.

Plants may not be able to utilize all of the phosphate fertilizer applied. As a consequence, much of it is lost form the land through the water run-off (Figure 2.13). The phosphate in the water is eventually precipitated as sediments at the bottom of the body of water. In certain lakes and ponds this may be redissolved and recyled as a problem nutrient. Animal wastes or manure may also be applied to the land as fertilizer. If misapplied on frozen ground during the winter, much of it may be lost as run-off during the spring thaw. In certain area very large feed lots of animals, may result in excessive run-off of phosphate and nitrate into streams.

Other human sources of phosphate are in the out flows from municipal sewage treatment plants. Without an expensive tertiary treatment, the phosphate in sewage is not removed during various treatment operations. Again an extra amount of phosphate enters the water.

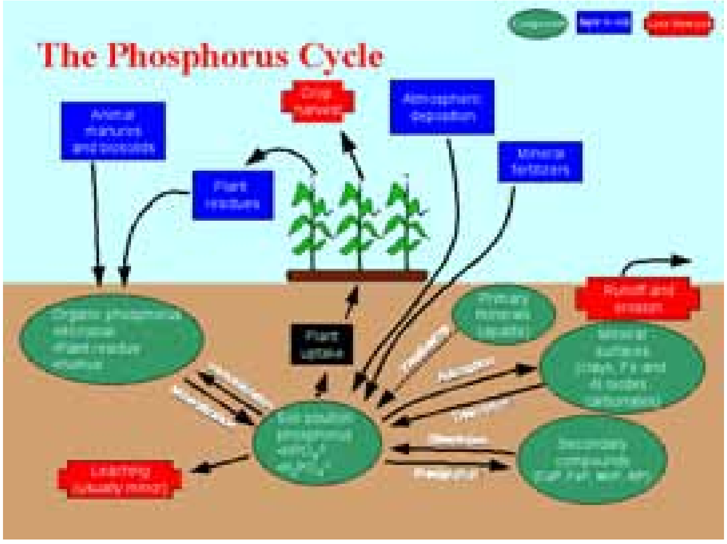


Figure 2.13. The phosphorus cycle (source: MSU, 2008)

At this point, the required revision on the parameters commonly used to characterize water quality is concluded. It has been developed along section 2.4 because, as indicated at its beginning, all those water quality features need to be clearly stated to go further in the analysis. The nitrogen and phosphor cycles have been quite in detail explained because of its high importance within the water cycle. Nitrogen and Phosphor compounds will be measured in the sampling stations along the river stream and they will be the basis for the exergy assessment. Understanding the successive transformations of those compounds facilitates the definition of the background parameters in the study.

Being already concern about the human effects on water, next 2.5 section is devote to describe the main water uses (demand, consumption and quality), and to put them in relation with the existing water scarcity and degradation.

2.5. Water uses, scarcity and degradation

Individual human bodies are 70% water. An average adult normally takes in two or three litres of water per day, mostly though drinking and eating. A similar amount is released mainly through urine, sweat and respiration. People begin to feel thirsty after a loss of only 1% bodily fluids and risk death if fluid loss nears 10% (Bansil, 2004). These figures highlight how important is water for human life. However, water is used for many other purposes further than survival.

Attending to the final water use in different world regions, the current water allocation can presented (Figure 2.14). There is increasing competition for water among the various water use sectors in many river basins. When the water demand by industry is compared to the two other main sectors, it is evident that industry uses only a fraction of the amount of water used by agriculture.

However, in East Asia and the Pacific, industrial water use has grown to a significant proportion of total use, in line with its significance to the economies of those countries. In sub-Saharan Africa, although overall water use is low, the water used by industry is a larger proportion of the total, because more agriculture is rainfed, rather than irrigated. These data exclude rainfed agriculture from the calculations of water use, and do not include environmental flow requirements as a water use category. In many catchment areas and river basins, environmental needs have not yet been calculated (UN-WWAP, 2006).

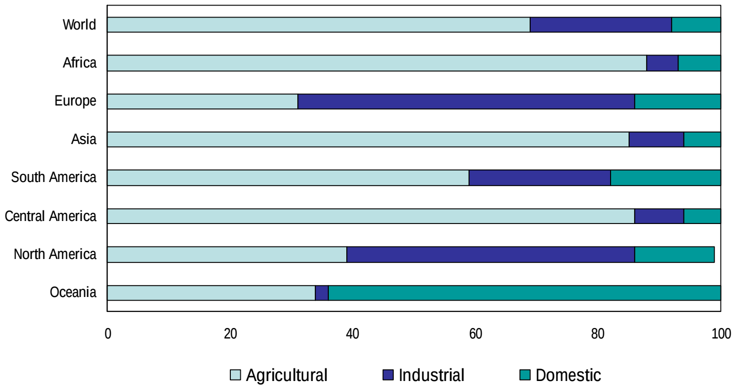


Figure 2.14. Water use by agricultural, domestic and industrial sectors (Source: UN-WWAP, 2006)

Withdrawal is defined as the *removal* of freshwater from water resources or reservoirs for use, while water consumption is understood as the *use of water by humans* from natural water resources or reservoirs for agriculture, industry or domestic purposes.

It is convenient to underline the return rate associated to each water use, that is, the difference between the demanded catchments and effective water consumed. Those water flows returned to surface and groundwater must be accurately depicted, in order to have the complete picture available. A realistic water balance for a given river basin or country be then prepared. Analyses of recent trends show, that under conditions of an increasing deficit in water resources, considerable changes have been observed in World water management practices. These are associated, first of all, with the development of the price of water resources and the need to preventing environmental degradation (Shiklomanov and Rodda, 2004). These trends are observed in charges in water use across the main sectors.

Urban and industrial water uses do not represent high water consumption and their return factor is usually taken as 95-98% or even 100%. Nevertheless, some other more conservative sources indicate return rates of 90%, 86% and 30% respectively for industry, municipalities and agriculture (Alcamo et al., 2000; EPRI, 2002; Martínez-Beltrán and Koo-Oshima, 2004). In the simulation model that will widely described in Chapter 6, no water consumption for these users has been assumed.

Agriculture consumes more water by far than any other societal use. Water is needed by plants in photosynthesis to form carbohydrates, the basic food supply of all life. The case of agricultural uses is quite different because only a part of the irrigation water comes back to the same watershed. The return rate is high, but so is (generally speaking) the uncertainty about return pathway as well. In this work, 10% of return flow in the same watershed is considered. If the boundaries of the analyzed system where enlarged, the complete IBC instead of isolated watersheds, the whole irrigation *missed* water could be better considered.

The proportion of water used in each sector changes over time. While the vast bulk of water is currently withdrawn for and consumed in agriculture, an increasing proportion of water is being taken for urban and industrial uses. Economic forces, and priority of uses in case of drought drive this switch (Shiklomanov and Rodda, 2004).

The difference among water withdrawal and water consumption are shown in Figure 2.15, for the different water users.

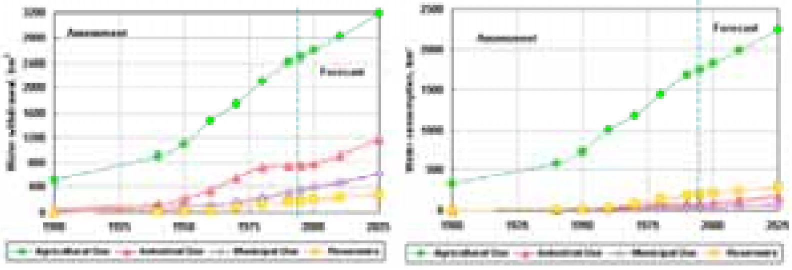


Figure 2.15. World water withdrawal and water consumption along the years, for different water uses (Source: UNEP, 2008)

Following major growth between 1960 and 1980, water withdrawal for use by industry worldwide has pretty much stabilized. Industrial water withdrawal in Europe has actually been dropping since 1980, although industrial output continues to expand. In Asia, the growth in industrial water withdrawal was rapid up to 1990, and has since then been growing much more slowly, despite the region's high growth in manufacturing output. The intensity of water use in industry is increasing in these regions, as is the value added by industry per unit of water used. In the industrial sector, the biggest share of freshwater is stored in reservoirs and dams for electrical power generation and irrigation. However, one of the greatest contributions to water losses around the world is the volume of water evaporated from reservoirs. Industrial uses account for about 20% of global freshwater withdrawals. Of this, 57-69% is used for hydropower and nuclear power generation, 30-40% for industrial processes, and 0.5-3% for thermal power generation (Shiklomanov, 1998).

However, the biggest user of freshwater is the agricultural sector. It agriculture accounted for 67% of the world's total freshwater withdrawal, and 86% of its consumption. By the year 2000, approximately, the 15% of the world's cultivated lands had been irrigated for food crops, accounting for almost half the value of global crop production (UNEP, 2009).

Agriculture is expected to increase its water requirements by 1.3 times, industry by 1.5 times, and domestic consumption by 1.8 times, by 2025 (Shiklomanov, 1999; Alcamo et al., 2000). Freshwater use by sectors at the beginning of the 2000s is summarized in Figure 2.16.

Figure 2.16. Freshwater use by sector at the beginning of the 2000s. (Source: UNEP, GRIDA, 2009)

As a particular part in the industrial use of water, hydropower has to be analyzed. Water is a key resource for energy generation, primarily through the use of hydroelectric power, but also in nuclear-based energy generation, coal slurry technology and small scale hydroelectric schemes, among others.

In 2000, one-third of the countries in the world relied on hydropower for more than half their electricity supply, and large dams generated 19% of electricity overall, although its importance varies from country to country. Twenty-four countries generate more than 90 percent of their electricity through hydropower, whereas others generate none at all. In the developed world, roughly 70% of hydroelectric power generation potential has already been developed; in the developing world, only about 10% (WEC, 2007).

Europe makes use of 75 % of its hydropower potential, while Africa has developed only 7 percent (Figure 2.17). This is viewed as a possible cornerstone of Africa's future development, with significant export potential and plans to establish a continent-wide electricity grid.

Hydropower brings flexibility to a national network grid, due to its ability to meet sudden demand. Run-of-river hydropower stations - from large to small - are clean, affordable and sustainable renewable energy providers. However, hydropower projects involving large reservoir construction fall into a different category. There remains considerable difference of opinion worldwide as to whether they should be classified as renewable energy and if they should be prioritized by developing countries for investment.

Figure 2.17. Percentage of hydroelectricity generation of the total by country. (Source:UN-WWAP, 2006)

For hydropower, dams are needed. In 2000, there were over 45,000 large dams worldwide (Figure 2.18). According to the International Commission of Large Dams, a large dam is one with a height of 15 m or more from the foundation, or a height of 5 to 15 m with a reservoir volume of more than 3 million m^3. Half of the world's existing large dams are built strictly for irrigation, while the remainders are built for hydro generation, water supply and flood control.

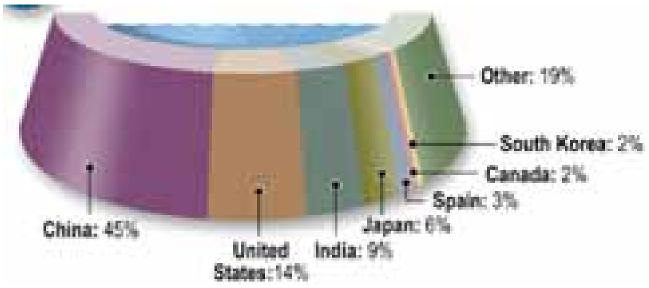


Figure 2.18. Distribution of large dams worldwide. Shown as a percentage of total large dams worldwide. (Source: ICOLD, 2008).

In the mid-1990s, there were 2,836 reservoirs with a storage capacity greater than 0.1 km^3 and a combined total volume of 6,384.5 km^3.

2.5.1. Main water uses

After the general vision given above, particular aspects about water uses are revised in the following sections. Demand, use and quality will be the field covered in each of them.

2.5.1.1. Municipal water use

Municipal or urban water use includes abstraction of water and its treatment and distribution mostly for domestic purposes to cities and towns and to public and private enterprises. The public supply also includes water for industry, which consumes high quality fresh water from the city water supply system. In addition to that, much of the domestic consumption in certain countries is for watering lawns and gardens, and car washing (Cech, 2003).

a. Water demand for municipal use

The volume of municipal water use depends on the number of people served and the degree to which they are equipped with services and utilities, i.e., the availability or unavailability of pipelines and conduits and a centralized hot-water supply. It also depends considerably on the climate conditions. Usually 150-250 l/day per head of water (including 2.5 - 3 l for drinking water and water for cooking) are considered to be sufficient to meet all personal demands. For operation of municipal enterprises and maintenance of cleanliness and hygiene in cities, additionally 150 to 200 l/day per head are required. Water use above these values is usually due to demand by industry and for garden-watering. In small towns and villages without effective distribution systems, water use is in the region of 75 to 100 l/day per head (Shiklomanov and Rodda, 2004). Data provided by UNESCO (2000) coincide with those mentioned values and indicate that: the average person in developed countries uses 500-800 litres per day (300 m^3 per year), compared to 60-150 litres per day (20 m^3 per year) in developing countries. Consumption can reach 40-60% of the total water intake.

Some countries have developed different designs for municipal water supply. For northern countries water supply norms are less, while for southern countries with hot dry climates they are considerably more. In some countries the norms of municipal water supply depend on the population served and on the sphere of activities. For example, in Japan, the water consumption is 150-300 l/day per head and this increase to 400-500 l for large cities with a population above one million. In addition there may be some variation for water in volume (between 5% and 10%) if there are large demands for water for a particular industry. These norms correspond, in general, to actual water use in many modern cities, where they are 300-600 l/day per head (Gleick, 2008).

Due to increasing urbanization, and a rising standard of living, together with higher cultural levels, more and more water is abstracted in most countries to meet municipal needs. A volume of 1000 l/day per head is assumed to be the maximum urban water supply in a hot climate where a complete range of domestic devices are available and where no restrictions are imposed on water use for swimming pools, garden-watering and car-washing. A figure of 600 l/day would apply in a moderately warm climate (Shiklomanov and Rodda, 2004). As an example, in Russia, at the beginning of the twentieth century, in the populated areas, piped water consumption was 15 to 30 l/day per head. At the present time, most of the population of Russia uses 300 l/day per head.

In the developing countries of Asia, Africa, and Latin America, the public water service supplies 50 to 100 l/day. Where water resources are under stress, it is usually not more than 10 to 40 l/day per head (Shiklomanov and Rodda, 2004).

The volume abstracted and the size of the population usually determines the total volume of the water used in public services. Annual values of municipal water supply are given in many national and international publications (for example, the World Resources Institute, WRI, or the World Bank, WB).

b. Water consumption in municipal use

When calculating the water balance, the values of water consumption for public services and water diversion volumes are very important. With an effective sewage system, the greater part of the water put into the supply system is returned as waste water (treated or not) to the rivers. A large part of the water consumed consists of water losses due to evaporation, leaks in the water supply and sewerage systems, and that water used for watering gardens, cleaning streets, for recreation, areas, and allotments (Marecos et al., 2007). In hot dry regions, the losses are certainly larger than in cold and humid ones. The water consumed for human use is often insignificant as compared with water losses due to evaporation in these areas.

The loss of water expressed as a percentage of water abstracted depends to a considerable extent on the volume abstracted. In modern cities equipped with public, well- managed and relatively news systems for water supply and sewage disposal, losses can be between 5% and 10% of the total intake water. For small cities with a large number of individual buildings not fully provided with such systems, losses can reach 40-60% of the water intake. Again, these losses are less in colder areas and higher in warmer ones.

In the developed world, most towns and cities and many rural areas are now provided with water supply and sewage systems maintained by municipal, public and private bodies. In the future, the demand for water is expected to increase, and the losses to decrease (Shiklomanov and Rodda, 2004). These conditions have to be taken into account in the forecasts of water use.

c. Water quality for municipal use.

In addition to the changes in quantity and quality of water resulting from domestic use in cities, the mere migration of water through a city in its transformation from precipitation to stream flow can significantly alter water timing, temperature and chemistry. Storm water flows over impervious surfaces such as roads, rooftops and parking lots. In the process, there is little potential for runoff to percolate into groundwater tables, but a great deal of potential for the water to absorb heat from paved surfaces and to entrain pollutants, such as oils and heavy metals, from contaminated surfaces. Large fluxes of polluted storm water can also trigger releases of raw sewage into receiving water bodies in cities where a single sewer system conveys both storm water and domestic waste. Sudden releases of polluted urban wastewater pose danger both for human health and for aquatic life.

In relation to legal aspects, the Council Directive 75/440/CEE, of 16 June 1975, concerning the quality required of surface fresh water intended for the abstraction of drinking water in the Member States, includes, in its *attached 2*, values of forty-six water parameters (as colour, temperature, NO_3^- , Fe^{2+}, or Cl^-). Some of them are mandatory (they must be assured for drinking water in the 95 % of the analyzed water), and the others are guide water parameters values. However, some exceptions will be considered if the parameters values are modified by inundations, or other meteorological disasters.

2.5.1.2. Water use by industry and for power production.

Water is used by industry in a myriad of ways: for cooling the equipment, mechanisms and instrumentation heated in the production process; for transportation and washing; as a solvent; for generating steam; in some industries it is a part of the composition of the finished product and as a constituent part of the product itself (e.g. in the beverage industry).

Some water is used for maintaining the necessary sanitation and for meeting the standards of hygiene in the workshops and in other parts of the different industries enterprises and for meeting the demands of the working personnel. The largest industrial use of water is in the generation of electricity in thermal and nuclear power stations (UN-WWAP, 2006). Here vast amounts of water are needed for cooling and smaller volumes to feed the steam cycles.

a. Water demand for industry use

The power industry is the second highest user of fresh water after irrigation among the different sectors. The volumes of industrial water used differ not only for the type of industry, but they also depend on the technology of the manufacturing process and also on climatic conditions. Next to power production, the principal water users are the chemical and petrochemical industries followed by ferrous and non- ferrous metal, the wood pulp and the paper industry, and in machine-building (Shiklomanov and Rodda, 2004).

Coming back to the energy production, the amount of water needed to that production varies greatly with the type of facility and the characteristics of the fuel cycle. Fossil fuel, nuclear and geothermal plants require enormous amounts of cooling water. Solar photovoltaic systems wind turbines and other renewable energy sources often require minimal amounts of water. The generation of hydroelectricity generally consumes water only through evaporation from the reservoir. Regulation of rivers for electricity production can substantially alter the timing and volume of flows with substantial implications for the physical-chemical and biological structure of the ecosystem.

In studies of water used by industry, certain indices of water consumption such as one tonne of finished production, one kWh or one million euros, are used. Shiklomanov and Rodda (2004) provide numerous examples. Some of them are summarized here: for mining and enriching 1 tonne of ore between 2 and 4 m^3 of water is used; to produce 1 tonne of cast-iron 40-50 m^3, rolled metal 10-15 m^3, copper 500 m^3, and nickel 4000 m^3. Very much fresh water is used for wood pulp and paper, and for the petroleum industries. For example, to produce 1 tonne of cellulose some 400-500 m^3 of water is required, viscose silk 1000-1100 m^3, synthetic rubber up to 2800 m^3, synthetic fibre and plastics 2500-5000 m^3, capacitor paper up to 6000 m^3. For a thermal power plant with a capacity of 1 million kW between 1.0 and 1.6 km^3 of water is required per year. Even more water is required for nuclear power plants of the same capacity- some need 1.5 times as much, others twice and some 3 to 4 times as much. Vast quantities of water are needed for the thermal and nuclear plants of 3-5 million kW capacity and for the even larger ones which are being designed. For a wood pulp and paper plant producing 500,000 tonnes per year, some 435 million m^3 of fresh water are required, and for an average metallurgical plant about 250 million m^{3}area needed (Levin, 1973).

During the past two to three decades, industrial water use has risen sharply, largely because electric power production has grown. The production of synthetic fibres, artificial rubber and plastics has also increased, with a concomitant increase in demand for water.

The nature of industrial water use depends to a very large extent on the type of water supply scheme being used. There are two basic schemes: inflow and circulating. In the first, water is abstracted from the source and after use it is discharged either treated or untreated into the receiving waters. With the circulating system the used water is cooled, treated, and returned to the water supply system for reuse. The fresh water intake for a circulating water supply is small and only sufficient to make up for the water lost in the production process or to periodically replenish water in circulation.

Technological progress in industrial water use, in terms of the rational use of water resources, relies not only on the wider application of circulating water but also on the introduction of dry technology to the production processes. Additionally there has been progress to reduce water use: for example where water is used for cooling, to substitute air cooling. By these and similar means water use can be reduced by 50-70% in the different types of industrial processes (Shiklomanov and Markova, 1987).

The Global 2000 report (Barney, 1980) contains data showing that in 1977, that world total industrial water use was 805 km^3, including 502 km^3 for thermal power production (62%). Gleick (2008) estimated that in 1980, industry and thermal power production used 710 km^3 per year, including water consumption of 62 km^3 or 8.7% of the intake water. About 75% of the industrial water was used in Europe and North America. Analysis of changes in industrial water use over the last 30-40 year points to a considerable growth for the globe as a whole. However, in many developed countries beginning with the 1980s, the demand for water by industry has not increased and has even decreased in some.

Estimates of the future volume of industrial water use should take into account these differing trends. On the one hand, this volume should increase due to the growth of industry and power production. On the other hand, this increase is not directly proportional to industrial growth, because in most developed countries there is a tendency to use recirculating systems, and dry technologies. The total world water use by industry seems likely to increase, at least over the next 15 to 20 years. However, the rates of increase could be 1.5-3 times less than the increase in the volume of industrial production (Shiklomanov and Rodda, 2004).

b. Water consumption in industry use

The water that evaporates in the industrial process must also be considered in accurate assessments as well as the water that remains in the product, by-products, and the solid wastes generated along the way. The balance is discharged after use as wastewater or effluent. The total water withdrawal from surface water and groundwater by industry is usually much greater than the amount of water that is actually consumed, as illustrated by the graphs in Figure 2.15. Industrial water use tends to be measured in terms of water withdrawal, not water consumption.

The quantity of water actually consumed by industry is usually a small fraction of the intake water. However, it varies considerably depending on the type of industry, the nature of the water supply, the technology involved in the process, and the climatic conditions. In thermal power production, this quantity is about 0.5-3.0% of intake water. In most of the sectors on industry, it is 5-20% and it can reach 30-40% in certain instances (UN-WWAP, 2006). It is obvious that with the inflow water supply system, water consumption, expressed as a percentage of the intake water, is considerably less than with the circulating system.

The water losses incurred by industry and during power production can be divided, according to Shiklomanov and Rodda (2004), into:

- Losses due to the additional evaporation occurring when water is moved from its source to the enterprise concerned along with those taking place in cooling and during the discharge of the warm cooling waters into the river channel
- Losses by evaporation inside the enterprise during the manufacturing process
- Losses due to its inclusion of water in the finished product.

The second and third groups do not depend on climatic conditions, unlike the first, which is likely to be more significant for drier climates nearer the equator rather than for the more humid areas farther away.

c. Water quality in industry use

Frequently, the negative impact of industry on the water environment is of greater concern than the actual volume of water used. Water quality is deteriorating in many rivers worldwide, and the marine environment is also being affected by industrial pollution. Effluent discharges from some industries have harmful consequences for freshwater ecosystems through changes in water temperature increases in chemical oxygen demand (the quantity of oxygen required to break down artificial chemicals) and toxic pollution. It takes place because much of the water used by industry is usually disposed of *to drain*. As far the UN-WWAP (2006) understands the situation, this can mean:

- direct disposal into a stream, canal or river, or to sea
- disposal to sewer (which may be discharged, untreated, further downstream, or may be routed to the nearest municipal sewage treatment plant)
- treatment by an on-site wastewater treatment plant, before being discharged to a watercourse or sewer treatment in a series of open ponds.

Thus, industrial water use has in general more implication for water quality than quantity. In turn, the implications of industrial use for water quality depends greatly on the industry.

On the other hand, industries may require water that is cleaner than can be provided by the environment. In these cases, which involve *clean* industries such as microelectronics and pharmaceuticals, the wastewater discharged into receiving waters may be higher than the ambient water quality. The resulting improvement in water quality can benefit aquatic ecosystems when it removes anthropogenic pollutants from the water, where water quality is naturally unsuited for human consumption. However, improvements in water quality may be harmful to native ecosystems and the species that inhabit them. Many species, including most river dolphins, have evolved in water that is very high in suspended sediment loads, for example. Reduction of suspended sediments in these systems could improve water quality from a human perspective, while rendering the ecosystem uninhabitable for the wild species that evolved there (Hunt, 2004).

Apart from the general ideas summarized above, it needs to be point out that the rapid rise in water use by industry is one of the main causes of the growth of water pollution. This growth is explained, first, by the pace of industrial development generally and then by the growth of production of synthetic fibres and petrochemical products, wood pulp and paper; next, by the rapid expansion of thermal power production and the construction of power plants; lastly, by the increasing volume discharged as waste water. In most cases, these discharges are not treated or are only part treated, often resulting in the serious pollution of the receiving waters (Shiklomanov and Rodda, 2004).

The water used by thermal and nuclear power plants is discharged into rivers and lakes at a temperature some 8-12ºC above the ambient temperature (Shiklomanov and Rodda, 2004). This disturbs the natural thermal regime of these water bodies significantly, changing many natural processes and raising the profile of the so- called *heat contamination* problem.

There are many instances of water reclamation (treating or processing wastewater to make it reusable), where industrial effluent is not returned immediately to the natural water cycle after use. It can be recycled or reused directly on-site, either before or after treatment. The water may also be treated and then reused by other industries nearby or agricultural or municipal users, as well as for cropland irrigation or local parks and gardens. All these possibilities for water reclamation and reuse are dependent on the quality of the discharge. Reclaimed water that has been treated can also help to conserve the water environment by being injected to replenish underground aquifers or prevent salt-water intrusion or by being discharged into a drought-stricken wetland. This issue will be further developed in section 2.7.2.

Of major concern are the situations in which the industrial discharge is returned directly into the water cycle without adequate treatment. If the water is contaminated with heavy metals, chemicals or particulates, or loaded with organic matter, this obviously affects the quality of the receiving water body or aquifer. The sediments downstream from the industrial discharge can also be contaminated. Water that has a high organic content often appears cloudy or foamy, and is characterized by the rapid growth of algae, bacteria and slime (Cech, 2003). The growth of these organisms depletes the level of oxygen in the water. It is more difficult for fish, insects, amphibians and many species of aquatic plants to live and breed in such oxygen-depleted water. If the water discharged is still hot, this *thermal pollution* may also affect the aquatic ecosystems downstream, which have to adjust to a temperature that is higher than normal. A much larger volume of water may actually be affected than the volume of the industrial discharge itself.

Industries and water quality regulators in some places still rely on the so-called *dilution effect* to disperse contaminants within the water environment to the point where they fall below harmful levels. In areas where industries are growing fast and more industrial plants are coming on-stream with many newly created discharge points, this approach can quickly result in polluted rivers and reservoirs. The toxicity levels and lack of oxygen in the water can damage or completely destroy the aquatic ecosystems downstream as well as lakes and dams, ultimately affecting riverine estuaries and marine coastal environments. In international river basins, routine pollution and polluting incidents such as industrial accidents and spillages may have transboundary effects.

Significant pollution sources in river basins, such as large industrial plants, may be termed *hot spots* and prioritized for clean-up within a river basin management plant. Authors like Hernandez (2001) provide wide information about the change in water quality due to different industrial activities, depending on the productivity sector. Those figures will be used later on in this work to characterize the exergy degradation provoked by the different water uses.

2.5.1.3. Water use by agriculture

Far more water is used by agriculture than by any of the other sectors and most of this water is employed for irrigation. The demands of irrigation can place water resources under stress, particularly in dry years.

a. Water demand in agricultural use

The bulk of the world's agricultural production is rainfed, not irrigated (Shiklomanow and Rodda, 2004). Claims that agricultural production is threatened by global water shortages usually fail to note that most of the world's food production does not rely on freshwater withdrawals at all and does not necessarily accelerate the naturally occurring rates of evapotranspiration.

The largest share of the water uptake by plants is transpired back into the atmosphere through plants' leaves. In addition to its energy dissipating role, the transpiration process is necessary for lifting nutrients from -photosynthesis takes place. If soil moisture levels fall below the wilting point, plant growth slows and eventually stops, and the potential crop yield is not fulfilled. Irrigation aims at ensuring that enough moisture is available at all times during the plant's life cycle to satisfy its water demand, thus supporting maximum crop yields.

The concept of *blue* and *green water* has been used for quite some time to distinguish between two fundamentally different elements of the water cycle (see section 2.2). When atmospheric precipitation reaches the ground, it divides into several sections, which pursue the terrestrial part of the hydrological cycle along different paths. Out of a total annual amount of 110,000 cubic kilometres (km^3) of precipitation on the land surface, about 40,000 km^3 is converted into surface runoff and aquifer recharge (blue water) and an estimated 70,000 km^3 is stored in the soil and later returns to the atmosphere through evaporation and plant transpiration (green water). Blue water is the freshwater that sustains aquatic ecosystems in rivers and lakes; it can also be applied to drinking or domestic purposes, to industry or hydropower or to irrigated agriculture (UN-WWAP, 2006).

Rainfed agriculture uses only green water. Irrigation uses blue water in addition to green water to maintain adequate soil moisture levels, allowing the crop plants to absorb the water and fulfil their crop yield potential. The green water/blue water concept has proven to be useful in supporting a more comprehensive vision of the issues related to water management, particularly in reference to agriculture (Ringersma et al., 2003). It is estimated that crop production takes up 13% (9,000 km^3 per year) of the green water delivered to the soil by precipitation, the remaining 87% being used by the non-domesticated vegetal world, including forests and rangeland.

Out of the world's total land area of 13 billion hectares (ha), 12 percent is cultivated, and an estimated 27 percent is used for pasture. The 1.5 billion ha of cropland include 277 million ha of irrigated land, representing 18 percent of cropland. In population terms, cropland amounts to a global average of 0.25 ha per person (UN-WWAP, 2006). Figure 2.19 shows the evolution of cropland compared to population between 1960 and 2000, illustrating the huge productivity increase of agriculture during that period. The intensification of agricultural production made it possible to limit the expansion of agricultural land to a few percentage points as the population was more than doubling.

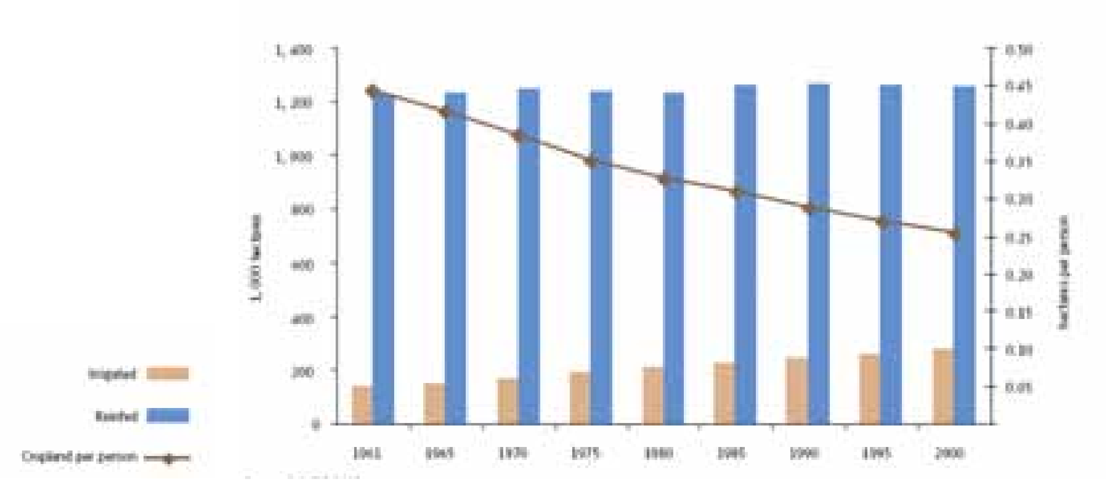


Figure 2.19. Evolution of cropland, 1961–2000 (source: FAOSTAT, 2005 cited by UN-WWAP, 2006)

During the twentieth century, the World population multiplied by three. At the same time, water used in irrigation increased sixfold. It was accompanied by the almost depletion of some major rivers. Specific management tools related to improved high-yielding varieties of cereals, irrigation, improved soil moisture utilization and the application of plant nutrients, pest control, where the talents of the named *green revolution*. As a result of those technology packages on good land in suitable socio-economic environments, the crop yields increased, as well as the incomes for millions of farmers, particularly in Asia. Statistics indicate that yields of rice, wheat and maize approximately doubled between the 1960s and the 1990s (UN-WWAP, 2006). The green revolution meant an important development, but it had also a negative face: fertilizers and agrochemical, based pest and weed control created environmental and health problems.

Along the second half of the twentieth century, while population rapidly increased, irrigation development became a core part of the strategy produce food. It meant, consequently an increase in the water consumption. As the food needs increase, the amount of land for agriculture is expected to grow. However, land has to be both suitable and available for conversion to agriculture. So, the options are limited.

b. Water consumption in agricultural use

While irrigation currently withdraws about 2,300 km^3 of freshwater per year from rivers and aquifers, only about 900 km^3 is effectively consumed by crops. As previously indicated, it represents about 60-70% of the water demand and 90% of the water consumption (Alcamo et al., 2000).

Rather than water use efficiency, the concept of water productivity is now widely accepted as a measure of performance in agricultural water use. By definition, productivity represents the output of any production process expressed per unit of a given input, in this case water. In agriculture, several types of output can be considered. In a strict commodity production vision, the output is usually expressed in volumes or value of a given agricultural production. However, productivity calculations are increasingly being extended to assess the water value of other outputs, including the social and environmental services provided by irrigation (Molden et al, 2003).

c. Water quality in agricultural use

It is quite difficult to define average values for the change in quality due to irrigation. It mainly depends on the kind of soil and on the crop. As an example, the more than 100,000 ha irrigated by the Bardenas Canal that originates in the Yesa Reservoir located in the Aragón River has an irrigation water of excellent quality (EC=0.32 dS/m; NO_3^- <2 mg/l) (Causapé et al. 2004)

Isidoro et al (2002) characterized the quality of drains water. The waste waters were characterized using an average small value conductivity (0.84 dS/m) and high nitrate concentration (54 mg/l). On the other hand, the values of some rivers used a higher average conductivity (0.97 dS/m) and a much more smaller nitrate concentration (27 mg/l).

Water that is available for reuse after application in irrigation often carries concentrations of agricultural pollution that render it unfit for many application –even for reuse in growing crops (Hunt, 2004).

Wastewater and water desalination constitute potential sources of water for agriculture and other uses. Technologies for tertiary wastewater treatment and desalination have very much in common. However, the cost of treatment varies depending on the type of treatment and the intended final use of product water. Treated wastewater reuse in agriculture is less expensive than is desalinated water. With its associated benefits, treated wastewater reuse also has problems in terms of public acceptance, and potential health and environmental risks.

Although the WHO and FAO have specified guidelines for wastewater reuse, no common standards have been set owing to difficulties in systematic implementation in countries around the world. For the reasons above, due consideration should be given to both the problems and benefits of wastewater reuse and water desalination.

The experts recommended wastewater treatment as a better option in sustainable development and the introduction of programmes to inform the public of the benefits of treated wastewater reuse. The group also suggested that hybrid solutions, a blend of wastewater plants coupled with desalination plants, may have a place in urban and peri-urban agriculture. However, of great importance is the setting of standards for the outflow quality of wastewater treatment plants and the associated effluent monitoring.

In relation with the suitability of desalinated water for crops, the Irrigation Water Salinity Index (IWSI) is defined by Cánovas (1986).

Eq. 2.5.
$$IWSI = \frac{\left[Na^{+}\right]}{\sqrt{\dfrac{\left[Ca^{2+}\right]\left[Mg^{2+}\right]}{2}}}$$

From Eq. 2.5, it can be concluded that a desalinated water have to be used carefully for crops. Since desalination efficiency is usually less than 100%, the remaining ions would be probably the Na^{+} (the smallest ones). Then, the IWSI would be infinity because the equation becomes $[Na^{+}]/0$.

On top of that, desalinated water is more expensive than conventional water resources and it is not affordable for most crops, although it might be affordable for high value crops, especially where subsidies on capital costs are provided.

Continuing with cost considerations, brackish water desalination is more suitable for agricultural production than is seawater desalination. Moreover, desalination facilities near the point of use are preferred in order to minimize transfer costs. In terms of operation and maintenance (O&M), small to medium plants are more problematic.

Finally, if desalinated water is used for agriculture, reverse osmosis (RO) is the best desalination technology because of the cost reductions driven by improvements in membranes in recent years.

Spain provides a significant example of the application of desalinated water in irrigation. Spain has more than 300 treatment plants (about 40 percent of the total number of existing plants) and 22.4 percent of the total desalinated water is used for agriculture. Most of these plants process brackish water (only 10 percent of the total desalinated water for agriculture originates from seawater) and are located in coastal areas or within 60 km of the sea (Martínez and Koo-Oshima, 2004). In this country, small and medium-sized brackish-water desalination plants, with a capacity of less than 1,000 m^{3}/d, are common because they adapt better to individual farmer requirements and to the existing hydraulic structures.

Desalination programmes are recommended to be integrated with water resources management, with application of best practices for water management (leaching requirements, and better irrigation methods) and selection of appropriate salt-tolerant crops. The optimal size and site of facilities should be studied, and better operating management of smaller plants is required (automatic plant operations, and farmer knowledge on operational processes).

2.5.2. Summary of quality for diverse water uses

Two main water quality parameters (conductivity and TOC) for different uses are collected in Table 2.14, in which the most relevant information in relation with previous sections has been summarized. Input water values (before use) and output water values (after use) can be shown in it.

	C (ppm)	COD (mg/l)
Dom.Low.in	32	50.75
Dom.Low.out	100	181.81
Dom. Medium in	32	50.75
Dom. Medium out	200	363.63
Dom. High in	32	50.75
Dom.High out	500	545.44
Irrig. None in	448	34.13
Irrig. None out	2,989	61.09
Irrig. Moderate in	1,000	34.13
Irrig. moderate out	6,400	61.09
Irrig. Severe in	1,920	34.13
Irrig. Severe out	12,800	61.09
Energetic in	1,920	140.0
Energetic out	2,240	232.7
Ind. Salt extract. In	960	50.8
Ind. Salt extract. Out	150	15,185
Ind. Gas product. In	960	50.8
Ind. Gas product. Out	937	272.7
Ind. Plastic in	960	50.8
Ind. Plastic out	50	45.4
Ind. Wash-mach. In	960	50.8
Ind. Wash.-mach.out	7,400	7,273
Paper Industry in	960	50.8
Paper Industry out	20	25.5
Fruits and veget. In	32	50.8
Fruits and veget. Out	1,944	5.5
Animal waste In	960	50.8
Animal waste Out	1,000	5,908
Ind. soap In	960	50.8
Ind. soap out	333	6,062

Table 2.14. Chemical features of the water before and after different common uses. (Sources: Metcalf and Eddy, 2003; Hernández, 2001; Causapé et al., 2005.)

Domestic input water quality parameters (potable/drinkable water parameters) are standard, irrespective of the kind of population nucleus. However, more output contamination/pollution can be considered in the urban ones.

On the other hand, irrigation water values have been divided into three groups, using different degrees of use restriction, since it is the most common standard quality parameters division found in bibliography. On top of that, many examples of different crops are available, and their individual study seems to be endless.

Because some of the most problematic output irrigation water parameters are conductivity, or nitrates, the TDS increments are very high, and the TOC can be considered almost constant.

Energetic water use (for cooling water or steam generation) input parameters are shown less restrictive than the preceding ones.

Finally, some examples of different industrial uses are included. Fruits and vegetables industry input parameters are the same as the domestic ones, since this kind of industry is a food manufacturer.

Recall that in some industrial uses examples, output conductivity is bigger than input conductivity. Nevertheless, it can be assured that this is a coherent affirmation in some of them, for instance, the salt extraction industry example.

2.6. Water demand management

A basic idea within the water management world, is the distinction between supply enhancement and demand management. Whenever water demand exceeds water supply, there are two general methods for addressing the problem: it may be either carry out alternative designed to enhance water supply, or pursue approaches meant to control and manage demand. The first harnesses another water source in some way, and the second invokes ways to operate within the limits of current supplies (Griffin, 2006). Of course, we can jointly undertake both types of measures, and this is normally best. Examples within each category are listed in Table 2.15.

Supply Enhancement Strategies	**Demand Management Strategies**
Build/enlarge dams	Establish water-conserving plumbing
	codes requiring certain fixture types
	(such as low-flow toilets and showerheads)
Drill/imrove wells	Establish contingency plants
Build interbasin water transfer facililities	Ration water or constrain water use
Repair leaky infraestructure	Buy/Lease/sell water rigths
Build desalination plants	Raise water rates
Reprogram reservoir operations	Educate population about conservation options

Table 2.15. Supply and demand strategies. (Source: Griffin, 2006)

Supply enhancement has dominated water resource planning in the modern era, but this dominance has been suspended in many developed countries. Traditional forms of supply enhancement have run much of their course, because fresh water supplies are physically limited. New dams and wells generally deprive water from some existing or future category, even if it is estuary inflows, which have become increasingly valuable due to great amount of human diversions of water from its natural courses. Moreover, these forms of supply enhancement are much more expensive than they have been in the past.

As the role for supply enhancement has ebbed, the opportunities of demand management have simultaneously increased. While individual demand management options lack the scales of supply enhancement facilities, and they are certainly not viewed as the monuments to human achievement that our dams have become, demand management strategies are powerful tools for balancing demand and supply.

Conserving available water and reducing demand is a necessary measure in water-short regions, especially those in arid climates. Water demand management (WDM) programmes select economic incentives to efficiently promote the responsible water use; they identify water conservation measures aimed at raising society's awareness of the resource. Such tendency differs from the traditional supply driven method, which makes all existing water available.

In those places where water was traditionally perceived as abundant, no WDM programmes have been implemented. Nevertheless, the benefits in the extended useful life of water supply and treatment plants and in the operating efficiency and duration of sewage disposal systems can be considerable in terms of higher economic return on investment (UN-WWAP, 2006). Water demand management meant to be the strategy that stresses on making better use of water already mobilised, thanks to a reduction in physical and/or economic waste. Typical phases when strategy is to be applied are: flow control, loss control, supply versus demand policy, metering, pricing, training, legislation, etc.

The increasing scarcity of water sources to meet societal demands is translated into the inclusion of planned water reclamation, recycling, and reuse in water resources systems.

WDM advocates a wide range of measures that go beyond conservation to broader sustainable resource management. It applies to the protection of water quality sources; reduction of wastage both in infrastructure leakage and by users; improvement of water allocation among competing uses, and creation of appropriate pricing mechanisms. One example of a situation where conservation measures are needed is the case of *undelivered water,* a commonly accepted result of utilities supplying water through piped distribution systems: losses are routinely reported as 40% and as high as 60 to 70% in some major cities (UN-WWAP, 2006).

By reducing leakage and demand, substantial reductions in the source volumes could be achieved. This should be a clear message in development settings. WDM may obviate the need for some of the proposed large-scale physical or infrastructure investments and thereby provide real efficiency gains to society (GWP, 2005a).

In the management of a sustainable industry sector, it is crucial the integration of water management. In addition, such a practice links environmental and economic outcomes. The management will very much depend on the activity, although water is present in an important amount of processes. In general, the most common actions to be implemented within the water consumption are the water balance, the environmental audits and the operational performance reviews. They all can help operational sites to develop specific solutions; the identification of the best technology to improve the process is fundamental.

Industry pays for potable water at processing plants and it generates wastes that pollute it. Reduction of water use through stromwater collection, general recycling or reclamation of used water is an appropriate method to reduce cost and water usage.

Agriculture and irrigation, the main water user sector on a global scale and there exist an increasing pressure for water to be used more efficiently. Demand reduction and modernization of irrigation systems are basic actions that are being implemented in agricultural water management.

2.7. Water supply technologies

The world's population growth will mean an increased need for water to meet various needs, as well as an increased production of wastewater. In addition to the common water supply from surface waters and aquifers after a proper treatment process, desalination and reuse are starting to play an important role in modern water supply systems.

In the following, a review of the current available technologies is developed. It is quite relevant to highlight that each option has to be carefully analyzed within its boundary conditions, specially its location and surrounding infrastructure.

Many communities throughout the world are approaching, or have already reached, the limits of their available water supplies; water reclamation and reuse have almost become necessary for conserving and extending available water supplies.

2.7.1. Water treatment plants

Two different types of water treatment plants, the most common ones, are considered here: plants for water potabilization and wastewater treatment plants.

2.7.1.1. Potable water plants

The first step in acquiring safe drinking water is to protect raw water at its source. Watersheds used for municipal water sources often have restricted land uses, recreational activities, and development controls. Water providers must limit erosion of sediments, body contact sport such as swimming and water skiing, and waste disposal in such areas.

The second step in acquiring drinking water is to divert it from a river, reservoir, or groundwater. Intakes are the permanent connecting structures (pies, cement conveyance structures, etc.) that capture raw water and transport it to a drinking water treatment facility. The intake of a groundwater well includes the screened well casing in the aquifer and a piping system that delivers groundwater to the treatment land or end user. The intake for surface water sources can include a diversion dam and head gate on a river, or pipes that divert water from a reservoir. Water intakes at reservoirs are usually located at different depths to obtain varying water temperatures and suspended sediments. Intakes are generally not placed near the water surface to avoid floating debris, or at locations that could collect bottom deposits. Drinking water sources can be intermingled to improve the temperature and water quality of raw water provided to the treatment plant from multiple sources.

Pretreatment

In pre-treatment of drinking water, once raw water is delivered to a water treatment plant through an intake pipe, pre-treatment usually occurs in large tanks or small reservoirs where a variety of water treatment steps begin. Pretreatment is particularly useful if water is diverted from a river that has high amounts of suspended sediments.

Screens are fist used to remove large floating items, fish, fine solids, and other objects. Next, water is allowed to stand in tanks or reservoirs to promote sedimentation whereby larger silts, fines, and clay particles settle out of suspension. Afterwards, treatment starts.

Treatment

The steps considered in the treatment are: flocculation/coagulation, filtration and the final drinking water treatment. The sources consulted for the elaboration of this treatment summary were, mainly, the works of Cech (2003), Metcalf and Eddy (2003), Klein et al. (2005) and Surampalli (2004).

a) Flocculation/coagulation.

It is the next step in drinking water treatment, and is the process of adding chemicals to water to cause very fine suspended matter to settle out. Chemicals, such as aluminium potassium sulphate, activated silica, clay, and soda ash have been found to assist in this process when agitated (flash mixing) into raw water. A precipitate of almost gelatinous particles will usually coagulate within 10 to 30 minutes after the chemicals are added. This coagulation of fine suspended matter is called flocculation and will gain enough mass and weight to settle out of the water as sludge.

The main objective of flocculation and coagulation is the formation of clear water that has flocculation visible and in suspension. This process can remove approximately 90 to 99 percent of all viruses present in water, although prechlorination and preozonation may be necessary if excessive organic material is present. Viruses are not actually killed during this process; instead they are contained within the settled floc and sediments, which are later removed.

Concrete or steel sediment basins, generally 2.4 to 6.1 m deep, are used to hold water during the flocculation/coagulation process. Pretreated water continuously flows through these tanks. Sludge, created by settling flocculation, is generally removed from the bottom of the sediment basins every six months.

b) Filtration

Filtration follows flocculation and coagulation, and is the process of passing water through layers of sand and gravel to eliminate turbidity, odour, and colour. The most common method of filtration is the gravity rapid sand filter in which water is passed through beds of sand. Some drinking water plants can eliminate the need for flocculation and coagulation if the raw water is obtained from protected (clean) sources of surface or groundwater.

Filtration is a relatively simple process. Raw or pretreated water is slowly sprayed or sprinkled onto filtering media (sand). Gravity forces water through the sand particles until it exits the bottom of the media: Filtered water is conveyed to a storage area for additional treatment (pH, fluoridation, and disinfection).

Filters can become clogged with sediments and other particulates, and must be backwashed (flushed) occasionally to remove unwanted materials. The backwashed material is considered waste and must be drained into the sewer system for treatment before being released back to rivers, lakes, or other water bodies. Improper backwash techniques can allow pollutants to contaminate a drinking water system.

c) Final Drinking Water Treatment

Alter filtration is completed, water is placed in holding basins where fluoridation, and disinfection can occur. Fluoridation is considered a preventive medicine program to improve the health of teeth. Sodium fluoride (NaF) is generally used in this process. Chlorine gas is a common method of disinfection, called chlorination. The gas is mixed with water to kill remaining bacteria and some viruses.

Chlorine odour and taste are common complaints of drinking water customers; activated carbon treatment can help reduce these complaints. Since chlorine is very toxic, safe storage and handling of the chemical at water treatment plants are extremely important. Chlorine compounds were used as early as the 1830s to eliminate foul smells.

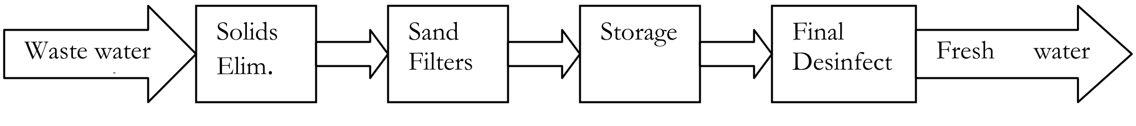
Ozone gas and ultraviolet (UV) systems may also be used in this final stage of water treatment to eliminate remaining bacteria and viruses. Ultraviolet treatment kills almost 100 percent of all microbiological organisms in water, but it is a very slow and expensive process. pH and corrosion control also occur at this stage of drinking water treatment by adding chemical such as lime and soda ash. However, it is necessary to add an excess of 0.3-0.5 mg/L of chemical substances, because of its evaporation in the urban supply circuit, and its necessary to use chlorine, since O_3 leaves water and does not persist time enough into the water which is being supplied using pumps.

The Council Directive 75/440/CEE, mentioned previously, includes, in its attached 2, quality values required for surface fresh water intended for the abstraction of drinking water in the Member States of forty-six water parameters (as colour, temperature, NO_3^-, Fe^{2+}, or Cl^-).

Three water quality levels are defined. Level A1 (very high quality waters), A2 (medium quality waters) and A3 (low quality waters). Each of them includes different treatment and phases, which are summarized in Figure 2.20, for A1 and A2. Intensive treatment, A3, is similar to A2 treatment scheme. However, includes two steps of oxidation, before the mix chamber and after the sand filters.

Drinking water treatment facilities are generally located at the highest topographic location in a city to allow treated drinking water to be delivered to customers by gravity.

A1 water treatment:



A2 water treatment:

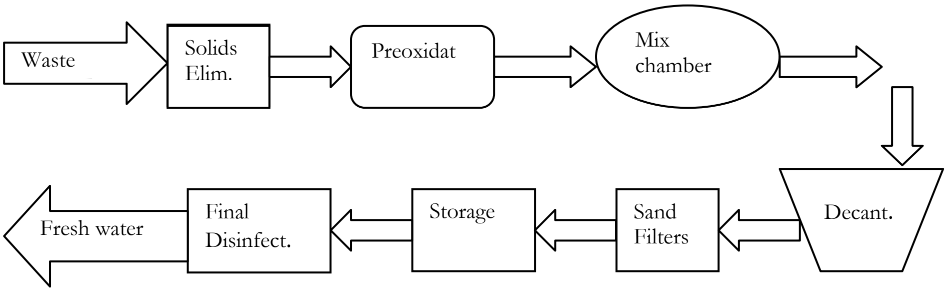


Figure 2.20. Potabilization treatments for different water qualities. (Source: adapted from Directive 75/440/CEE)

2.7.1.2. Wastewater Treatment Plants

Large-scale treatment of waste water became commonplace during the twentieth century. Wastewater facilities are generally located at a geographic low point in the topography of a city so that most wastes flow by gravity to the wastewater treatment facility. Areas that cannot be served by gravity require pump stations to lift wastewater to the treatment plant.

Complete sewage treatment includes three steps: primary, secondary, and tertiary. Primary treatment involves little more than removing suspended solid materials from wastewater and the returning liquids to a stream. Secondary treatment removes suspended solids and a larger percentage of organic matter. More elaborated systems (usually found in larger cities) include a third cleansing step called tertiary treatment. The numerous steps existing in large facilities are shown in Figure 2.21. All combine to remove biosolids and, ultimately, to discharge treated effluent back to a river, lake, or other water body.

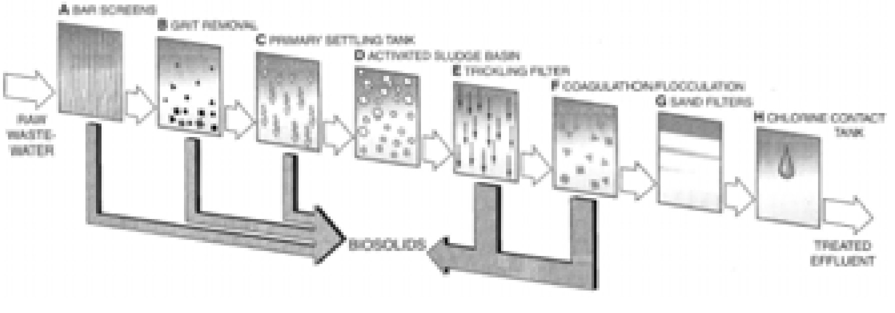


Figure 2.21. Wastewater treatment process (Source: Cech, 2003).

Primary treatment

Primary treatment includes screening, sand removal, and primary settling. Raw sewage that arrives at treatment plants contains floating materials (wood, paper, grit, oils, etc.) that must be removed early in the treatment process to protect mechanical equipment such as pumps and aerators and to prevent blockage of pipes. These materials are extracted with mechanical rakes or revolving screens. Since these contaminants contain potentially hazardous materials, they are discharged into containers and disposed of by incineration or are transported by truck to a landfill site. Efficient screening is extremely important in the wastewater treatment process.

Water then moves into a grit chamber to allow cinders, sand, and small stones to settle to the bottom. Grit chambers are particularly important in communities with combined storm drainage and sewer systems where stand and gravel can wash into sewers after storms. Wastewater next enters primary settling tanks that are used to remove suspended solids that settle as sludge. This process is very similar to drinking water sedimentation. Time is allowed for remaining grit and other suspended particles to settle from the wastewater, and chemicals can be added to accelerate this process. Wastewater floes into the thanks at a constant rate so that heavier solids are deposited at the inlet end and lighter solids settled out at the outlet end. The bottom of settling tanks is usually a V-notch design (an inverted pyramid) which allows sludge to be mechanically scraped off the bottom of the tank. Radical (circular) settling tanks have floors that slope toward the center of the tank (an inverted cone) for easier sludge removal.

Secondary Treatment

The purpose of secondary treatment is to reduce the demand for dissolved oxygen (BOD) that wastewater will place ion a waterway after discharge. This reduction in BOD is done by the aerobic oxidation of nutrients in the water. Microorganisms are used in this denitrification process to consume nutrients that would act as food for dissolved oxygen in rivers and other water bodies.

There are two types of secondary treatment processed; trickling filter and activated sludge systems. Aerobic microorganisms are used in both to decompose organic materials. BOD levels are high in these processes so that aeration of effluent is continuous.

Another secondary treatment method is the activated sludge process. Effluent is constantly agitated and aerated to assist in bacterial activity. The sludge contains large numbers of aerobic organisms that digest organic material. Microorganisms that grow transform the organic material into new bacteria. Carbon dioxide, and water.

The primary function of the activated sludge process is the removal of material that requires dissolved oxygen, or biological oxygen demand. Sludge flocs also promote good settlement in secondary sedimentation tanks. Flocs are continually flushed from the tank to make for influent. Some flocs return to the activated sludge tank to provide sufficient bacterial growth to reduce BOD.

The remainder of the floc is removed as sludge. Oxygen is required by microorganisms and is provided by mechanical aeration (agitation or stirring) or by the diffusion (release) of air at the bottom of the tank. Air bubbles automatically form and create currents in t he wastewater as the buddles rise to the surface of the tank. This air/liquid interface is an efficient method of transferring oxygen to water.

Microorganisms play a large role in wastewater treatment. These microorganisms consume nutrients and pathogens if pH, temperature, flow rates, and dissolved oxygen are closely monitored by the plant operator. Bacterias grows best in a narrow range of pH near neutrality, about 6.5 to 7.5. The other requirement for bacterial growth is the availability of carbon.

Trickling filters are rectangular or circular beds filled with coarse media or rock and gravel diameters of 5 to 10 cm. Wastewater is sprayed on the surface and trickles down the filtering rocks until it reaches a drain system at the base of the filter system. A microbial film will develop on the surface of the coarse media and remove BOD as sewage trickles through the bed. Since no straining of particles occurs, this filtering treatment is strictly biological.

Air must also be distributed through the filtration system to promote aerobic oxidation. Air circulation is encourage by the temperature differences between the air and wastewater, and causes upward air movement in tubes located at the sides of the filtering systems. Circular trickle systems have a rotating pipe that sprays effluent onto the surface of the coarse rock media. Rectangular trickle systems have a distributor (pipe) that is driven forward and backwards across the media surface to spray effluent for treatment. Depth of these filtering systems is usually 1 to 4 m. Trickling filters are relatively simple and inexpensive to operate and are widely used. Disadvantages are the substantial land areas required, fly and odor nuisance, and the removal of only approximately 80 percent of organic matter from water. (Horan, 1990).

Tertiary treatment

Effluent from secondary treatment contains only 5 to 20 percent of the original quantity of organic matter and is generally discharged safely into rivers or lakes. However, nitrates and phosphates may still remain and can require tertiary treatment. Tertiary treatment is very expensive since it involves physical and chemical methods such as flocculating chemicals, denitrifying bacteria in sand filters, and chlorine to remove additional contaminants. Ultraviolet lights are also used in some plants instead of chlorine since chlorination can combine with methane gases under some conditions to form carcinogens. A dense network of UV lights placed across the effluent will further disinfect wastewater

Wastewater effluents are major source of nutrient pollution in waterways around the world. (EPA, 2001) Municipal effluent can cause problems with algal blooms and eutrophication if ammonia or nitrates are present. Nutrients can be removed during the wastewater treatment process, through ammonia stripping, additional chlorination, and selective ion exchange. However, these processes can be very expensive, unreliable, and unpopular.

The most common nutrient treatment is the use of natural nitrogen removal processes of the nitrogen cycle. The bacterial oxidation processes can be enhanced by increasing the time wastewater resides in filtering tanks and by adding oxygen. However, these processes create capacity problems that require more tanks, additional wastewater treatment personnel, and other expenses. Economics always plays a major factor in wastewater treatment, and additional treatment requirements are sometimes resisted due to economic concerns.

2.7.2. Reuse Technologies.

The terminology used in the area of water reclamation and reuse difference various main concepts as follows.

Wastewater reclamation is the treatment or processing of wastewater to make it reusable, and *water reuse* is the use of treated wastewater for beneficial purposes such as agricultural irrigation and industrial cooling.

Reclaimed water is a treated effluent suitable for an intended water reuse application. In addition, *direct* water reuse requires the existence of pipes or other conveyance facilities for delivering reclaimed water. *Indirect* reuse, through discharge of an effluent to receiving water for assimilation and withdrawals downstream, is recognized to be important but does not constitute planned direct water reuse.

In contrast to direct water reuse, *water recycling* normally involves only one use or user and the effluent from the user is captured and redirected back into that use scheme. Water recycling is reusing treated wastewater for beneficial purposes such as agricultural and landscape irrigation, industrial processes, toilet flushing, and replenishing a ground water basin (referred to as ground water recharge). In this context, water recycling is predominantly practiced in industry (Metcalf and Eddy, 2003).

Early developments in the field of water reuse are synonymous with the historical practice of land application for the disposal of wastewater. With the advent of sewerage systems in the nineteenth century, domestic wastewater was used at "sewage farms" and by 1900 there were numerous sewage farms in Europe and in the United States. While these sewage farms were used primarily for waste disposal, incidental use was made of the water for crop production or other beneficial uses (Asano, 2006). During the past century, a number of water reclamation and reuse projects have been developed as a matter of necessity to meet growing need for reliable water.

Planned water reclamation and reuse have gained considerable attention worldwide in recent decades as an alternative and new water resource in the context of integrated water resources management.

Water reuse may also present communities with an alternate wastewater disposal method as well as provide pollution abatement by diverting effluent discharge away from sensitive surface waters. Already accepted and endorsed by the public in many urban and agricultural areas, properly implemented nonpotable reuse projects can help communities meet water demand and supply challenges without any known significant health risks.

Nevertheless, the legal frame for this activity is not clear. Water reclamation for nonpotable reuse has been adopted in different countries without the benefit of national or international guidelines or standards (EPA, 2004). The WHO's guidelines for agricultural irrigation reuse (dated 1989) are under revision (WHO, 2003). Recently, the 2004 EPA Guidelines for Water Reuse (EPA, 2004) have been presented. Its primary purpose is to summarize water reuse guidelines, with supporting information, for the benefit of utilities and regulatory agencies, particularly in the U.S. The Guidelines cover water reclamation for nonpotable urban, industrial, and agricultural reuse, as well as augmentation of potable water supplies through indirect reuse. However, neither the U.S. Environmental Protection Agency (EPA) nor the U.S. Agency for International Development (USAID) proposes standards for water reuse in any publication. These guidelines are not themselves any kind of regulation.

As the link between wastewater, reclaimed water, and water reuse has become delineated more clearly, increasingly smaller recycle loops are possible (Asano and Levine, 1996). Traditionally, the hydrologic cycle has been used to represent the continuous transport of water in the environment.

Recent documents from WHO (Aertgeerts and Angelakis, 2003) and the US EPA (2004) address the state-of-the art aspects and future trends in water use, both of which predict increased development and use of the practice to augment water supply sources in order to meet demands. The WHO guidelines for wastewater reuse first published in 1995 are being updated with a planned release date of 2006 (WHO, 2005).

Levine and Asano (2004) recently summarized the more important challenges associated with water reclamation and reuse. They noted that the technique of water reuse is being applied in many countries including the United States, Mexico, Germany, Mediterranean and Middle Eastern countries, South Africa, Australia, Japan, China and Singapore. Its increased application is being facilitated by modern wastewater treatment processes, which advanced substantially during the twentieth century. These processes can now effectively remove biodegradable material, nutrients and pathogens so the treated waters have a wide range of potential applications.

2.7.2.1. Water reuse as source substitution

The annual reclaimed water volumes total about 2.2 billion m^3, based on 2000 and 2001 figures from the World Bank. Recent projections indicate that Israel, Australia and Tunisia will use reclaimed water to satisfy 25 percent, 11 percent and 10 percent, respectively, of their total water demand within the next few years (Lazarova et al., 2001).

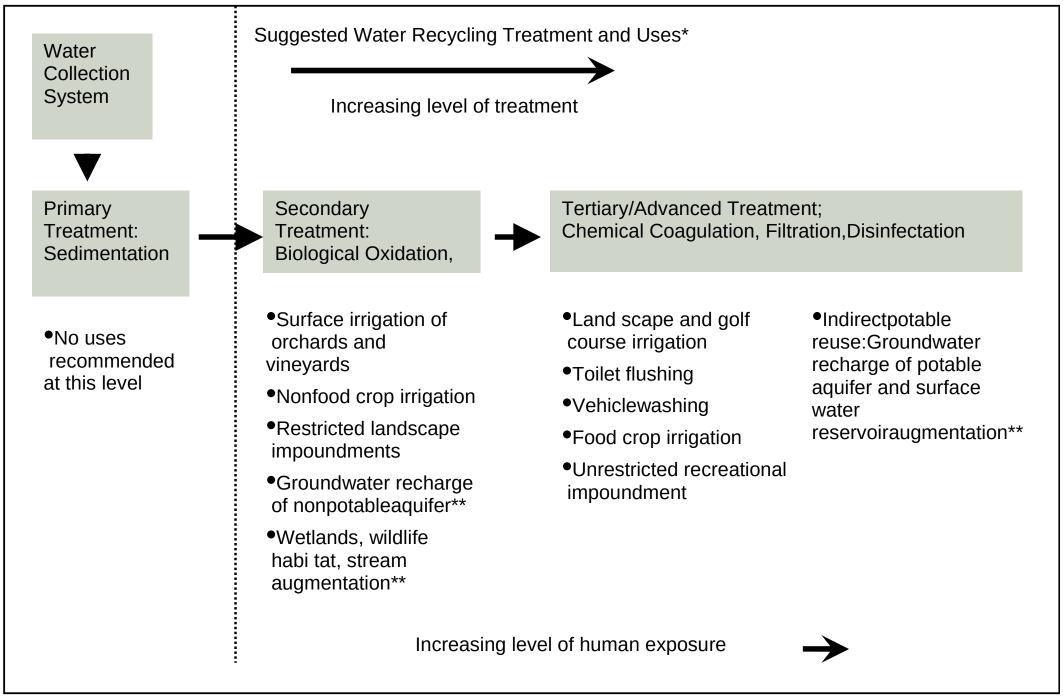
In Jordan, reclaimed water volumes are predicted to increase more than four times by 2010 if demands are to be met. By 2012, Spain will need to increase its reclaimed water use by 150 percent and, by 2025, Egypt will need to increase its usage by more than ten times. A number of Middle Eastern countries are planning significant increases in water reuse to meet an ultimate objective of 50 to 70 percent reuse of total wastewater volume. The growing trend of water reuse is not only occurring in water deficient areas (Mediterranean region, Middle East and Latin America), but also in highly populated countries in temperate regions (Japan, Australia, Canada, north China, Belgium, England and Germany). This method of augmenting natural water sources is becoming an integral component to many water resources management plans and future use policies.

Under the broad definition of water reclamation and reuse, sources of reclaimed water may range from industrial process waters to the tail waters of agricultural irrigation systems. However, the sources of reclaimed water are limited to the effluent generated by domestic wastewater treatment facilities (WWTFs) in many countries.

In Spain, reuse water quality is defined in the previously mentioned RD 1620/2007. The main included measure parameters are: intestinal nematodes, Escherichia Coli, suspended solids, turbidity, and other criteria.

The use of reclaimed water for non-potable purposes offers the potential for exploiting a "new" resource that can be substituted for existing potable sources. This idea, known as “source substitution” is not new. In fact, the United Nations Economic and Social Council enunciated a policy in 1958 that *No higher quality water, unless there is a surplus of it, should be used for a purpose that can tolerate a lower grade.* Many urban, commercial, and industrial uses can be met with water of less than potable water quality. With respect to potable water sources, EPA policy states, *…because of human frailties associated with protection, priority should be given to selection of the purest source* (EPA, 1976). Therefore, when the demand exceeds the capacity of the purest source, and additional sources are unavailable or available only at a high cost, lower quality water can be substituted to serve the non-potable purposes.

Since few areas enjoy a surplus of high quality water, and demand often exceeds capacity, many urban residential, commercial, and industrial uses can be satisfied with water of less than potable water quality. In many instances, treated wastewater may provide the most economical and/or available substitute source for such uses as irrigation of lawns, parks, roadway borders, and medians; air conditioning and industrial cooling towers; stack gas scrubbing; industrial processing; toilet flushing; dust control and construction; cleaning and maintenance, including vehicle washing; scenic waters and fountains; and environmental and recreational purposes.



* Suggested uses are based on Guidelines for Water Reuse, developed by U.S. EPA.
** Recommended level of treatment is site-specific.

Figure 2.22. Suggested water recycling treatment and uses (Source: EPA, 2004)

The economics of source substitution with reclaimed water are site-specific and dependent on the marginal costs of new sources of high-quality water and the costs of waste.

Finally, the chart shown in Figure 2.22 illustrates the possible water reuse pathways. Each use requires a specific treatment of reused water. In addition, these ideas have been drawn in Figure 2.23 as suggested water recycling.

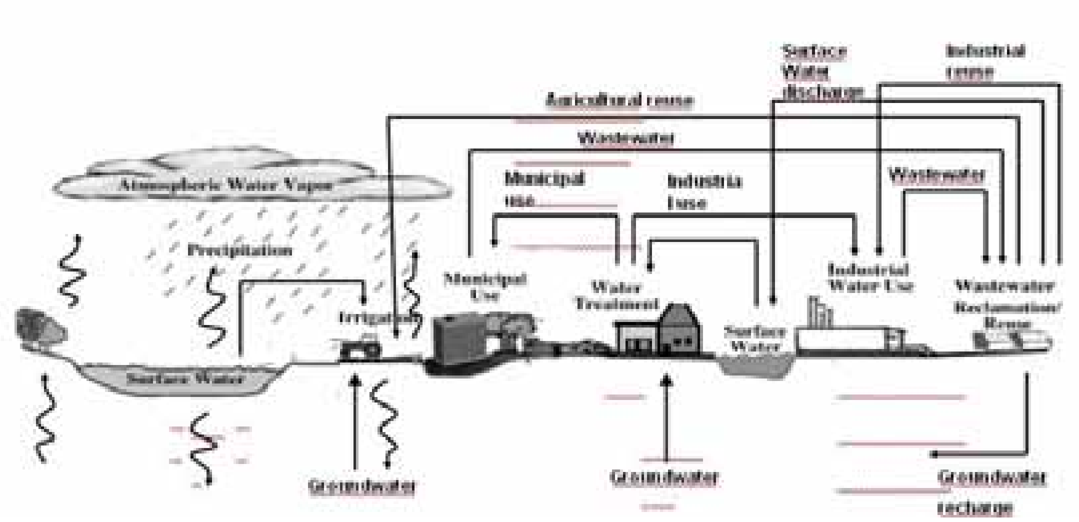


Figure 2.23. Reclamation and reuse facilities in the cycling of water through the hydrologic cycle (Source: adapted from Asano and Levine, 1995).

2.7.2.2. Wastewater reuse applications

In the planning and implementation of water reclamation and reuse, the reclaimed water application will usually govern the wastewater treatment needed to protect public health and the environment, and the degree of reliability required for the treatment processes and operations. In general, water reuse applications fall under one of five categories. The relative amount of water used in each category varies locally and regionally due to differences in specific water use requirements and geopolitical constraints.

In Spain, the criteria of reused water utilization are defined in the R.D. 1620/2007 (*REAL DECRETO 1620/2007, de 7 de diciembre, por el que se establece el régimen jurídico de la reutilización de las aguas depuradas*). The existing categories are: urban uses, agricultural uses, industrial activities, recreational uses and environmental uses.

i) *Urban uses* include fire protection, air conditioning, toilet flushing, construction water, and flushing of sanitary sewers. Typically, for economic reasons, these uses are incidental and depend on the proximity of the wastewater reclamation plant to the point of use. In addition, the economic advantages of urban uses can be enhanced by coupling with other ongoing reuse applications such as landscape irrigation.

ii) *Agricultural use* represents the largest current use of reclaimed water throughout the world. This reuse category offers significant future opportunities for water reuse in both industrialized countries and developing countries.

iii) *Industrial activities* represent the third major use of reclaimed water, primarily for cooling and process needs. Cooling water creates the single largest industrial demand for water and as such is the predominant industrial water reuse either for cooling towers or cooling ponds. Industrial uses vary greatly and water quality requirements tend to be industry-specific. To provide adequate water quality, supplemental treatment may be required beyond conventional secondary wastewater treatment.

iv) *Recreational uses* involve non-potable uses related to land-based water features such as the development of recreational lakes, marsh enhancement, and stream flow augmentation. Reclaimed water impoundments can be incorporated into urban landscape developments. *Landscape irrigation* is the second largest user of reclaimed water in industrialized countries and it includes the irrigation of parks; playgrounds; golf courses; freeway medians; landscaped areas around commercial, office, and industrial developments; and landscaped areas around residences. Many landscape irrigation projects involve dual distribution systems, which consist of one distribution network for potable water and a separate pipeline to transport reclaimed water.

v) *Environmental use* constitute the fifth largest use of reclaimed water in industrialized countries. Reclaimed water has been applied to wetlands for a variety of reasons including: habitat creation, restoration and/or enhancement, provision for additional treatment prior to discharge to receiving water, and provision for a wet weather disposal alternative for reclaimed water. Falling under this use, *groundwater recharge* is the fourth largest application for water reuse, either via spreading basins or direct injection to groundwater aquifers. Groundwater recharge includes groundwater replenishment by assimilation and storage of reclaimed water in groundwater aquifers, or establishing hydraulic barriers against salt-water intrusion in coastal areas.

Potable reuse is another water reuse opportunity, which could occur either by blending in water supply storage reservoirs or, in the extreme, by direct input of highly treated wastewater into the water distribution system. However, according to the R.D. 1620/2007 (Art.4), this use is prohibited. Only in the case of a disaster water could be use, previously defined the quality parameter values by the sanitary authorities.

On top of that, because of the costs of treatment and safety concerns, water reuse applications have been limited primarily to nonpotable uses. However, some communities are continuing to investigate and evaluate the potential for indirect and direct potable reuse options. While the quantities of reclaimed water involved in these potable water reuse projects are small, the technological, public health, aesthetic, and public acceptance issues are of fundamental importance and are a greater challenge in water than in drinking water supply.

While potentially large quantities of reclaimed municipal wastewater can be used in the first five categories, the quantities associated with the sixth and seventh reuse categories are minor at present; particularly potable water reuse. Some water reuse examples are summarized in Table 2.16.

Application settings	Examples
Urban use	
Unrestricted	Landscape irrigation (parks, playgrounds, school yards), fire protection, construction, ornamental fountains, recreational impoundments, in-building uses (toilets, air conditioning)
Restricted-access irrigation	Irrigation of areas where public access is infrequent and controlled (golf courses, cemeteries, residential, greenbelts)
Agricultural irrigation	

Application settings	Examples
Food crops	Crops grown for human consumption and consumed uncooked
Non-food crops, food crops consumed after processing	Fodder, fibre, seed crops, pastures, commercial nurseries, sod farms, commercial aquaculture
Recreational use	
Unrestricted	No limitations on body contact (lakes and ponds used for swimming, snowmaking)
Restricted	Fishing, boating, and other non-contact recreational activities
Environmental use	Artificial wetlands, enhanced natural wetlands, and sustained stream flows
Groundwater recharge	Groundwater replenishment, saltwater intrusion control, and subsidence control
Industrial reuse	Cooling system makeup water, process waters, boiler feed water, construction activities, and washdown waters
Potable reuse	Blending with municipal water supply (surface water or groundwater)

Table 2.16. Reuse examples. (Source: Levine and Asano, 2004)

2.7.2.3. Treatment and Water Quality Considerations

Understandably, the construction of reclaimed water transmission and distribution lines to existing users in large cities is expensive and disruptive. As a result, wastewater reclamation and reuse will continue to be most attractive in serving new residential, commercial, and industrial areas of a city, where the installation of dual distribution systems would be far more economical than in already developed areas.

Use of reclaimed water for agricultural purposes near urban areas can also be economically attractive. Agricultural users are usually willing to make long-term commitments, often for as long as 20 years, to use large quantities of reclaimed water instead of fresh water sources. One potential scenario is to develop a new reclaimed water system to serve agricultural needs outside the city with the expectation that when urban development replaces agricultural lands in time, reclaimed water use can be shifted from agricultural to new urban development.

Water reclamation and non-potable reuse typically require conventional water and wastewater treatment technologies that are already widely practiced and readily available in many countries throughout the world. When discussing treatment for a reuse system, the overriding concern continues to be whether the quality of the reclaimed water is appropriate for the intended use. Higher level uses, such as irrigation of public-access lands or vegetables to be consumed without processing, require a higher level of wastewater treatment and reliability prior to reuse than will lower level uses, such as irrigation of forage crops and pasture. For example, in urban settings, where there is a high potential for human exposure to reclaimed water used for landscape irrigation, industrial purposes, and toilet flushing, the reclaimed water must be clear, colourless, and odourless to ensure that it is aesthetically acceptable to the users and the public at large, as well as to assure minimum health risk. Experience has shown that facilities producing secondary effluent can become water reclamation plants with the addition of filtration and enhanced disinfection processes.

A majority of the states have published treatment standards for guidelines for one or more types of water reuse. Some of these states require specific treatment processes; others impose effluent quality criteria, and some require both. Many states also include requirements for treatment reliability to prevent the distribution of any reclaimed water that may not be adequately treated because of a process upset, power outage, or equipment failure. Dual distribution systems (i.e., reclaimed water distribution systems that parallel a potable water system) must also incorporate safeguards to prevent cross-connections of reclaimed water and potable water lines and the misuse of reclaimed water. For example, piping, valves, and hydrants are marked or colour-coded (e.g. purple pipe) to differentiate reclaimed water from potable water. Backflow prevention devices are installed, and hose bibs on reclaimed water lines may be prohibited to preclude the likelihood of incidental human misuse. A strict industrial pre-treatment program is also necessary to ensure the reliability of the biological treatment process by excluding the discharge of potentially toxic levels of pollutants to the sanitary sewer system. Wastewater treatment facilities receiving substantial amounts of high-strength industrial wastes may be limited in the number and type of suitable reuse applications.

Differences are also apparent in the distribution of reclaimed water for these different purposes. Where disposal is the objective, meters are difficult to justify, and reclaimed water is often distributed at a flat rate or at minimal cost to the users. However, where reclaimed water is intended to be used as a water resource, metering is appropriate to provide an equitable method for distributing the resource, limiting overuse, and recovering costs.

Until this point, the sections 2.7.1 and 2.7.2 have covered the issues related to the water treatment plants main features and the existing water reuse technologies. In addition to treat the used water for giving it back to the river, or for directly reusing it, an alternative water source is obtaining fresh water from the seawater. It is an initially expensive option, but the feasibility of each study has to be study before judging it; the suitability of the desalination option will always depend on the comparing factors. In the next section 2.7.3, the most relevant desalination options are summarized.

2.7.3. Desalination as a new water supply technology.

Desalination technologies are currently a solution to obtain a healthy freshwater under cost and environmental optimum conditions. On top of that, some places have been highly developed (e.g the Persian Gulf) because of their fossil fuels abundance.

Desalination can be achieved either by removing salt from water, or by removing pure water from a saline or polluted source. For producing large quantities of freshwater from a saline source, it is necessary to remove the water from the salt. This process leaves behind a highly concentrated saline solution, or brine, which must be disposed of as a waste product, often in the sea.

Two desalination methods are in common use: thermal and membrane separation. The general desalination process is schematized in Figure 2.24.

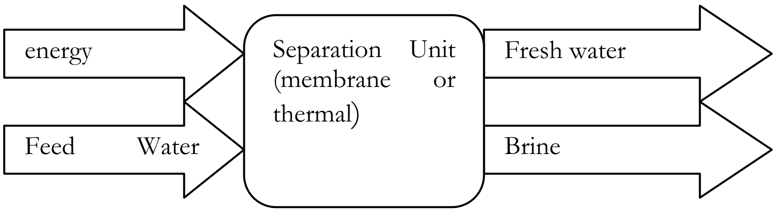


Figure 2.24. The desalination process

There are two main phase-change separation methods. In the first, the most common desalination process, water is evaporated and the vapour is condensed. An alternative consist on freezing the water and melting of ice crystals.

Evaporation can be carried out by bringing water in contact with a heat transfer surface (boiling process, for example, MSF, MED, SEE-VC, humidification-dehumidification, and a number of methods based on the use of solar energy) or bulking feed water (to produce vapour through what is termed a flashing process).

To improve thermal efficiency, vapour compression is combined with desalination processes. In the VC process, low temperature vapour formed in the same effect or the preceding evaporation effect is compressed and used to initiate the evaporation process in the first or the same evaporation effect. The VC process incorporates component devices that include mechanical compressors, steam-jet ejectors, TVC components, adsorption/desorption beds, and absorption/desorption columns. Variants of the single effect VC process include mechanical vapour compression (MVC), thermal vapour compression (TVC), absorption vapour compression (ABVC), adsorption vapour compression (ADVC), and chemical vapour compression (CVC).

On the other hand, membrane desalination processes, in which a highly concentrated brine stream is formed on the other side of the membrane, include Reverse Osmosis and Evaporated Distillation.

In the RO process, high pressure forces fresh water to permeate through a semi-permeable membrane, leaving behind a highly concentrated brine solution. ED is activated using electrical energy, causing electrically charged salt ions to move through selective ion exchange membranes, leaving behind low salinity product water.

An overview of the main desalination categories is summarized in Figure 2.25.

Traditionally, thermal desalination or distillation has been the most commonly used technology for producing large quantities of freshwater from seawater. Different thermal desalination processes require different magnitudes and combinations of heat and electricity. The economic efficiency of desalination plants is improved by combining the purposes of power and water production. Most of the desalination plants operating in the Middle East and elsewhere are dual-purpose multistage flash distillation plants that produce both water and electricity, using oil as the energy source. However, oil price rises undermine the economic performance of these plants, even in the Arabian Gulf region. As a result, nuclear power is increasingly being considered as a viable energy source for thermal desalination plants, particularly in countries that have local uranium reserves. The advantages include fuel price stability and the long-term availability of the fuel, but these need to be balanced against the well-known drawbacks of high initial investment costs and the disposal of spent nuclear fuel.

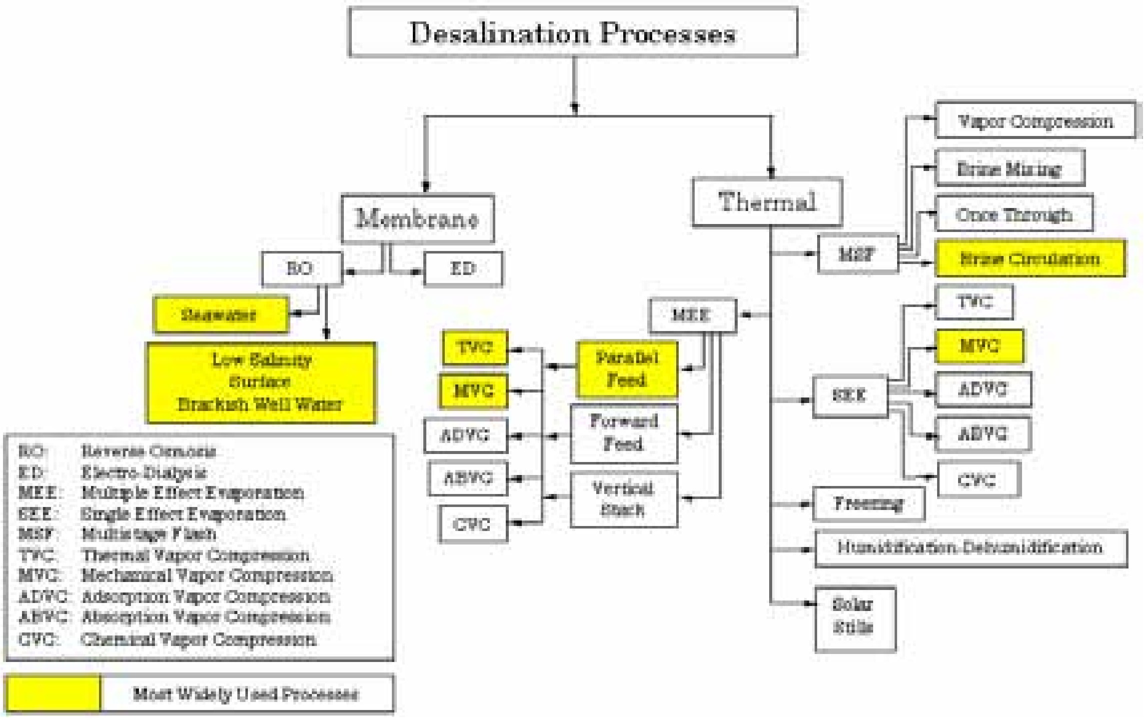


Figure 2.25. Desalination processes schema. (source: ESCWA-UN, 2001a).

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On the other hand, the freezing desalination was extensively developed in the 1950s and 1960s. It has some advantages which include lower theoretical energy requirements and limited corrosion, scaling and salt precipitation in plant components. However, the process involves dealing with ice and water mixtures that are mechanically rather difficult to handle.

During the freezing, dissolved salts are excluded from ice crystals. Before the entire mass of water has frozen, the mixture is usually rinsed to remove the salts in the remaining salt-laden water adhering to the ice crystals. The fresh ice is then melted to produce fresh water.

Desalination development is enormous. Nowadays, its installed capacity is 47 Mm^3/d (more than the urban consumption). Expected desalination average growing by 2005-2015 is 101%, with a maximum value in Mediterranean region (179%).

Ninety-seven percent of the world's water is too salty for consumption or agriculture. Desalination is not a new concept, as it has been practised since biblical times. However, the process typically consumes large quantities of energy in order to produce drinking water from seawater or polluted water, making energy cost the major determinant of the desalination cost. Hence desalination technology has tended to be used in water-scarce countries where energy is cheap and plentiful.

As of June 30, 2008, there were 13,872 "contracted desalination plants" worldwide, according to Global Water Intelligence and the International Desalination Association. As Table 2.17 indicates, an important percentage of the world's desalination plants are located in the Arabian Gulf Countries.

COUNTRY	**m^3/d**	**% of the world desalted water**
Saudi Arabia	10,759,693	17%
United Arabia Emirates	8,428,456	13%
USA	8,133,415	13%
Spain	5,249,536	8%
Kuwait	2,876,625	5%
Algeria	2,675,958	4%
China	2,259,741	4%
Katar	1,712,886	3%
Japan	1,544,849	2%
Australia	1,493,158	2%

Table 2.17. Top ten desalination countries (Source: EMIS, 2008 and GWI-IDA, 2008)

Desalination in the Middle East usually comes in the form of thermal processes: MSF & multi-effect distillation (MED). This is mainly due to the low cost of energy in these countries and the problems faced by membrane processes in dealing with the high salinity of the Arabian Gulf water. The desalination market in the Middle East and North Africa, is expected to increase significantly as drought conditions worsen, populations grow and water demand per capita increases due to expansion in industrial activities and development of tourism.

In Europe and in most of the rest of the world, the dominant technology is RO. Reverse osmosis has seen the most rapid growth in the last 30 years mainly due to technological developments in the membrane manufacturing process. The advantages of RO are that it is an economical process that consumes little energy. The low investment and operation costs of this widely accepted technology add to its appeal.

All major desalination technologies have demonstrated their ability and reliability to produce fresh water in an economical manner. Each technology has found their supporters and users, stimulating competition between them and provoking the continuous improvement of all of those technologies.

According to the experts, the best desalination technologies are distillation (multistage flash, MSF) and membrane technologies (reverse osmosis, RO, and reversal electro-dialysis, EDR). RO and EDR are applied to desalinate brackish water, with salt concentrations of less than 10 g/litre, while RO and distillation are applied for seawater, with a salt concentration of more than 30 g/litre.

The percentage and desalinated water produced volume by technology are summarized in Figure 2.26.

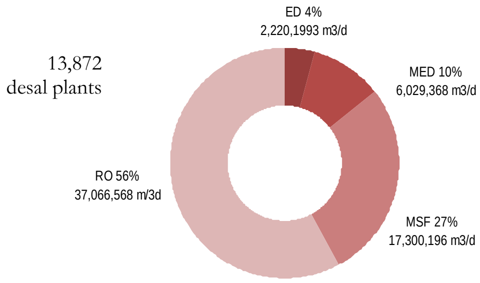
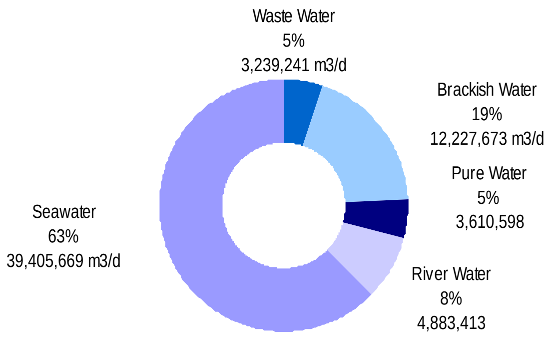


Figure 2.26. Contracted desalination plants by technology. (source: GWI, 2008)

The increase in contracted MED capacity since 2004 have been a 103 %, and nearly 3.1 Mm^3/d of capacity was contracted between the end of 2004 and mid-2008 (GWI, 2008)

The experts recommended that each specific case be studied carefully before selecting the technology. The expert group designed by FAO considered membrane technologies as being most adaptable with EDR being promising for future applications. (FAO, 2006)

Different feedwater qualities and off-takers of desalinated water are summarized in Figure 2.27 and Figure 2.28.



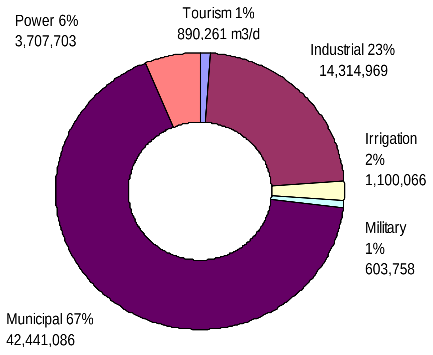


Figure 2.27. Feed water quality of desalination plants. (source: GWI, 2008)

Figure 2.28. Off-takers of desalination plants. (source: GWI, 2008)

2.7.3.1. Distillation thermal processes

Industrial thermal desalination was greatly developed with the introduction of submerged evaporators. The tubes of submerged heating steam evaporate feed water, as salt formation on the outer surface of the evaporator tubes occur.
Nevertheless, one of the main reasons to replace evaporators by flash distillation mechanisms was the scale's low thermal conductivity, which drastically reduced heat transfer efficiency.

The first unit was installed in 1960 in Kuwait (ESCWA-UN, 2001b). The initial design was progressively developed, incorporating the features of the present MSF process.

a. Multistage Flash (MSF) Distillation

Multistage Flash distillation is the most widely form to produce water from seawater, especially common wherever the temperature, salt content, biological activity or pollution level of seawater is high, as in the Middle East. This process has been in large-scale commercial use for over 30 years, coupled to power stations. In general, MSF plants are more common because they are simple and robust, although their specific consumption may be higher than other technologies. Other advantage of MSF plants are their unit size, considered of large scale (more than 50,000 m3/d of capacity per unit).

The Multistage Flash process (Figure 2.29) is described as follows: seawater pumped through heat exchanger tubes installed in the various evaporator stages, is heated to a certain temperature. Final heating is performed by steam (coming from a power station) in a brine heater. The hot seawater then goes into flash chambers where the pressure is maintained below the equilibrium pressure corresponding to the temperature at which the brine enters. Part of the brine flashes into vapour and after passing a demister, it condenses outside the tubes while heating the seawater flowing through the tubes. The multistage flash distillation unit contains cells assembled in series, at a different pressure. The water produced in each stage is collected in a trough mounted below the tube bundle which collects the fresh water end product. These widely used units perform recycle brine in order to reduce the quantity of the make-up seawater needed to produce fresh water. The concentrated seawater is also removed from the last stage by a pump or by gravity.

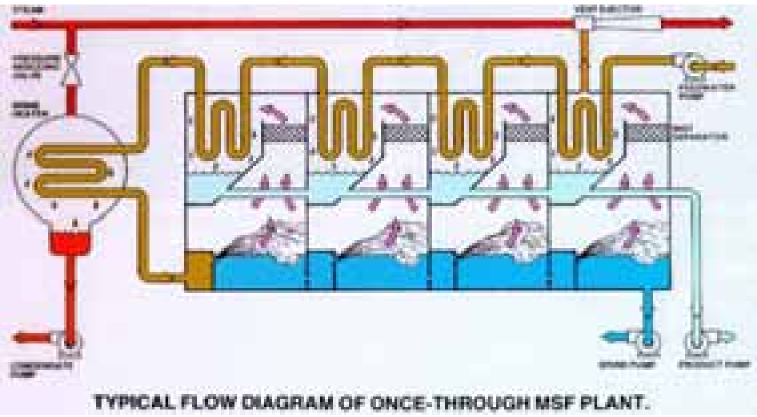


Figure 2.29. Sketch of a typical MSF unit. (source: Uche et al, 2006)

b. Multi-Effect Distillation (MED)

Contrary to MSF, in Multi-Effect Distillation evaporation takes place on surfaces, by exchanging the latent heat through the heat transfer surface between condensing vapor on one side and evaporating brine on the other (Figure 2.30).

The MED plant also has several stages, each with a heat exchanger tube bundle. Seawater is sprayed onto the tubes and the condensing heating steam inside the tubes evaporates part of the seawater on the outside. The steam produced is used as heating steam in the next stage, where it condenses inside the tubes. The condensate is the water product. Obviously, the boiling temperatures and pressures in the different evaporators cannot be the same. The first stage is heated by external steam from a heat recovery steam or a back-pressure steam turbine, but in most cases, MED plants are equipped with thermal vapor compressors for better efficiency. The steam produced in the last stage is condensed on the outside of exchanger tubes in a separate condenser, which is cooled by incoming seawater. Part of the heated seawater is then used as feedwater. Product water and concentrated seawater are then pumped out from the last stage of the evaporator.

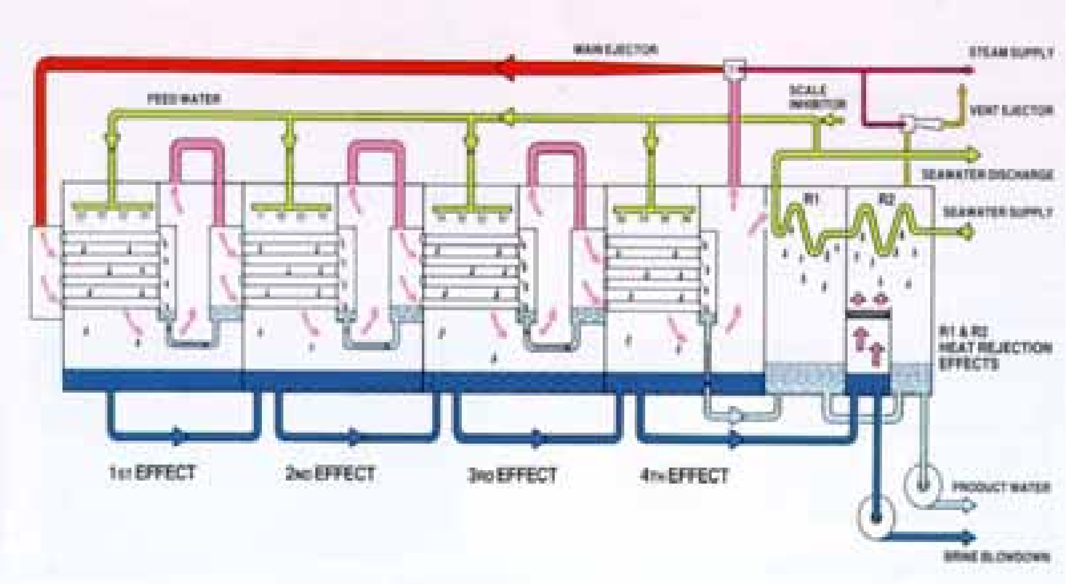


Figure 2.30. Scheme of a MED unit with thermocompressor (TVC) (source: Uche et al, 2006)

The major advantage of MED with respect to MSF is the ability to produce more water per steam consumed (Performance Ratio). MED plants could reach a value of 15 while MSF almost 10, and includes lower specific power consumption (< 1.5 kWh/m^3) than MSF (> 3 kWh/m^3). Furthermore, their efficiency does not depend on the steam temperature coming from the turbines as MSF plants, so MED plants are the most promising for thermal distillation technologies for desalination. However, the unit size of MED plants is up to the third with respect to MSF units at present.

c. Vapor Compressor Distillation (VC)

Vapor compression distillation is similar to multi-effect distillation, but the main difference is that the vapor produced by the evaporation of the brine inside is not condensed in a separate condenser. In this case, that vapor enters in a centrifugal, single-stage type designed for high-volumetric flows, and this high-energy compressed steam is discharged into the evaporator onto the outside of the enhanced surface tubes, where it condenses and provide its latent heat energy to the boiler seawater inside the tubes.

Note that the process is very efficient thermodynamically, because most of the shaft work required by the compressor is used to avoid the boiling point elevation of seawater. In comparison with thermal desalination plants, no cooling water is required resulting in smaller intake and pumping systems and lower energy requirements (up to 9 kWh/m^3 of product). Unfortunately, the maximum size of VC plants is only about 3,000 m^3/d but they could grow in capacity and number of effects in order to improve its efficiency and reduce its cost (Figure 2.31).

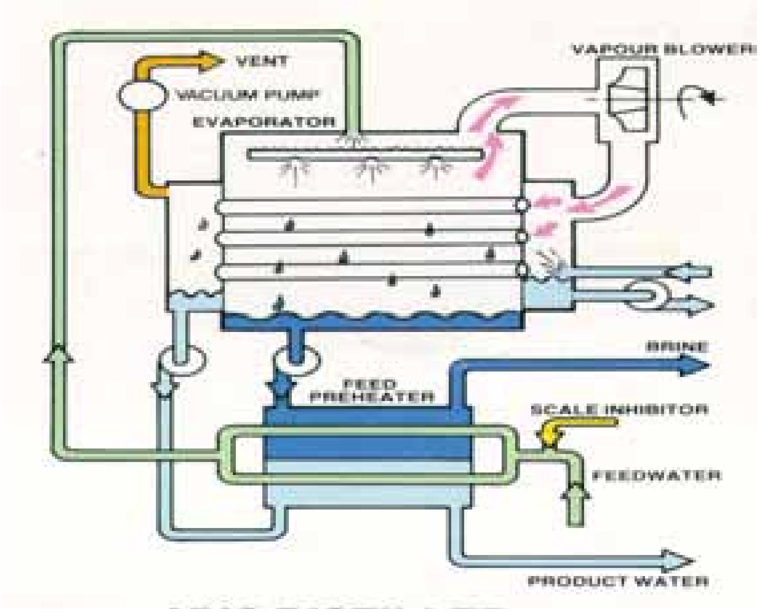


Figure 2.31. Typical one-stage vapor compressor distillator (VC). (source: Uche et al, 2006)

2.7.3.2. Desalination membrane processes

Although introduced in the 1960s, synthetic membranes began to play an important role in the early 1980s. Membrane-based processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).

The size of ions, molecules, suspended particles, which are allowed to pass or retain is the main difference between these processes. In MF and UF, commonly used to remove suspended material, a membrane retains the largest one particle and allows smaller than its pores to pass through. In the RO, the solvent passes through the membrane, which retains the solute. This mechanism allows direct and effective desalination. NF, in an intermediate position, allows the passage of ions and other entities of suitable size.

Microfilters allow the passage of micron-sized particles, ranging from 10^{-2} to 10 microns; ultrafilters allow much smaller-sized particles in the range of $2 \cdot 10^{-3}$ to $8 \cdot 10^{-2}$ microns through; and NF membranes permit particles in the nanometer (nm) range, from $8 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ microns, to filter through. RO membranes allow the passage of particles ranging from 10^{-4} to 10^{-3} microns (ESCWA-UN, 2001a).

Table 2.18 provides some further information on the principal characteristics of membrane systems.

Separation process	Pore size or maximum molecular weight rangea/	Operating pressure (kPa)	Substances removed	Alternative traditional water treatment method
Microfiltration (MF)	0.1 to 10 microns	140 to 5,000	Bacteria, viruses, larger colloidal particles, precipitates and coagulates	Ozonation, chlorination, sand-bed filtration, bioreactors, coagulation and sedimentation
Ultrafiltration (UF)	10 to 1,000 Å 1,000 to 500,000 daltons	200 to 1,000	High molecular weight proteins, large organic molecules and pyrogens	Sand-bed filtration, bioreactors and active carbon treatment
Nanofiltration (NF)	2 to 70 Å 180 to 10,000 daltons	550 to 1,400	Large divalent and some monovalent ions, colourants and odorants	Lime/soda softening and ion exchange
Reverse osmosis (RO)	1 to 70 Å	1,400 to 7,000	All of the above in addition to monovalent ions	Evaporation, freezing and electrodialysis

Note: Å = angstroms; kPa = kilopascals.
a/ The maximum molecular weight range, expressed in Daltons, refers to the molecular weight cut-off (MWCO) allowed by
membrane pores.

Table 2.18. A summary characterization of membrane separation processes. (Source: ESCWA-UN, 2001a)

a. Reverse Osmosis (RO)

Reverse osmosis (membrane desalination) is an electrically-driven process that uses special membranes through which water molecules may pass under pressure, leaving behind larger molecules, including salt. The capital cost of reverse osmosis units is dropping, and they are now the most common choice for new desalination plants.

Seawater reverse osmosis plants allow to demineralize water in a reliable manner. In RO desalination (Figure 2.32), seawater (or brackish water in case of inland territories that suffer from saline aquifers) is pretreated to avoid membrane fouling. It then passes through filter cartridges (a safety device) and is sent by a high-pressure pump through the membrane modules (permeators). Because of the high-pressure, pure water permeates through the membranes and the seawater is concentrated. The water product flows directly from the permeators into a storage tank, and the concentrated seawater (at high pressure) is sent via an energy recovery system back into the sea.

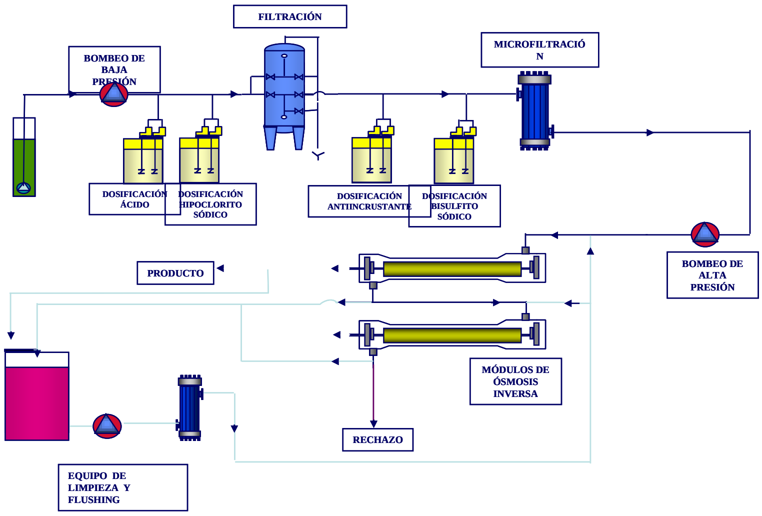


Figure 2.32. Diagram for a seawater RO unit. (Source: Uche et al, 2006)

Seawater RO process uses only electrical energy, and the higher consumption occurs in the high-pressure pump. Nowadays, energy recovery systems, as those: Pelton or Francis turbines, which takes profit of the pressurized brine as water stored in reservoirs. Inverse pumps (or turbochargers), that allow to impulse a great part of the energy required for the high-pressure pump, therefore they are mounted in a unique shaft.

Pressure exchangers, translating the brine pressure into the feed water, by means of ceramic rotors or a set of valves and closed cylinders could recover more than the 95% of the energy stored in the reject brine, so the total energy consumption for seawater could be from 3 to 5 kWh/m^3, depending on the feed water salinity and temperature. The modularity of RO systems also provokes that those systems have been rapidly installed in all over the world.

Seawater RO is a membrane technology (see a symplified schema in Figure 2.33) . Other membrane processes as nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) are rapidly growing to be used in brackish desalination or waste water reuse, with very low energy consumptions (less than 1 kWh/m^3).

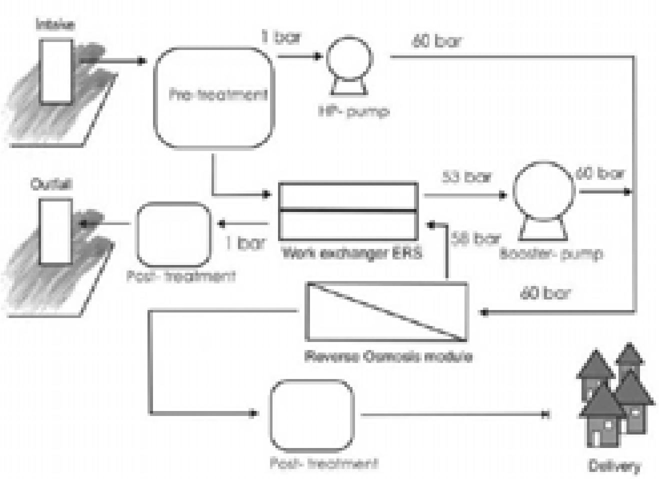


Figure 2.33. Simplified reverse osmosis scheme with energy recovery system. (Source: Fritzmann, 2007)

Although RO systems have a relatively low rate of energy consumption, RO desalination uses high-cost electrical energy. Improvements still need to be made to reduce energy usage. One way could be RO that takes advantage of low-grade heat energy to increase flux through the membrane for a given pressure drop. This thermally enhanced RO can be used in locations where waste heat energy is available, typically from co-located electrical power generation and RO desalination plants. Hybrid desalination plants would combine thermally enhanced RO and thermal desalination to further lower electrical energy consumption per unit of product water, while achieving higher water recoveries than RO alone.

Desalination of inland saline waters, which are present on most continents in quantities similar to freshwater, can also be used to increase water supplies, but disposal of the residual concentrate is a major problem. Hybrid desalination technologies that concentrate precipitates and salts while extracting the water with membranes can potentially process the brine (Uche et al, 2006). One of the largest barriers to desalinating inland salt waters found in lakes and deep aquifers, a use which is becoming more common due to overpumping of aquifers worldwide, is the high cost – or complete inability – to dispose of the brine. Techniques that can concentrate the brine to approach the zero-discharge limit will permit desalination in arid inland regions of the world. Two alternative desalination technologies currently under investigation, forward osmosis and membrane distillation, can also use low-grade heat energy. They may be used alone, or as hybrid systems with RO, to achieve high water recovery.

There are further potential improvements in RO on the horizon that could help reduce the cost of standard and hybrid desalination technologies. RO membranes that are chemically resistant to chlorine are being developed, so that more powerful cleaning materials can be used to keep flux up and operational costs down. Anti-fouling membranes are also being developed to reduce unrecoverable biofouling. Super-flux membranes, using now-exotic technologies such as carbon nanotube membranes, can potentially increase the flux through the RO system 10 times or more. This would reduce overall energy use by 20 percent compared with the most efficient systems. To reduce energy costs to near the natural law limits, nature-inspired membranes that actively pump hydrated salt ions out of the salt water are being researched. While these developments are years away from being implemented (if ever), they do show that new concepts are being developed that could dramatically improve desalination technologies, reducing operational costs, energy use, and capital costs, since smaller systems can be used for the same average output of product water (Uche et al, 2006).

b. Electrodyalisis (ED)

This process is used to demineralize brackish water by making different ions migrate through selective membranes in electric field made by the direct difference of voltage potential between two electrodes connected at the boundaries of the membranes. Whenever salt water is flowing in a cell, the cations are attracted by the anode and the anions by the cathode. If not constrained, these ions discharge on the electrodes of opposite sign. In return, if a set of selective and permeable membranes is placed between the electrodes, salt concentration decreases in some compartments of the cell where salt water becomes even more concentrated. This process is suitable for desalinating brackish waters with an average salt content between 1 to 3 g/l (for other salinities the process is not profitable) with a very low power consumption (less than 1 kWh/m^3) and a salt rejection of more than 80%. For seawaters, the process is also feasible but with very high energy costs, so it is generally discarded for those proposes (Figure 2.34).

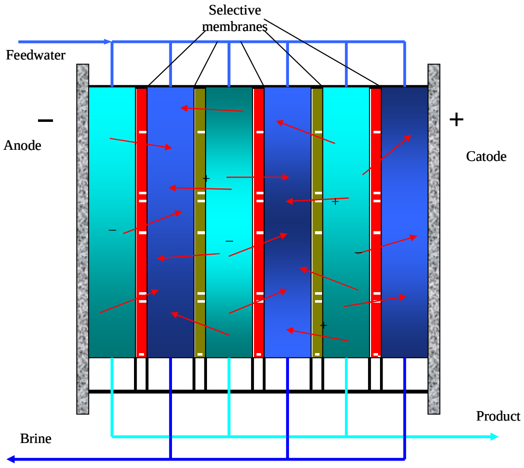


Figure 2.34. Principle of operation of a single electrodialysis (ED) cell.

2.7.3.3. A comparison between desalination processes

Each desalination process is highly recommended in one area, but under some other circumstances should also be convenient to replace the previous process with some others. Table 2.18 summarizes the main characteristics of the referred processes.

	MSF	MED	VC	RO	ED
Energy requirements (MJ/m³)	Thermal 250-300	Thermal 150-220	Mechanical	Mechanical	Electrical
Operating temperature range (°C)	90-120	< 80	60-105 (MVC) < 80 (TVC)	15-40	15-40
Operating pressures range (Mpa)	Sub-atmosph	Sub-atmosph	Atmospheric and Sub-atmosph	2.0-8.0	Atmospheric
Electrical requirement (kWh/m3)	3.5-5	1.5-2.5	1.5-2	5.0- 9.0	1
Unit capacity (m3/d)	5,000-60,000	100-20,000	20-2,500	100-100,000	
Feed water salinity range	seawater	seawater	seawater	Brackish and seawater	Brackish and seawater
Sensitivity to feed water quality	Low	Low-medium	Low-medium	High	Medium-high
Pre-treatment requirements	minimum	minimum	minimum	extensive	minimum
Product water quality (ppm)	very high <10	very high <50	very high <50	100-500	250-500
Product water recovery percentage	10.0-15.0	10.0-25.0	40-55	25-50	
Plant reliability	high	medium	low	high	high
Turnkey capital investment cost	Moderate	Low-moderat.	Low-moderat.	Low-moderat.	Low

	MSF	MED	VC	RO	ED
Surface required	high	medium	low	low	low
Scaling/fouling and corrosion potential	low-moderate	moderate-high	moderate-high	low-moderate	low
Spare parts replacement rate	Moderate (large pumps)	Low (small pumps)	Moderate (vapour compressor)	High (pumps and membranas)	Low (membranas)
High technology components	pumps, instrum, control	Intruments and control	Compresor, instr. and control	pumps, memb, instrum., and control	membranes
Maintenance requirements	low-medium	low	low-medium	high	medium
Operator´s skill requirements	highest	high	high	medium	medium
Potential for further process developments	low	medium	high	medium	low
Market potential for the next 10-15 years	moderate	high	high	high	low-moderate

Table 2.19. A comparison between the most widespread desalination processes (Own elaboration from FAO, 2006; Fritzmann et al., 2007; Uche, 2000; Splieger et al., K.S; 1994; and Uche et al., 2006)

The total cost per unit of desalinated water produced is determined by the cost of capital, energy use, and operational costs. The capital cost, including cost of membrane lifetime for RO, which strongly depends on flux of water throughput, is ~40 percent of the total product water, energy is ~40 percent, and operational costs for pre-treatment, post-treatment, and cleaning are ~20 percent. If one were to minimize only one of the three main categories – such as energy, by reducing flux through the membrane – the energy savings would be more than offset by increased capital costs. In fact, the total cost for desalinated water near the point of use can actually be lower than using conventional sources that must be conveyed long distances, particularly if pumped over hills and mountains.

2.7.3.4. Trends in desalination technology

Thermal desalination

Significant technological developments to the distillation processes are not expected as the technology is fairly mature. However, according to the ESCWA-UN (2001a), there will be changes in the materials that constitute the plant (particularly in the tubing used in the heat exchangers), in larger plant unit sizes producing as much as 76,000 m^3/d for MSF and 23,000 m^3/d for MED, and in the faster delivery of plants (becoming of the order of 1–2 years).

Membrane desalination

There is always room for development in membrane technologies. Development is driven by the fact that membranes are gaining wider use in water/wastewater treatment as well as pre-treatment for desalination. Technological trends include integrated membrane solutions, increased energy efficiency, and increased recovery ratio for seawater RO. New developments will also witness lower use of materials, fewer chemicals and smaller footprints (ESCWA, 2001b).

As the success of RO desalination hinges on the proper pre-treatment of the feed water, various membranes could precede the removal of the monovalent ions by the desalination membrane in order to selectively remove suspended solids and decrease turbidity (microfiltration), organics (ultrafiltration) and hardness and sulphates (nanofiltration). Various energy recovery devices are now available, such as Pelton wheel turbines, work and pressure exchangers as well as hydraulic turbochargers that can reduce energy requirements by as much as 50 percent.

Larger plant size also contributes to the economy of scale that is significant between a plant producing 1,000 m^3/d and that producing 40,000 m^3/d, where the capital cost per cubic metre of water can decrease by a factor of 2.5. However, RO plant sizes larger than 40,000 m^3/d will not have any further considerable effect on cost reduction.

Other trends

Owing to the difference in the demand growth factors (11% for water and 4% for power), a decoupling between power and desalination plants is expected. Where dual-purpose plants are planned, a major trend in technological development is the utilization of more than one process in combination. Such hybrid thermal/membrane combinations offer several advantages including the use of the steam to de-aerate the feed water and optimization of its temperature for RO, application of the post treatment to the combined product, use of the same seawater intake, and combining the discharged brine with the recycled brine.

Hybrid systems of RO and thermal processes utilize seasonal surpluses of idle power and address the power/water mismatch caused by differences in either daily or seasonal demands. The largest such hybrid plant is in Fujeirah, United Arab Emirates, where MSF desalinates 284,000 m^3/d and RO desalinates 170,000 m^3/d. To further address power/water mismatches, using idle power to desalinate would lead to greater water production, hence the need for storage of this excess desalinated water. Therefore, desalination aquifer storage and recovery (DASR) is considered strategic in terms of cost and security.

In addition, using filtration processes in conjunction with thermal processes to remove the hardness in the feed water theoretically reduces the scaling potential and allows the thermal plant to be operated at higher temperatures, hence, greater productivity.

Trends that are also worth tracking are the use of renewable energies in desalination, and the growing importance of the environmental impacts of desalination plants.

Desalination development potential

Desalination has great development potential on a global scale. This is attributed to the fact that out of 71 large cities that do not have local access to new freshwater sources, 42 are coastal. Out of the entire world population, 2 400 million inhabitants (39 percent) live within 100 km of the sea. Current production of desalinated seawater corresponds only to the demand of 60 million inhabitants. Although desalination has been considered among the non-conventional water resources, it can no longer be considered as a marginal resource because some countries such as Kuwait and Qatar rely 100 percent on desalinated water for domestic and industrial uses (nearly 60 percent in Saudi Arabia).

Other than the fact that desalination may be the only option for some countries, there are driving forces behind its development potential, making it more favourable than conventional resources. Being independent of climate conditions, rainfall and so on, a primary force is its identification as a secure source of supply. Compared with conventional civil engineering projects, desalination offers advantages in terms of the length of the construction period, which is in the order of 1–3 years, as well as its modular construction allowing the increase in supply to be in line with that of the demand. In addition, a desalination project is less likely to encounter opposition from local groups or problems associated with construction right of way. Furthermore, it is much more attractive to private-sector investment than is a dam or a conveyor system. Given these factors, it appears that desalination is the only resource for regions with overdrafted groundwater aquifers, albeit in combination with integrated management (primarily that of water demand).

2.8. Summary of the chapter

In this chapter, general aspects about water resources are reviewed. It has been elaborated after a wide bibliography review. Having such an introductory chapter facilitates the understanding of all the following ones, since all the considered items appear disseminated along this work.

The distribution of water resources on Earth is shown and the main uses of the renewable fresh water are analyzed. Water quality characterization is also treated, as well as the main strategies in water management. Key issues brought here to be analyzed are related to the rapid growth of the population, putting more pressure on water supply (demand is increasing), the amount of water is effectively reduced by pollution (supply is decreasing) and the draw of the coming situation.

Future tendencies on a global level indicate spectacular growth in the domestic and industrial sectors (especially in underdeveloped countries) and less growth of the water dedicated to irrigation. In developed countries there is even a certain reduction of demand because of more efficient use and also for other reasons not directly related with water management, such as industrial delocalisation, as well as, in the European Union, the pressure of conservation policies such as, for example, those resulting from the Framework Directive.

In the last part of the chapter, water demand and water supply issues are considered. The different water treatment technologies are analyzed, from potabilization to desalination. Inflows and outflows that take part in each process are summarized. Their performance and suitability depending on the situation also appear, since they will be used in the following chapters.

Chapter 3

Statement of the problem

What is the value of water? This chapter tries to approach the question to give an answer to the matter. First of all, it is worth to bring forward here again the already introduced idea in Chapter 2 regarding that water is a natural resource, rather than a molecule or a source of economic utility. Water is, from the very beginning, the primary life-support of a system. In consequence, the answer will never be universal. In the broadest sense, *good* or *bad* is a value. So we are not interested in desires nor wants or, in other words, in *values*. Instead, the interest is focused on the value of an asset in relation to humankind's values. Therefore, the value of water will always be subjective as subjective are the man values. No general theory of the value of things can be stated accordingly. Also we are looking for numbers. We are accustomed to using sentences like *the value of that is... a number*, or we *evaluate* projects or men´s work by putting numbers and elaborate rankings. So, the numerical value of a thing serves primarily to make comparisons among the different states of that issue or a set of similar things. Besides of that, we are not intending to evaluate the concept *water* in relation to man, but evaluating some properties of water. In the range of human behaviour, these properties can be physical, chemical, biological, ecological, economic, social or even political and religious ones. Reduction of one type into another may be fruitless in many cases. However, two aspects of reality have been quantitatively developed more than others: the scientific and the economic aspects. Science quantifies physical, in a general sense, and biological properties, meanwhile Economics do the same with costs and prices. Both aspects help us to appreciate water qualitatively and quantitatively. These two features interact each other. For instance, dirty waters affect health and need depuration that increases its cost. In spite of it, in the field of water treatment and management, physical aspects and economics are poorly connected.

To sum up, a new question can be formulated: Is there any systematic relationship between the scientific parameters affecting the quality and quantity of water with the economic ones? Answering this question highly reduces the scope of the previous question regarding the *value of water*, since many aspects of the *value* concept have been left aside. We are not interested in social, political or ethical values concerning the water world. In this sense, many scientific as well as economic features of water will not be accounted for. For instance, we exclude from our analyses, in the context of this thesis, any biochemical, biological and/or ecological characteristics of waters, apart from the included in the definition of parameters that we do use, such as the environmental or minimum flow or rivers. At this stage of the presented methodology, the interest is concentrated in physical-chemical properties. The same happens with economic concepts: *prices* of water are not the matter, but *costs*. *Price* is what someone actually pays for a property. It is formed in the interchange. On the contrary, *cost* refers to production rather than to the exchange.

Then, the ideas developed in this thesis could help managers to rationally assess water costs in regular water supply systems. We do not intend to contribute with a theory of everything that substitute broader managing and political views in the social issue of water.

In addition to the development of that message, in this chapter, the concretion to water world is brought through the concept of *overcoming scarcity*, which is being transformed into the development of *means to live with scarcity*. Scarcity, water management and the development of social coordination mechanisms for living with it, should be the central focus of water economics.

Afterwards, the first Spanish attempt to relate Thermodynamics and water assessment is summarized. The Spanish water accounts improved the OCDE methodology for water accounting by introducing the quality concept on it, apart from the prescribed quantity.

Finally, the currently world-wide most important initiative regarding water accounting is *UN's System of Environmental-Economic Accounting for Water (*SEEAW). It is a conceptual framework for the organization of physical and economic information related to water using concepts, definitions and classifications

3.1. Market value, price and cost.

The concepts of value, cost and price have appeared in the introduction, although none specific clarifying about them has been done yet. Cost, value, and price are three distinct concepts. However, they are usually confused and used interchangeably, although it is not strictly correct.

Market value, unlike cost and price, is always expressed as a subjective fact or estimation that unavoidably introduces an error. Buyers and sellers add another margin of error because they make decisions based on emotions and personal preferences, not just rational thought. In consequence, it can be said that value is a theoretical concept based on complex human behaviour, i.e., because there are a wide variety of beliefs and assumptions about economics and human nature, there is an ongoing controversy regarding the definition of *value*. As a result, people have created different value definitions for different uses. The market value has no specific units.

The *price* is what someone actually pays for a good. It can give an idea of its value, but it only happens sometimes; what means that a buyer may pay more or less for a property than its theoretical market value. Price is expressed in monetary units.

Cost may be more precisely defined because it accounts for the different expenses along the production chain, it is the sum of resources to produce something. It comes from actual measurements like the amount of resources entering the production process, their prices at the moment of analysis, and other conditions previously defined. The precise assessment of its measurement does not tell us about its objectivity. This is because it depends on the prices of resources entering the system which depend on market subjectivities. It may be argued that we always can substitute prices of resources by their production costs but, at the chain end, we find the Nature. We are radically ignorant on how many resources were needed to produce natural goods we take for free. Therefore production costs can be precisely evaluated and they are as objective as the prices of consumed resources are. However, cost is calculated from a mixture of physical magnitudes and economic ones. In this sense, cost is closer to the objectivity of physical facts.

Unfortunately, because of the confusion among cost, value, and price, parties to a transaction often have difficulty in truly communicating with each other. The inclusion of physical laws, more specifically of Thermodynamics, in the analysis could help to manage with those concepts: in particular, the exergy concept.

As an example, the exergy content of a bohemian glass or a stone sculpture, or even gold is zero in practical terms. Many things that society values, thermodynamics does not. The source of value may be or may not be related to its exergy content, even for the case of fuels. Thus, the only thing that Physics can do is to assess the physical cost of objects, i.e., the amount of energy units required to produce a given product, namely embodied energy.

The concept of embodied energy comes from the 1970s, when it was a great concern with the first global energy crisis. The problem with energy is the lack of techniques to allocate values of embodied energy when two products are produced simultaneously. A more precise concept then came: the *exergy cost* proposed by Valero or the *cumulative exergy consumption* proposed by Szargut, which are in fact similar concepts to embodied energy but using exergy. That cost could be defined as the amount of resources needed to obtain a functional product.

Cost is therefore an emergent property. It cannot be measured as a physical magnitude of a flow stream as temperature or pressure; it depends on the system structure and appears as an outcome of the system analysis. In consequence, it needs precise rules for calculating it from physical data. Cost is a property that cannot be found in the product itself.

On one hand, resources take a general meaning. On the other hand, cost is associated to the purpose of production. It is associated neither with price nor with the resources that could be saved if the production process were less efficient or more conventional one. Any resource is measured in some specific units and, in consequence, the introduction of the monetary unit became necessary to unify all the cost. However, the *profit* concept, inherent to the market, makes the cost concept to disappear in that transformation. Cost is partially erased in the units change.

Generally, monetary costs are more objective than price. Prices are formed in the market and are only perfectly presented in economic books. On the contrary, cost of products and services are calculated by adding (objectively) the resources required to produce them. But resources are, in turn, the products of a previous process that consumed new resources, and so on.

However, moving backwards to Nature, it is very difficult to know the fair price (the willingness to pay) of the free resources and services that are continuously taken from Nature. Usually it is decided that the cost of natural resources is the *imperfect* price that they will fetch on the market. In this way, the chain of the objectivity of cost is broken since this is also formed by price policies that are not based on Physics. In other words, converting monetary cost into energy cost based on the technical input–output coefficients is only justifiable when no alternative and more rigorous methods are available.

Furthermore, the price-fixing mechanisms rarely take into account the concrete physical characteristics that make them valuable. But natural capital has at least two physical features which make fresh water, for example, unusual: a particular composition which differentiates it from the surrounding environment, and a distribution which places it in a specific concentration. These intrinsic properties, can be in fact evaluated from a thermodynamic point of view in terms of exergy

The calculation of exergoecological costs can be proposed for all those products and services, which our society produces from ecosystems and consumes, although they could be sometimes really complicated to estimate due to lack of information. The development of a methodology to objectively asses water cost through the exergy concept is the main objective of this dissertation.

3.2. Economic assessment of the environmental services

In economics, the environment is viewed as a composite asset that provides a variety of services (Tietenberg, 2006). It provides the life-support systems that sustain our existence, so it is a fundamental asset. As it happens in relation to other assets, it is wished to avoid undue depreciation of the value of this asset so that it can be able to continuously provide aesthetic and life-sustaining services.

As Figure 3.1 summarizes, raw materials and energy are provided by the environment. Materials are transformed into consumer products through the production process, run by energy. After their use, materials and energy are returned to the environment as waste products. The breathed air, the protection, the provision of nourishment or the landscape are environmental services that consumers also obtain from the environment. The energy received on Earth is mainly from the Sun, either directly or indirectly.

The treatment of our Planet and its immediate environment as a closed system has an important implication: the mass of materials flowing into the economic system from the environment is return to it as waste in the same amount (assuming no accumulation) in the system. In consequence, an excessive waste can depreciate the asset. If the absorptive capacity of nature is exceeded, wastes reduce the services that the asset provides.

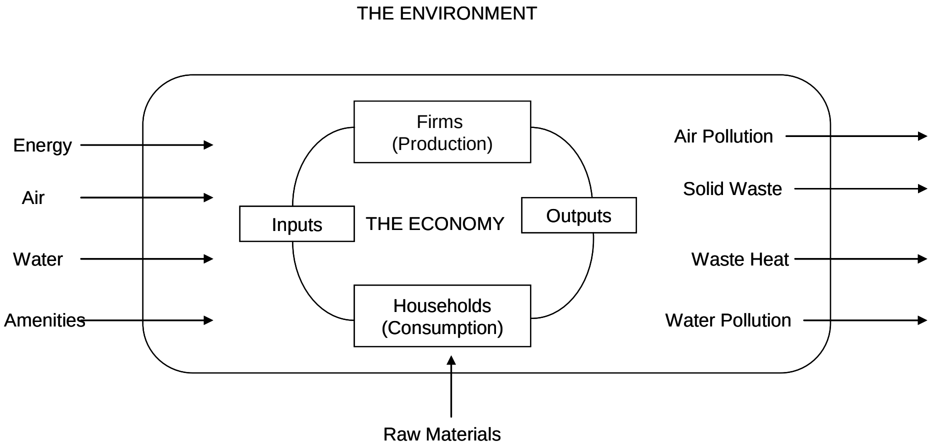


Figure 3.1. The economic system and the environment (Source: adapted from Tietenberg, 2006)

The Second Law of Thermodynamics states the irreversibility of any consumption of energy, that is, the entropy increases because some energy is always lost during the conversion, and the rest, once used, is no longer available for further work. The Second Law also implies that in the absence of new energy inputs, any closed system must eventually use up its energy. Since energy is necessary for life, life ceases when energy ceases.

Our planet is not even approximately a closed system with respect to energy because of the energy gained from the sun. The Entropy Law suggest, however, that this flow of solar energy established an upper limit on the flow of energy that can be sustained. In the future, if the stored energy in fossil and nuclear fuels is depleted, the amount of energy available for useful work will be only determined by this flow and by the amount that can be stored in dams or biomass. Assuming this situation the growth process, over the long run, will be limited by the availability of solar energy and our ability to put it to work.

Whatever the chosen approach to asses natural resources, it must be first well understood the relationship between the economic system, natural resources, and the environment. That is why, in this chapter, a brief historical review about the nature environment and economics interaction is carried out. Special attention is devoted to Georgescu-Roegen, Daly or Naredo, whose ideas are considered as milestones for the framework of this dissertation: the *Ecointegrator* approach.

3.2.1. The accounting systems: from Mercantilism to the Physiocrats and the Ricardian Earth.

The genesis of the theoretical background for the current national accounting Systems, guiding the macroeconomist' thought, dates from 18th Century (Naredo, 1987). Before that time, the Mercantilism was the dominant school of thought throughout the early modern period (from the 16th to the 18th Century).

Mercantilism's background is based on the statement that the prosperity of a nation is dependent upon its supply of capital. In this economic theory, it is assumed that the global volume of international trade is unchangeable and that the economic assets or capital are represented by gold, silver, and trade value (defined as bullion). It is held by the state and can increase through a positive balance of trade with other nations. The economic system is seen as a zero-sum game, in which any gain by one party required a loss by another. Thus, any system of policies that benefited one group would by definition harm the other, and there was no possibility of economics being used to maximize the common good (Landreth and Colander, 2002). Mercantilists' interest lies in rationalize particular practices rather than in establishing the best policies (Landes, 1997). They defend a protectionist role of the government in relation to the economy of the country, by encouraging exports and discouraging imports, by using tariffs and subsidies.

From there Montesquiev considered the Economy as the science of *richness acquisition*. Having this in mind, it can be understood, as Naredo mentions (Naredo and Valero, 1999), that the Spaniards in America, when offered mirrors and glass pieces to the aborigine in exchange for gold and gemstones, were perfectly conscious about committing an unfair trade. Nevertheless, natural resources are nowadays extracted from poor countries in exchange for less valuable assets such as informatics or financial products, and the conscience about the swindle does not exist any more.

Thus, the strengthening of Economics was not any more based on the acquisition, but on the richness production. It was needed to wait until the works of the today called Physiocrats, to establish the notion of *production* as centre of the modern version of the economic system. The group of economics designed as Physiocrats thought that the wealth of nations was exclusively derived from the development of land and agriculture, and the value that is produced. Physiocrats' theories were initially developed in France and their popularity increased by the second half of the 18th Century, becoming a very well structured theory of Economics. Two important leaders of this current were Anne-Robert-Jacques Turgot and François Quesnay. Quesnay published the famous *Tableau économique* in 1758, trying to orientate the techniques to obtain higher efficiency rates in all the productive activities. Physiocracy immediately preceded the first modern school, classical economics, which began with the publication of Adam Smith's *The Wealth of Nations*, in 1776 (Nell, 2009).

The Physiocrats' emphasis on productive work as the only source of national wealth is in contrast to earlier schools which often focused on the accumulation of bullion or the balance of trade. However, they only considered agricultural labour as valuable, what is seen as an important weakness from the point of view of modern tendencies. The modern economists understand the production of goods and services as productive activities to be added to the national income. However, for the Physiocrats, precursors of the anti-mercantilist movement, those were the investment of the agricultural surplus.

Physiocrats developed their theory in a completely agricultural French economy (agriculture was 80% of the country's wealth). Quesnay's ideas against industry and international trade are based on the belief that industry production does not mean any gain in wealth. If labour from agriculture is invested into industry, the overall wealth would decrease. As a consequence, population should decrease if the available land to produce food disappears in favour of industry. In addition to that, the trade proposed by Mercantilists assumes that there exits more of a resource than it needs for internal consumption and therefore that resource can be tradeable. As a summary, it can be said that Physiocrats linked all the generation capacities to the *Mother Earth*.

Once established the economic system idea with its production and consumption carousel, and accepted the target of its expansion and continuous growth, a movement of this ideal system from the physical context (where it was initially formulated) to the universe of monetary values, was operated. Such a displacement happens at the same time that the developments of the Nature sciences invalidated the archaic vision of the world and the eagerness of controlling the underlying physical growth.

As a matter of fact, when the mineralogy, supported by the modern Chemistry knowledges, refuted the ancient believes about the growth of the minerals inside the Earth, and when Geodesy obtained accepted measurements of the Earth meridian, the ideas of production and growth of the aggregates of the economic system distanced from the physical world until being completely confined in the self-sufficient value universe.

Those authors finished the cut of the nexus that still joined the idea of economic system to the surrounding physical world trough the concept of *ricardian earth*: the Earth, with all its resources, as well as work, are replaceable by capital. Ricardo's most famous work is his *Principles of Political Economy and Taxation* (1817), where he states the labour theory of value: the relative price of two goods is determined by the ratio of the quantities of labour required in their production. From it, it is derived that the effects on income are always beneficial because foreign trade does not affect value and it is always benefits (comparative advantage). Net product is selling off with profit. Ricardo was an opponent of protectionism for national economies, as also Adam Smith was.

The central aggregate of the current national accounting systems is an added-value balance resulted from subtracting the sale value from the import spent in their obtaining. The physical processes are left out.

It is relevant to add at this point that the developed countries, cradle of the Industrial Revolution, are used to derivate an important part of their negative externalities far from their own territories, charging them on the rest of the Planet. This issue is related to the existing deep asymmetry between the monetary valuation and the physical cost along the whole general economic process. It leads to the physical inequality related to the costs, that underlies from the monetary equality of the interchanges in the own world trade. In this context, appeared new concepts such as the ecological rucksack, which estimates the ecological deterioration dragging by the products along their production process; or the ecological footprint, a measure of human demand on the Earth's ecosystems that represents the amount of biologically productive land and sea area needed to regenerate the resources a human population consumes and to absorb and render harmless the corresponding waste (Naredo and Valero, 1998).

3.2.2. Georgescu-Roegen: the change of the paradigm.

Although the idea of getting closer the environment and the economy had been largely treated, the Nicolas Georgescu-Roegen's contribution deserves a special attention. He is considered as one of the most remarkable and profound thinkers in modern economics.

Georgescu-Roegen filled up the gap between two far natural resources conceptions, providing a link to join the mecanicism leading the traditional economy, where the imperative perception was that any process can be reversible (and the consequent idea that any asset is replaceable), and the Ecological Economics, where entropy straightens up as the most suitable valuation tool.

In 1966, Georgescu-Roegen, published *Analytical Economics*, where he developed his initial ideas on a new biological or evolutionary approach to economic theory. His ideas were further developed and consolidated in his magnum opus, *The Entropy Law and the Economic Process* (1971). Today, his work is becoming more and more relevant, and his insights are being grafted into the evolutionary economics, already postulated by Schumpeter (first half 20th century) and linked to Darwin's evolutionary biology (Martínez-Alier, 1987).

3.3. Environment and Economics: two different ways of facing the interrelationship.

From all the previous revision, it can be concluded that two approaches exist in addressing natural resources Economics: the standard neoclassical mainstream of Economics that applies economic concepts to the environment through the named Environmental Economics; and the approach known as ecological economics, which seeks to place economic activity in the context of the biological and physical systems that support life, including all human activities. The latter implies, in some way, a modified look back to the *Mother Earth* concept of the world defended by the Physiocrats.

A simple and schematic review of the main features of these two approaches has been done next.

3.3.1. Environmental Economics.

Environmental Economics is a subfield of traditional Economics concerned with environmental issues. Particular issues include the costs and benefits of alternative environmental policies to deal with air pollution, water quality, toxic substances, solid waste, and global warming (NBER, 2007).

When the optimal commercial exploitation of natural resource stocks started to be an important concern, the Economics of natural resources began. Resource managers and policy-makers paid attention to the broader importance of resources and their associated externalities.

Markets fail to allocate resources efficiently, and this is the starting point of Environmental Economics. According to Hanley et al. (2007), a market failure occurs when the market does not allocate scarce resources to generate the greatest *social welfare*. A disequilibrium in market prices implies inefficiency and wastefulness of goods. Then, resources can be reallocated to make at least one person better off without making anyone else worse off. Market failure includes externalities, non excludability and non rivalry. These three concepts are summarized, according to Hanley et al. (2007) in the following:

Externality: it is a market failure in which the market does not lead to an efficient outcome. It can be summarized with the idea that an externality exists when a person makes a choice that affects other people that are not accounted for in the market price. For instance, a firm pouring wastes on water will probably not take into account the costs that its behaviour imposes on others.

Common property and non-exclusion: If the scarcity value of the *commons* (environmental asset) is ignored, resources can be over harvested. When it is too costly to exclude people from accessing a desired environmental resource, market allocation is likely to be inefficient.

Hardin, in 1968, theorizes that in the absence of restrictions, users of an open-access resource will use it more than if they had to pay for it and had exclusive rights, leading to environmental degradation (Ostrom, 1990). His concept of the tragedy of the commons popularized the challenges involved in non-exclusion and common property. There exist two basic concepts, the *common property*, where a property right regime that allows for some collective body to devise schemes to exclude others, thereby allowing the capture of future benefit streams; and the *open-access*, which implies no ownership in the sense that property everyone owns nobody owns.

Public goods and non-rivalry: It appears when market price does not capture the social benefits of its provision. For example, protection from the risks of floods is a public good since its provision is both non-rival and non-excludable. Non-rival means that flooding protection provided to one country does not reduce the level of protection to another country; non-excludable means that it is too costly to exclude any one from receiving that protection.

3.3.1.1. Natural resources valuation from the Environmental Economics perspective

The main issue within the Environmental Economics context is assessing the economic value of the environmental services. Different uses can be distinguished: use and indirect use, which are tangible benefits accruing from them; and non-use values, including existence, option, and bequest values, and which are estimated using stated preference methods such as contingent valuation or choice modelling.

Contingent valuation typically takes the form of surveys about the people's willingness to pay or their willingness to accept compensation for the destruction of the environmental good. Hedonic pricing examines the effect the environment has on economic decisions through housing prices, travelling expenses, and payments to visit parks (Harris, 2006).

The solutions advocated correcting such effects and externalities include, according to the environmental economics methodology:

Environmental regulations, whose economic impact is usually calculated by a cost-benefit analysis estimated by the regulator. There is a proliferation of these *command and control* instruments, which derive directly form conventional economics. In general, regulations are implemented by fines, which operate as a form of tax if pollution rises above the threshold prescribed. Other option would be that the pollution must be monitored and laws enforced, whether under a pollution tax regime or a regulatory regime.

Quotas on pollution. With the final objective of getting a pollution reduction in the cheapest way, the tradeable emissions permits are played into the market. Then, a firm can reduce its pollution load by paying a different firm to make the same reduction. In practice, tradeable permits approaches have had some success, such as the EU's carbon dioxide trading program, though interest in its application is spreading to other environmental problems.

Taxes and tariffs on pollution. It is also know as removal of *dirty subsidies*. It consists on setting a tax on polluting. It is considered a dynamic incentive because the tax continues even as pollution levels decreases. This idea is sometimes named as green tax.

Better defined property rights. To assign property rights can mean an optimal solution if there is no transaction cost, regardless of who receives them. For example, if people living near a factory had a right to clean air and water, or the factory had the right to pollute, then either the factory could pay those affected by the pollution or the people could pay the factory not to polluted. Many markets for *pollution rights* have been created in the late twentieth century. The assertion that defining property rights is a solution is somehow controversial within the field of environmental.

The main academic and professional organizations for the discipline of Environmental Economics are the Association of Environmental and Resource Economists (AERE) and the European Association for Environmental and Resource Economists (EAERE).

3.3.2. Ecological Economics

Ecological Economics addresses the interdependence of human economies and natural ecosystems. This transdisciplinary discipline studies the metabolism of society and is based on a conceptual model of the economy connected to, and sustained by, a flow of energy, materials, and ecosystem services.

According to Faber (2007), Ecological Economics is defined by its focus on nature, justice, and time. Issues of intergenerational equity, irreversibility of environmental change, uncertainty of long-term outcomes, and sustainable development guide the analysis and valuation.

Ecological Economics theorists emphasize the importance of energy resources, especially fossil fuels, in current economic systems. All ecological systems depend on energy inputs, but natural systems rely almost entirely on solar energy (this statement is the based where, as it will be seen later on, Odum founded the *Emergy* approach).

In the 1960s, started the interest in ecology and economics. As Constanza relates (Constanza, 2003), the first meetings occurred in the 1980s. It began with a symposium in Sweden which was attended by people who would later be instrumental in the field, including Costanza, Daly, Hall, Odum, and Pimentel. Most were ecosystem ecologists or mainstream environmental economists, with the exception of Daly. In 1987, Daly and Costanza edited the first issue of the journal *Ecological Modelling* to test the waters.

The rapid growth of economic production during the twentieth century required enormous energy inputs, and global economic systems will make even greater energy demands in the twenty-first century. Energy availability and environmental implications of energy use are central issues for Ecological Economics. As previously indicated, Nicholas Georgescu-Roegen provided Ecological Economics with a modern conceptual framework based on the material and energy flows of economic production and consumption. He has been highly influential in this field and can be considered the father of this new way of thought.

A fundamental principle of ecological economics is that human economic activity must be limited by the environment's carrying capacity. Carrying capacity is defined as the population level and consumption activities, whether of humans or animals, that the available natural resource base can sustain without depletion. As an example of non carrying capacity observation, the conditions on the Mexico-US border (too many people, industries and pollution because of low-cost labor and lax environmental controls) constitute an excellent example of incrementalization (Ganster, 2002). This situation could be illustrated through the well-worn parable of the frog and the saucepan: dropped into a pan of hot water, the frog instantly jumps out. However, when placed in cool water that is gradually heated, the frog remains passive until it boils. Not noticing gradual change, it is incrementalized to death.

To sum up, the main objective of Ecological Economics is to link the physical reality with the economic thinking and practice. The physics laws and the knowledge of biological systems are the milestones, focussing on uneconomic growth and quality of life. Ecological economists are inclined to acknowledge that much of what is important in human well-being is not analyzable from a strictly economic standpoint and suggests an interdisciplinary approach combining social and natural sciences as a means to address this.

The main academic and professional organization for the discipline of Ecological Economics is the International Society for Ecological Economics (ISEE). It is a not-for-profit, member-governed, organization dedicated to advancing understanding of the relationships among ecological, social, and economic systems for the mutual well-being of nature and people.

3.3.2.1. Natural resources valuation from the Ecological Economics perspective

Two concepts, commonly confused by the traditional economy, need to be distinguished within the Ecological Economics framework: *growth*, a quantitative concept; and *development*, meaning a qualitative improvement of the quality of life. Ecological Economics challenges the common normative approach taken towards natural resources, claiming that it misvalues nature by displaying it as interchangeable with human capital-labour and technology. In Ecological Economics, natural capital is added to the typical capital asset analysis of land, labour, and financial capital.

Ecological economists belief that standard economics theory does not considered all the importance of the energy supplies, the scarce natural resources, and cumulative environmental damage. They assumed that human capital is not complementary to, but dependent upon natural systems, since human capital inevitably comes from natural systems.

The whole idea of treating ecosystems as goods and services to be valued in monetary terms remains controversial. A common objection is that life is precious or priceless, but this demonstrably degrades to it being worthless under the assumptions of any branch of Economics. Reducing human bodies to financial values is a necessary part of every branch of Economics and not always in the direct terms of insurance or wages (Mishra, 2008).

Costanza el al. (1997) presented a study to determine the *price* of the services services provided by the environment. This was determined by averaging values obtained from a range of studies conducted in very specific context and then transferring these without regard to that context. Dollar figures were averaged per hectare number for different types of ecosystem e.g. wetlands, oceans. A total was then produced which came out at 33 trillion US dollars (1997 values), more than twice the total GDP of the world at the time of the study. This study was criticized by pre-ecological and even some environmental economists (for being inconsistent with assumptions of financial capital valuation), and ecological economists (for being inconsistent with an Ecological Economics focus on biological and physical indicators), (Norgaard and Bode, 1998).

Although, as it has been clearly seen, the fact of using physical laws to assess natural resources is agreed by ecological economist, the way to do it is somehow diverse. Initially, the valuation methods based on the First Thermodynamics Law appeared and its followers are known as Energeticist. A more elaborated approach comes from the Second Thermodynamics Law, including the quality of the energy flows.

Energeticists: First Law of Thermodynamics

The energeticists were the ecological economics's pioneers at the beginning of the 20th century. The viewed clear that the monetary system is not the adequate way of valuing environment and developed their value theory based on the calorie unit. They defended that any item can be translated into that energy unit. This current keeps the knowledge in a mechanicist paradigm, but open the door to a new form of analysis.

Energy accounting and balance is one of the most powerful tools used by Ecological Economics. An energy balance can be used to track energy through a system, and is a very useful tool for determining resource use and environmental impacts, using the First and Second laws of thermodynamics, to determine how much energy is needed at each point in a system, and in what form that energy is a cost in various environmental issues (Cleveland, 2006). The energy accounting system keeps track of energy in, energy out, and non-useful energy versus work done, and transformations within the system.

One of the most important and comprehensive contributions to the energy and Thermodynamics history and its relationship with the Economy, was published by Martínez-Alier in 1987 under the title *Ecological Economics: Economics, environment and society* (Martínez-Alier, 1987).

Odum's Emergy concept

An especially interesting branch withing the energeticist approach to relate environment and economics is *Emergy*, defined as the available energy of one kind previously used up directly and indirectly to make a service or product by Odum (1996). He is known for his pioneering work on Ecosystem Ecology, and for his provocative proposals for additional laws of Thermodynamics, informed by his work on general systems theory.

Emergy analysis has evolved from the field of *eco-energetics* (Odum, 1971) and its empirical origins stem from the study of the patterns of energy flow which ecosystems and economic systems develop during self-organization (Odum, 1988). The theoretical foundations of emergy analysis are based on the observation that both ecological systems and human social and economic systems. They are fundamentally energetic systems exhibiting characteristic designs and organizational patterns that reinforce energy use. Moreover, emergy analysis posits that the dynamics and performance of environmental systems are best measured and compared on an objective basis using energy metrics. Earlier applications of this concept used the term 'embodied energy' (Costanza, 1980; Odum and Odum, 1976) to signify that the energy expended during production in ecological and economic systems can be considered to be embodied in the system's products.

Furthermore, it is held that this embodied energy informs a product's potential importance, or value, to both the production system that created the product and to its end-users. Odum (1988) later adopted the word emergy to differentiate the concept from other similar concepts in use in the field of ecological economics (Brown and Herendeen, 1996). By utilizing concepts and data from many different scientific disciplines, emergy analysis is in many respects a transdisciplinary science, and can be thought of as a synthesis of systems theory, ecology and energy analysis.

Emergy values are most often quantified and expressed as solar energy equivalents, and the unit used to express emergy values is the solar emJoule (seJ). By tracking all resource inputs back to the amount of solar equivalent energy required to make those inputs, emergy analysis accounts for all the entropy losses required to make a given product, and thereby allows for qualitatively different resources to be considered on a common basis. Emergy has elsewhere been referred to as the 'memory of energy' that was dissipated in an energy transformation process (Odum, 1996; Brown and Ulgiati, 1999). In contrast to economic valuation, which assigns value according to utility - or what one gets out of something - and uses willingness-to-pay as its sole measure, emergy offers an opposing view of value where the more energy, time and materials that are invested in something, the greater is its value. According to Odum, the principles of energetics take into consideration a hierarchical ordering of energy forms, which aims to account for the concept of energy quality, and the evolution of the universe.

Emergy analyses have been used to assess the sustainability of environmental systems of all scales, from economic activity within the Biosphere of the Earth (Brown and Ulgiati, 1999), to the sustainability of national economies (Ulgiati et al., 1994; Lagerberg and Brown, 1999), to bio-fuel production (Ulgiati, 2001; Bastianoni and Marchettini, 1996), water supply alternatives (Buenfill, 2001a), municipal wastewater treatment (Björklund et al., 2001), and historical comparisons of industrial and pre-industrial agricultural systems (Rydberg and Jansén, 2002).

Because of its interest and the provided complementary vision, this emergy approach will be further developed in the Chapter 7 of this dissertation.

Second Thermodynamics Law as working tool

A further step in the valuation of Environment within Economics is including the quality and degradation aspects in the analysis. From a physical perspective, it means to include the Second Thermodynamics Law (entropy law). That is, taking exergy as the working tool.

From the Industrial Revolution until today, the development and continuous efficiency improvements of the energetic and industrial sectors have been tightly joined to the Thermodynamics principles. None of the advances can be understood without its proper thermodynamics context.

In addition to its traditional industrial trajectory, the Exergy analysis has been performed in the field of Industrial Ecology to use energy more efficiently (Wall, 1986). In recent decades, utilization of exergy has spread outside of physics and engineering to the fields of Industrial Ecology, Ecological Economics, Systems Ecology, and Energetics (e.g., Jørgensen et al., 2000; Rosen and Dincer, 2001; Gong and Wall, 2001; Wall, 2002; Szargut, 2003, 2004; Chen, 2006).

The resource accounting in terms of exergy has been carried out based on nation or industrial sector scales (Chen, 2007). Dincer (2002) paid much attention to the relationship between energy utilization and the environmental impacts, and highlighted the implication of the exergy analysis to the sustainable development.

Hellstörm (1997, 2003) estimated and compared the exergy consumption of physical resources in some wastewater treatment plants and sewerage systems. Finnveden and Östlund (1997) and Ayres et al. (2002) have developed an Exergy Based Life Cycle Analysis, introducing the concept of exergy into the methodology of environmental life cycle assessment and using it as a uniform indicator of total environmental impact.

In a framework for systems evaluation based on exergy circuit language, ecological value for a waste stream is defined negative and equal in magnitude to corresponding embodied exergy in terms of the total exergy consumed in human helped treatment or natural degradation of the waste water stream (Chen, 2006).

Chen (2007) developed for a unified objective assessment of water quality, the chemical exergy based evaluation method. While a quantity termed specific standard chemical exergy based on the global reference substances might be adopted, an indicator as specific relative chemical exergy with reference to a spectrum of substances associated with the specified water quality standard is proposed for water quality evaluation. So it has more practical implications, resulting in unified objective quantifiers for the carrying capacity and carrying deficit of water resources. With data collected in the GEMS/WATER project, water qualities of 72 rivers and 24 lakes over the world were evaluated as a detailed case study to illustrate the adaptability of the chemical exergy based indicators for water quality evaluation.

3.3.3. Comparative: Environmental Economics vs. Ecological Economics.

Ecological Economics seeks to recognize what traditional economics often ignores; that the Economy is embedded in wider social and biophysical systems (Dodds, 1997). Ecological economics is distinguished from Environmental Economics by its connection to disciplines within the natural sciences and its focus on how to operate an economy within the ecological constraints of Earth's natural resources.

Ecology deals with the energy and matter transactions of life and the Earth, and the human economy is by definition contained within this system. Economic theory, as encapsulated in general equilibrium models, assumes both an infinite resource base and also infinite waste sinks with no feedbacks. This allows neoclassical economics to claim theoretically that infinite economic growth is both possible and desirable, what disagrees with much of what the natural sciences have learned about the world and, according to Ecological Economics, completely ignores the contributions of Nature to the creation of wealth. As an example, the planetary endowment of scarce matter and energy, along with the complex and biologically diverse ecosystems that provide goods and ecosystem services directly to human communities: micro- and macro-climate regulation, water recycling, water purification, storm water regulation, waste absorption, food and medicine production, pollination, protection from solar and cosmic radiation, the view of a starry night sky, etc.

Resource and neoclassical economics focus primarily on the efficient allocation of resources, and less on two other fundamental economic problems which are central to Ecological Economics: distribution (equity) and the scale of the economy relative to the ecosystems upon which it is reliant (Daly and Farley, 2004).

Ecological economics uses tools from mathematical economics, but may apply them more closely to the natural world, i.e., the physical laws. Whereas mainstream economists tend to be technological optimists, ecological economists are inclined to be technological pessimists. They reason that the natural world has a limited carrying capacity and that its resources may run out. Since destruction of important environmental resources could be practically irreversible and catastrophic, ecological economists are inclined to justify cautionary measures based on the precautionary principle (Costanza, 1989).

These two groups of specialists sometimes have conflicting views which can often be traced to the different philosophical underpinnings of the two fields. Some ecologists subscribe to deontological ethical systems; other economists subscribe to teleological ethical systems (Mazilu and Ciobanu, 2009). Ethical system can not be demonstrated to be right or wrong, but they may sometimes have different implications for environmental policy. Environmental economics is viewed as relatively more pragmatic in a price system; ecological economics as relatively more idealistic as it supposedly does not use money to arbiter decision making as much.

3.4. Water as an economic good

Starting from the Agenda 21 and the Dublin Principles, which put the concept of *water as an economic good* on the global agenda, Peter Rogers tried to clarify the substantial confusion about its meaning (Rogers et al, 1998). He addressed the lack of understanding by formulating the concept of water as an economic good and explaining, in practical terms, the economic tools that can be used to effect the environmentally, socially, and economically efficient use of water. He defends the potential role of economic tools in providing socially acceptable public decisions.

As a summary of that work, some useful ideas are reproduced here in order to correctly locate the WFD's requirement regarding water costs.

In assessing the economic value of water and the costs associated with its provision, two main aspects have to be observed: the cost involved in the provision of water and the value of the use of water. Regardless of the method of estimation, the ideal for the sustainable use of water requires that the values and the costs should balance each other; full cost must equal the sustainable value in use (see Figure 3.2).

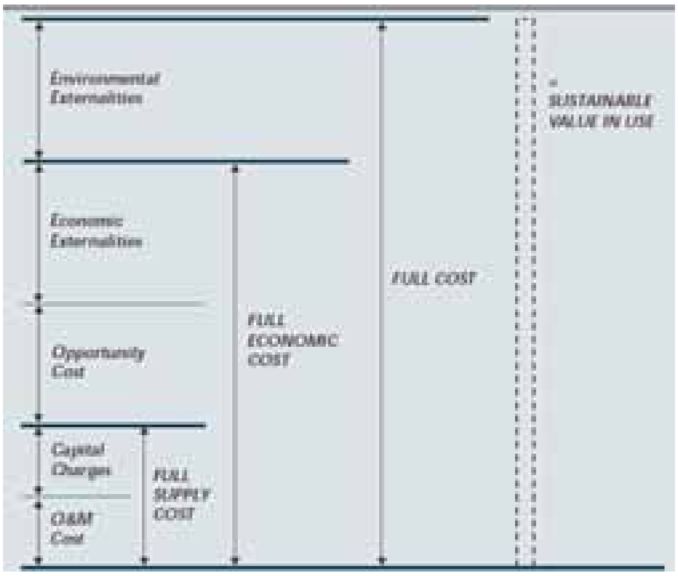


Figure 3.2. General principles for cost of water according to Roger's work (Rogers et al, 1998)

Three important concepts can be identified: the Full Supply Cost, the Full Economic Cost; and the Full Cost.

The Full Supply Cost includes the costs associated with the water supply to a consumer without consideration neither of the externalities imposed upon others nor of the alternate uses of the water. Full Supply Costs are composed of two separate items: Operation and Maintenance (O&M) Cost, and Capital Charges, both of which should be evaluated at the full economic cost of inputs.

The Full Economic Cost of water is the sum of the Full Supply Cost, the Opportunity Cost associated with the alternate use of the same water resource, and the economic externalities imposed upon others due to the consumption of water by a specific actor.

The Full Cost of consumption of water is the Full Economic Cost, given above, plus the Environmental Externalities. These costs have to be determined based upon the damages caused, where such data are available, or as additional costs of treatment to return the water to its original quality.

According to Rogers et al. (1998), for economic equilibrium, the value of water, which is estimated from the value in use, should just equal the full cost of water. The value in use is typically expected to be higher than the estimated full cost. This is often because of difficulties in estimating the environmental externalities in the full cost calculations.

3.5. Costs definition in the WFD.

The European legislation (WFD) explicitly says in its Article 9 that *Member States shall take account of the principle of recovery of the costs of water services, including environmental and resource costs, having regard to the economic analysis… and in accordance in particular with the polluter pays principle.*

In consequence, water pricing policies should be readjusted by 2010 following the guidelines of the Full Cost Recovery Principle (FCR) stated in the Directive. That text does not explicitly use the term full or integral cost recovery (in Article 9, as reproduced in previous paragraph, it just mention that the cost recovery principle concerning water has to be taken into account). This fact leads to consider the possibility of modulating the principle and of establishing exceptions, as long as they are suitably justified. Regarding users, at least industry, households and agriculture will be taken into account by using the *Polluter Pays* Principle.

However, it does clearly state that, when it talks about the cost concept, it is not just referring to costs in the conventional economic sense but that it considers *even the environmental costs and those concerning the resource.* The FCR concept contains diverse terms, which according to the WATECO group guide (ECO2, 2004) are:

- *financial costs (or services costs)* include the cost of providing and administering water services, such as supply, sanitation, transport and storage, which at present are reflected to users in minor or major quantity. They include all operation and maintenance costs, and capital costs (principal and interest payment), and return on equity where appropriate, i.e., the costs of depreciation of capital, the costs of financing, the costs of maintenance and running, the administrative costs and other direct costs that could be included.
- *environmental cost* regarding the alteration of the physical and biological aspects of water bodies due to human activities. It represents the cost of damage that water uses impose on the environment and ecosystems and those who use the environment (e.g. a reduction in the ecological quality of aquatic ecosystems or the salinisation and degradation of productive soils). In consequence, the environmental cost also includes "economic externalities" such as the loss of employment in the services sector in rural areas due to the impacts of a social nature due to the degradation of the water resources.
- *resource cost* as the cost of foregone opportunities which other uses suffer due to the depletion of the resource beyond its natural rate of recharge or recovery,

derived from an inefficient or alternative use (for example, linked to the over-abstraction of underground waters).

The first term could be easily calculated from classical economic accountancy. However the second and third terms are obviously more difficult to evaluate, at least with current analysis tools in existing water management policies.

3.5.1. The *Ecointegrator* approach

As measurements are gradually introduced to restore water bodies, they should be considered as financial costs following the FCR concept, and therefore double accounting could appear if this circumstance is not taken into account. This idea has been already highlighted by many authors. Naredo (2007) presented some interesting graphics showing this idea; they have been adapted and reproduced in the Figure 3.3.

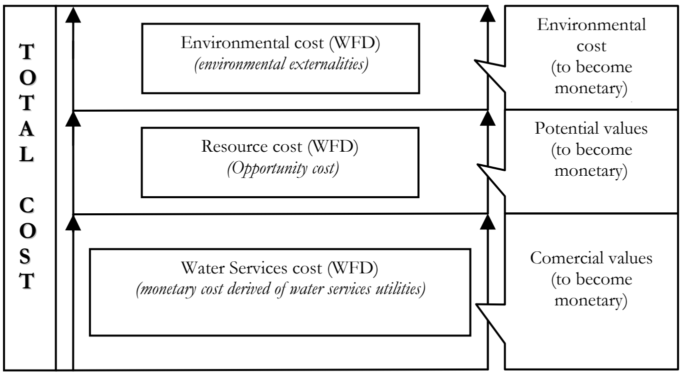


Figure 3.3. Costs in the standard economic approach, adapted to the WFD requirements (Source: Naredo, 2007)

According to Naredo, the underlying hypothesis comes from traditional Economics and indicates that the mentioned costs are one- dimension (only expressed in monetary units), they do not overlap (forming disjoint sets) and they are additive (they have to be added to obtain the total cost to be assigned to the users).

After a detailed analysis of the restrictions included in the WFD's costs definitions by a traditional economics interpretation (see Naredo, 2007), this author describes a new methodological proposal aimed to open the closed (and generally one-dimensional) reasoning outlines. In this way, the approach could be open to open, multidimensional and transdisciplinary treatments, more adequate for the management of the current industrial society.

Naredo's proposal does not try to eliminate or marginalize the monetary and hydraulic traditional approaches, but relocate them in the wider frame of the new approaches. As an example, the study and good information of the environmental costs of water body is not called to exclude the studies devoted to know the willingness to pay for its environmental quality. It just derivates to further exercises of informed social participation serving to reach a consensus about quality standards with full knowledge of the reason why cost are originated and their payment repercussions.

The proposed calculation methodology for the water costs affirms its pluridimensionality, what does not denies, but reinforce, the monetary approaches offering new support points. It also considers that the service, environmental and resource costs are not disjoint sets (and therefore neither additive), but they overlap: water management must precisely be able to play with those intersections and overlaps in order to design reasonable economic tools.

These ideas are summarized in the called *Ecointegrator Approach*, whose main interest is in orienting the water costs to get that the cost of the water service fairly reflects the environmental and recource cost, attending to the good water management principles and passing from the case A to the case B represented in Figure 3.4 and Figure 3.5.

Case A: The service costs (monetary) hardly account for the environmental and resources cost.
Case B: The service costs (monetary) reflect an important part of the environmental and resource costs.

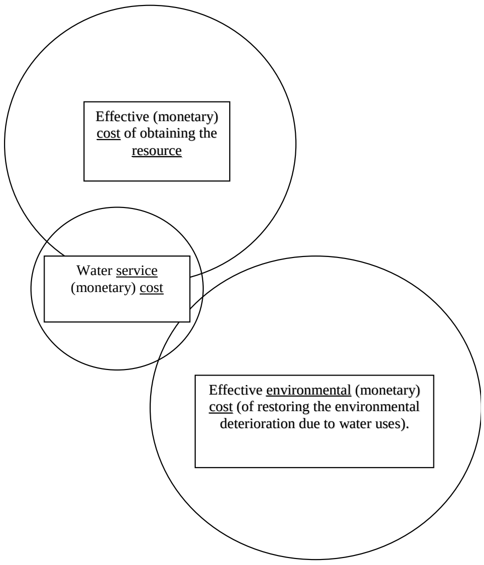


Figure 3.4. Small overlap of the different water costs (Source: Naredo, 2007)

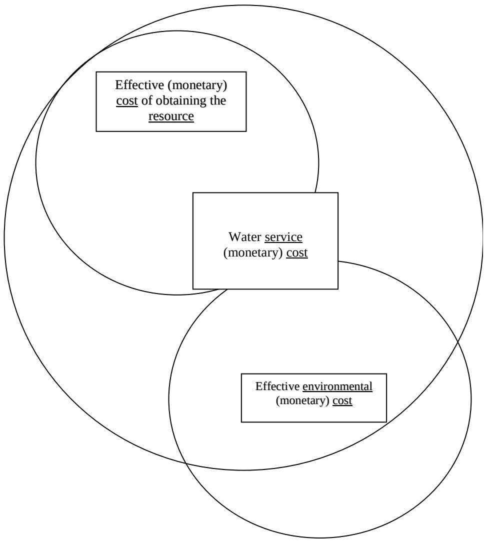


Figure 3.5. Overlap of the different water costs, *Ecointegrator* approach (Source: Naredo, 2007)

The implicit hypothesis is: 1º) The costs are pluri-dimensional (they can be quantified in monetary and physical units), 2º) Its monetary version changes with the institutional Framework, which provokes overlapping of the environmental and resource (obtaining) costs with the service cost, and 3º) The three costs are not additive: the service costs has to account for the environmental and resource costs.

A water management system that observes the WFD Principles about the costs recuperation and the degrader pays principle, the service cost of water should account for the environmental costs as well as for the resource cost. At the same time, the water tariffs regime should be adapted to the resulting costs panorama, except in specially justified exceptions.

3.6. Water, scarcity and their management.

Like many natural products, water's worth has increased as its usage has risen. A huge amount of water-related issues are growing interest for the last years. Its availability has also been affected by the notion that has come to be called the environmental *Kuznets curve*– rising income levels bring even greater increases in the demand for a better environment and this often incorporates the non-use of rivers, forests and land. Kuznets curve is the graphical representation of Simon Kuznets's theory that economic inequality increases over time while a country is developing, then after a critical average income is attained, begins to decrease.

Despite the best efforts of scientist and engineers, scarcity prevails today. Demands for water have continued to increase with expansions of irrigated agriculture, resource processing, industrial application and domestic use. There has also been a growing recognition of the inverse relationship between the health of riverine ecologies and the extent of water extractions. This has promoted the emergence of demands for environmental flows in rivers. At the same time, the total amount of water available remains constant (if somewhat stochastic) and the possibilities for relocating water have been reduced through increased competition for the environmental resources required for the construction of dams. Furthermore, water supply is, in places, becoming increasingly compromised in terms of its suitability for different purposes because of quality deteriorations.

Hence the saga of *overcoming scarcity* is being transformed into the development of *means to live with scarcity*. This means attempting to make the most of the water that is available, primarily through the establishment of institutions that provide the incentives for society to derive maximum social well-being through its access to the water resource. Scarcity, and the development of social coordination mechanisms for living with it, is the central focus of water economics.

Water management, understood as the practices of planning, developing, distribution and optimum utilizing of water resources under defined water polices and regulations, is the instrument to deal with the giving situation.

In general terms, the concept of water as a resource or as a natural heritage element subject to accounting derives from the attempt to find the interaction between the discipline that studies the behaviour of water as a *natural entity* (Hydrology) and that which tries to regulate its management (Water Economy or Hydroeconomy). The search of this interaction has given rise to different accounting procedures in different countries, until finally arriving at the methodology proposed by the Organisation for Economic Co-operation and Development (OECD). It only referred to Water Quantity Accounts.

The currently world-wide most important initiative regarding water accounting is UN's System of Environmental-Economic Accounting for Water (SEEAW). The SEEAW is a conceptual framework for the organization of physical and economic information related to water using concepts, definitions and classifications consistent to those of the System of National Accounts (UN-SNA, 1993).

In Spain, the first attempt to relate Thermodynamics and water assessment is known as the Spanish Water Accounts (Naredo, 1997). They were primarily established to assemble water-related information (both physical and monetary) within the consistent and useful framework needed to regulate water management with economic criteria. Besides being of critical importance to all governments endowed with legal responsibility and authority over the economic management of water resources, this objective concurred with the demands of the 1985 Spanish Water Act (WA) which recognised, for the first time ever, the unitary character of the hydrological cycle (thus repealing the deep-rooted yet artificial division made between surface and ground waters) and laid down the unitary character of the management of the "public ownership of the continental waters".

Title III of this Act entrusted the entity in charge of Hydrological Planning with the task of drawing up a water policy based on this unitary and comprehensive view of the hydrological cycle and on rational and economic criteria for the management of the country's water resources, considered to be "scarce and essential", among other tenets. In light of this, it becomes apparent that the Water Accounts were expected to furnish a complete and orderly system of information on which to base the design and application of hydrological planning policies.

In addition to the above-mentioned objective, the WA was also destined to serve other purposes. Since its establishment required that all the available data were employed to construct a complete system of information relating the water situation from the view point of both the resource (Hydrology) and the economic agents or transactors involved in its utilisation (Economy), they made it possible to detect gaps and inconsistencies in the statistics used and gave rise to new appraisals of water economy problems that had gone unnoticed with the traditional parcelling approaches.

Finally, the development of Spanish WA also met the need to place the water management concerns peculiar to Spain within the context of the more ample Natural Resources Accounts established by other European countries (Naredo, 1997). During the last decades, Spain has been very active in this field. The development of the Spanish Water Accounts resulted, in part, from the OECD request that the Spanish government apply the pilot water account methodology adopted by this organisation (a simplified version of the methodology applied in France in 1986) in Spain, where dryness and aridity are prevailing characteristics. It constituted a milestone in water quality accounting because, at that time SEEAW did not exist (the current document was the SEEA, which accounted only for quantity).

The results of applying an adapted version of the mentioned accounting exercise in Spain concurrently enriched and synthesised the OECD (and even the original French) methodology. Thus, they met the twofold purpose of contributing relevant methodological observations and of placing data (both physical and monetary) within the global framework needed to take economic water management decisions in Spain, where water scarcity and ill-quality problems are more pressing that in the European countries lying north of the Pyrenees (Naredo, 1997).

These two works, which are the background for the methodology developed in this dissertation, are going to be explained next.

3.6.1. System of Environmental-Economic Accounting (SEEA)

Environmental–economic accounting is a response to the need for integrating environmental policies into the overall system of decision making. The European Environment Agency has started the implementation of a programme of land use and ecosystem accounts, following the System of Environmental and Economic Accounts (SEEA) guidelines of the United Nations (UN-SEEA, 2003). The purpose is to integrate information across the various ecosystem components and to support further assessments and modelling of these components and their interactions with economic and social developments.

The construction of land and ecosystem accounts is now feasible due to continuous improvements in monitoring, collecting and processing data and progress with the development of statistical methods that facilitate data assimilation and integration. The accounts are based on explicit spatial patterns provided by comprehensive land cover accounts that can be scaled up and down using a 1 km^2 grid to any type of administrative region or ecosystem zone (e.g., river basin catchments, coastal zones or bio-geographic areas). Land cover accounts have been produced for 24 countries in Europe and first results published in the European Environment State and Outlook 2005 report of the EEA (EEA, 2006).

It aims first at clarifying and quantifying the use of the environment in the broader sense, marketed resources as well as services not presently internalized by the economy. The purpose is to assess public and private benefits and costs and to optimize the use of environmental resources taking into account a longer time frame and future options. Direct benefits and costs have to be assessed together with indirect – sometimes "hidden" – ones, in order to supply private and public decision makers with adequate information about the trade-offs they face. This means addressing in clear terms the possible impacts of environmental degradation on the economy, on population as well as on the ecosystems themselves.

The ecosystem concept is certainly not new in ecological economics, and has existed within environmental accounting since the very beginning of the formal developments that resulted in the SEEA 2003. Ecosystem accounts are in no way a substitute for ecological or economic modelling. Instead, they aim to organise and present data in a way that facilitates their assimilation and use by researchers and decision makers.

This idea has been developed in the water management field through the Integrated Water Resource Management in agreement with the WFD. Main characteristic of this propose actuation way are collected in the following, with special attention to its accounting tool: the SEEAW.

3.6.1.1. Integrated Water Resource Management (IWRM)

Integrated water resources management (IWRM) is based on the perception of water as an integral part of the ecosystem, a natural resource and a social and economic good, whose quantity and quality determine the nature of its utilization. To this end, water resources have to be protected, taking into account the functioning of aquatic ecosystems and the perennially of the resource, in order to satisfy and reconcile needs for water in human activities. In developing and using water resources, priority has to be given to the satisfaction of basic needs and the safeguarding of ecosystems. Beyond these requirements, however, water users should be charged appropriately (UN-Agenda 21, 1992).

IWRM calls for a sustainable management of water resources to ensure that there is enough water for future generations and that water meets high quality standards. An IWRM approach promotes the coordinated development and management of water, land and related resources in order to maximize the resultant economic and social welfare in an equitable manner without compromising the sustainability of vital ecosystems. This includes more coordinated development of (a) land and water; (b) surface and groundwater; (c) the river basin and its coastal and marine environment; and (d) upstream and downstream interests (Global Water Partnership, 2004).

For policy-making and planning, taking an IWRM approach requires that (a) policies and priorities take water resources implications into account, including the two-way relationship between macro-economic policies and water development, management and use; (b) there is cross-sectoral integration in policy development; (c) stakeholders are given a voice in water planning and management; (d) water-related decisions made at local and river-basin levels are in-line with, or at least do not conflict with, the achievement of broad national objectives; and (e) water planning and strategies are integrated into broader social, economic and environmental goals (GWP, 2004).

The SEEAW is a useful tool in support of IWRM by providing the information system to feed knowledge into the decision-making process. Because of its features, outlined in the previous section, the SEEAW can assist policy makers in taking informed decisions on allocating water resources efficiently, improving water efficiency, understanding the impacts of water management on all users, getting the most value for money from investment in infrastructure, Linking water availability and use, providing a standardized information system which harmonizes information from different sources, is accepted by the stakeholders and is used for the derivation of indicators and getting stakeholders involved in decision-making.

System of Environmental-Economic Accounting for Water (SEEAW)

The System of Environmental-Economic Accounting for Water, commonly referred to as SEEAW (UN-SEEAW, 2007), has been prepared by the United Nations Statistics Division in collaboration with the London Group on Environmental Accounting, in particular, with its Sub-Group on Water Accounting along the last three years.

Because water is critical and intimately linked with socio-economic development, it is necessary for countries to move away from sectoral development and management of water resources and to adopt an integrated overall approach to water management (UN-WWAP, 2006).

The SEEAW is a conceptual framework for the organization of physical and economic information related to water using concepts, definitions and classifications consistent to those of the System of National Accounts 1993 (UN-SNA, 1993). The SEEAW framework is an elaboration of that in the handbook Integrated Environmental and Economic Accounting 2003 (UN-SEEA, 2003) which describes the interaction between the economy and the environment and covers the whole spectrum of natural resources and the environment.

The SEEAW is complemented with a set of standard tables focusing on hydrological and economic information. It also includes a set of supplementary tables covering information on social aspects which permits the analysis of the interaction between water and the economy. Standard tables constitute the minimum data set that all countries are encouraged to compile. Supplementary tables consist of items that should be considered by countries in which information would, in their particular cases, be of interest to analysts and policy makers, or for which compilation is still experimental or not directly linked with the 1993 SNA. The set of tables, standard and supplementary, were designed with the objective of facilitating the compilation of the accounts in countries and to obtain information, which is comparable across countries and over the time.

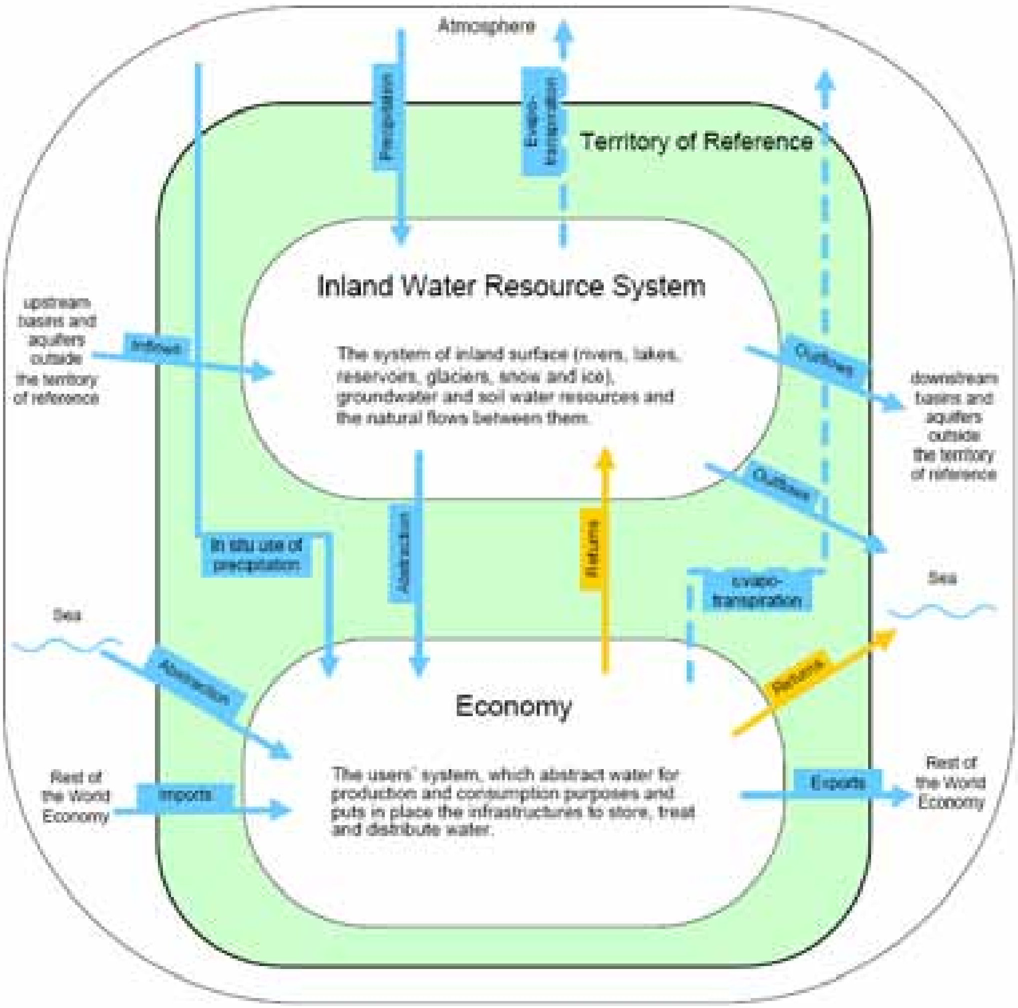


Figure 3.6. Flows between the economy and the water environment (Source: UN-SEEAW, 2007)

The framework of the SEEAW is presented in the simplified diagrammatic form in Figure 3.6, which shows the economy, the system of water resources and their interactions. The economy and the inland water resource system of a territory – referred to as *territory of reference* - are represented in the figure as two separate boxes. The inland water resource system of a territory is composed of all water resources in the territory (surface water, groundwater and soil water) and the natural flows between them. The economy of a territory consists of resident water users who abstract water for production and consumption purposes and put in place the infrastructure to store, treat, distribute and discharge water.

Only by integrating information on the economy, hydrology, other natural resources and social aspects can integrated policies be designed in an informed and integrated manner. Policy makers taking decisions on water need to be aware of the likely consequences for the economy. Those determining the development of industries making extensive use of water resources, either as inputs in the production process or as sinks for the discharge of wastewater, need to be aware of the long-term consequences on water resources and the environment in general.

The SEEAW consist of two parts:

Part I comprises the categories of accounts for which there is considerable practical experience and a consensus on best practices has emerged. It includes internationally agreed concepts, definitions, classifications, accounts and tables. The accounting categories are:

- *Physical supply and use tables* provide information on the volumes of water abstracted, supplied within the economy and discharged back into the environment by economic activity and households.
- *Emission accounts* provide information on the release of pollutants in wastewater in physical units.
- *Hybrid supply and use tables* present side-by-side economic information on the use and supply of water within the economy with the corresponding physical flows. This module also provides information on the expenditure and financing of water-related activities as well as the stocks of water-related infrastructure in place.
- *Asset accounts* provide information on the stock levels of water resources in the environment and their changes brought about human activities (i.e. abstraction and returns) and natural events (such as precipitation and evapotranspiration).

Part II comprises those accounts that are considered of high policy relevance but still experimental because a international accepted best practices did not emerge. They include:

- *Quality accounts* provide information on the quality of water resources in the environment and their changes.
- *Valuation of non-market flow of water* is a review of valuation techniques commonly used, given the controversial nature of water valuation. Flow accounts for pollution, energy and materials. These accounts provide information at the industry level about the use of energy and materials as inputs to production and the generation of pollutants and solid waste.

- *Examples of application of water accounts* provide examples of how the accounts have been used in countries for the derivation of indicators to monitor and evaluate policies; and for scenario-modelling.

The UN Statistical Commission (UNSC), upon recommendation by the UN Committee of Experts on Environmental-Economic Accounting (UNCEEA), has adopted Part I of the SEEAW as an interim international statistical standard subject to re-evaluation when the SEEA 2003 is adopted as an international statistical standard. Further, the UNSC encouraged its implementation in countries.

From the perspective of this work, however, the fact about that SEEAW also presenting quality accounts is the most relevant issue, since they describe water resources in terms of their quality.

These accounts, together with the economic valuation of water resources, are included in the SEEAW for the sake of completeness. However, these modules are still experimental and they are presented in terms of issues in implementation and illustrated by country practices, rather than providing guidelines on the compilation.

3.6.2. Spanish water accounts: methodological innovations and conceptual specifications.

The inland water resource accounts were tabulated in terms of quantity in Spain for a mean hydrological year (1980 to 1989) (Naredo and Gascó, 1994) following the pilot methodology adopted by the OECD. However, calculating inland water resource accounts in terms of quality is problematic due to the concept of water resource quality and its measurement (Naredo, 1997). Water resource quality has been studies several times, analysing chemical properties like dissolved oxygen, conductivity or alkalinity (Interlandi et al., 2003) or nutrients and metals in the surface water (Simeonov et al., 2003). However, since water quality and water quantity are often closely linked, modelling methods (Malan et al., 2003) or other tools should be used to integrate water quality and water quantity in river basins.

Peninsular Spain has a surface area of 493,771 km^2 divided into 11 administrative hydrographical basins corresponding mostly to natural hydrographical catchments. The climate is Mediterranean and seasonal except in the north where it is humid and in the south-east where it is semi-arid. Climate, topography and rock weathering determine salt-water concentration associated with osmotic energy. The relief, with a mean altitude of 568 m, determines a topographical position associated with potential hydraulic energy.

The establishment of WA in Spain followed this methodology insofar as quantity is concerned, not only by filling in the three tables of results that form part of it, but also by drawing up many more detailed and intermediate tables and charts. The three OECD tables record annual water movements including origins and destinations, water stock composition and evolution, and primary withdrawals and final uses broken down into sectors, respectively.

Spanish Water Accounts (Naredo and Gascó, 1994) introduced by first time the Thermodynamics in the water accounting. These authors stated that while the Law of conservation of matter and energy governs water quantity accounts, the Law of entropy governs water quality accounts.

The Law of conservation gives rise to the well-known formula that equates, within a period of time, the accumulated flow of water input in a particular territory with the water output plus the water stock variation reflected therein. The framework for all water quantity accounts rests on this formula, better known in its more widely-used version that equates (in the absence of other external inputs) precipitation inputs with final infiltration, evapo-transpiration and run-off outputs plus stock variation.

Together with the Entropy Law, the Conservation Law must also be applied to water matter-energy relations: water quantity refers to the quantity of mass (or volume, since water density is the same as water unit), while water quality refers of available energy or exergy it contains, identified with its capacity to react spontaneously. Not intending to deal with the fields of energy involved in the movement of water in the biosphere, this line of research will be opened with the calculation of the fields considered to be more relevant and more easily quantifiable in the case of Spain: those related (1) directly with the altitude; the *hydraulic power* (HP) measurable according to mass and height above sea level and (2) inversely with the content of solutes by unit of water mass or volume, or directly with its dilution capacity -*osmotic power* (OP) measurable according to the osmotic pressure exercised by saltwater over the semipermeable piston that puts it in contact with better-quality water-. More details about the methodology can be found in Annex B of this dissertation.

In countries where aridity is a dominant feature, soils tend to be poor in organic matter and rich in salts, so that water is not only scarce and irregular in quantity, but also in quantity. In Spain natural water quality oscillates from seasonal thaw waters to water in which salinity is close to that of sea water. The dryness of the territories not only places the volume of irrigation water demand above that of urban-industrial supply, but also heightens the risk of soil salinisation as poor-quality water is increasingly used. Hence the need for these territories to develop a sound water management policy, founded on a deep understanding of the map of natural qualities available and of the different water uses made, to guide human intervention. If, as is the case in Spain, a marked orography is added to the aridity of the greater part of the territory, then the two dominant competitors for water in large quantities are the agricultural and the hydroelectric sectors, highlighting yet again the importance of measuring the " natural" or "innate" quality if water as an obligatory backdrop to water management.

Despite the fact that the results of the Water Quantity and Quality Accounts are of interest in themselves as management guidelines, the WA system acquires its full impact with the Water Monetary Accounts. This explains why it has also been necessary to develop a specific methodology to suit the nature of the institutional framework and the statistical sources available.

Lastly, and as a result of relating the quantity of distributed water (recorded in the Quantity Accounts) with the expenditure of the user agents (recorded in the Monetary Accounts), the implicit prices or mean unitary values for water were calculated and compared with those featured in the sources available (Naredo, 1997).

3.7. Summary of the chapter

Nature has been always present in the economic system, even when it was not called so. During 16th to 18th century, when the mercantilist was the dominant school of throughout, economic assets or capital were represented by bullion held by the state and the economic system was seen as a zero-sum game in which any gain by one party required a loss by another. From then on, the strengthening of Economics was not any more based on the acquisition, but on the richness production. The most significant contribution of the Physiocrats was their emphasis on productive work as the source of national wealth. This is in contrast to earlier schools, in particular mercantilism, which often focused on the ruler's wealth, accumulation of gold or the balance of trade. The Physiocrats meant the beginning of the anti-mercantilist movement: they established the notion of *production* as centre of the modern version of the economic system.

Afterwards, the economic system accepted the target of its expansion and continuous growth and the separation between the physical system and the universe of monetary values, was operated. Such a displacement happens at the same time that the developments of the Nature sciences invalidated the archaic vision of the world and the eagerness of controlling the underlying physical growth. The growing feeling was that resources and work were replaceable by capital, as Ricardo sustained.

Ecological Economics and Environmental Economics are somehow the two currently existing environment-related disciplines to assess natural resources with in Economy. Ecological economics is sometimes described as taking a more pluralistic approach to environmental problems and focuses more explicitly on long-term environmental sustainability and issues of scale. Despite the best efforts of scientist and engineers, scarcity prevails today. Demands for water have continued to increase with expansions of irrigated agriculture, resource processing, industrial application and domestic use. Hence the saga of 'overcoming' scarcity is being transformed into the development of means to live with scarcity. There, Economics has an important role to play.

Two important contribution for water resources assessment have been shown in this chapter: SEEAW and the Spanish Water Accounts, which represented the first official connexion between Thermodynamics and Economics.

The accounts described in SEEAW describes the stock of water in terms of its quantity and its quality. The quality accounts are still experimental and there is yet to be agreement on a standard way of compiling them. Since it is generally difficult to link changes in quality to the causes that affect it, quality accounts describe only the total change in an accounting period, without further specifying the causes.

The Spanish Water Accounts, in quantity and quality, were carried out in 1994. The followed methodology, which is partially the background of the Physical Hydronomics proposed in this study, has been briefly explained in this chapter (more information is provided in Annex B).

In summary, it can be said that something is still missing in the explained water accounting methodologies. They mainly focus on quantitative analysis and, although partially go over the water quality, the analysis is not depth enough. It is desired that the quality burden in water accounting goes further than just knowing the salinity (or any other chemical parameter) category of the rivers. Those water accounts allow seeing the situation, but the actions of judging and executing remain pending.

As indicated in Chapter 1, the European WFD is called to fill the gap between the physical water world and its economic conceptualization. It launches different statements for the rivers and some of them are even unreal (the objective states of the water bodies). WFD set out a bunch of situations and asks for a *planning of measurements* in order to achieve the established (objective) states of the water bodies.

The water costs, the corrective measurements and its application, and the costs allocation can be performed by PH. PH is much more than an accounting tool; it can become a powerful instrument in water management and planning.

Chapter 4

Exergoecology applied to global water resources

In this chapter, the application of the Second Law of Thermodynamics to the natural resources assessment is considered. This application is called Exergoecology (Valero, 1998). In particular, the world fresh water resources are evaluated.

Firstly, a general description of the methodology is done, focussing on exergy as the property to measure water availability, on the exergy components of a water flow, and identifying the most suitable reference environment for the fresh water resources assessment. Secondly, a thorough study of the exergy of organic matter in water bodies is carried out. The biological exergy is also analyzed.

Thirdly, the exergy assessment of the renewable fresh world water resources and the world water withdrawal is done. Since we are dealing with global resources, the chemical and potential components of water are considered. After obtaining the exergy replacement of those water resources, they are translated into land requirements if that energy were obtained from renewable resources.

Finally, the exergy assessment of ice caps and glaciers is performed, attending to chemical, potential and thermal exergy components of water.

4.1. Exergoecology

The thermodynamic value of a natural resource is defined as the minimum work necessary to produce it with a specific structure and concentration from common materials in the environment. The process should be reversible and heat should only be exchanged with the environment. That minimum amount of work is theoretical and equal to the material's exergy (Riekert, 1974). As it is well known, the exergy of a system gives an idea of its potential for not being in thermodynamic equilibrium with the environment or, what is the same, for not being in a dead state related to the Reference Environment (RE).

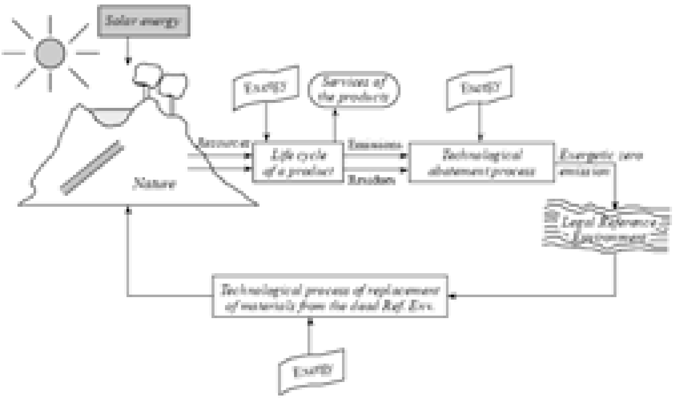


Figure 4.1. General sketch of the main processes involving natural resources evaluation. (Source: Valero, 1998)

Figure 4.1 shows a simplification of the cycle followed by any natural resource from nature which is used as a service product. It is finally degraded when it reaches its equilibrium with the Environment. If it is desired to restore the resource, a certain amount of exergy has to be introduced in the replacement way, by means of a technological process

Exergoecology is the application of the Second Law of Thermodynamics analysis through the exergy analysis in the assessment of natural fluxes and resources on the Earth (Valero, 1998). The consumption of natural resources implies destruction of organized systems and dispersion, which is in fact generation of entropy or exergy destruction. This is why the exergy analysis can describe perfectly the depletion of natural capital and, specifically, the degradation of water bodies.

4.1.1. Exergy as the property to measure water availability

The availability of a renewable resource can be understood as *how accessible it is*. In order to be used, a resource must be changed chemically and physically to the required conditions (e.g., for human consumption, water must be extracted from a river or sea, must be purified and finally sent to end users). In consequence, the exergy of a system gives an idea of its potential for not being in thermodynamic equilibrium with the Environment or, what is the same, for not being in a dead state related to the RE.

4.1.2. Reference Environment (RE)

It is clear at this point that, in order to calculate the exergy of any natural resource, a RE should be defined. This RE must be determined by the natural environment and it has conventionally been assimilated to the most degraded thermodynamic state, i.e., a dead Planet where all materials have reacted, dispersed and mixed. That is, all the resources are chemically degraded and completely dispersed.

In the exergy field, there have been many contributions to the determination of a RE. Each RE is fixed by their chemical composition. They have therefore different values of reference exergy and will generate different exergies. This implies that the determination of the natural capital exergy (in this case, fresh water exergy assessment) is necessarily linked to the definition and thermodynamic properties of the RE. Hence, the importance of an appropriate selection of an adequate RE for evaluating natural resources. The two main groups are Partial and Comprehensive Reference Environments.

Some authors such as Gaggioli and Petit (1976) and Sussman (1979) established that the R.E. should be defined according to the specific characteristics of the analyzed process (Partial Reference Environment). This criterion is based on that being the exergy a parameter that quantifies the theoretical evolution of a system with respect to the RE, some of the possible evolutions of the system, cannot be attained because of process limitations. Hence, only possibilities of evolution that the system can practically attain are analyzed. The RE is not a *dead state* anymore, but it can vary depending on the analyzed process.

For computing exergy changes of variable composition or chemically reactive steady flow processes, a comprehensive RE is generally unnecessary. However, this is not the case when the target is focused on the analysis of the natural capital on Earth. In this case, there are no process limitations and the resources can follow an evolution process towards the dead state, thus a comprehensive RE is required.

Within the known comprehensive RE, all authors agree in dividing the reference substances that compose the RE into gaseous components of the atmospheric air, solid components of the external layer of the Earth's crust, and molecular components of seawater. Nevertheless, there are also criterion differences between the different authors. They could be classified into environments based on (Szargut et al., 2005): Szargut's criterion, Chemical equilibrium and abundance criterion.

Abundance and Szargut's criterion are not opposite criteria. According to Szargut's criterion, among a group of reasonable abundant substances, the most stable will be chosen if they also complain with the *Earth similarity criterion.* That is, if the stability of the possible different reference substances for a specific element (measured in terms of the formation Gibbs energy) is within a certain threshold, then the most abundant R.E. will be chosen. If the differences exceed this threshold, the most stable substance will be taken as R.E. as long as it does not contradict the *Earth similarity criterion.* The stability threshold has not a fix value and depends on each element considered, since it is subjected to geological uncertainties. Therefore, Szargut's dead environment is similar to the real physical environment and should represent the products of an interaction between the components of the natural environment and the waste products of the processes. The most probable products of this interaction should be chosen as reference species (Szargut et al., 2005). Szargut's methodology for obtaining the chemical exergy of the elements from the RE is detailed in Annex B.

Some authors define the chemical exergy by means of the chemical equilibrium with the real environment. Ahrendts (1977) and Diederichsen (1999) stated that if the amount of different elements in the reference system is known and the temperature of the system is fixed, the quantity of each chemical compound and the value of each chemical potential is uniquely determined by the condition of chemical equilibrium. Even though Ahrendt's RE only included 15 elements, they represented more than 99% of the Earth's crust and thus his RE can be considered as a Comprehensive Reference Environment. He calculated the composition of this environment in chemical equilibrium, having as a variable parameter the thickness of the crust layer. Ranz (1999) explained why Ahrendt's RE was not suitable to evaluate the natural capital on Earth. Most of the metals cannot be evaluated because they form part of the 1% of the Earth's crust neglected by Ahrendts. His obtained RE is very different from the real environment and it is very unlikely an eventual evolution biologically and/or geologically blocked.

Diederichsen updated and extended Ahrendt's model with new geochemical data and obtained among others, a RE including 75 elements. Furthermore, he allowed the composition of this environment to change with two variable parameters: thickness of the Earth's crust and ocean's depth. The final chosen environment should comply with the *Earth similarity criterion*. The similarity with the Earth was measured with the equilibrium pressure, the oxygen and nitrogen content in the gas-phase and the equilibrium salt content in the oceans. Even though Diederichsen (1999) added more elements than Ahrendts (1977) and included a new variable parameter, the composition of his new Reference Environment is still too different from the real Earth. According to the *Earth similarity criterion*, the RE that best fits with the Earth's Environment takes a crust thickness of only 0.1 m and an ocean's depth of 100 m.

Keeping in mind that background, the RE for any analysis has to be carefully thought before calculation. The natural reference for the system has always to be observed. Different types of waters are analyzed and used, so the appropriate RE selection is needed to perform the adequate analysis.

4.1.3. Exergy analysis of a natural resource

The analogy between the availability of a natural resource and its exergy helps us to relate each resource parameter with its exergy components. These parameters are physical and also chemical. As an example, for mineral resources assessment, concentration and chemical composition are the more significant features; in water resources assessment, however, altitude, temperature and chemical composition will give the most important information.

Although each natural resource assessment needs a particular analysis framework, a general explanation of the procedure to evaluate a natural resource could be as follows:

- Identifying the most relevant features of the resource and obtaining its physical and chemical characterization, which makes it differ from the surroundings.

- Selecting the most suitable RE for the resource. In general, as an example, sea water is a proper reference for a fresh water resources evaluation.

- Calculating the exergy of the evaluated resource and analyzing it according to the aim of the study. For example, if the target is to compare two possible states for a resource, both exergy values will be compared and the exergy gap will be determined.

4.2. Exergy value of water

It is perfectly clear that the value of water resources is huge. The purpose of this section is firstly presenting the different exergy components of a water mass, including a discussion about the most suitable parameter to measure the organic matter content in a water body. Secondly, a definition of the most suitable reference environment was analyzed in order to perform an accurate exergy assessment of those resources and confirm such that huge value of water in the Planet.

4.2.1. Exergy components of a water flow

The exergy of a water body is defined by its mass flow and six parameter measurements that characterize the physical conditions of water: temperature, pressure, composition, concentration, velocity and altitude (Zaleta, Ranz and Valero, 1998). The exergy method associates each parameter with its exergy component: thermal, mechanical, chemical, kinetic and potential.

Therefore, and starting from these components, it is possible to evaluate in quantitative (flow, Q) and qualitative (specific exergy, b) terms a water body and any water resource will be characterised by its exergy components. The proposed model considers temperature, pressure, height, velocity, concentration and composition. The model assumes the approximation to an incompressible liquid (Martínez and Uche, 2009).

Eq. 4.1.

$$\underbrace{b_{H_2O}\,(kJ/kg)}_{Total\ .specific\ .exergy\ ,b} = \underbrace{c_{p,H_20}\left[T - T_0 - T_0 \ln\left(\frac{T}{T_0}\right)\right]}_{Thermal\ .Ex\ ,b_t} + \underbrace{v_{H_2O}\left(p - p_0\right)}_{Mechanical\ .Ex\ ,b_{mch}} +$$

$$\underbrace{\left[\sum_i y_i\left(\Delta G_{f_i} + \sum_e n_e b_{ch,n_e}\right)_i\right]_p}_{Chemical\ .Ex\ ,b_{ch,c}} + \underbrace{RT_0 \sum_i x_i \ln\frac{a_i}{a_0}}_{Concentrat\ ion\ .Ex\ ,b_{ch,f}} + \underbrace{\frac{1}{2}\left(\frac{C^2 - C_0^2}{1000}\right)}_{Kinetic\ .Ex\ ,b_k} + \underbrace{g\left(z - z_0\right)}_{Potential\ .Ex\ ,b_p}$$

where subindex *0* denotes the water properties of the reference. C_p stands for the specific heat at constant pressure; y represents the moles of the substance i divided by the total mass of the dissolution (it can assumed equal to the molality); ΔG_f is the Gibbs free energy; n_e is the moles number of the elements (e) forming a compound (i) and $b_{ch,ne}$ its corresponding specific chemical exergy; x_i is the molar fraction and *a* is the activity.

Each component should be separately calculated. The sum of all components expresses the exergy of the given water resource and can be understood as the minimum energy required to restore the resource from its RE. Each component in Eq. 4.1 will be explained in detail in the next sections.

An adequate RE has to be defined as one in which its level, pressure, temperature and composition has minimum exergy (all the parameters referred to the RE are noted with the index $_0$). The RE proposed by Szargut (Szargut el al, 2005) can be taken as the most convenient to evaluate the exergy in the water cycle. However, as it will be explained in the next section, some further considerations need to be observed regarding the presence (or not) of organic matter in that RE.

4.2.1.1. Thermal exergy component

Thermal exergy depends on the specific heat of the aqueous solution $c_{p,H2O}$, which could be assimilated to that corresponding to pure water (for river and lake waters), (see Perry and Green, 1997) and its absolute temperature, *T(K)*, as indicated in Eq. 4.2.

Eq. 4.2. $$b_t = c_{p,H_2O}\left[T - T_0 - T_0 \ln\left(\frac{T}{T_0}\right)\right]$$

This term is usually not representative since this heat source has low quality with respect to the RE (it means a low exergy value). However, it can have a representative value in some given situations such as cooling systems or recreational uses such as thermal spring water sources in a river basin.

4.2.1.2. Mechanical exergy component

The mechanical exergy term is calculated from the specific volume of the solution vH2O, which is calculated without serious error if it is considered pure water (Perry and Green, 1997) and approximately has a value of 0.001 m3/kg, and the pressure difference with the reference environment RE$(p - p_0)$, Eq. 4.3.

Eq. 4.3. $$b_{mch} = v_{H_2O}\left(P - P_0\right)$$

This component could be representative if pumping stations and buried pressure piping systems are analyzed in the study, as well as water collected in reservoirs, since they would raise the capability of that water flow to produce power. When a river or any water body is studied, a value could be assigned to this component, if the flow altitude were known at each point, area, or river reach.

4.2.1.3. Potential exergy component

The potential exergy term (Eq. 4.4) is calculated taking into account the height z (m) where the measurement is taken. Parameter g represents the gravitational force of the earth (9.81 m/s^2) and z_0 the altitude of the reference level (z_0=0 at sea level).

Eq. 4.4. $$b_p = g\left(z - z_0\right)$$

Although this term is quite important in the river source of a basin, it should be considered with special attention the case of reservoirs with installed hydropower utilities: this potential exergy will be converted successively in kinetic, mechanical and electrical energy within the power station.

No matter the disaggregation level, this potential component will be present in any water analysis related to energy. Therefore, the minimum energy required to set a given amount of water in its original altitude conditions is going to be studied here.

4.2.1.4. Kinetic exergy component

The kinetic exergy is calculated by taking the absolute velocity *c* (in m/s) at the sampling site, as indicated in Eq. 4.5.

Eq. 4.5. $$b_k = \frac{1}{2}\left(\frac{c^2 - c_0^2}{1000}\right)$$

Unless the sampling station is located in rapids or in the core of a waterfall, this term should not be a very relevant component in any case. RE is considered static, so C_0 is zero by definition.

4.2.1.5. Chemical exergy component

The intrinsic chemical exergy of any element is easily found in any chemical exergy table (Szargut et al, 2005) and its expression is given in Eq. 4.6:

Eq. 4.6. $$b_{ch,f} = \sum_i y_i \left(\Delta G_{f_i} + \sum_e n_e b_{ch,n_e} \right)_i$$

where ΔG_f is the formation Gibbs energy, n_e is the amount of kmol of the element e and b_{chne} is the standard chemical exergy of the element. This component gives an idea about the energy required to form a molecule from the existing substances in the RE. If the molecule takes part of the RE, its formation exergy component is equal to cero (since it already exists in that RE).

4.2.1.6. Concentration exergy component

In addition to the chemical exergy, the concentration of the substance in the water body has to be compared with its concentration in the RE. This term, defined by Eq. 4.7, is the most complex term to calculate since three different contributions have to be considered: the concentration of pure water and the contributions corresponding to the dissolved inorganic and organic substances.

Eq. 4.7. $$b_{ch,c} = R\,T_0 \sum x_i \ln \frac{a_i}{a_0}$$

Where x_i is the molar concentration and a_i is the activity coefficient of substance *i* on water. Activities are rather used than molar concentrations, since we are dealing with solutions.

The *dissolved inorganic substances* are evaluated from their direct measurement in the river throughout the sampling stations. Starting from the sample concentration of each electrolyte, the activity of each of them could be calculated by applying the simple formula given in Eq. 4.8:

Eq. 4.8. $$a_i = \gamma_i \cdot m_i$$

where γ_i is the activity coefficient, and m_i is the molality of the *i* substance. The first term could be calculated by applying the Debye-Hückel Theory (Klotz and Rosenberg, 1977) for dilute aqueous solutions that explains the unexpected behaviour of electrolyte ions in a dilute solution by accounting for their electrostatic interactions (Eq. 4.9):

Eq. 4.9. $$\ln \gamma_i = \frac{-A \cdot z_i^2 \sqrt{I}}{1 + B \cdot \phi_i \cdot \sqrt{I}}$$

where A and B are constants that only depend on temperature for aqueous solutions, z_i is the ionic charge (valence), ϕ_i is the effective diameter of the ion in the solution, and I is the ionic force that takes into account the effect of the rest of ions in the solution (Eq. 4.10):

Eq. 4.10. $$I = \frac{1}{2} \sum_i m_i \cdot z_i^2$$

The contribution of pure water can be calculated in two different ways:

a. From its conductivity

In the first of them, activity of *water* is obtained from the measure of its conductivity, taken into account that such conductivity comes from the dissolved ions and its relation to the colligative property of osmotic pressure. That is, conductivity is more or less proportional to the salinity of water.

The activity of water (as liquid) a_{H2O} is obtained from the measurement of the electric conductivity of the water (Eq. 4.11), taken into account that such conductivity comes from the dissolved (strong) ions in water and its relation to the water osmotic pressure π (a typical colligative property of aqueous solutions).

Eq. 4.11. $$\pi_{H_2O} = -\frac{R \cdot T_0}{v_{H_2O}} \ln\left(a_{H_2O}\right)$$

b. As a component in the mixture

The second option to obtain the exergy of water is treating it as a component of the mixture, whose concentration is calculated as $1\text{-}m_{tot}$. In this case the activity of water derivates as a function of the addition of the molality of the solutes.

The exergy of the *dissolved organic substances* can be calculated in the same way as the inorganic ones. If they take part of the reference environment, Eq. 4.7 will be applied. If those organic substances are only found in the studied water body but not in the reference environment, Eq. 4.6 will give their exergy value.

As it was already indicated in the potential component, the chemical component is really relevant in any water resources analysis, since chemical quality degradation accounts for the effect of human presence.

In the previously defined exergy components, it is clear than the exergy difference between to given states represents the minimum energy required for filling the gap. In this way, it is easy to see, as an example, that the minimum energy for pumping will be given by Eq. 4.4.

When dealing with the chemical concentration exergy component, the minimum energy needed for restoring fresh water has to be analyzed. The complete analysis can be seen in Annex B, where the description given by Hanbury et al. (1993) has been followed.

4.2.2. Referent environment for water bodies analyses.

As it has been repeatedly indicated, the composition of the chosen RE has to be carefully studied because it can lead to inconsistencies in the chemical exergy calculation, taken into account that it is an additive property. Then, choosing a determined Reference Environment affects the final exergy value of a water body that, in any case, will be positive for a water flow at a pressure equal or higher than the atmospheric pressure.

The important point is that the exergy differences among two given water bodies will differ if the adopted reference environment is different. Then, choosing the proper and most representative reference is a key issue. The adequacy to the end objective of the exergy analysis has also to be observed: in this case, the environmental and resource costs evaluation, able to restore the deterioration and damage caused by human action.

When the sea is considered as the RE, most of the inorganic dissolved electrolytes in the surface water are also present, in a minor quantity; consequently, the concentration chemical exergy due to salts is negative. However, some other important elements such as nitrates, nitrites, phosphates or organic matter are not found in the sea water, or their presence is negligible.

Inorganic substances are evaluated from their direct measurement in the river in the sampling stations. All the inorganic compounds are assumed to exist also in the RE, so their exergy is calculated according to Eq. 4.7.

The cutt-off rules for the set of components that the RE could content are crucial for the later study of the water bodies attending to their composition. There will be always traces of some elements in the sea water, but a low limit has to be established in order to determine if they are considered or not as a component of the RE. When the concentration is negligible, they are assumed as absent.

In the following, different possibilities for the reference environment composition are analyzed. Finally, a suitable reference is defined after the analysis of the results.

4.2.2.1. Sea water

Sea is the natural reference for water bodies involved in the hydrological cycle: the river losses its capacity to produce work when it dilutes in such that huge reservoir. The river water reaches the thermodynamic equilibrium with seawater in some few kilometres far from the coast.

The power moving all that exergy contribution is the sun, since the hydrological cycle with evaporation, rainfall and runoff renovates the exergy river profile. Consequently, it makes sense to think on oceanwater as the most adequate RE for a flow of water following the hydrological cycle. However, as it is going to be explained in the following, the proposal of adopting the sea as exergy reference to analyze surface or ground water profiles (whose chemical composition is quite different from the sea) has to be carefully considered and analyzed.

The idea of all the exergy being "lost" in the river mouth must be explained with caution: the availability of a water flow in the mouth with disequilibrium in composition, temperature, velocity, pressure…with respect to the sea is lost when it completely diluted with the surrounding sea. It happens at certain distance from the coast, after being partially invested in the transitional waters. There, the chemical disequilibrium is a basic life generator (beaches, fishing shoals…). This consideration is further commented and studied in Chapter 5, where the real exergy profiles of rivers are presented.

The sea composition that was chosen as reference environment has to be studied because it can lead to inconsistencies in the chemical exergy calculation, taken into account that it is an additive property (that is, all the components contributions to the chemical exergy can be added, what can lead to misinterpretation of some of them). Most of the dissolved electrolytes in the surface water are also present, in a minor quantity, in the sea (the concentration chemical exergy due to salts is negative according to Eq. 4.7). However, some other important elements such as nitrates, nitrites, phosphates or organic matter are not in the seawater, or their presence is negligible, but they do exist in the river water.

The chemical exergy contribution of the inorganic matter in water is usually denoted as b_{IM} and it can be defined as the sum of the salts exergy plus the exergy of the pure water (Eq. 4.12). Although b_{salts} is usually a negative value, the global value is positive because of the higher positive value of b_{H2O} that compensates b_{salts}.

Eq. 4.12. $$b_{IM} = b_{salts} + b_{H_2O}$$

In addition to the inorganic contribution to the chemical exergy, the organic part has also to be included. The aim of this section is to determine if the organic compounds should be present in the chosen RE. Their presence in the RE (seawater) is extremely low. The inclusion (or not) of this components in the reference environment has different consequences for their exergy assessment within the river. When the substance is taking part of the reference environment, its chemical exergy contribution is calculated from its concentration exergy (Eq. 4.7). However, if the substance does not exist in the RE, its chemical exergy is represented by the formation chemical exergy (Eq. 4.6).

Two possibilities are directly derived from the previous statement of the problem: a reference environment with organic matter, denoted as *CONC*, and a reference environment without it, denoted as *COMP*.

a. Reference environment: sea water with organic matter (CONC).

If the organic matter is included in the RE, only their concentration chemical exergy is considered, as it happens with the rest of the inorganic dissolved electrolytes. Since nutrients and organic matter have a higher concentration in the river (surface water) than in the sea, they lead to positive exergy values for the concentration chemical exergy (Eq. 4.7). Then, the obtained exergy value would contradict the idea of correspondence between degradation and lower exergy value: a high polluted and eutrophized water will have a high exergy content.

Considering a practical case, comparing for example surface water before and after a secondary wastewater treatment, this reference would work out that the exergy of the inflow could be higher than the effluent exergy, if all the chemical components were added with their corresponding sign. Then, the exergy value contradicts the idea of correspondence between degradation and lower exergy value.

b. Reference environment without organic matter (COMP).

If neither the OM nor the NP are included in the reference environment, their exergy contribution will be their composition (or reaction) chemical exergy and its value will be positive or negative depending on the component and its balance according to ΔG_f, and the b_{ch} of reactives and products (Eq. 4.6). Opting for this alternative, the exergy value of these components (nitrates, nitrites, ammonia, phosphates, organic matter, nitrogen and phosphor), which is very important in surface waters, is amplified comparing with the previous option. This circumstance allows visualizing much better the differences among different ecological states of water bodies.

In addition to that, organic matter (OM), nitrogen and phosphor (NP) are compound coming mainly from the antropic degradation. Keeping in mind one of the future task in this work (the definition of restoration measures), it will be useful to have its exergy separately calculated because different depuration technologies will be required. Each of them will have a different associated exergy cost.

Table 4.1 shows the composition of the previously explained reference environments. For the sake of clarity, it is remembered that the REs are called *CONC* (the one with OM, N and P in its composition) and *COMP* (the one without those components).

Ref Env	**Ca**	**Cl**	**HCO3**	**K**	**Mg**	**Na**	**NH_4**	**NO_2**	**NO_3**	**PO_4**	**SO_4**	**TOC**
CONC	416	19,345	145	390	1,295	10,752	0.1021	0.0329	0.3395	0.0627	2,701	0.65
COMP	416	19,345	145	390	1,295	10,752	---	---	---	---	2,701	---

Table 4.1. Chemical composition (in mg/l) of the two analyzed marine reference environments, considering (or not) NO_3, NO_2, NH_4, PO_4, OM in their composition.

The exergy values for two different water masses (one of them with salinity equal to 360 ppm and the other one with 560 ppm) have been calculated using alternatively the two reference environments. Results are shown in Table 4.2

	T [° C]	TOC [mg/l]	Cond [µS/cm]	Dens [kg/m^3]	$b_{ch,tot}$ [kJ/kg]	$b_{ch,H2O}$ [kJ/kg]	$b_{ch,salts}$ [kJ/kg]	$b_{ch,IM}$ [kJ/kg]	$b_{ch,OM}$ [kJ/kg]	$b_{ch,NP}$ [kJ/kg]
COMP	10.41	2	360	999.2	2.4909	2.4065	-0.01672	2.3898	0.09	0.01067
	10.41	3	560	999.4	2.4888	2.3989	-0.01754	2.3814	0.135	0.01664
CONC	10.41	2	360	999.2	2.5061	2.5219	-0.01721	2.5047	0.0004079	0.0005982
	10.41	3	560	999.4	2.4982	2.5143	-0.01830	2.496	0.0008418	0.001065

Table 4.2. Comparison of two water masses analyzed with the two previous marine reference environments.

The exergy values for the components OM and NP are considerably higher when the COMP reference environment is used (see, for example, 0.09 vs. 0.004079 for the $b_{ch,OM}$ or 0.1067 vs. 0.0005982 for the $b_{ch,NP}$. There is a minimum difference of two orders of magnitude, what is clearly meaningful to perform the analysis. In the CONC reference environment, lightly higher values are obtained for the b_{IM} component, since there is the contribution of more elements in the RE.

In any case, whatever the chosen option is, it is highly recommended the exergy contribution of the organic elements to be computed separately, i.e., it should not be added to the other electrolytes in the aqueous solution contributing to the chemical exergy of the water body.

Diverse REs were analyzed along this study. In addition to the RE as seawater that considers (or not) OM in its composition that were studied in detail, some other different reference environments were considered were finally discarded when the appropriate RE was analyzed, in particular:

- A completely degraded RE, with very high N, P and OM concentration values could be proposed. Apart from being a non-realistic RE, by using this reference, negative contributions will be obtained for any water mass. Thus, it would contradict the idea of "cleaner" water means "higher" exergy, following the reasoning based on a RE that should be as realistic as possible .
- A "virgin river" (or spring waters) could be also taken as RE. Although it could be a good chance to know the degradation of each river, it has an important disadvantage: the RE would be different for each river basin and, in consequence, the comparison would not be accurate for a global exergy assessment.
- Pure water could be a common RE that would allow comparison among water bodies. This possibility is analyzed in the next section.

4.2.2.2. Pure water

If pure water is taken as reference, all the dissolved components in the river will be more concentrated than in the RE. In this case, the limit is the pure water, without any pollution. Then, there would not be any controversy related to the sign of the exergy component. The parameters b_{IM} and b_{salts} would be equal in this case, since b_{H2O} would be zero.

Since pure water does not content any element apart from the water molecule, the chemical exergy of any water mass would be calculated from the composition chemical exergy of the different elements in the sample (whose sign is negative or positive depending on the molecule). The calculation could also be done by means of the concentration exergy expression, adopting a very small (close to cero) amount for all the components in the RE. Then, all the exergy components (pollutants) would be always positive.

The calculation has been made opting for the first option, including the chemical composition exergy. Results of the analysis are presented in Table 4.3. Two water types (the same as in previous section) have been evaluated. In this example, organic matter, nitrogen and phosphor does not change. So it can be appreciated that the increase in salinity (conductivity) is translated in a higher value for the $b_{ch,IM}$. It contradicts in some way the pre-established perception that *cleaner* water has higher exergy.

Cond (µS/cm)	**TOC** mg/l	$b_{ch,tot}$ [kJ/kg]	$b_{ch,H2O}$ [kJ/kg]	$b_{ch,IM}$ [kJ/kg]	$b_{ch,OM}$ [kJ/kg]	$b_{ch,NP}$ [kJ/kg]
360	1.0	0.2794	0.0000	0.1556	0.1556	0.1125
560	2.0	0.4846	0.0000	0.2421	0.2421	0.2250
3510	4.0	2.0770	0.0000	1.5170	1.5172	0.4500
35000	0.5	5.6229	0.0000	5.5640	5.5640	0.0563

Table 4.3. Exergy values for two water masses. The reference environment is pure water.

4.2.2.3. Effect of the salts, organic matter and nitrates concentration.

The proposed reference environments could be considered as limit cases: high salinity (sea), on the one side, and pure water (null salinity) on the other side. However, the specific concentration for the reference is still pending. In order to show the different exergy assessment depending on the concentrations adopted in the reference, two variation analyses are developed in this section.

- The first one analyzes the effect of changing the reference at low concentrations (water bodies with salts content from 50 to 5,000 ppm), that is, surface or brackish water, with a typical electrolytes distribution for those type of waters.

- The second one is saline-seawater in the range of 5,000-95,000 ppm of salts, with a typical share of seawater content prevailing chlorides, sodium and traces of magnesium, potassium, bromide and iodide.

The three mentioned REs have been taken: seawater (with the organic and diffuse pollution components included or not in the RE composition) and the pure water. As it can be observed in the graphs, the different chemical exergy parabolas have different curvature and, in consequence, the exergy value differs depending on the adopted reference.

The salts concentration has been reduced in the two cases where the RE is seawater: from its initial value, 35,046 ppm for the standard ocean, to 10, 100 and 1,000 times lower, until reach a water quite similar to pure water.

Surface water analysis – salts variation

Figure 4.2 presents the graphs for the different components of the chemical exergy of surface water vs. the salts concentration in the river, when the reference environment is the *CONC* one (RE containing OM), with 35,000, 3,500, 350 and 35 ppm respectively.

Figure 4.2 shows that the slope of the curves rises as the salts concentration in the RE decreases. As an example, if a river water with a 1000 mg/l of salts content (blue vertical line), has an exergy value of the H_2O equal to about 2.5 kJ/kg for the RE with 35,000 ppm, about 0.23 for the 3,500 ppm, and negative values for the other alternatives (as it can be expected, since the salinity of the river is higher than the salinity of the reference). The effect of the salts concentration in the RE for the OM and the NP exergy components is hardly appreciated in comparison with the other components. Suspended solids contribution is very low.

In Figure 4.3, a similar analysis has been carried out, but with the COMP reference environment (none OM presence in the RE), and also changing from 35,000 to 35 ppm in the salinity of that reference.

The OM and NP components are constant because, as it has been defined in the COMP RE, they are represented by its formation exergy, which is a constant value independently of the rest of parameters.

When pure water is taken as reference, the chemical components behaviour as the salts concentration in the river changes presents significant differences. It is shown in Figure 4.4.

The organic matter component has not been changed with the salts concentration, so it is represented as constant. NP and SS are lightly changed, as it can be seen in Figure 4.4. The contribution due to salts is represented by the yellow line and it grows as the salt concentration increases. It is a straight line, as the rest of components, because, as explained in section 4.2.2.2, each component is included in the analysis by means of its formation exergy. In conclusion, the exergy increases as the salinity increases, what does not meet the idea of cleaner water having higher exergy.

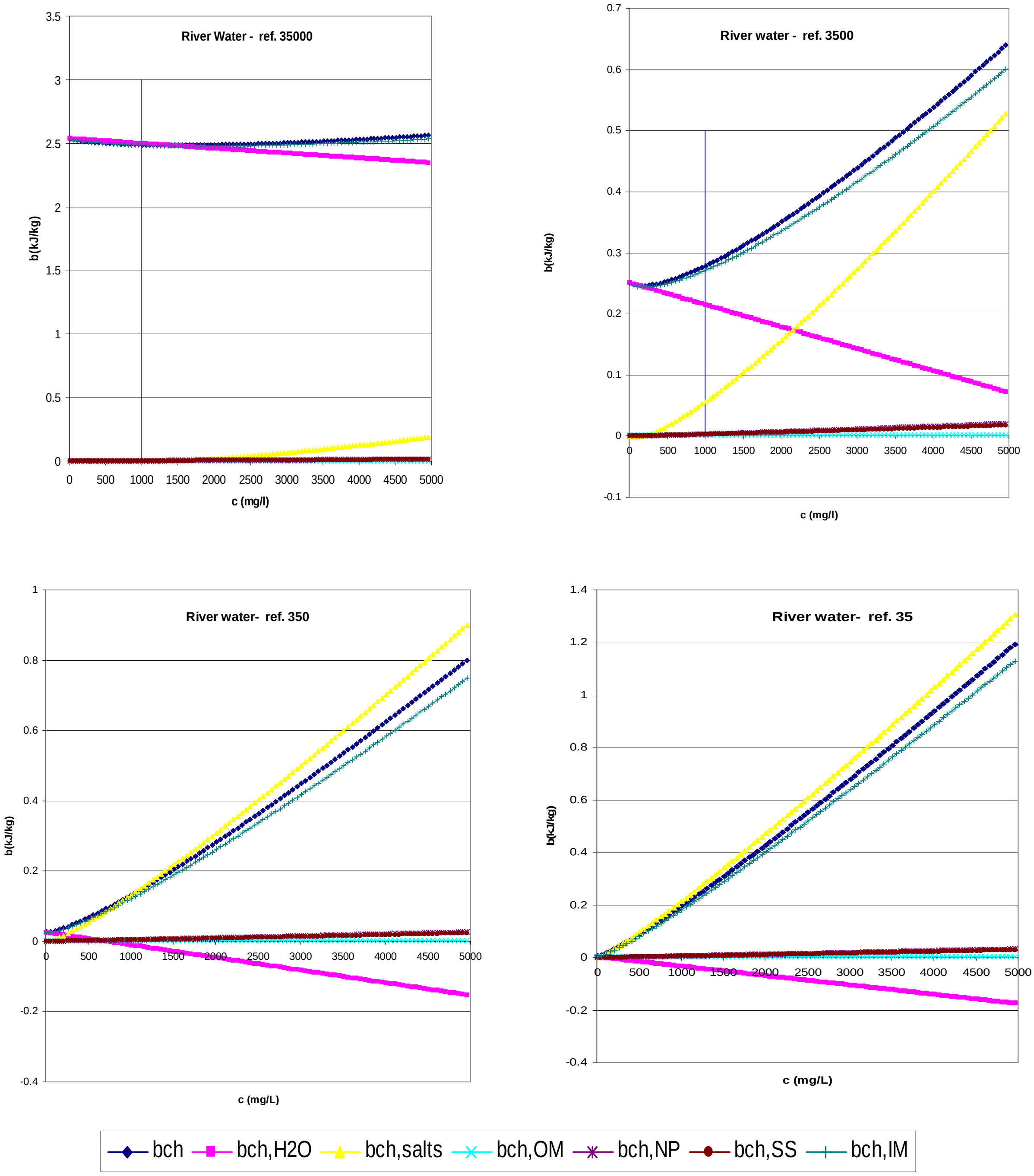


Figure 4.2. Chemical exergy of a surface water vs. salts concentration of this water. The RE is seawater with organic components (CONC) and its salts concentration has been varied: 35000, 3500, 350 and 35 ppm.

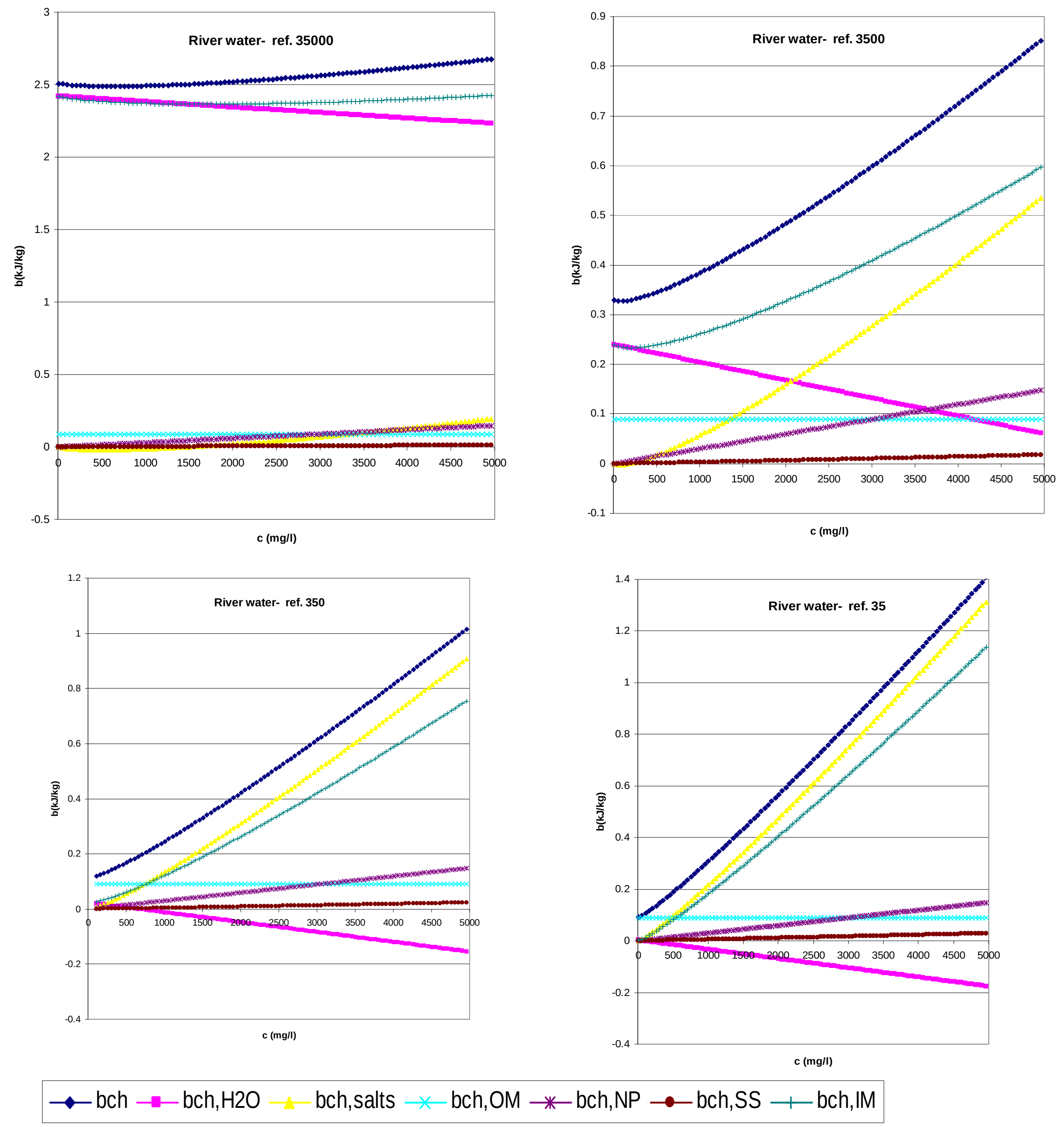


Figure 4.3. Chemical exergy of a surface water vs. salts concentration of this water. The RE is seawater without organic components (COMP) and its salts concentration has been varied: 35000, 3500, 350 and 35 ppm).

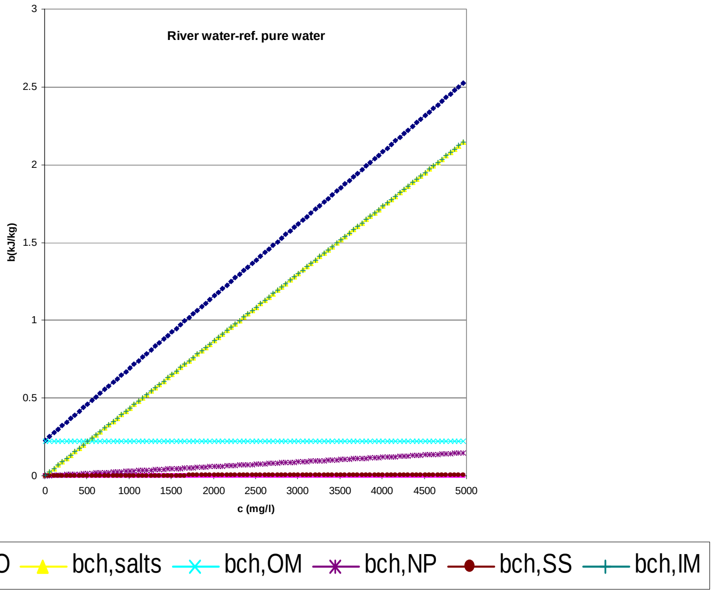


Figure 4.4. Chemical exergy of a surface water vs. salts concentration of this water, taking pure water as the RE.

Seawater analysis – salts variation

A similar analysis has been carried out for the sea water evaluation. Alternatively, the salts concentration in the RE has been changed, both with the COMP and the CONC reference environments.

The graphs show the chemical exergy of a marine water vs. salts concentration of this water.

The considered concentration are, in this case, the corresponding to saline waters from 5,000 to 95,000 ppm. It can be observed in Figure 4.5 that the salts exergy contribution is positive when the salts concentration in the studied seawater is higher than the salts concentration in the RE.

The important differences that can be observed among the water exergy depending on the chosen RE have to be highlighted. A water exergy analysis in the Mediterranean Sea or in the Dead Sea will lead to considerably different for the same water sample.

Figure 4.6 summarizes the results of seawater with changing salinitiy, being evaluated in the different COMP REs (RE without OM).

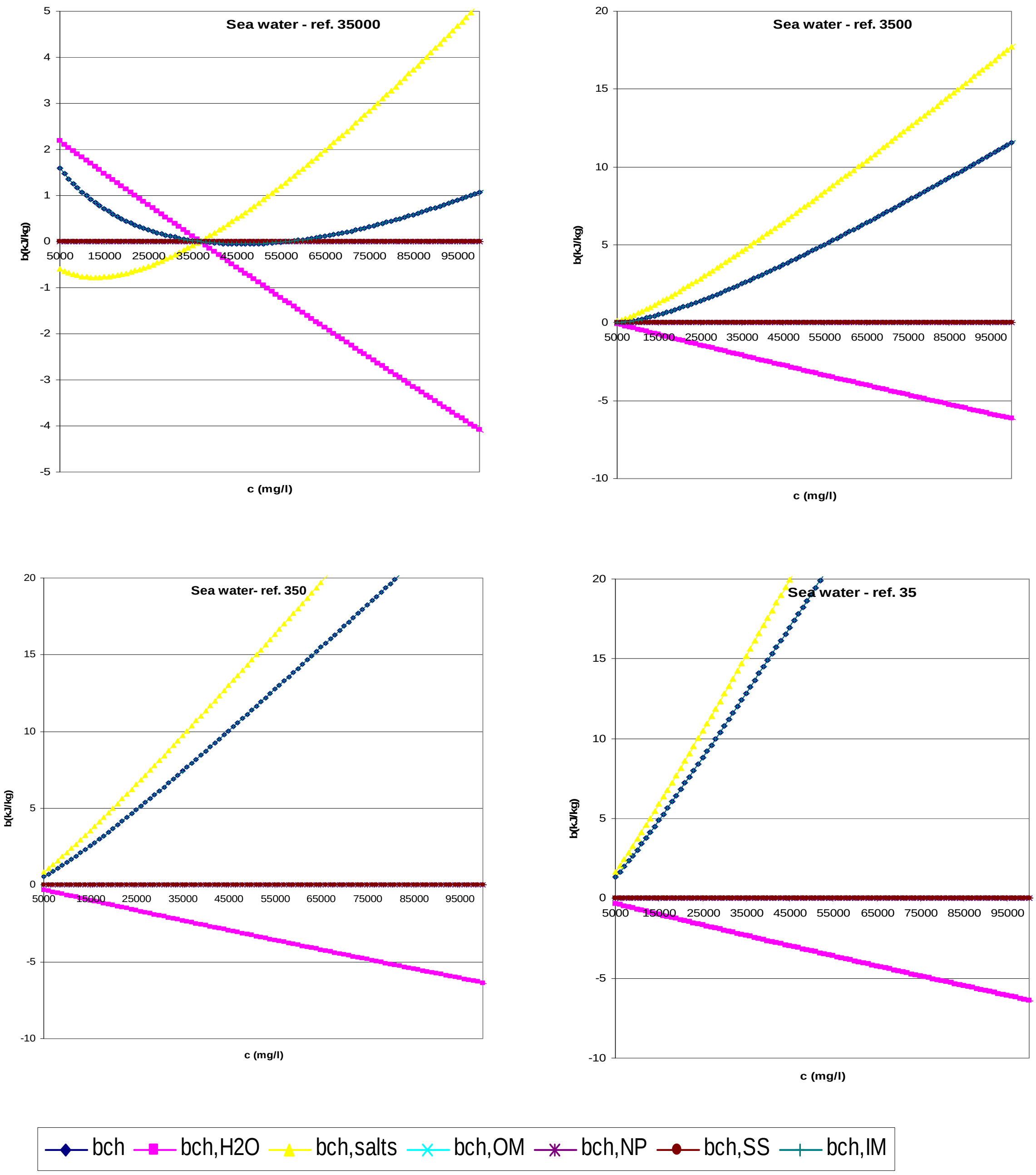


Figure 4.5. Chemical exergy of a marine water vs. salts concentration of this water. The RE is seawater with organic components (CONC) and its salts concentration has been varied: 35000, 3500, 350 and 35 ppm).

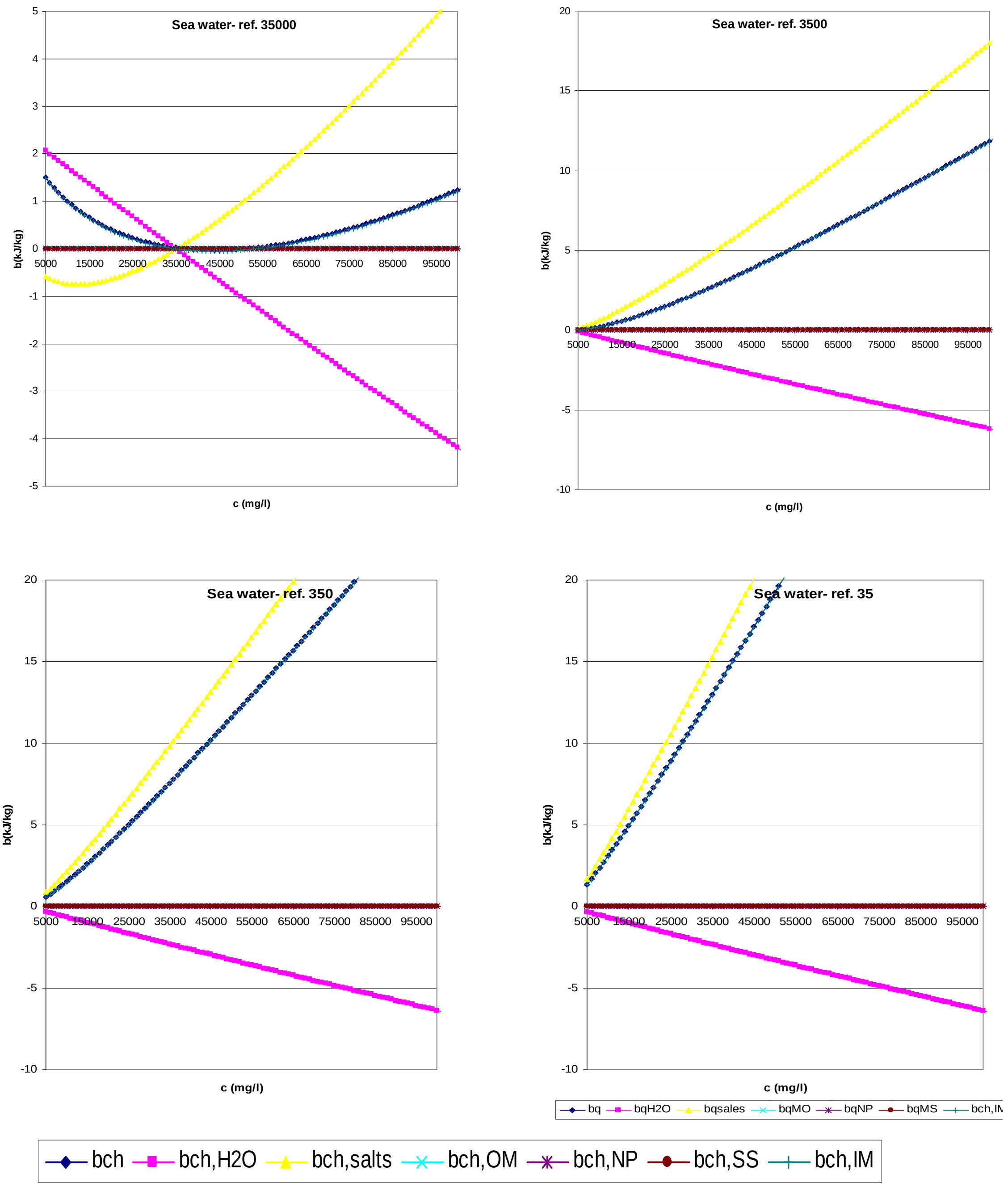


Figure 4.6. Chemical exergy of a marine water vs. salts concentration of this water. The RE is seawater without organic components (COMP) and its salts concentration has been varied: 35000, 3500, 350 and 35 ppm).

The only differences between Figure 4.5 and Figure 4.6 are mainly related to the OM, NP presence. However, it can not be appreciated because of the scale of the graphs. For example, in the case of 35,000 ppm in the reference, the chemical exergy of sewater due to OM is 0.0225 (constant) in the *COMP RE*, and it is around 10-5 (varying) in the *CONC RE*.

Next, the exergy of seawater with changing salitiny has been calculated taking pure water as RE (Figure 4.7). It is clear in this case that the idea of null exergy value for seawater would not be adequate anymore. Pure water having the lowest exergy value is not consequent with the water cycle, where the not availability of water is associated to seawater.

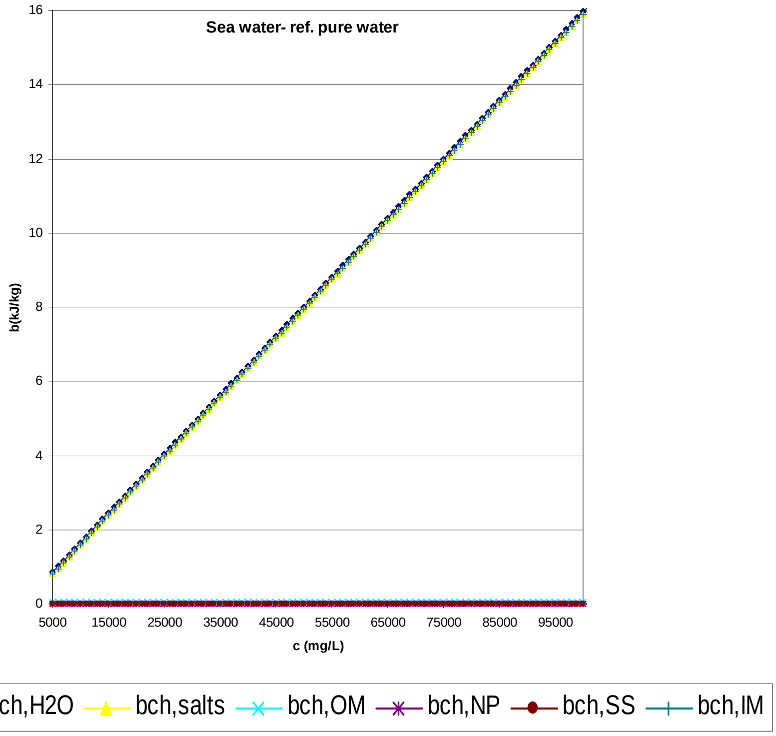


Figure 4.7. Chemical exergy of a marine water vs. salts concentration of this water. The RE is pure water.

Surface water analysis – Nitrates, Phosphates and Organic Matter variation

In the same way, the analysis of different N and P concentrations, as well as organic matter (as TOC in mg/l) has been done for typical surface water, for the three selected REs. Results show that a more significant effect (value) for the chemical exergy is obtained when the seawater RE does not content any nitrogen, phosphor and organic matter –COMP RE- (blue line) and when the RE is pure water (pink line) than when the CONC RE is considered (yellow line).

Firstly, the effect of the nitrates variation in a surface water on the chemical exergy of those nitrates is presented in Figure 4.8. The rest of the parameters on water remain constant, while the nitrates concentration varies from 0 to 100 mg/l. In the pure water and COMP reference environments, the exergy is calculated from the chemical exergy value of the nitrate molecule (formation exergy). Then, the value for $b_{ch,NO3}$, in KJ/kg, is higher than the obtained value when the CONC reference environment is considered. In the latter, the nitrates chemical exergy is calculated by means of the chemical concentration exergy expression.

The lines representing the pure water RE and the *COMP* RE seem are quite close, although values lightly differ. It is not clearly appreciated because of the small obtained numbers. The RE COMP gives rise to a parabolic shape in the representation, but it is not appreciate because of the slow change.

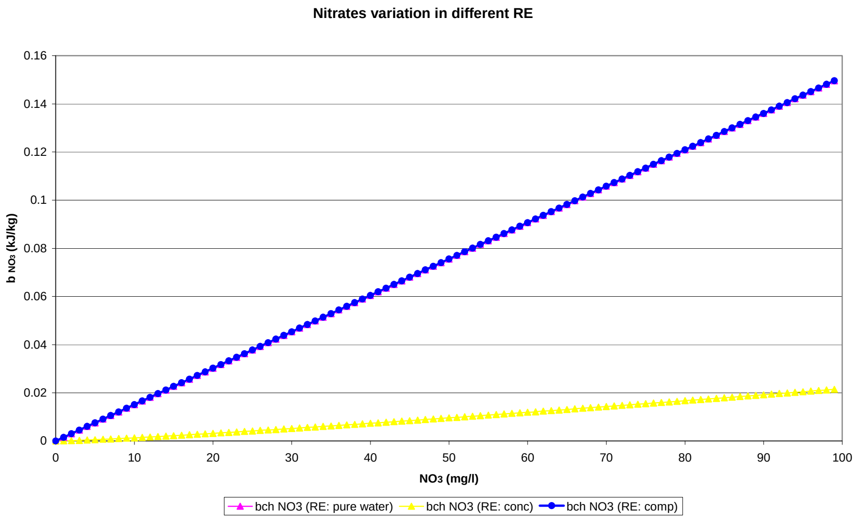


Figure 4.8. Nitrate chemical exergy vs. nitrates concentration in water for three different REs: pure water and seawater with and without organic matter.

A very similar analysis can be done for the phosphates variation in a surface water and their effect on the chemical exergy value. That variation has been graphed in Figure 4.9, where the PO4 content, in mg/l, changed from 0 to 50.

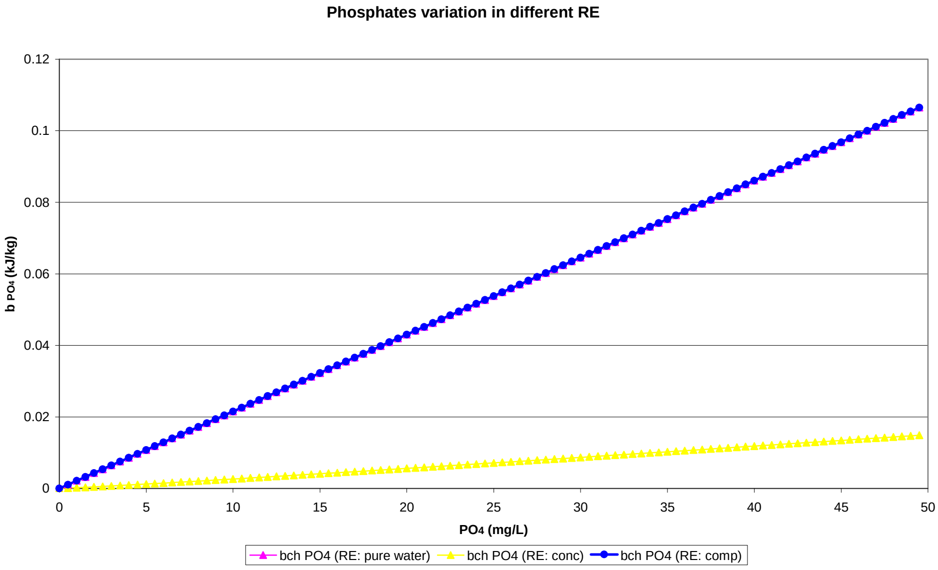


Figure 4.9. Phosphate chemical exergy vs. nitrates concentration in water for three different REs: pure water and seawater with and without organic matter

Finally, the analysis is performed with the organic matter present in a surface water. The chemical exergy varies linearly, as in the previous cases, when the RE is pure water or the in the COMP RE case (Figure 4.10). In the analysis, TOC, in mg/l, changed from 0 to 50.

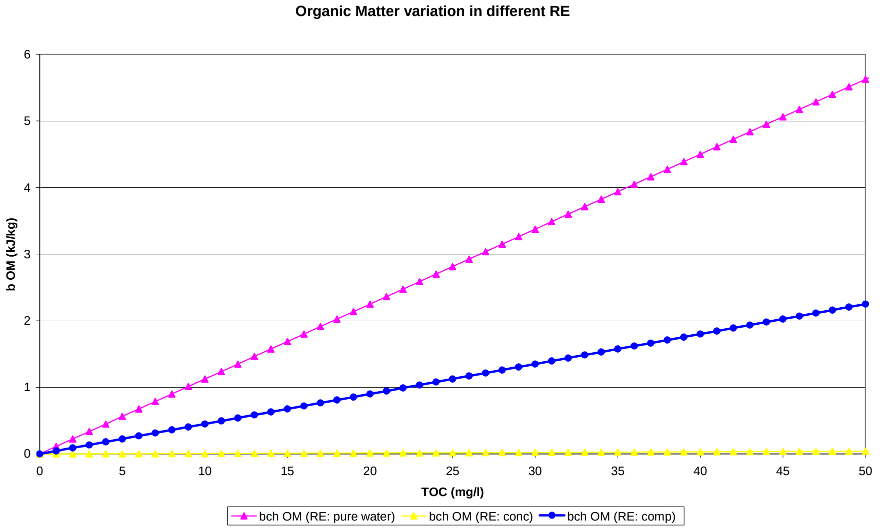


Figure 4.10. Chemical exergy of OM vs. nitrates concentration in water for three different REs: pure water and seawater with and without organic matter

4.2.2.4. Characterization of the chosen Reference Environment

As concluding remark, we can say that the RE election is not a banal decision because the calculated exergy values depend on it.

The quality degradation of surface water because of its use makes usually present by means of high IM and OM presence in the river. Therefore, the importance of this study to analyzed the exergy value of them with the different RE alternatives. It is a relevant issue because, as it will be seen in next chapter, the available technologies to carry out river restoration have to be considered: depuration for OM and distillation for IM. Thus, the presence of these polluting substances needs to be easily observed from an exergy perspective.

The choice for this study is considering an idealized sea water without organic matter, nitrogen and phosphor (blue line in Figure 4.10), i.e., the named COMP RE. In consequence, the differences between the river and the reference are slightly amplified in OM and NP, what is useful for our final target: the exergy profile of the river, disaggregated by exergy components. This is the most suitable RE for the analysis and it is also coherent with sea water as a very important part of the hydrological cycle.

In particular, the composition of the reference used in this study is the average composition of the Mediterranean Sea (CWA, 2008a), since the considered case studies (chapter 6) are located in the eastern Spanish coast (Table 4.4).

	ppm		ppm
Cl	19,345	Na	10,752
HCO_3	145	SO_4	2,701
K	390	MS (SiO_2)	0,477
Mg	1,295	Ca	416

Table 4.4. Average composition of the chosen RE

The NP component is represented by NH_4, NO_2, NO_3 and PO_4 and their concentration in the RE is taken as zero (as it has been previously explained). The same happens with the OM, represented by the TOC measurement and the CH_2O molecule.

For the chosen RE, Figure 4.11 shows the behaviour of the chemical component when the salinity of the evaluated water sample varies from zero to more than 80,000 ppm. Since the reference has been taken in a seawater with 35,000 ppm, there is the point with null exergy when C=35,000 ppm.

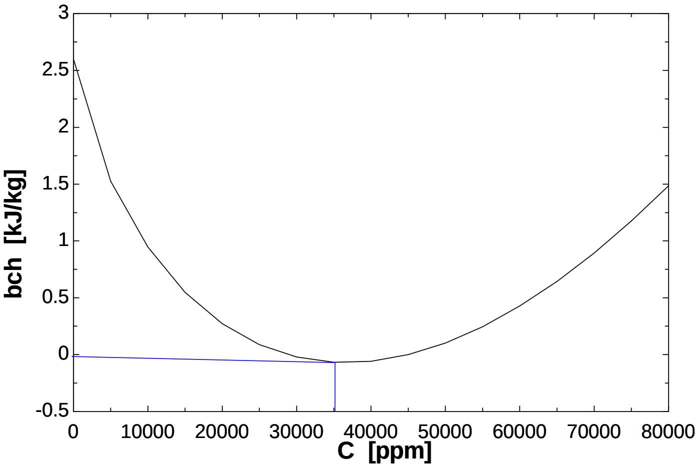


Figure 4.11. Behavior of the concentration exergy with water conductivity.

4.2.3. Exergy of organic matter in water bodies

It has been stated, after the previous analysis in this chapter, that the organic matter is not present in the RE. It is the time now to clearly define the procedure to measure the exergy of organic matter in the studied water bodies.

Oxygen and carbon equivalent indicators have been traditionally adopted to indirectly reflect the concentration of organic matters in water by some authors. Organic matter measurements explained in chapter 2 are going to be applied here.

In this sense, the dissolved organic substances are estimated from the measures related to the organic material in water. Once that measure is given, there are different alternatives to calculate the exergy of organic matter in water, according to the literature.

Tai et al. (1986) suggested alternatively the chemical exergy of organic contaminants in wastewater can be calculated by using the data of TOD with the converted coefficient of 13.6 kJ/g of TOD (Eq. 4.13) or by means of the TOC, with the converted coefficient 45 kJ/g of TOC (Eq. 4.14):

Eq. 4.13. $b_{ch}(J/l) = 13.6 \times TOD(mg/l)$

Eq. 4.14. $b_{ch}(J/l) = 45 \times TOC(mg/l)$

Tai stated that, even if we could determine the standard free energy of formation of organic substance in wastewater, it would be difficult to find a definite relation between it and the measures of the organic substance content (COD, BOD, TOD or TOC). To overcome this circumstance, he expressed the generic organic compound in waste water as $C_aH_bO_c$ and established a pattern of oxidation to obtain Eq. 4.13 and Eq. 4.14. This provides a first approximation for practical estimations. Hellstörm (1997, 2003) used those relationships in his estimation of physical resources consumption in the exergy analysis of a wastewater treatment plant and suggested alternatively that chemical exergy of organic contaminants in water can be calculated by using the data of COD with the converted coefficient of 13.6 kJ/g of COD. In consequence, it provides relative values.

Chen and Ji (2007) developed a unified assessment of water quality, the chemical exergy based evaluation method. As opposed to the specific standard chemical exergy based on the global reference substances, he proposed an indicator called specific relative chemical exergy with reference to a spectrum of substances associated with the specified water quality standard.

Zaleta-Aguilar et al. (1998) used a typical organic molecule to represent the 'mean organic substance' to facilitate the estimation of the order of magnitude of exergy value for the organic components. Their proposal was a fat molecule, $C_{39}H_{80}O_3$. He supposed the combustion of that molecule (Eq. 4.15) and introduced in the reaction the BOD measured in the river to determine (by means of the stoiquiometry relation) the amount of oxygen required by the organic molecule oxidation.

Eq. 4.15. $$C_{39}H_{80}O_3 + \frac{115}{2}O_2 \leftrightarrow 39CO_2 + 40H_2O$$

Some other studies (Foster, 1943; Surampalli, 2004) have used the molecule CH_2O as an average organic compound representing the biodegradable organic matter in a river water. It is a formaldehyde, the simplest sugar type. The molecule of formaldehyde consists of a water molecule kept separated into its parts, in a potential energy state, by a central carbon atom. The general formula for carbohydrates is $(CH_2O)_n$.

A molecule of formaldehyde reacts with a molecule of oxygen to produce a molecule of carbon dioxide, a molecule of water, and energy. The formaldehyde is technically a carbohydrate food source, capable of supplying energy for cell life under the proper conditions. Therefore, it could be chosen as the average molecule representing organic matter in water.

In this dissertation, taking the mentioned sugar molecule and the organic matter measurement in the studied water flow, both ways (through TOC and assuming a combustion reaction showed in Eq. 4.16) have been calculated in order to obtain a value for the chemical exergy.

Eq. 4.16. $CH_2O + O_2 \leftrightarrow CO_2 + H_2O$

Trying to summarize and compare all those methodologies, Table 4.5 shows the obtained figures that have been obtained after following the previously described procedures.

Data used in the analysis are real sampling data of the Foix watershed (see Chapter 6 for a detailed description of this basin). TOC and BOD values are directly obtained from the river basin simulation. COD was estimated from bibliography relations among these three parameters (Metcalf and Eddy, 2003).

				Chemical Exergy (kJ/l)						
	mg/l			**TOC**		**COD**			**BOD**	
River reach	**TOC**	**COD**	**BOD**	**Tai**	**CH_2O**	**Tai**	**CH_2O (comb)**	**$C_{39}H_{80}O_3$ (comb)**	**CH_2O (comb)**	**$C_{39}H_{80}O_3$ (comb)**
1	0.4	0.7	0.51	0.01845	0.01770	0.00954	0.01137	0.00964	0.00822	0.00697
2	0.4	0.7	0.51	0.01890	0.01814	0.00954	0.01137	0.00964	0.00822	0.00697
3	0.5	0.88	0.63	0.02430	0.02332	0.01193	0.01421	0.01205	0.01028	0.00871
4	0.5	0.88	0.63	0.02025	0.01943	0.01193	0.01421	0.01205	0.01028	0.00871
5	0.4	0.7	0.51	0.01665	0.01598	0.00954	0.01137	0.00964	0.00822	0.00697
6	2.8	4.91	3.55	0.12470	0.11960	0.06679	0.07960	0.06748	0.05754	0.04878
7	2.6	4.56	3.30	0.11750	0.11270	0.06202	0.07391	0.06266	0.05343	0.04530
8	1.8	3.16	2.28	0.07965	0.07643	0.04294	0.05117	0.04338	0.03699	0.03136
9	1	1.75	1.27	0.04410	0.04232	0.02385	0.02843	0.02410	0.02055	0.01742
10	1.4	2.46	1.78	0.06300	0.06045	0.03340	0.03980	0.03374	0.02877	0.02439
11	1.1	1.93	1.39	0.04860	0.04663	0.02624	0.03127	0.02651	0.02261	0.01916

Table 4.5. Results for chemical exergy by different procedures for the eleven stretches of the analyzed river.

Column 5 shows the results after applying Eq. 4.14, proposed by Tai et al. (1986). In column 6 are presented the figures obtained assuming that the measured TOC in the river is in CH_2O form. The amount of sugar is calculated and multiplied by its chemical exergy. In column 7, Eq. 4.13 is applied, assuming the equivalence between TOD and COD. At this point, it is worth to remember that Tai's relations are obtained for waste water (therefore the factor 3 in the obtained exergies coming from the ratio between Eq. 4.14 and Eq. 4.13). That is, the ratio between the two measurements (TOC/COD) is equal to 3.

The four following columns summarize the results of assuming, alternatively, the combustion of the two proposed molecules. First identifying the O_2 in Eq. 4.15 and Eq. 4.16 with the calculated COD and then with the measured BOD. As it was expected because BOD values are lower than COD values; latter results for chemical exergy are lightly diminished.

One of the found difficulties was that the formation chemical exergy of the organic molecules was not available in the usual exergy tables. Then, we calculated its formation enthalpy by means of its high heating value (according to Lloyd and Davenport's relation, 1980), its entropy (correlation proposed by Ikumi -1982- for incompressible fuels) and the basic thermodynamic relation given in Eq. 4.17,

Eq. 4.17.

$$b_{ch}{}^{o} = \Delta h_f^o - T^o s^o - \sum f_j \mu_j^{oo}$$

where Δh_f^o is the formation enthalpy, s^o the entropy, f_j the coefficient depending on the number of atoms of each component and μ_j is the chemical potential of each component. Table 4.6 shows the results. As it was expected, the chemical exergy by gram has same order of magnitude while, when the molar basis is taken, the fat molecule contains much more exergy.

	CH_2O	**$C_{39}H_{80}O_3$**
b_{ch} (kJ/mol)	518.64	25,280.64
b_{ch} (kJ/g)	17.25	42.42

Table 4.6. Results for chemical exergy of the considered molecules.

In this study, whatever the taken chemical measured parameter is, given information is only about the chemical exergy content, ignoring if the elements are forming a live organism or not.

To sum up, it can be said that the determination of the chemical exergy of organic matter in water bodies is an unclear issue, largely considered in exergy literature but also commonly overlooked.

Since organic matter is the most changing component in water (due to pouring and leaks from different pollutant sources) and therefore restoration treatments will need to be implemented, it is crucial to clearly define the exergy content of aqueous organic matter.

Results showed in Table 4.5 indicate that procedures based on TOC measurement seems to be the most accurate for the calculation of the chemical exergy of organic matter in surface waters. BOD and COD based methods lead also to coherent results. However, they are parameters joined to wastewater treatment plants and our interest is focussed on whole watersheds.

If TOC data are not available but BOD or COD do, combustion reactions could be used. Contrary to the expected results, no high differences are found between assuming a simple sugar or a fat as average organic molecule in the water flow, since their exergy content on a mass basis has the same order of magnitude.

Nevertheless, from the experience with chemical quality parameters data bases, it is concluded that the most important consideration is to perform the calculations using the measured parameter (that is, the one that is actually measured) for each type of water. The inherent error associated to the appropriate parameter that measures the OM content in water bodies is higher than the error introduced by the methodological approach used to calculate its exergy. Then, if we are dealing for example with a waste water treatment plant effluent, BOD will be the parameter giving the most accurate results. In this way, we avoid the inherent inaccuracy of relations among parameters.

Although the showed accounting gives us an idea about the organic matter content, it is clear that the described procedure does not provide any information about the eventual organic toxics in water because the exact composition of organics is not detailed, and furthermore its exergy could be very low despite of its danger. In addition to that, the exergy of living organism has not been considered.

Next section is devoted to the analysis of Jorgensen's proposal, whose works have been directed to analyze ecological systems (live organisms) from an exergy approach.

4.2.4. Biological exergy component. Eco-exergy.

In the last two decades, several mathematical functions have been proposed as holistic ecological indicators with a double purpose. On the one hand, they intend to express emergent properties of ecosystems arising from self-organisation processes in the run of their development. On the other hand, to act as orientors or goal functions in models development. Such proposals resulted from a wider application of theoretical concepts, following the assumption that it is possible to develop a theoretical framework able to explain ecological observations, rules, and correlations on basis of an accepted pattern of ecosystem theories (Jørgensen et al, 2002).

The thermodynamic concept of exergy as a unified measure of the deviation of a system from its environment has gained wide acceptance in environmental and ecological fields (Jørgensen, 1999, 2001, 2006; Szargut et al., 2002; Chen, 2006) and has been tested in several studies.

Jørgensen and co-workers have made a considerable effort in exergy modelling for aquatic systems such as lakes and coastal areas, by demonstrating and illustrating the relationships between exergy and biomass, biodiversity, species composition, and other properties of ecosystems.

The modified exergy function proposed by Jørgensen, later defined as eco-exergy (Jørgensen, 2006), was born as a developing tool for structural dynamic models of aquatic eco-systems. The application field of this new function is highly different from the original application field of exergy, and the way of calculating eco-exergy also differs from the classical one. There are basically two main innovations:

- The first one involves the choice of a different reference state, that allows to difference among the existing structures and between dead and living systems.

- The second one consists of considering, not only the chemical-physical exergy content (corresponding to the classical exergy), but also the exergetic content related to the system structure. Jørgensen showed how, in biological systems, in fact, info-exergy content is much higher than the exergy of chemical bonds of organic structures. For instance, in order to distinguish two different species living in an ecosystem, it is essential to evaluate the complexity of their structure and the information related to it, rather then the *pure* chemical free energy owned.

Susani et al. (2006) used several examples to show the importance of including information exergy when approaching the study of complex biological systems through thermodynamic laws. For all these examples, both classical and ecoexergy are calculated in order to understand the difference between the two approaches and to show how classical theory is not sufficient in describing living systems, where information and genetic structures make the difference among organisms. The examples developed in section 4.2.4.3 of this dissertation are derived from them.

In order to follow without difficulty the obtaining the factors defining the eco-exergy value for different organism, it is important to remember at this point the relation between exergy and information theory, whose basic expression is the Boltzman's Equation (Eq. 4.18). It accounts for the existing strong link, in statistical mechanics, between entropy and probability (Boltzmann, 1886).

Eq. 4.18. $$S = k_b \ln W$$

Where k_b is the Boltzmann's constant and W is he number of microstates that will yield one specific macrostate.

W is proportional to the probability p that a particular microstate will occur; in fact, the more number of microstates, the lower probability of completely describing the system. A high number of microstates also means a high level of disorder and a low level of information about the real state of the system.

Entropy function grows with the uncertainty about the system, and reaches its highest value exactly when the system reaches its thermodynamic equilibrium. The difference between the entropy level of a system and the entropy level of the same system at thermodynamic equilibrium is a measure of information and order.

After some more mathematical considerations (see the complete development in Annex B), Eq. 4.19 shows the direct relation to obtain the exergy of a system from the Kullback information function, $K\left[p^{(0)};p\right]$.

Eq. 4.19. $$B = k_b T_0 \ln 2 K\left[p^{(0)};p\right] = k_b T_0 \ln 2 \sum_i p_i \log \frac{p_i}{p_i^{(0)}}$$

where p_i is the probabilities distribution for all possible states (i=1, . . ., n).

4.2.4.1. Eco-Exergy definition

As it is well-known, Exergy (B) is directly derived from the Second Law and can be expressed as Eq. 4.20 indicates:

Eq. 4.20. $$B = S(T - T_0) - V(P - P_0) + \sum_{i=0}^{n} (\mu_i - \mu_{i0}) n_i$$

As the chemical energy embodied in the organic components and the biological structure contributes far more to the exergy content of the system, there seems to be no reason to assume a (minor) temperature and pressure difference between the system and the reference environment. Under these circumstances exergy is calculated only from the chemical potentials, which are extremely dominant for ecosystems, the Eq. 4.21 is valid with good approximation:

Eq. 4.21. $$B_{ch} = \sum_{i=0}^{n} (\mu_i - \mu_{i0}) n_i$$

where component 0 represents all the inorganic components, n=1 corresponds to detritus and i≥2 are the organisms.

Starting from exergy function defined in Eq. 4.21 and introducing the chemical potential definition (Eq. 4.22), the Eq. 4.21 becomes (Jørgensen and Mejer, 1977) the Eq. 4.23:

Eq. 4.22. $$\mu_i = \mu_{i,0} + RT \ln \frac{c_i}{c_{i,0}}$$

Eq. 4.23. $$B_{ch} = RT_0 \sum_{i=0}^{n} c_i \ln \frac{c_i}{c_{i,0}}$$

where R is the gas constant; T_0, the temperature of the environment; c_i, the concentration of the *i*th chemical component of the system and $c_{i,0}$, the concentration of the ith component at the equilibrium.

As already specified, exergy can be calculated only by setting a reference environmental state. To perform the calculation of eco-exergy, the chosen reference state is composed by all inorganic elements that form a living organism in their highest oxidation state (when no chemical exergy is left). Physical exergy is equal both for detritus and any more complex structure, but the informational exergy is very different.

Classical exergy theory suggests that the exergy of structurally complicated material can be estimated on the basis of the elementary composition of the material itself (Shieh and Fan, 1982). In this case, classical exergy does not distinguish between different organisms with the same elementary composition, and it ignores the possibility that complex organisms have a lower probability of existence. In consequence, carbon oxide and diamond will have the same classical chemical exergy.

Coming back to Eq. 4.23, let's consider that the phytoplankton in a lake is studied. The concentration c_i could be expressed as mg/l of a local nutrient. c_{io} is the concentration of the i^{th} component at thermodynamic equilibrium and n is the number of components. The value c_{io} is very low for living components because the probability of those living components to be formed at thermodynamic equilibrium is very low. This implies that living components have a high eco-exergy. c_{io} is not zero for organisms, but will correspond to a very low probability of forming complex organic compounds spontaneously in an inorganic soup at thermodynamic equilibrium. c_{io}, on the other hand, is high for inorganic components, and although c_{io} is still low for detritus, it is much higher than for living components.

Shieh and Fan (1982) have suggested the estimation of the exergy of structurally complicated material on basis of the elementary composition. However, this has the disadvantage that a higher organism and a micro-organism with the same elementary composition will have the same exergy, which is in complete disagreement with the lower probability of forming a more complex organism, i.e. the lower concentration of c_{io} in Eq. 4.23.

The weighting factor β, defined as Eq. 4.24 indicates, has been calculated for several organisms based upon the number of non-nonsense (coding) genes (Jørgensen et al., 1995, 2000; Jørgensen, 2002). It is assumed that an organism is represented by the enzymes, which determine the life processes and that c_{io} can be calculated from the probability of random formation of these enzymes. The coding genes are considered blueprints of life.

Eq. 4.24. $$\beta \equiv \frac{c_i}{c_{i0}}$$

Therefore, exergy estimations based on biomass and information for organisms can with good approximation be found as:

Eq. 4.25. $$Ex = \beta \cdot c$$

where c is the concentration of biomass and β the weighting factor, that accounts for the information that the organisms carry (Jørgensen, 2006). Determination of β for various organisms has been based on the number of coding genes, but recent research has shown that some of the non-coding genes are crucial for the control, maintenance and development of the organisms. The results of ongoing whole-genome projects have therefore be applied in order to obtain more accurate β-values (Eichler and Sankoff, 2003).

These new β-values are several times bigger than the previously applied values. The number of amino acids coding per gene was probably underestimated in previous calculations. However, applications of the former values, for instance in ecosystem health assessment, where exergy is used as ecological indicator (referred as exergy index) and in the development of structurally dynamic models, are still valid because the exergy calculations were applied only as relative measures.

A complete table with the last published β factors, as well as a detailed develop of the way of calculation of Jørgensen's eco-exergy by means of the Information Theory, can be found in Annex B.

4.2.4.2. Eco-Exergy calculation for organic matter and organism.

The concentrations of each organism can be measured, but the concentrations in the reference state (thermodynamic equilibrium) are based on the usual chemical equilibrium constants (see Annex A) and the exergy content due to information is calculated using Kullback's information formula (Kullback, 1959 cited by Jørgensen, 2006).

The reasoning chain for obtaining the eco-exergy for organic matter and organism is based on the idea that living organisms use four different nucleotides which are responsible for coding amino-acids and their proteins. Each organism has, in its DNA, a given number of nucleotides (a_i) structured in genes and a given percentage of repeating genes (g_i). The probability of each of them, p_i, can be found as the number of permutations among the four characteristic nucleotides sequences for the considered organism genome, taking into account only the non-repeating genes which are presented in the DNA chain.

After the mathematical procedure explained in Annex B, the general expression for eco-exergy is obtained (Eq. 4.26).

Eq. 4.26. $$\left(\mu_1 - \mu_1^{eq}\right)\sum_{i=1}^{n} c_i - RT_0 \ln 4 \sum_{i=2}^{n} c_i a_i (1 - g_i)$$

Total exergy is called eco-exergy and contains both physical (classical) and info exergy. Since this total exergy can be expressed as equivalent detritus, as showed in Eq. 4.27, the useful β value is alternatively expressed in Eq. 4.28

Eq. 4.27. $$B_{total} = \sum_{i=1}^{N} \beta_i c_i$$

Eq. 4.28. $$\beta = \frac{ex^{eco}}{ex^{phys}} = 1 + \frac{ex^{\inf o}}{ex^{phys}}$$

Where the total exergy is called eco-exergy and defined as the sum of the physical exergy and the info exergy (Eq. 4.29).

Eq. 4.29. $$ex^{eco} = ex^{phys} + ex^{\inf o}$$

Finally, it can be seen that the two main innovations exposed in section 4.2.4 have been covered: detritus as reference environment and different β factors depending on the coding genes number in each specie.

4.2.4.3. Eco-exergy calculation examples

In this section, several examples about eco-exergy calculation are showed in order to analyze the differences between the ecological and the physical exergy concepts. They have been elaborated based on the work developed by Susani et al. (2006).

Both classical (physical) and info-exergy are going to be calculated in order to obtain the eco-exergy value of the considered elements. In every example, the calculation procedure to estimate the info exergy starts with the calculation of the information content of the object by means of its probability. Then, exergy is obtained as Eq. 4.19 indicates.

House made of bricks.

Let's assume a simple parallelepiped house design, with a squared base of 100 m^2, and two floors high 2.5 m each. Its total volume is 500 m^3. The bricks used in the building are standard bricks (28 cm×6 cm×13 cm). About 5500 bricks will be need to complete the house. The house has a strong exergy content inside the building materials, but it also has some information content related to its structure and design.

Classical exergy

Each brick made of clay has a generic chemical composition of kaolinite, $Al_2Si_2O_5(OH)_4$, and 3 kg of weight. According to Szargut et al. (1988), this compound has a chemical exergy of content of 197.8 kJ/mol. Then, the exergy content of the whole house regarding the bricks is 12.6 GJ.

Info exergy

In order to calculate the information content of the described house, the probability is of putting a single brick in a useful position in order to build up the exact house structure has to be found out. According to Boltzmann's theory, all the possible microstates that a brick can assume in the house volume have to be considered.

The choice of considering the house volume is set to maximize the possible microstates or position of the bricks, to reduce the a priori knowledge about house building and to maximize the information content of the house structure itself (Susani et al., 2006). So the a priori probability of placing a brick in the right position is given by the ratio between the brick's volume and the volume of the whole house:

Eq. 4.30. $$p_{brick} = \frac{V_{brick}}{V_{house}} = \frac{0.002184}{500} = 4.37 \cdot 10^{-6}$$

so the Kullback information related to the position of each brick is

Eq. 4.31. $$I_{brick} = \ln \frac{1}{p_{brick}} = 12.34$$

The info exergy is obtained after applying Eq. 4.19 (at 27°C) and it is equal to $1.95 \cdot 10^{-19}$ kJ. It does not affect the β value that remains basically equal to 1, according to Eq. 4.28.

For this example the amount of exergy related to the information is completely negligible compared to the high value of exergy content of matter.

130-pages book

A book is a way of information storage in the form of matter. In this example, a 130-pages book is considered.

Classical exergy

If the book has a mass of 1.5 kg and a regular paper composition, its classical exergy content can be calculated from the paper Low Heating Value (LHV). Then, taking the LHV equal to 20 MJ/kg, the physical exergy of the book is 30 MJ.

Info exergy

The information content of the book can be calculated by applying the Kullback's formula. If the book, containing N characters (both letters and symbols), is written using an alphabet of n characters, it can be stated that the a priori probability that a character is written in the right position is equal to Eq. 4.32 and the information content for the whole book equal to Eq. 4.33:

Eq. 4.32. $$p_c = \left(\frac{1}{n}\right)^N$$

Eq. 4.33. $$I_{book} = N \ln \frac{1}{p_c}$$

Assuming a book with 3 million characters and an alphabet of 50 possible characters (letters of the alphabet plus symbols), the final exergy content of information can be calculated by applying Eq. 4.32, Eq. 4.33 and Eq. 4.19. It results $1.01 \cdot 10^{-10}$ kJ at the temperature of 27 ºC

A similar reasoning way can be followed to calculate the exergy content of a picture with 10^{24}x768 pixels with 65,000 colours available. Its info exergy content is about $2 \cdot 10^{-11}$ kJ and, assuming the weight of the picture as 15 g, its classical exergy is 300 kJ.

Both the book and the picture, which apparently contain a lot of information, still have β values basically equal to 1. In these cases, information exergy has a completely negligible weight in respect to the classical one. Moreover, even the most advanced computers, able to store millions of books or pictures in a single hard drive, still do not have an exergetic information content comparable to their classical one ($\beta \approx 1$). The capacity of packaging information in smaller and smaller quantities of matter is the key for the computer evolution, that is still now far away from the packaging of information typical of microscopic and biological structures (Susani et al., 2006).

Crystal lattice structure

In this example a microscopic level of the matter is tackled in order to understand how important is the microscopic structure to show the crystal features at a macroscopic level. The information exergy content related to the lattice in a glass made of crystal is analyzed.

The main difference between a common glass and a crystal one consists in the presence of lead oxide molecules in the crystal lattice that confers special resistance to the end product, which becomes more workable and mouldable.

The specific composition of the considered crystal is shown in Table 4.7. The main component (over 60% in weight) is the silicate; then, there is about 20% in mass of lead oxide, and smaller quantities of potassium and sodium oxides (10 and 5%, respectively), which are also important for the glass features. All these compounds are mixed together in a physical mixture and no chemical reactions occur, but all the minor compounds assume a well-defined position inside the silicate amorphous structure. Moreover, the compounds tend to be distributed in a uniform way inside the crystal, and it is possible to identify a microscopic cluster which is repeated several times (Vogel, 1994).

Classical exergy

From the classical exergy theory (Szargut et al., 1988), the total amount of exergy associated with those kinds of materials is given by the weighted average of the specific exergies of the single chemical compounds. Using the exergy values given in Table 4.7., the specific exergy of crystal results as 69.2 kJ/mol.

This way of calculating the exergy content completely forgets to take into account the peculiar microscopic structure which gives new chemical and physical features to this material. Furthermore, if the high exergy invested in terms of heat in obtaining the new material from the starting compounds is considered, it can clearly be understood how valuable the crystal is compared with the random mixture of its basic compounds.

	% weight	% moles	b_{ch} (kJ/mol)
SiO_2, amorph	62	75.4%	7.9
PbO, red	23	7.5%	45.9
K_2O	10	7.8%	413.1
NaO	5	9.4%	296.2

Table 4.7. Composition of the analyzed crystal in weight and mol percentage and chemical exergy of the components.

Info exergy

The crystal's properties, in fact, are related to its microstructure, and a well made crystal is produced only through the knowledge of its chemical composition and mixture. If a crystal is made of repeated clusters with a given structure, it is possible to calculate the probability of producing the exact lattice at the microscopic level. According to the chemical composition of the crystal studied, the percentage of molecules in its single cluster is known. These values represent exactly the existing a priori probabilities of finding each molecule in the right position inside the crystal cluster.

Applying Eq. B.26, it can be found out the Kullback information content of each cluster and, using Eq. 4.19, its exergetic content of information. This exergetic content is, again, a very low value of 2.24×10^{-20} J, but it has to be multiplied for an Avogadro number of clusters (6.02×10^{23}) that form a mole of crystal; therefore, the exergetic content of information embodied in a mole of crystal is equal to about 13.5 kJ, and its β value calculated following Eq. 4.29 is equal to 1.2.

This example shows how the amount of information embodied in microscopic structures is so high that it can also have a non-negligible value in terms of exergy. This exergy content becomes of the same order of magnitude and directly comparable with the classical one.

Living organism

Classical exergy

It is equal for any kind of organism, since the constituent chemical elements are the same. The detritus reference value is 18.7 kJ/mol.

Info exergy

According to Eq. 4.26 and Eq. 4.28, it is possible to write a new equation expressing β value for living systems as follows:

Eq. 4.34. $$\beta = 1 + \frac{a_i(1-g_i)}{5.28\cdot10^5}$$

where a_i are the nucleotides structured in genes and g_i is the percentage of repeating genes. The bacteria DNA is composed of 6.7 million genes ($a_i = 6.7\cdot10^6$) and only 16% are repeating ones ($g_i = 0.16$). By introducing these values in the Eq. 4.34, the β of bacteria results 11.7.

In Table 4.8, the procedure has been repeated for different organisms, with different degrees of complexity. The input values for the genoma size and the number of repeating genes have been taken from Jørgensen's works (Jørgensen et al., 2005).

Organism	**Genome size (Mb)**	**Repeat (%)**	**β value**
Bacteria	6.7	16%	11.7
Intracellular parasite	34	0.5%	65.1
Scial amoebe	34	0.5%	65.1
Mustard weed	125	14%	204.6
Fruit fly	137	2%	255.3
Sea squirt	155	10%	265.2
Malaria mosquito	280	16%	446.5
Tiger puffer fish	400	9%	690.4
House mouse	2,500	38%	2,937
Human	2,900	46%	2,967

Table 4.8. Genome size (a_i) and repeating genes (g_i) and β value for different organism (Source: Jorgensen et al., 2005)

The β values are directly related to the complexity of the genetic structures of each organism; in fact, they start from about 11 for the bacteria to almost 3,000 for a human being.

The info-exergy content becomes even more important than classical exergy in living systems, and it grows along with the complexity of the living system itself.

Summary of the results of the examples

Very different elements have been analyzed. Final results for each of them are reproduced in Figure 4.7 in order to get an easier comparative. In the fifth example, classical specific exergy is 18.7 kJ/g for all the organism, the eco-exergy value is obtained from Eq. 4.27 and info exergy as subtraction of them (Eq. 4.29).

As a conclusion, it can be said that a very simple biological structure, such a bacteria, has a β value and information content ten times higher than an inorganic structure, such as glass.

This circumstance can be not very important for non-alive systems, but information and structure play a very significant role when an ecosystem or any complex system is studied. Although, as previously shown, there exists a clear relationship between information and thermodynamics, classical exergy have not traditionally included the information content in its analysis.

The eco-exergy function incorporates information content that facilitates to distinguish and classify different species based on a quality factor related to their genetic content. From an exergy perspective, information has significance for systems with high information, such as a book or a picture. However, it requires relevant the information embodied in microscopic structures to be included in the analysis. That information is enormous when compared to any man-made information storage (Susani et al., 2006).

Even the most advanced computers are many orders of magnitudes less efficient in storing and transporting information than living systems (Wall and Gong, 2001). The evolution of living systems is due to their capacity of storing information. The eco-exergy function measures that information.

System	**Classical exergy (J)**	**Info exergy (J)**	**Eco-Exergy (J)**
Inorganic			
House	1.61E+10	1.95E-19	1.61E+10
Book	3.00E+07	1.01E-10	3.00E+07
Picture	3.00E+05	1.97E-11	3.00E+05
Crystal (1 mol)	6.92E+04	4.20E+06	4.27E+06
Organic ***(1 mol)***			
Bacteria	1.87E+04	1.99E+05	2.18E+05
Intracellular parasite	1.87E+04	1.20E+06	1.22E+06
Scial amoebe	1.87E+04	1.20E+06	1.22E+06
Mustard weed	1.87E+04	3.81E+06	3.83E+06
Fruit fly	1.87E+04	4.76E+06	4.77E+06
Sea squirt	1.87E+04	4.94E+06	4.96E+06
Malaria mosquito	1.87E+04	8.33E+06	8.35E+06
Tiger puffer fish	1.87E+04	1.29E+07	1.29E+07
House mouse	1.87E+04	5.49E+07	5.49E+07
Human	1.87E+04	5.55E+07	5.55E+07

Table 4.9. Summary of the exergy results for the studied systems

In spite of the eventual advantages of having wider data about the organic water content on water, eco-exergy is not going to be included in the PH's methodology. The most relevant reasons are:

- There exits a non-closed argument about the accurancy of the β factors. Going deeper in such a debate clearly exceeds the scope of this Ph.D. thesis.
- The higher order of magnitude of the eco-exergy would hide the classical exergy results.
- There are available real data neither about the species living in the rivers studied in this dissertation, nor for global water resources.

4.2.5. Total exergy of a given water body, water mass or water flow

After reviewing and analyzing each of the specific exergy components, it can be concluded that the Eq. 4.1 can be used every time, but with a previous careful analysis leaded to focus the case study. The reference state is going to be defined in this work as idealized sea water without organic matter. In general studies, the world oceans water chemical composition is considered, while in specific areas' studies, the proper sea water composition will be taken as reference state. As an example, for the rivers in the Spanish east coast, the Mediterranean Sea.

Regarding the exergy components, all of them will be considered in very detailed analysis, but only the most important (representative) ones in global analysis. Then, in a general sense, the total exergy of a water mass or flow, in power units (kW) can be calculated with Eq. 4.35:

Eq. 4.35. $$B\,(kW) = Q(m^3/s)\cdot b(kJ/kg)\cdot \rho_w(kg/m^3) = \dot{m}\,(kg/s)\cdot b(kJ/kg)$$

where *Q* is the water flow of a river/channel/pipe, ϱ_w is the density of the aqueous solution, which could be assumed as pure water without any significant error. Those two terms constitute the mass flow ($\dot{m}$); and finally *b* is its specific exergy, where the considered water exergy components are included.

Once the boundary conditions determined to calculate the total value of water, the more relevant aspects about the exergy cost of water resources are going to be developed in the next section.

Afterwards, in the last part of this chapter, the global fresh water resources on earth are going to be assessed. For this task, only chemical and potential exergy component are taken into account. The study of the world icecaps is also included and, at that point, the thermal component will be added.

In next chapter, Chapter 5, the study area will be much more limited and the methodology will be adapted to watersheds studies.

4.3. Exergy Cost

4.3.1. Historical overview

According to the review carried out by Torres and Valero (2007), the first proposal in the literature to use the Second Law analysis for costing purposes was made by Keenan in 1932, where he indirectly refers to exergy costing as the means for appropriately apportioning cost associated with the cogeneration of electric power and steam for distribution. In particular, Keenan pointed out that the value of those products rest in their *availability*, not in their energy. This author, together with Benedict, kept on working on the idea of coupling exergy and cost streams.

In the 1960's, Tribus and Evans, made exergy analysis of desalination processes, which led them to the idea of exergy costing and its applications to engineering economics, for which they coined the word *Thermoeconomics*. In addition, at that same time, Obert and GAggioli were working on rules to provide a rational distribution of the cost (Torres and Valero, 2007).

The effort of comprehensively apply Termoeconomics to the analysis, optimization and desing of thermal system was leaded by Gaggioli on the 1980s. From then on, the works regarding to exergy analysis increased. In 1985, Tsatsaronis introduces the key concept of Fuel and Product. Frangopoulos (1983) and Spakovsky (1986) kept working on Evan's proposals.

The General Theory of the Exergy Cost was firstly presented by Valero, Lozano and Muñoz (1986) through a set of three papers published by the American Society of Mechanical Engineers (ASME). They stated the fundamental task of costing as the problem of obtaining the cost of all the physical flows comprising a system, once its limits, as well as its subsystem aggregation level, have been defined. In this sense, they define the exergy cost as the *real amount of exergy required to produce any physical flow in a system whose limits, aggregation level and subsystem efficiencies have been defined.*

From then on, many other authors have contributed to the development of exergy and thermoeconomic accounting, completing the existing theories and even opening new research lines.

Szargut (1987) gave rise to the *cumulative exergy consumption* concept, an idea intrinsically similar to the *exergy cost* defined by Valero et al. (1986), i.e., a close to embody energy concept, but using exergy.

Gong and Wall (2001) also pointed out that exergy can be defined as a sustainable development registration that emphasizes the connection between generated services or products and used resources. Exergy can be then considered, a good ecological index, since a high exergy efficiency means less exergy wastes to the environment or less environmental damage. Based on this premise, some authors such as Mora and Oliveira (2006) have more recently used the exergy efficiency as an environmental performance index which includes the aspects of energy efficiency and environmental impact of the energy conversion processes.

4.3.2. Exergy cost background

When the exergy difference between two given thermodynamic states is calculated, the time arrow of the process that joins them has to be carefully observed. Processes that may have happened spontaneously cannot be performed in the opposite way unless some extra exergy is added in the system. Real processes are far from reversibility: they unavoidably imply an exergy loss defined by the Second Thermodynamics Law. As mentioned, this idea has already been applied by different authors in the resources analysis demanded by a process.

In the following, some basic ideas on exergy analysis and Thermoeconomics are presented. Most of the information in this section has been taken from the summary report on Thermoeconomics published by Torres and Valero (2007).

The search for the cost formation process is where physics connects best with economics, and thermoeconomics can be defined as a general theory of useful energy saving, where conservation is the cornerstone.

The exergy balance accounts for the degradation of the exergy. The input exergy into a process will always be greater than the exergy output (Eq. 4.36 and Eq. 4.37).

Eq. 4.36. $$ExergyInput(B_{input}) - ExergyOutput(B_{output}) = Irreversibilities(I) > 0$$

Eq. 4.37. $$B_{fuel} - B_{product} = B^{*}_{fuel} - B_{product} = \sum I$$

where $B^*_{fuel} = \sum B_{input}$

This expression only keeps in mind the irreversibilities of the process. The purpose of this process is set by means of the definition of its efficiency. This is to say, that there is an implicit classification of the flows crossing the boundary of the system: the flows that are the *production* objective, the *resources* required to carry out the production and those that are *residual*. This information is not implicit in the Second Law and is the most important conceptual leap separating and at the same time joining Physics and Economics. Eq. 4.38 is of utmost importance because it places *purpose* in the heart of thermodynamics.

Eq. 4.38. $$\mathrm{Re}sources(F) - \mathrm{Pr}oducts(P) = \mathrm{Re}sidues(R) + Irreversibilities(I) > 0$$

On the other hand the concept of efficiency defined as *efficiency=product/resource* is older than Thermodynamics and measures the quality of a process. The desire to produce a certain product is external to the system, and must be defined beforehand. Once this has been done, the design of the system and its functional structure will fit the aim of using available resources. Every definition of efficiency demands a comparison of the product obtained with the resources needed to obtain it. Its inverse value is *unit consumption=resources/product.*

This expression is also a definition of the unit average cost when resources refer to the overall plant instead of individual processes. This concept is the key of Thermoeconomics. A logical chain of concepts can be established as shown in Figure 4.12, allowing to connect Physics and Economics.

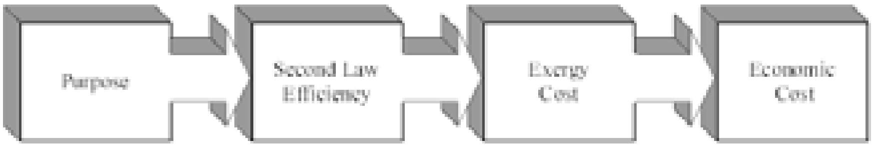


Figure 4.12. Logical chain of Thermoeconomic concepts.

When the problem of calculating the average costs of the final products is faced, it is not needed to disaggregate the system unless several products are simultaneously produced and appear allocation problems. As stated above, the most important application of Thermoeconomics lies in the search of the causes of cost and how to decrease it. This means that the analysis must be as detailed as possible. Not only physical components can be disaggregated, exergy itself can also be disaggregated into its mechanical, thermal, chemical or physical components that have their own history of formation. Each sub-process has consumed its resources to produce a particular increase of pressure, temperature or chemical potential. The flow history and its physical cost can always be reconstructed i.e. the amount of given resources to produce the flow. By a systematic account of these consumed resources, a physical cost to each identified flow can be associated, representing the sum of the resources needed to produce it under the given circumstances. The basic statement is the Cost balance proposition.

> *The cost balance*: The cost is a conservative property. The average cost of inputs is equal to the average cost of outputs

The problem arises with allocating costs to co-products, by-products and wastes of any component in a system, namely when there appear flow bifurcations. Thus, any bifurcated flow, according to Valero (Valero et al., 1986 and Valero, 2009), will belong to one of three categories: resource, F, product,P, or waste,R. Therefore, some additional F-P-R propositions are needed, which can be summarized as follows:

> *F proposition*: The output flow of a subsystem, identified as a non-spent resource, maintains the same cost per unit of exergy as at the input.
> *P proposition*: The cost of products, obtained simultaneously in a single subsystem, are allocated in proportion to their exergy.
> *R proposition*: The cost of wastes is as much negative as the additional resources needed to dispose of them.

Therefore, to sum up, three conditions are needed to allocate costs. First the definition of the boundaries of the system. Second, a structure of the system in which all the components or processes are described in terms of black boxes interacting to each other through energy flows. And, third, the definition of the purpose of production for each and every component. In Thermoeconomics, the words *history, degradation, exergy, quality, cost, resource, consumption, purpose and causality* are related between them. In the *cost formation process*, it is essential to analytically search for the locations and physical mechanisms that make up a specific productive flow. The resources are used up to provide physicochemical qualities to the intermediate products until a finished product is obtained.

In this context, *cost* could be defined as the amount of resources needed to obtain a functional product. On one hand, resources take a general meaning. On the other hand, cost is associated to the purpose of production. It is associated neither with price nor with the resources that could be saved if the production process were less efficient or more conventional one.

Cost is an emergent property. It cannot be measured as a physical magnitude of a flow stream as temperature or pressure; it depends on the system structure and appears as an outcome of the system analysis. Therefore, it needs precise rules for calculating it from physical data. Cost is a property that cannot be found in the product itself (see Chapter 3).

As it was explained in the first chapter, the parameter firstly considered in this dissertation is the exergy of the resource, in energy units. In a first approximation, minimum exergy cost is defined as the exergy gap between two different exergy states, therefore it has energy units.

In short, it can be said that exergy cost of a mass or energy stream is the amount of exergy required to produce it. The unit exergy cost of a mass or energy stream represents the amount of exergy required to obtain a unit of exergy of the product stream. If B_i represents the exergy of the *i-th* product stream and B^*_i its exergy cost, the unit average exergy cost is written as indicated in Eq. 4.39:

Eq. 4.39. $$k_i^* = \frac{B_i^*}{B_i}$$

Then, taking advantage of the information provided by the unit exergy cost, k, the reversible exergy cost will be obtained as real needed energy units by means of the exergy replacement cost ERC. In an ulterior step, it will be expressed in economic units, after obtaining the proper conversion factors.

Traditionally, in Exergoecology, several terms related to costs have been used. For the sake of clarity, their definitions are given here:

Minimum Exergy Cost*:* it is the exergy difference among two physical given states. Its units are energy units. It is also called *exergy gap* and gives idea of the exergy distance among these states. If one of them is the reference state, B and ΔB coincide. In addition to that, since exergy has different components, as it was explained in section 4.2.1, it is important to underline that the distance among to states can be small for a component but higher attending to other features. Its units are MJ/u, where u stands for kg, m^3 or similar.

Unit Exergy Cost (k^*)*:* it is the inverse of the exergy efficiency, as it has been shown in Eq. 4.39. Considering a given process, it is calculated as the ratio between the exergy needed to produce (fuel, F) a resource and the exergy of the resource where the interest is focused (product, Pr). If the process were reversible, its value would be 1. Therefore, it gives information about the process irreversibility. It is dimensionless.

Eq. 4.40. $$k^* = \frac{F}{\mathrm{Pr}}$$

Specific Exergy Replacement (Restoration) Cost (SERC): it accounts for the irreversivility of the process, in MJ/u, where u stands for kg, m^3 or similar. It is obtained by multiplying the exergy gap or minimum cost times the unit exergy cost.

Eq. 4.41. $$SERC = k^* \cdot \Delta b$$

Exergy Replacement (Restoration) Cost (ERC): In relation to global resources assessment, it represents the exergy flow required a given available technology to return a resource into the physical and chemical conditions in which it was delivered by the ecosystem (Valero, 2001). The analysis can be also focussed on restoring a system to some specific previous or desired state, not necessarily to the initial natural state. Its units are energy per time (MJ/yr, as an example). The term Q represents the considered flow (m^3/yr or kg/yr, as examples) or mass (such as m^3 or kg).

Eq. 4.42. $$ERC = SERC \cdot Q$$

4.3.3. Exergy cost of the process and exergy cost of the product

Following the theoretical studied background, two different exergy cost have been defined in this dissertation for the analysis of the water-related processes: on the one hand, the exergy cost of the process and, on the other hand, the exergy cost of the product. In the latter, the whole process is comprised and all the flows are considered in Eq. 4.43, since the total exergy behaviour of the plant wants to be studied. All the outputs are taken as coproducts.

Eq. 4.43. $$k^*_{process} = \frac{F}{\mathrm{Pr}}$$

Where F represents the exergy of the fuels required for running the process and P stands for the addition of all the products present in the process.

In the former, only the desired output is considered and all the inputs are assigned to it, as shown in Eq. 4.44. In this situation, the rest of the outputs are not considered valuable. The exergy cost of the product is obviously higher than the exergy cost of the process.

Eq. 4.44. $$k^*_{product} = \frac{F}{\mathrm{Pr}_{fresh/clean\_water}}$$

Where F is the exergy coming into the process and $\mathrm{Pr}_{\mathrm{fresh/clean\ water}}$ is the exergy of the desired product, fresh or clean water depending on the studied water treatment process. The arising question at this stage is which of the calculated cost should be applied for the water cost calculation searched in this work.

Since the river exergy profiles have been calculated exclusively attending to the water features, it has sense to apply the cost of the product, where the product is the water that needs to be cleaned or replaced.

As the diverse outflows of the process are getting valuable for any other process or final user, they can be considered as products (co-products of the desired clean water) and the cost of the process could be reconsidered. If, for example, the brine obtained in the desalination processes were generally used by a given industrial sector, it could be established a lower exergy cost for the desalted water.

4.3.4. Exergy cost of pumping

According to the definition for the unit exergy cost given in the previous section, the simplest way of calculating the k^*_{pump} is as the inverse of the exergy efficiency of a conventional pump (about 0.7). Thus, 1.43 is the value that will be used for the pumping unit exergy cost.

4.3.5. Exergy cost of desalination technologies

The main desalination techniques, according to the description realized in Chapter 2, have been analyzed to obtain their respective exergy costs.

Seawater, electricity and heat (where needed) have been taken as main inputs of the process for the desalination technology. The outputs are fresh water and brine. An average recovery ratio of 45% has been estimated for the calculations and the obtained fresh water is considered free of salts.

Table 4.10 shows the considered values for sea water (input water, iw) and energy inputs in the system (electricity, W, and heat, Q, when needed). The electricity energy flow is equal to its exergy and the exergy of the heat flow has been calculated considering the working temperature, according to the information given in Chapter 2. Seawater has exergy equal to zero, as it is clear. The notation kg* indicates that values are per kg of treated water

	C_{iw} (ppm)	T_{iw} (K)	T_{iw} (ºC)	W (kWh/m^3)	Q (MJ/m^3)	$b_{ch,iw}$ (kJ/kg)	$b_{t,iw}$ (kJ/kg)	b_W (kJ/kg*)	b_Q (kJ/kg*)	b_{in} (kJ/kg)
MSF	45,000	298.15	25	3.5	250	0	0.4312	1.512	7.3	9.2
MED	45,000	298.15	25	1.5	200	0	0.4312	1.08	6.2	7.7
RO	35,000	293.15	20	4	0	0	0.06199	6.48	0	6.5
ED	2,000	293.15	20	1	0	2.1325	0.06423	0.45	0	2.6

Table 4.10. Input flows and input exergy values for the desalination technologies

The output flows are, for all the technologies, distilled water (D) and brine (BD). In addition to that, for the thermal technologies, the cooling water (CW) has to be added. The more general schema of the flows of a desalination plant is shown in Figure 4.13.

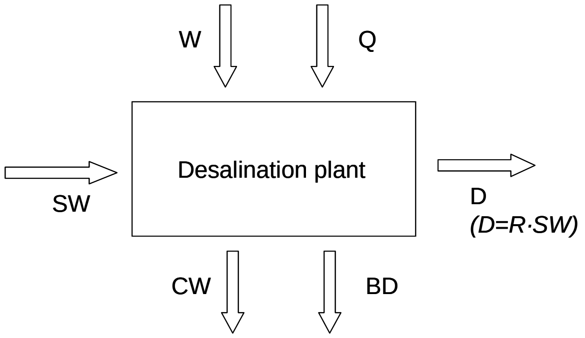


Figure 4.13. General flows diagram for a desalination plant.

In addition to chemical components, the thermal ones are also important for the calculation, since they account for a significant amount of available energy. The recovery ratio is quite different depending on the technology, so this data must also be included in the out flow exergy.

	R_c	C_D (ppm)	T_D (K)	C_{CW} (ppm)	T_{CW} (K)	C_{BD} (pmm)	T_{BD} (K)
MSF	0.12	0	293.7	45,000	310.2	63000	305.2
MED	0.20	0	303.2	45,000	305.2	69000	303.2
RO	0.45	300	293.7	_	_	63391	293.7
ED	0.13	250	293.2	_	_	2250	293.2

	$b_{ch\,D}$ (kJ/kg*)	$b_{t\,D}$ (kJ/kg*)	$b_{ch\,CW}$ (kJ/kg*)	$b_{t\,cw}$ (kJ/kg*)	$b_{ch\,BD}$ (kJ/kg*)	$b_{t\,BD}$ (kJ/kg*)	$b_{ch,out}$ (kJ/kg)	$b_{t,out}$ (kJ/kg)	b_{out} (kJ/kg)
MSF	3.50	0.0841	0	2.59	0.0968	1.464	0.45	1.95	2.40
MED	3.50	1.1060	0	1.464	0.2203	1.097	0.84	1.15	2.00
RO	2.56	0.0840	_	_	0.47	0.08167	1.41	1.20	2.61
ED	2.58	0.0664	_	_	2.0821	0.06421	2.14	0.06	2.21

Table 4.11. Exergy flows calculation for desalination technologies.

Finally, after characterizing all the mass and energy flows, the unit exergy cost for the desalination technologies are calculated. Results are collected in Table 4.12.

	$k_{process}$	$k_{product}$
MSF	3.8	21.4
MED	3.8	8.3
RO	2.5	5.5
ED	1.2	8.0

Table 4.12. Exergy costs for desalination technologies.

Reverse osmosis, as known, is the most efficient desalination technology. MSF presents the higher value when the attention is focuses in the products, since this technology provides an important amount of released heat.

In this study, the unit exergy cost of the product is the parameter to be used, since the attention is focussed on water resources.

Electrodialysis has also a relatively low exergy cost. However, it has to be remembered that it is a technology only applicable to salty waters, not to seawater. In spite of that, it is less efficient than the RO because of its low recovery ratio. (ED process will be later proposed as the restoration technology for the inorganic matter component). Thermal technologies present the highest values, that is, they are less efficient. The $k_{product}$ of the MSF is especially high because, as the definition of the product unit energy cost indicates, the heat is not considered (what is a non-realistic situation in a MSF plant).

4.3.5.1. Exergy content in the brine

An important issue not very often treated is the useful energy that brine contains, a waste product in desalination plants. An important amount of energy has been invested in the separation process to obtain fresh water, but also to concentrate the salts initially dissolved in seawater: both streams contain exergy. One of the advantages of exergy analysis is that it permits to discover energy losses consumed in producing by-products or wastes in a process. Main inefficiency of RO lies in the available energy (exergy) contained in the brine which is not converted into any useful energy nowadays, but promising advances are being found (Ahmad et al., 2008). The other main source of thermodynamic inefficiency (or irreversibility) is the additional pressure drop (with respect to osmotic pressure, the theoretical minimum) that it is needed to apply in present RO modules in order to obtain a competitive permeate flux.

Figure 4.14 shows the chemical specific exergy profile with salinity in a reverse osmosis desalination process with seawater salinity (RE) of 35,000 ppm. For instance, if a RR of 45% was considered, brine would lead to 63,000 ppm, and has a chemical exergy value which obviously is different from zero. Brine discharge and further dilution is then a very important exergy loss (or thermodynamic inefficiency) in desalination processes, in some way contradicting the present use of techniques to improve as much as possible brine dilution in order to minimize its environmental impact.

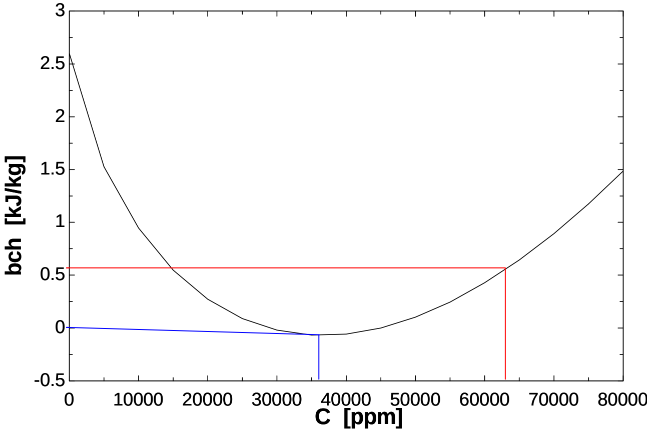


Figure 4.14. Behavior of the concentration exergy with the conductivity of the water

4.4. Exergy value of the hydrologic cycle

The Hydrosphere analysis from an exergy approach can be aimed at different levels, attending to the system boundaries and to the desegregation level the study is interested in. As final section of this chapter, the explained exergy concepts are applied to the global renewable water resources.

As seen in section 4.2.1, the thermodynamic value of water is given by exergy and has, in general, five components: thermal, mechanical, chemical, kinetic and potential (Valero et. al, 2007). However, there are two main basic components: its composition (chemical exergy), which makes it useful for different urban, industrial and agricultural uses, and its altitude (potential exergy), that can be used to produce shaft work and electricity.

Getting detailed information about all global fresh water resources features is a hazardous task due to the lack of data and the reported information would not improve that much the results. Therefore, only the two mentioned and more representative exergy components of water are considered: chemical quality and geopotential. The first one is the minimum energy needed to return the quality characteristics to water and could be obtained by desalination techniques. The second one is the minimum energy needed to return the resource to its condition of potential disequilibrium as delivered by the hydrological cycle. That is represented by the energy needed to lift this resource to the determined height.

The reference for this analysis is, clearly, the ocean. It is considered as the reference state and its main features are altitude equal to cero (no geopotential exergy) and chemical composition equal to the average oceans composition seen in Chapter 2 (Millero, 1996). Then, when a water flow reach the ocean after being used and mixes into it, it has zero chemical exergy as well.

Fresh water stocks have been previously studied from the exergy perspective (Botero, 2000; Valero et al., 2002). However, attending to the real human water appropriation, it could be more interesting and accurate to evaluate the renewable annual water flows, taking into account that they become free every year from the hydrological cycle. In addition to that, the previous studies considered the quality of the restore water equivalent to pure water, after a desalination process. Here, the final restored water has the quality of average river water.

4.4.1. Methodology

The ERC of water resources on the Earth was calculated at two different perspectives: first, renewable fresh water provided by the hydrologic cycle is considered, and second, only world water withdrawal is included. First number gives an idea of the huge amount of energy that would be theoretically consumed if natural hydrologic cycle were moved by humans' technology, and the second one estimated the energy required if all used waters were restored from ocean. This last figure was also compared with present energy consumption in order to propose desalination and pumping as the end solution to water scarcity in the near future

Summing up, the general steps to be follow for water resources assessment, that were briefly described in section 4.1.3 are:

- Defining the water resources to be assessed: world renewable water resources and annual world water withdrawal.
- Defining the reference to be applied. It is clearly seawater, since the idea is calculate the Exergy Replacement Cost of those water resources.
- Characterizing the water resources (physically and chemically), in order to estimate their exergy value. It has been done attending to the potential (altitude) and chemical (salinity of average surface water on rivers) quality of water.
- Applying the unit exergy cost of the required technologies to restore the water resource. Then, as indicated in Eq. 4.41, the SERC (MJ/m^3) is calculated.
- Finally, the ERC is estimated taking into account the yearly water flow (see Eq. 4.42)

4.4.1.1. Exergy required to restore the potential exergy component

The exergy needed to return a consumed water resource to its conditions of physical disequilibrium (or potential) with the chosen reference level (the ocean) is its potential Exergy Replacement Cost (ERC_{pot}), and it can be calculated using Eq. 4.45. In order to find it, the $SERC_{pot}$ value is required. $\mathrm{SERC_{pot}}$ is, in turn, a function of the potential exergy b_{pot} (proportional to the height above the sea level, z) and the unit exergy cost of pumping processes, k_{pot}, which is the inverse of the exergy efficiency (η) of a pump. Such efficiency is a well-known parameter in Thermodynamics. Eq. 4.45 shows the argument followed here:

Eq. 4.45. $$ERC_{pot} = SEC_{pot} \cdot WR \approx k_{pot} \cdot b_{pot} \cdot WR \approx \frac{1}{\eta_{pump}} \cdot b_{pot} \cdot WR \approx \frac{1}{\eta_{pump}} \cdot g \cdot z \cdot WR$$

Where b_{pot} and z can be also expressed as Δb_{pot} and Δz respectively, since the starting point (and reference) is the sea level, with $z=0$.

When the ERC_{pot} of water resources is searched on a global scale (global renewable water resources, world water withdrawal), data on the altitude at which the hydrological cycle discharges in the different countries and continents would be needed. A detailed description of water courses (and their available water flows) would be required in order to calculate the mean value for the attitude z of the water course or annual consumptions in each area. A good attempt could be using the mean attitude of the territories, extracted from available geodata (see Table 4.15 for details).

A different alternative to obtain the ERC_{pot} is suggested from the point of view of the Second Law of Thermodynamics: the minimum energy to elevate water (potential exergy) coincides with the maximum energy obtained when it is turbinated using a reversible machine. Therefore, available figures from the inventory of the world's hydropower capacity can be used to calculate the minimum energy required for pumping (or restoring potential exergy component).

To calculate this component on a global scale, data on the height at which the hydrological cycle discharges the resources in the different countries and continents would be needed. It is practically impossible to calculate the pumping energy everywhere in the world, since we would need data on precipitation, evaporation and runoff in every country at different heights.

From the point of view of the Second Law, the minimum energy to elevate water coincides with the maximum energy obtained when it is turbined using a reversible machine. Therefore, global detailed figures about the world's hydroelectric power can be used to calculate the minimum energy required for pumping.

In 2005, renewable energy represented one-fifth of total power generation. Hydropower is the most advanced and flexible of the renewables and represents 87% of this production REF. During 2005 alone, 18 GW of new hydro capacity was commissioned (WEC, 2007). Notwithstanding this, the entire renewables portfolio for heat, power and transportation offers an enormous potential. As far as hydropower resources are concerned, the IHA (IHA, 2008) estimates that only one-third of the realistic potential has been developed.

Hydropower generation is measured on a large scale in TWh/year and different associated parameters are defined (0). The *gross theoretical capability* (GTC) expresses the total amount of electricity which could potentially be generated, if all available water resources were turned to this use. Those figures are estimated on the basis of atmospheric precipitation and water run-off. The *technically exploitable capability* (TEC) means the hydropower capability which is attractive and readily available with existing technology. The *economically exploitable capability* (EEC) is that amount of hydropower generating capacity which could be built, after carrying out a feasibility study on each site at current prices, and producing a positive outcome.

	Gross Theoretical Capability (TWh/yr)	**Technically exploitable Capability (TWh/yr)**	**Economically exploitable Capability (TWh/yr)**
Global	39,388	16,326	8,725
Africa	2,488	1,852	1,007
Asia	16,285	5,523	3,279
Australia and Oceania	495	189	69
Central America	1,353	279	77
Europe	4,945	2,714	1,632
North America	6,701	2,733	1,037
South America	7,121	3,036	1,624

Table 4.13. Gross theoretical, technically exploitable and economically exploitable capabilities in the continents and global (WEC, 2007).

The current hydropower development status is very different from one continent to another. Figure 4.15 shows the economically feasible hydropower in the world regions versus the percentage of potential development. As an example, hydropower in Europe is highly exploited, although its economically feasible possibilities as lower than in any other continent. However, Asia has the highest potential but it is just used in about 25%.

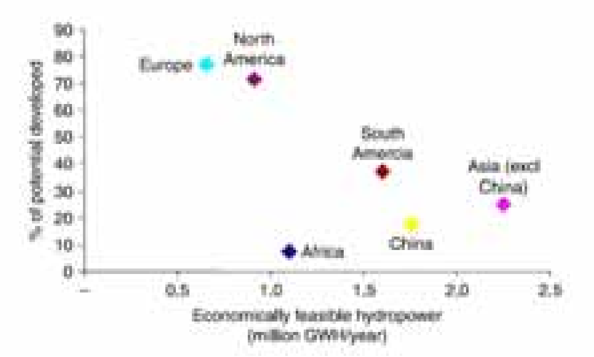


Figure 4.15. Economically feasible hydropower vs. potential development. (Source: Gabbrielli, 2008)

The parameter used in our alternative study for the available fresh water is the *GTC*, since is the only one that accounts for the global hydrologic cycle.

The first procedure (the average altitude of continents as parameter to calculate the potential component) has been chosen in this paper and figures will be presented in the last part of the paper.

The k_{pot} is assumed constant and equal to the inverse of the exergy efficiency of a pump, taken as 0.7. Then, the k_{pot} is 1.43 in all the cases, assuming that similar pumps were taken for this labour.

4.4.1.2. Exergy required to restore the chemical exergy component

The exergy required to restore the chemical exergy component is equivalent to the energy required to obtaining fresh water from its most degraded state (seawater). The minimum *cleaning* or *separating* energy for obtaining a useful water resource (WR) from oceans is its Replacement Exergy Cost (ERC_{ch}), corresponding to its quality component and described in Eq. 4.46. As in the potential case, apart from the considered WR, the ECR_{ch} depends on the chemical Specific Exergy Cost ($SERC_{ch}$), which is a function of the exergy gap between the reference and mean river waters (b_{ch}) and the unit exergy cost (k_{ch}) of the technology required, which could be any kind of desalination-type.

Eq. 4.46.
$$ERC_{chm} = SEC_{chm} \cdot WR = k_{chm} \cdot \Delta b_{chm} \cdot WR = k_{chm} \cdot \left(R_0 \cdot T_0 \cdot \sum_i x_i \ln \frac{a_i}{a_0} \right) \cdot WR$$

At this point, it is necessary to bring here the different available technologies to obtain fresh water and the calculated k for those technologies, as it has been done for the potential component, with the pumping process.

The present study has disaggregated the water resources by continents. It means that having the unit exergy cost, k_{ch}, for the different desalination technologies it not enough. The technologies share in each continent needs to be included in the analysis. Most of the times, it is not the most energy-efficient technology but the most suitable one, the chosen in a given place. Then, in the Middle East, for example, presents mixture between MSF (85.5%), RO (8.5%) and MED (6%) has been applied (see Chapter 2). However, RO is the predominant technology in Europe and America. In some other areas, there is too few desalination plants than no available data have been found and the world average (MSF: 27.6%, MED: 9.6%, RO: 59.2% and ED: 3.5% according to GWI, 2008) has been taken.

	MSF	**MED**	**RO**	**ED**	**k_{ch} (av)**
Global	27.6%	9.6%	59.2%	3.5%	8.25
Africa	27.6%	9.6%	59.2%	3.5%	8.25
Asia	85.5%	6.0%	8.5%	0.0%	19.03
Australia and Oceania	27.6%	9.6%	59.2%	3.5%	8.25
Central America	1.5%	3.5%	95.0%	0.0%	2.99
Europe	1.5%	3.5%	95.0%	0.0%	2.99
North America	1.5%	3.5%	95.0%	0.0%	2.99
South America	27.6%	9.6%	59.2%	3.5%	8.25

Table 4.14. Technologies in the continents and average k_{chm}.

Then, an average k_{ch} has been obtained for each continent and for the world as a whole. It is a very useful figure for being able to analyze the ERC_{ch} of the water resources in the different part of the earth.

4.4.2. Exergy Replacement Cost of worldwide water resources

The ERC of water resources has been calculated at two different levels: firstly, to the total yearly renewable fresh water on the Earth and, secondly, for the yearly world water withdrawal. In the first case, the number gives idea of the exergy that would theoretically be necessary to consume in order to restore all the renewable fresh water on the planet. In the second one, comparisons are carried out to connect the yearly-generated electricity with the exergy needed to restore the annually withdrawn water.

	Renew. water (km^3/yr)	**withdrawal (km^3/yr)**	**h_{av} (m)**	**Electricity generation (TWh/yr)**	**Surface ($\cdot 10^3$ km^2)**
Global	42,862	3,714	855	19,020	134,220
Africa	4,151	213	750	515	30,300
Asia	13,509	2,295	960	6,540	44,900
Australia and Oceania	2,402	26	340	432	8,500
Central America	1090	101	720	88	2,720
Europe	2,900	392	340	3,436	9,900
North America	6,780	522	720	4,797	20,000
South America	12,030	165	590	792	17,900

Table 4.15. General figures for renewable water resources and water withdrawal, by continents. Average altitude, surface and electricity generation.

In Table 4.15, the general figures needed to carry out the calculations are presented. Renewable water and water withdrawal are the two water resources (WR) to be evaluated. The average altitude in each continent is used in the $SERC_{pot}$ obtaining. Electricity generation and surfaces will be use in the last part of the paper, for performing the comparisons and to translate the energy requirements into land demand (if the electrical energy is going to be obtained from renewable energy sources).

4.4.2.1. Exergy cost assessment of the annual renewable fresh water resources.

Assuming that all those renewable fresh water resources (renovated every year by the hydrological cycle) and presented in Table 4.15 were depleted, the minimum energy (exergy) required to restore them is going to be calculated.

The chemical and potential Unit Exergy Costs were calculated in sections 4 and 5 respectively. The potential component is calculated from the known data about the mean attitude per continent, given in Table 4.15. An alternative could be the use of the GTC above mentioned. The chemical specific exergy was calculated from the average river composition, as indicated in section 3.1. Main obtained figures for the ERC_{pot} and ERC_{ch} are presented in Table 4.16.

The ERC would rise until about 380,000 TWh/yr, where about 63% of its contribution comes from the chemical component. By continents, highest ERC is obtained, by far, for Asia, followed by America. The reason for this results are partially different. In Asia, in addition to the clear fact about their richness in renewable water (13,509 km^3/yr), the predominant desalination technology is MSF, the less exergy efficient one. In consequence, high $SERC_{ch}$ and ERC_{ch} values are obtained. In America, the high ERC is due exclusively to the quantity contribution, since it is a big area with important renewable fresh water resources.

	potential component					chemical component						
	b_{pot} (MJ/m³)	**B_{pot} (MJ/yr)**	k^*_{pot}	**$SERC_{pot}$ (MJ/m³)**	**ERC_{pot} (MJ/yr)**	**b_{ch} (MJ/m³)**	**B_{ch} (MJ/yr)**	k^*_{ch}	**$SERC_{ch}$ (MJ/m³)**	**ERC_{ch} (MJ/yr)**	**SERC (MJ/m³)**	**ERC (TWh/yr)**
Global	7.8	3.6E+14	1.43	11.22	5.1E+14	2.41	1.0E+14	8.25	19.90	8.5E+14	31.12	379,842
Africa	6.9	3.1E+13	1.43	9.85	4.4E+13	2.41	1.0E+13	8.25	19.90	8.3E+13	29.74	12,152
Asia	8.8	1.3E+14	1.43	12.60	1.8E+14	2.41	3.3E+13	19.03	45.91	6.2E+14	58.51	50,697
Australia and Oceania	3.1	8.0E+12	1.43	4.46	1.1E+13	2.41	5.8E+12	8.25	19.90	4.8E+13	24.36	3,195
Central America	6.6	7.7E+12	1.43	9.45	1.1E+13	2.41	2.6E+12	2.99	7.22	7.9E+12	16.67	3,060
Europe	3.1	9.7E+12	1.43	4.46	1.4E+13	2.41	7.0E+12	2.99	7.22	2.1E+13	11.69	3,847
North America	6.6	4.8E+13	1.43	9.45	6.8E+13	2.41	1.6E+13	2.99	7.22	4.9E+13	16.67	19,032
South America	5.4	7.0E+13	1.43	7.75	9.9E+13	2.41	2.9E+13	8.25	19.90	2.4E+14	27.64	27,718

Table 4.16. ERC of world renewable water resources.

As a conclusion, it can be said that the available water is the more weighting factor in the calculations, since the differences among the k_{ch} in different countries is much less important.

4.4.2.2. Exergy cost assessment of annual world water withdrawal

When only the real yearly demanded water is analyzed, more realistic results and conclusions are obtained for the energy assessment of water resources. This ERC value can be understood as the energy that would be needed to invest in pumping and desalination utilities in order to replace the fresh water taken by humans from the hydrologic cycle every year.

The yearly water withdrawal in each continent was presented in Table 4.15. As it was done in the previous study, ERC_{ch} is calculated through the share of desalination technologies by continent and the rivers composition, and the ERC_{pot} by means of the inverse of the energy efficiency of a typical pump. In this case, the potential component is also calculated from the known data about the mean attitude per continent. An alternative could be the use of the EEC above mentioned.

The total ERC of the global water withdrawal is about 33,000 TWh/yr (almost twice the world electricity production). By continents, it can be seen that this ERC would represent 42% of the electricity production in Australia, 38% in Europe and 52% in North America. For the rest of the continent, the comparison is dramatic: 163% in south America, 350% in Africa and 551% and 579% for Central America and Asia respectively.

	potential component					chemical component						
	b_{pot} (MJ/m^3)	B_{pot} (MJ/yr)	k_{pot}	$SERC_{pot}$ (MJ/m^3)	ERC_{po} (MJ/yr)	b_{ch} (MJ/m^3)	B_{ch} (MJ/yr)	k_{ch}	$SERC_{ch}$ (MJ/m3)	ERC_{ch} (MJ/yr)	SERC (MJ/m^3)	ERC (TWh/yr)
Global	7.8	3.1E+13	1.43	11.2	4.4E+13	2.41	8.9E+12	8.25	19.88	7.4E+13	31.1	32,895
Africa	6.9	1.6E+12	1.43	9.8	2.2E+12	2.41	5.1E+11	8.25	19.88	4.2E+12	29.7	1,802
Asia	8.8	2.2E+13	1.43	12.6	3.1E+13	2.41	5.5E+12	19.03	45.87	1.1E+14	58.5	37,846
Australia and Oceania	3.1	8.8E+10	1.43	4.5	1.3E+11	2.41	6.3E+10	8.25	19.88	5.2E+11	24.3	180
Central America	6.6	7.1E+11	1.43	9.5	1.0E+12	2.41	2.4E+11	2.99	7.22	7.3E+11	16.7	485
Europe	3.1	1.3E+12	1.43	4.5	1.9E+12	2.41	9.5E+11	2.99	7.22	2.8E+12	11.7	1,306
North America	6.6	3.7E+12	1.43	9.5	5.3E+12	2.41	1.3E+12	2.99	7.22	3.8E+12	16.7	2,510
South America	5.4	9.5E+11	1.43	7.7	1.4E+12	2.41	4.0E+11	8.25	19.88	3.3E+12	27.6	1,288

Table 4.17. ERC of annual world water withdrawal.

4.4.2.3. Use of solar energy to restore the annual water withdrawal

Global energy use has risen by 70% since 1971 and continues to increase at the rate of about 2% per year; this demand comes from both developed and developing countries. As previously indicated, fresh water demand is growing faster and, in consequence, also the desalination infrastructure utilities. The scarcity is exacerbated by groundwater pollution, such as has occurred in China, and above-average population growth in areas of limited water resources such as the Arabian Gulf states, southern Spain and the American southwest. It is estimated that by 2025, 3.5 billion people will live in areas facing severe water shortages. These areas are also characterized by its dry, sunny climate. It is therefore clear that this solar potential is the natural renewable energy source (RES) to be used for desalt or pump fresh water.

Once the ERCs to restore the fresh water withdrawal have been calculated, this part of the study is aimed to translate them in land requirements if the solar power were the only source. Firstly, the photovoltaic (PV) technology is studied, analyzing different alternatives (fixed or tracking systems, more and less efficient modules). Secondly, the solar energy generation systems using parabolic through collectors (PTC) are considered.

PV systems to restore fresh water

In Table 4.18 the solar potential for each continent is given, with the corresponding differences among the PV technologies. Different figures are given for fixed PV installation and two-axis tracking systems because, as it is well known, the tracking systems increase the incoming radiation: amorphous silicon is about 10% efficient, so the generated electricity per m^2 is lower than with other technologies. Conventional monocristaline silicion (about 15% efficiency) are considered with and without tracking in the analysis.

Looking at the previously calculated energy requirements (Table 4.17) and dividing by the solar potential in each case, the renewable power to be installed is obtained. The radiation is given in equivalent solar hours ($kWh \cdot m^{-2} \cdot d^{-1}$) and the global efficiency of the solar power plant –performance ratio- has already been included.

Table 4.18 also shows the land requirements for PV modules, if all the required energy to produce and elevate fresh water was obtained from this renewable technology. Fix technology is studied both with 10%-efficiency modules (e.g. amorphous silicon or a Si-triple junction) and with 15%-efficiency modules (e.g. regular mono-crystalline silicon). The tracking system was only analyzed with highest efficiency because there is no sense in using less efficient technologies in tracking systems (Bayod, 2009).

	Solar potential ($kWh \cdot m^{-2} \cdot d^{-1}$)			**PV power (TW) to be installed**			**Land requirements (km^2)**			
	without tracking (Amorph)	**without tracking**	**with tracking**	**Fix (Amorp)**	**Fix**	**Track.**	**Fix (Amorp)**	**Fix, 15% eff**	**Track. 15% eff**	**% land (max)**
Africa	1,600	2,000	2,700	1.1	0.9	0.7	11,260	13,345	40,034	0.13%
Asia	1,200	1,500	2,025	31.5	25.2	18.7	315,386	373,790	1,121,371	2.50%
Australia and Oceania	1,520	1,900	2,565	0.1	0.1	0.1	1,187	1,407	4,221	0.05%
Central America	1,360	1,700	2,295	0.4	0.3	0.2	3,564	4,224	12,673	0.47%
Europe	1,200	1,500	2,025	1.1	0.9	0.6	10,886	12,902	38,707	0.39%
North America	1,200	1,500	2,025	2.1	1.7	1.2	20,917	24,791	74,373	0.37%
South America	1,200	1,500	2,025	1.1	0.9	0.6	10,735	12,723	38,168	0.21%

Table 4.18. Continents surface, power and land requirements to restore the yearly water withdrawal, with different PV configurations and technologies.

The percentage of covered land is also shown in Table 4.18. Only the maximum of the three alternatives has been reproduced here. It can be observed that land requirements are less than 1% of the continent surface in all the cases, except in Asia, where the Middle East area contribution appears.

PTC systems to restore fresh water

When the PTC technology is considered, similar land demands result. Solar potential includes 1-axis tracking system and, eventually can be operated with a storage unit in order to maintain a continuous operation. Table 4.19 shows the obtained results, classified by continents.

	Solar potential ($kWh \cdot m^{-2} \cdot d^{-1}$)	**STC power (TW) to be installed**	**Land req (km^2)**	**% of the continent land**
Africa	2,700	0.67	26,689	0.1%
Asia	2,025	18.69	747,581	1.7%
Australia and Oceania	2,565	0.07	2,814	0.03%
Central America	2,295	0.21	8,449	0.3%
Europe	2,025	0.65	25,805	0.3%
North America	2,025	1.24	49,582	0.2%
South America	2,025	0.64	25,445	0.1%

Table 4.19. Power and land requirements to restore the yearly water withdrawal, with PTC technology.

As it happened in the previous study, demanded areas are quite low and Asia is the highest, with 1.7% of its territory to be devoted to PTC power plants.

Analysis of results for the exergy value of the hydrologic cycle.

Global figures to assess the energy freely given by the Earth through its hydrologic cycle have been obtained in this part of the dissertation. They have been studied from a physical approach, based on the Second Law of Thermodynamics: the Exergy Replacement Cost (ERC) of those resources has been calculated in each continent, separating chemical and potential contribution.

Two levels of analysis have been performed. First, in order to highlight the huge importance of the hydrologic cycle, the total available renewable fresh water on Earth was studied. Secondly, only present world withdrawal was considered in order to compare the magnitude and to quantify it from an energetic (and technologic) perspective. This second study provides a more realistic panorama, since it allows the comparison of the energy involved in the water cycle and the world energy demand.

Results show that ERC value for all the renewable fresh water is twenty times higher than the yearly world electricity consumption. When the study is focused only in the water withdrawal, the required energy *only* doubles the above mentioned demand. Chemical component account for 63% of that energy on average and the potential component represent the remaining 37%. It is due to the thermodynamic efficiency of desalination technologies), which is lower than the pumping efficiency. These both technologies have been analyzed through their UEC in this study.

Furthermore, the possibility of obtaining the exergy demand represented by the ERC, by only taking solar energy (SE) as primary source, was studied. Fixed-PV technology gives the lower surface requirements: although PV tracking systems increase the power generation, they do not compensate their additional space required to avoid shadowing. Asia would need the highest occupation of the territory if SE was selected (about the 2% by using PTCs, and the 2.5% in case of PV tracked systems).

As a conclusion, despite of the very low energy efficiency of the hydrologic cycle, if that huge amount of energy naturally obtained would be totally restored by desalination plus pumping systems, the required energy would not be affordable in the present context of the scientifically demonstrated climate change. Moreover, as exergy analysis gives the picture of the energy efficiency of water treatment processes, it could suggest new guidelines to reduce energy consumption in present desalination technologies, which seem to be the end solution to support human life needs in coastal areas, once water demand strategies have been fully implemented.

4.5. Exergy value of ice caps and glaciers.

The exergy assessment for the ice caps and glaciers was done in the same methodological way as followed for the renewable fresh water on the Earth. The exergy content on ice was firstly calculated. In this case, the thermal component has been considered in addition to the chemical and potential components because, as it is clear, the low water temperature is a key point for analyzing the value of those water bodies. First attempt to asses the exergy value of the ice on Earth was developed by Valero et al. (2002).

The world glaciers were separated intro three study areas: Artic (Greenland), Antarctic and the rest of the glaciers and ice caps in the world. In this study, the thermal, potential and chemical exergy components have been considered to be the most representatives. Values of temperature, altitude and composition have been taken from the physical description of them presented in Chapter 2.

Greenland and the Antarctic region have an average temperature of -10.8 ºC and -37.5 ºC respectively. The average temperature taken for the rest of glaciers is -28.9 ºC. The average altitude values are 1,524 m, 1,600 m and 1,500 m (Shiklomanov, 2004). Finally, the average chemical compositions were already detailed in Table 2.4.

Potential and chemical components were calculated as it was explained in sections 4.4.1.2 and 4.4.2.1. The thermal exergy component as obtained by addition of the three needed steps to produce ice from seawater at 15ºC: *(i)* cooling process until freezing point, *(ii)* phase change from solid to liquid and *(iii)* ice cooling from 0ºC to the established average ice temperature in each case. This is the usually called refrigeration demand Q_{cool}.

Eq. 4.2 has been applied for the cooling processes (1.63 kJ/kg in the first step) and the exergy of the heat flow has been calculated as well (18.4 kJ/kg). The exergy in the last cooling step depends on the ice temperature and values range from 3.32 kJ/kg for the Greenland to 13.38 kJ/kg for the Antarctic and 60.40 kJ/kg in the rest of the ice areas.

Eq. 4.47.
$$b_{thermal} = c_{H_2O}\left[T_H - T_0 - T_0 \ln\left(\frac{T_H}{T_0}\right)\right] + L\left(1 - \frac{T_0}{T_H}\right) + c_{ice}\left[T_C - T_H - T_0 \ln\left(\frac{T_C}{T_H}\right)\right]$$

Where L is the heat in the change of phase (334 kJ/kg), T_0 is the reference temperature (15ºC), T_H is the phase change temperature (0ºC) and T_C is the final ice temperature.

	Volume (km^3)	b_t (kJ/kg)	b_p (kJ/kg)	b_{ch} (kJ/kg)	b (kJ/kg)	B (kJ)
Artic (Greenland)	2,340,000	23.31	7.5	2.5235	33.3	7.8E+19
Antarctic	21,600,000	40.35	7.8	2.5013	50.7	1.1E+21
Others	207,639	33.37	7.4	2.5033	43.2	9.0E+18
					TOTAL	1.2E+21

Table 4.20. Volume, specific and total exergy of the thermal, potential and chemical component and total exergy content in the world ice sheets.

Results are showed in Table 4.20. The total exergy content in the world ice sheets is $1.2 \cdot 10^{21}$ KJ (1,200,000 EJ or 28,000 Gtoe), what is more than 2,300 times higher than the world annual primary energy demand, or 175 times higher than the proved world oil reserves. The world annual primary energy demand is about 500 EJ and the proved world oil reserves are about $162 \cdot 10^9$ toe ($1.2 \cdot 10^{12}$ barrels).

4.5.1. Exergy replacement cost of the world ice sheets and glaciers

Until this point, only the exergy content of the world ice sheets and glaciers has been accounted for. Next, the ERC of the ice sheets and glaciers is estimated, as it was already done for the fresh water resources, by considering technologies able to restore them as they are found in Nature (in this case, thermal, potential and chemical value). The corresponding unit exergy cost is taken for each of the processes: desalination for the chemical component, pumping for the potential and cooling for the thermal component.

The unit exergy cost for pumping remains 1.43 (defined in section 4.3.2). However, the desalination one, stated in section 4.3.3, varies here lightly because of the different chemical composition of the glaciers areas: calculations carried out for the general desalination analyses were reproduced, but changing the final composition of the fresh water (glaciers composition instead of rivers composition). The difference between those procedures is negligible (about 10^{-3}). Again, the RO desalination technique is the most efficient option; k_{des} is equal to 5.49.

Regarding the cooling unit exergy cost, the maximum efficiency of the refrigeration cycle can be easily calculated using the Carnot's Coefficient of Performance (COP_{Carnot}), so the minimum work needed is immediately obtained (Eq. 4.48).

Eq. 4.48. $$COP_{Carnot} = \frac{T_C}{T_H - T_C} = \frac{Q}{W_{theor}}$$

However, for obtaining the COP of the real cooling process some additional considerations needed to be done.

The practical COP can be obtained from the Carnot factor multiplied by a factor α as indicated in Eq. 4.49 (IDAE, 1998). Different α values are assumed for the heating pump depending on the kind of equipment that is being considered: 0.65, 0.5 and 0.3 for big facilities with advanced designs, residential and commercial with high efficiency and domestic equipments, respectively.

Eq. 4.49. $$COP_{HP} = \alpha \cdot COP_{Carnot,HP}$$

The different curves have been drawn, together with the COP_{Carnot}, in Figure 4.16.

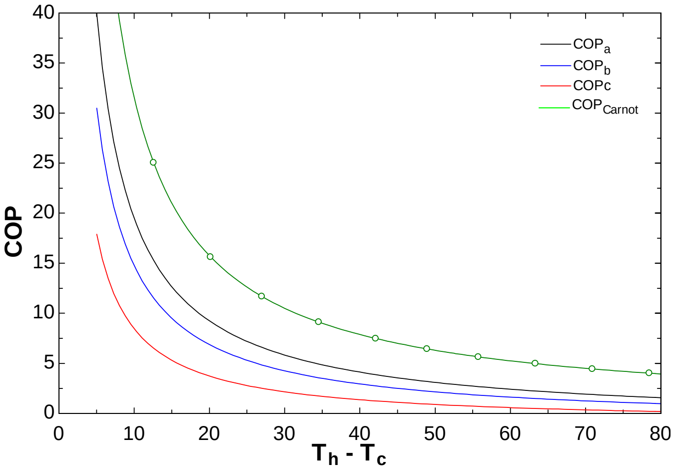


Figure 4.16. COP_{cool} for different equipments: big facilities with advanced designs (a), residential and commercial with high efficiency (b) and domestic equipments (c) vs the temperature difference among the hot and the cold focus. Green line represents the COP_{Carnot}. (Source: adapted from IDAE, 1998).

Once the real COP of the hypothetical cooling system was calculated, the associated required work is immediately obtained (Eq. 4.50), since the refrigeration demand Q does not varies.

Eq. 4.50. $$W_{real} = \frac{Q}{COP_{HP}}$$

For the world ice sheets and glaciers replacement, the best available technology needs to be considered. Consequently, the factor α for big facilities with advances designs was taken.

The summary of results can be seen in Table 4.21. Successive columns show the COP_{Carnot}, calculated according to Eq. 4.48; the COP_{cool}, directly read from Figure 4.16; the refrigeration demand Q; and the theoretical and real cooling works.

	COP_{Carnot}	COP_{cool}	Q (kJ/kg)	W_{theor} (kJ/kg)	W_{cool} (kJ/kg)
Artic (Greenland)	10.17	6.94	464.82	45.71	67.01
Antarctic	4.49	2.90	520.62	115.99	179.52
Others	5.56	3.66	502.65	90.34	137.18

Table 4.21. COP values for the theoretical and real cooling processes, cooling heat and energy demand by the theoretical and real cooling processes.

Finally, the unit exergy cost of the cooling process can be obtained by comparing the real and the theoretical required works (Eq. 4.51). Since the characteristic temperature for each of the studied ice areas is different, also the k^*_{cool} values slightly differ (Table 4.22).

Eq. 4.51. $$k^*_{cool} = \frac{W_{cool}}{W_{theor}}$$

Table 4.22 shows the k^*s and the SERCs for each of the exergy components and, finally, the ERC of the Earth's ice sheets and glaciers. It rises up $4.7 \cdot 10^{21}$ kJ, one order of magnitude higher than the glaciers and icesheets' total exergy content showed in Table 4.20. It is almost 700 times the energy content in the proved world oil reserves or 2,300 times the annual world primary energy demand.

	k^*_{cool}	k_{pum}	k_{des}	**SERC$_{\_t}$ (kJ/kg)**	**SERC$_{\_p}$ (kJ/kg)**	**SERC$_{\_ch}$ (kJ/kg)**	**SERC (kJ/kg)**	**ERC (kJ)**
Artic (Greenland)	1.47	1.43	5.49	67.01	10.68	13.86	91.55	2.1E+20
Antarctic	1.55	1.43	5.49	179.52	11.21	13.74	204.47	4.4E+21
Others	1.52	1.43	5.49	137.18	10.51	13.75	161.44	3.3E+19
							TOTAL	**4.7E+21**

Table 4.22. Unit exergy costs (cooling, dumping and desalination), specific exergies replacement costs (thermal, potential and chemical) and final ERC for each ice area and total ERC.

4.6. Summary of the chapter

This fourth part of the dissertation is a wide chapter with two well defined parts. In the first one, the exergy components of water are reviewed and their calculation way for this work has been established. Potential, chemical and, in some cases, thermal components are concluded to be the more relevant parameter to be studied in general water bodies analyses.

As a key point of the calculation, the most adequate Reference Environment for the water bodies exergy assessment has been proposed. The finally chosen RE was a sea water state without organic matter, nitrogen and phosphor. This is considered as the most suitable RE for our analysis and it is also coherent with sea water as a very important part of the hydrological cycle.

The Jorgensen's Eco-exergy approach has been considered in this chapter as well. However, since classical exergy does not take into account information content, it is not included in the analysis. The available information it not enough to go through the eco-exergy calculation and, in addition to that, the final aim of this work (water quantity and quality restoration) can not be tackled when life organism are included.

Once the exergy considerations are stated, the exergy cost definition and extension are considered in the second part of this chapter. The essential difference between the reversibility of processes (ideal process) and the real irreversible processes make necessary to define the exergy cost attending to the purpose of the process. The unit exergy cost, understood as the inverse of the exergy efficiency, and the exergy replacement cost, that gives information about the exergy needed to restore a resource, are the two main introduced concepts.

Finally, in the third part of the chapter, an attempt to valuate the hydrologic cycle has been performed. The exergy replacement cost of global fresh water resources and of the annual world water withdrawal have been calculated. The required exergy to restore the water freely yearly provided by the hydrological cycle is translated into land requirements by continents, assuming electricity production with RES (PV and STC).

Results show that REC for all the renewable fresh water is twenty times higher than the yearly world electricity consumption. When the study focuses only in the water withdrawal, the required energy doubles the mentioned world electricity demand. Chemical component accounts for 70% of that energy on average and has a higher unit exergy cost (between 5 and 6 depending on the continent). Potential component represent the remaining 30%, with a potential unit exergy cost of 1.43.

Furthermore, as mentioned, the possibility of obtaining the ERC with RES has been analyzed. Fix PV technology gives the lower surface requirements because, although the PV tracking systems make higher the production, they need about three times more space to avoid the shadow losses. South America is the continent where more surface would be needed to produce the energy with RES, until 6% of its territory in the PTC case.

As a conclusion, that huge energy that Earth give us in a natural manner, should not be totally restored by desalination plus pumping systems, since associated environmental impacts could provoke dramatically new environmental impacts and thus accelerate the climate change. Such systems should only be devoted to areas without fresh water supply for drinking uses.

Regarding the world glaciers and ice sheets, its exergy value has also been calculated. Thermal exergy component is also included, in addition to potential and chemical. Results show that the exergy value of the icecaps is even higher than the hydrological cycle one. It gives idea about the damaging consequences associated to the climatic change.

Chapter 5

Exergy assessment in a water course: Physical Hydronomics

The hydrologic cycle is a basic concept that water managers need to keep in mind in their daily work. When the flow of water is manipulated to fulfil human needs, it is necessary to understand how these actions will affect the hydrologic cycle and, ultimately, the availability and quality of water to downstream users. Thorough understanding of the hydrologic cycle is absolutely necessary if maximum use of water resources is to be achieved, while avoiding detrimental effects to wildlife and the environment as a whole.

The application of the Exergoecology approach to watersheds is developed in this chapter. The general methodology shown in Chapter 4 is here carefully adapted and applied to the study of a river basin. In this chapter, the watershed information requirements are reported and the calculation procedures are explained, after analyzing different procedure possibilities. The application of Exergoecology to a specific water-resources area or watershed is defined as Physical Hydronomics (PH).

The assessment of environmental and resource costs stated by the WFD requires the search of new theoretical and applied approaches able to lead to a comprehensive analysis based on a physical evaluations, that details quality but also quantity degradation. PH can play an important role in such undertaking.

This chapter is structured in fifteen points, which cover all the relevant aspects related to PH development and its application. First, the area of study, the different values of exergy depending on the type of considered water and the application of the Exergy anaylis to define the exergy profile of a river are tackled. Secondly, several river states are defined in accordance with the European WFD and the procedure to obtain their corresponding exergy profiles is detailed, attending to their quantity and quality components as well as to their main components: potential, organic matter, inorganic matter. Thirdly, as difference between river states, three exergy cost –coinciding with the WFD cost- are defined as exergy gaps: service cost (SC), environmental cost (EC) and remaining resources cost (RRC). The three can be added to obtain the integral replacement cost (IRC), understood as the difference between the river in its natural state and the same river in its more degraded situation with the river without any WTP and all their uses computed. Afterwards, a detailed interpretation of the expected sign for those exergy cost is done.

Point 5.12 marks the beginning of the section where the operative procedure to apply PH needs to be supported. Watersheds simulation models are crucial for the PH application. In most of the real river monitoring networks, only very few points are available on data bases. Then, in order to obtain a good enough exergy profile of the river, the simulation is needed. A review of the available watershed modelling softwares was done, and the Qual2kW was chosen.

The next step in the chapter is considering the exergy degradation along the river due to water uses is treated and its relationship with the already presented IRC is analyzed in detail. To illustrate the hypothesis of equivalence, some simple examples are developed and explained.

Finally, the unit exergy cost concept within the PH is launched. It accounts for the irreversibility of the real desalination and other water treatment processes, and makes possible the translation of the theoretical exergy gap between to given states of the river into a real exergy gap that is covered by means of real technical processes. In this way, the exergy needed to restore the river until its original state or until the legally defined desired state can be calculated in energy terms. If desired, the monetary cost of such measurements can be also obtained by introducing the energy monetary cost.

5.1. Introduction. Physical Hydronomics definition.

Global water analyses from an exergy perspective have been developed in Chapter 4. The total exergy replacement costs give an indication of the actual effort that should be made to restore the water stock or consumption because of its departure in quality and quantity from the sea. It measures the cost for producing water (through desalination) and restoring it to its original location (through pumping), with the available technology. This measure is useful for establishing an objective guide for water management, as it offers a map of maximum costs in a certain territory. They provide useful tools to assess fresh water values and help to quantify the natural resources given by the Nature for free.

However, when the objective is to calculate the degradation costs of a certain water body or flow due to the anthropogenic presence, those previous costs are not representative because it is not necessary to desalt and pump seawater to bring existing waters to a better status. At this stage, the interest resides in comparing the exergy difference existing between two given states of the river. It is obtained through the total exergy profiles of water courses under present or any other objective conditions.

Therefore, in this chapter, the area of study is reduced. It allows a more detailed analysis and opens the way to apply exergy approach in a broader sense, being even able to implement WFD through the branch of Exergoecology called Physical Hydronomics.

Physical Hydronomics is the specific application of Thermodynamics to physically characterize the degradation and correction of water bodies. i.e., the physical application to European Water Framework Directive. While Thermodynamics is interpreted here as the framework, Physical Hydronomics can be understood as the Accounting Principle. The final objective of PH is to use those calculated physical costs as a guide to allocate the environmental and resource costs proposed by the WFD.

5.2. The area of study: a watershed.

A watershed, which is sometimes called a drainage or river basin, is an area of land where all the water that falls on it will drain to a body of surface water, such as a stream or lake. It collects water and delivers it to the watershed outlet, which commonly is a stream or river.

Because fresh surface water and fresh groundwater are mainly the only parts of the hydrologic cycle that are directly taken for human uses, water managers are focused on these resources. Although it is important to know how much water is stored in groundwater, lakes, and wetlands, the understanding of the movement of water to, within, and from watersheds is far more important and a far greater challenge. Indeed, most research in the hydrologic sciences is devoted to understanding the movement of water, and the movement of chemicals and sediment transported by water in watersheds.

To assure adequate water resources for human use, water managers need to be able to measure the amounts of water that enter, passes through, and leave watersheds. This is a challenge because the relative magnitudes of the individual transfers in the hydrologic cycle can vary substantially. For example, in mountainous areas, precipitation is more difficult to measure high in the mountains compared to in the valleys. Mountain snowpack and the amount of melt water it can deliver can vary widely, thereby affecting natural water budgets at lower elevations.

As a second example, evaporation rates may differ greatly among an agricultural field. a nearby woodland, and a nearby wetland. Thirdly, the discharge of groundwater to surface water may vary in different parts of watersheds because different rock and sediment types may be present.

5.3. Exergy of different types of water

Different types of water have different exergy values because of their different quality characteristics. To illustrate this fact with real figures, the exergy value of specific types of water has been calculated. If the reference is 1 kg of water, the values for different exergy components are given in Table 5.1.

The chemical component designed as inorganic matter (bch_{IM}) is the addition of the chemical exergy of salts (bch_{salts}) and the chemical exergy of pure water (bch_{H20}). Chemical exergy of organic matter (bch_{OM}) and chemical exergy of nitrogen and phosphor (bch_{NP}) are presented separately because, as explained in chapter 4, their addition could hide the bch_{IM} presence. Finally bch_{tot} is the addition of all the components.

Attending to b_{ch_IM}, pure water, as expected, has the higher value because it has no salts presence and, in consequence, such water presents the best quality. Organic matter, nitrogen and phosphor are present in urban waste water, what conduce to a high value of bch_{OM} and bch_{NP} and, therefore, to a higher bch_{tot}.

Values used to calculate the exergy of what can be named *legal water* (OS) are taken from legislation and it has to be said that they are limit, maximum values. In consequence, the obtained exergy results have to be correctly interpreted.

5.4. Exergy of a river

In the exergy study of a river basin, all the exergy components presented in section 4.2.1 are considered. It means that a more detailed information about the study area than in global water analysis is needed: altitude, temperature, pressure and chemical composition, both for the actual state or the river and for the adopted reference environment. That RE keeps the features described in point 4.2.2, but its temperature and its salts composition can lightly vary depending on the sea where the river under study dies.

The PH's main objective is to obtain objective water costs. According to the WFD, different water costs are defined and, following basic Thermodynamic Laws, they are calculated through the exergy analysis.

5.4.1. Exergy profile of a river

The exergy profile of the river is a very useful tool that will help in the proposed task: each river exergy profile represents one of the statuses of the river. Total exergy is obtained by multiplying the specific exergy times the water flow (see Eq. 4.35).

According to Valero et al. (2007), the exergy profile of a river along its course has a characteristic curve, which is quite similar for all of them. This fact can be explained analysing the typical profiles of the specific exergy and of the water flow in a river.

The ideal and simplified specific exergy profile of a river is illustrated in the top of Figure 5.1. At the river source, water is found at the highest elevation and at the most pure state, therefore its physical and chemical exergies are the highest at that point. As it flows into the mouth, the water body loses height and purity and therefore its specific exergy decreases until it reaches the point of minimum exergy (maximum degradation) which is the sea (reference environment). On the other hand, the water flow usually follows exactly the opposite path: minimum at the source and maximum at the mouth because of the received contributions. Both effects together give an ideal total exergy pattern of the bell-shaped curve given at the bottom of Figure 5.1.

TYPE OF WATER		TOC	Cond	Cl	SO_4	NO_3	NO_2	NH_4	PO_4	Ca	HCO_3	K	Mg	Na	MS	$b_{ch.tot}$	$b_{ch.H2O}$	$b_{ch.salts}$	$b_{ch.IM}$	$b_{ch.OM}$	$b_{ch.NP}$
		mg/l	µS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	kJ/kg	kJ/kg	kJ/kg	kJ/kg	kJ/kg	kJ/kg
(1)	H2O	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	2.5388	2.5388	0.0000	2.5388	0.0000	0.0000
(2)	Rainfall	0.0	10.6	10.2	23.0	8.5	0.5	0.1	0.0	13.1	18.0	1.06	0.9	4.8	1.0	2.5368	2.5352	-0.0135	2.5218	0.0000	0.0150
(3)	surface water (Muga)	0.6	374.6	23.0	39.3	0.9	0.3	0.4	0.1	62.1	177.7	4.87	7.8	17.9	0.8	2.5361	2.5234	-0.0250	2.4983	0.0276	0.0101
(4)	deep water (MAS 32)	1.6	784.9	55.2	129.3	53.7	0.1	0.3	0.2	133.3	269.4	4.04	18.5	32.5	0.0	2.6253	2.5074	-0.0395	2.4679	0.0696	0.0878
(5)	waste water (urban)	125	574.6	58.0	61.8	1.1	0.3	20.4	10.1	95.2	272.6	7.46	11.9	27.5	1.2	8.2611	2.5107	-0.0364	2.4744	5.3970	0.3892
(6)	"legal" water	0.0	2500	250.0	250.0	50.0	0.5	0.5	0.0	100.0	500.0	0.00	50.0	200.0	50.0	2.4363	2.4666	-0.1249	2.3417	0.0000	0.0859
(7)	bottled Mineral water (Pascual)	0.0	32.62	33.8	19.8	5.0	0.1	0.0	0.0	66.4	333.0	0.00	26.3	29.3	12.0	2.5009	2.5145	-0.0228	2.4916	0.0000	0.0078
(8)	bottled Mineral water (Font vella)	0.0	29.40	16.2	16.4	5.0	0.1	0.0	0.0	38.5	149.0	0.00	9.7	13.2	0.0	2.5158	2.5273	-0.0193	2.5079	0.0000	0.0078
(9)	bottled Mineral water (Veri)	0.0	17.82	1.1	14.6	5.0	0.1	0.0	0.0	69.0	197.0	0.00	1.5	0.6	0.0	2.5335	2.5267	-0.0011	2.5256	0.0000	0.0078
(10)	bottled Mineral water (Fontecabra)	0.0	22.27	12.3	14.5	5.0	0.1	0.0	0.0	34.0	115.0	0.00	4.0	10.0	0.0	2.5213	2.5299	-0.0165	2.5134	0.0000	0.0078
(11)	tap water	0.0	1009.0	152.5	172.0	13.0	0.0	0.0	0.0	97.8	200.0	0.00	20.8	10.0	5.0	2.4693	2.5085	-0.0593	2.4492	0.0000	0.0196
(12)	reuse water	0.0	10.0	0.4	1.5	7.0	0.1	0.0	0.8	0.7	50.0	0.00	0.2	7.0	0.1	2.5416	2.5359	-0.0068	2.5291	0.0000	0.0125
(13)	desalted water	0.0	29.7	66.5	15.0	5.0	0.05	0.1	0.0	0.001	0.5	0.01	0.01	38.0	0.0	2.4967	2.5304	-0.0432	2.4872	0.0000	0.0095
(14)	desalted water (EXPO Zaragoza 08)	0.0	68.8	154.1	34.8	5.0	0.05	0.0	0.0	0.002	1.2	0.02	0.02	88.1	0.0	2.4429	2.5195	-0.0843	2.4352	0.0000	0.0077

(1) Pure water
(2) Average rainfall composition. Sources: Malecki and Szortakiewicz, 2006 and Daifullah and Ad Shakour, 2003
(3) Average values for the Muga Watershed (Catalonia, Spain). Owned elaboration from data of the Catalan Water Agency (CWA, 2008a)
(4) Catalan Water Agency (data of deep water mass number 32)
(5) Average values for urban waste water (Source: Metcalf and Eddy, 2003 and Hernández, 2001)
(6) RD 1074/2002 and RD 140/2003. They regulate the limit values for potable and mineral bottle water respectively. They both give the same values.
(7) to (10) Real values for bottled mineral waters in Spain. The brand is detailed in brackets.
(11) Real average value for tap water in Zaragoza (Spain). (Source: Ayuntamiento de Zaragoza, 2008)
(12) Real values for reused water in the Comunidad de Regantes de Arrato. Vizcaya (Spain)
(13) Average value for desalted water in the Spanish Mediterranean coast (CWA, 2008a).
(14) Prepared water for public supply, distributed to the public during the Water EXPO 2008 in Zaragoza. 75% of the bottle comes from the desalination plant "San Pedro del Pinatar" (Murcia) and 25% from rivers and springs in the area "Mancomunidad de los Canales de Taibilla". This mixture is drunk by more than 2.3 million people in Alicante and Murcia Provinces.

Table 5.1. Exergy of different types of water.

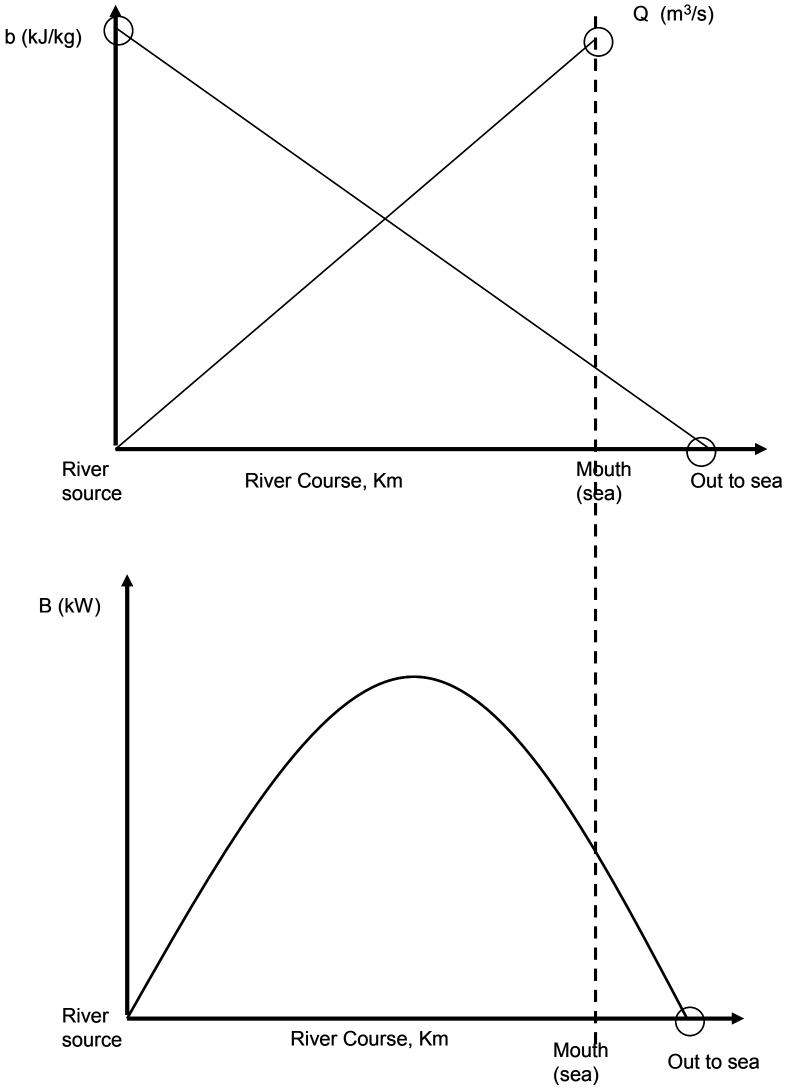


Figure 5.1. Typical specific exergy (b), water flow (Q) and total exergy ($B=b \cdot Q$) profiles of an ideal river. (Source: Valero et al, 2008).

This ideal pattern (for a regular river without special catchment or contributors) is modified in real rivers, since the specific exergy and water flow lines do not follow a perfect straight line. Furthermore, the existence of tributary rivers, filtrations to aquifers, catchments to diverse consumptive uses, solar evaporation, spill outs, etc. create positive or negative deviations in the river flows. The chemical exergy may also increase downstream, because of the addition of spurious chemical substances and organic matter. According to our definition, maximum exergy would correspond to pure, distilled water. However, since organic matter, nitrogen and phosphor add positive exergy, a water sample with a high organic content has also a higher exergy. As it was already explained in Chapter 4, the key point is to analyze the chemical exergy components separately. Additionally, a significant loss of exergy occurs by mixing river and seawaters in the river mouth.

The profile of a river is a function of time because of their torrential nature and seasonal uses. Therefore, in practical terms, the exergy profile of a given river will be better described monthly or even daily, if available data exist.

In other words, it could be said that the exergy in the source and in the mouth of the river is null. However, this statement has to be correctly understood, keeping in mind the importance of the nutrients that the river provides to its mouth area. Such a contribution is fundamental for the maintenance of the biological life in the area. In this sense, the null value of the exergy is reached some kilometres far from the coast, when the equilibrium with the ocean water has been reached. The biological contribution to exergy is analyzed, but not evaluated in this work (see section 4.2.4 in Chapter 4).

5.5. Environmental and Maintenance Flows

From the general idea regarding the theoretical exergy curves, it is needed at this point to start focussing the calculation specific issues. A fundamental part is the flow determination. Real flows are measured in gauging station and the natural flow regime is obtained from mathematical studies. However, the environmental and maintenance flows need to be determine by agreement, after performing the corresponding calculations. This section is devoted to clarify this matter.

Environmental flows are flows that are left in, or released into, a river system with the specific purpose of managing some aspect of its condition (Dyson et al., 2003). Their purpose could be as general as maintenance of a healthy riverine ecosystem, or as specific as enhancing the survival chances of a threatened fish species. They could be targeting the river channel and its surface waters, groundwater, the estuary, linked wetlands or floodplains, the riparian zone, and/or any of the plant and animal species associated with any of these system components.

Strictly speaking, *Maintenance Flows* (MF) are different from *Environmental Flows* (EF). The term EF has other designations or variants like *Environmental Water Requirements* or *Environmental Water Demand.*

However, the EF should not be confused with some similar terminologies like *Instream Flow Requirement* (IFR), mostly focused on flow for fish; *Draught IFR*, which is a reduced flow in dry years to maintain aquatic species without assuring their reproduction, or *Minimum Flow* that merely limits the abstraction of flow in the dry seasons. However, the *Maintenance IFR*, although not synonymous to EF, is similar. It refers to the flow regime required for maintaining all river ecosystem functions. But unlike EF, *Maintenance IFR* does not assure the socio-economic or hydrological benefits. Despite this consideration, the experience looking at the common use of these terms indicates that they are commonly mixed and used as synonyms.

As the condition of river systems deteriorates globally, environmental flows are increasingly appearing on national and international political agendas, and the requirement to use them, in legislation. The science of advising on environmental flows is relatively young (about 50 years), but more than hundred methodologies and methods now exist for such assessments and at least 30 countries are using them routinely in water resource management, with the number growing annually (Tharme and King, 1998).

The first environmental flows assessments (EFA) used mainly single issues and, in consequence, environmental flows were set to maintain the habitat for these species. Methods focused on few species without consideration for the whole ecosystem components may fail to capture system processes and biological community interactions that are essential for creating and sustaining the habitat and well-being of that target species. Then, flow management is best addressed for the entire ecosystem. Recent advances in EFAs reflect this knowledge and they increasingly take a holistic approach (GEFN, 2008).

The environmental flow (EF) is defined as an only value, while the environmental flow regime (EFR) is understood as a set of value giving the river flow at different stages and times.

5.5.1. Environmental flow methodologies

The EFA, which is based on environmental flow methodologies (EFM), can be classified into: hydrological, hydraulic rating, habitat simulation, holistic, or a combination of them (Palau, 2009).

5.5.1.1. Hydrological Methods

Typically simple, these primarily EFMs use hydrological data. They rely primarily on historical flow records - historical monthly or daily flow- , to derive EF recommendations. EF is usually given as a percentage of average annual flow or as a percentile from the flow duration curve, on an annual, seasonal or monthly basis; most methods simply define the minimum flow requirement.

The EFMs may incorporate various hydrological indexes, include catchment variables, or be modified to take account of hydraulic, biological and/or geomorphological criteria. They require only hydrological and some ecological expertise.

Hydrological Index Methods provide a relatively rapid, non-resource intensive, but low resolution estimate of environmental flows. These methods are most appropriate at the planning level of water resources development, or in low controversial situations where they may be used as preliminary estimates.

Recent approaches are more complex and hence, flexible. As a result of their rapid, non resource intensive, but low resolution outputs, and low flexibility, hydrological EFMs are most appropriate at the planning/reconnaissance level of WRDs, or in low controversy situations where the EFR estimates may be used as preliminary flow targets or as block-booked allocations. Hydrological EFMs may be used as tools within habitat simulation, holistic or combination EFMs. They have been applied in developed and developing countries.

5.5.1.2. Hydraulic rating

Hydraulic Rating Methods utilise a quantifiable relationship between the quantity and quality of an instream resource to calculate EFRs. They are based on historical flow records and cross-section data in critically limiting biotopes (e.g. riffles). Hydraulics is modelled as function of flow and the model assumes links between hydraulics (wetted perimeter, depth, velocity) and habitat availability of target biota. That is, hydraulics is used as a surrogate for the biota. Environmental flow is given either as a discharge that represents optimal minimum flow, below which habitat is rapidly lost, or as the flow producing a fixed percentage reduction in habitat availability (GEFN, 2009).

Hydraulic EFMs are combined desktop-field methods requiring limited hydrological, hydraulic modelling and ecological data and expertise. Due to their low-moderate resource intensity and complexity, and low resolution EFR output, they have low flexibility and are the most appropriate for application in WRDs where no limited negotiation of tradeoffs is required, or as a method within a habitat simulation or holistic type EFM. They represent the precursors of more advanced habitat simulation EFMs. They have been applied primarily in developed countries.

In recent years, however, they have been superseded by Habitat Simulation Methodologies or absorbed within Holistic Methodologies.

5.5.1.3. Habitat simulation

Habitat simulation methodologies are based on hydrological, hydraulic and biological response data. Environmental flow is predicted from habitat-discharge curves or habitat time and exceedence series. The EFMs obtained from the habitat simulation model, derive EFRs through analysis of the quantity and suitability of instream physical habitat available to target typically fish or invertebrates under different flow regimes, on the basis of integrated hydrological, hydraulic and biological response data.

Typically, the flow changes in the microhabitat are modelled in several hydraulic programs, using as input data hydraulic variables such as depth, velocity, substratum composition, cover and, more recently, complex hydraulic indices, collected at multiple cross-sections within the river study reach.

The available habitat conditions, simulated using various habitat modelling programs, are linked with information on the range of preferred to unsuitable microhabitat conditions for target species, lifestages, assemblages and/or activities, often depicted using seasonally defined habitat suitability index curves. The resultant outputs, in the form of habitat-Q curves for the biota, or extended as habitat time and exceedence series, are used to predict optimum flows as EFRs (Bejarano, 2009).

Some habitat simulation EFMs consider ecosystem subcomponents in addition to instream biota (e.g. sediment transport, water quality, riparian vegetation, water dependent wildlife). Data requirements are moderate-high, and include historical flow records, hydraulic variables for multiple cross-sections, and habitat availability and suitability data for various biota. A high degree of expertise in advanced, dynamic hydrological and hydraulic habitat modelling, land surveying, and in physical habitat-flow needs of target species.

The EFMs are complex, highly resource-intensive, moderately flexible, and with a moderate to high resolution EFR output. Habitat simulation EFMs are applied in cases of medium/large-scale WRDs involving rivers with economically important fisheries, of high conservation and/or strategic importance, and/or with complex, negotiated tradeoffs among water users. They may comprise tools within holistic type EFMs. They have been applied primarily in developed countries (Smakhtin, 2009).

5.5.1.4. Holistic methods

Holistic methodologies incorporate hydrological, hydraulic and habitat simulation models. These methodologies explicitly adopt a holistic, ecosystem-based approach to environmental flow determinations, what is an exclusive feature of them. Important and critical flow events are identified in terms of select criteria defining flow variability, for major components or attributes of the riverine ecosystem (riparian vegetation, geomorphology, floodplain wetland). This requires considerable multidisciplinary expertise and input.

The basis of most approaches is the systematic construction of a modified flow regime from scratch with an element-by-element basis of, at least, monthly periodicity. Each element in the procedure represents a well defined feature of the flow regime intended to achieve particular ecological, geomorphological, water quality, and in some cases social or other objectives in the modified river.

The resulting EFMs are of moderate-high resource intensity, complexity and output resolution. Holistic EFMs range from moderately to highly data intensive. They require, among other inputs, multiple river stretches, historical flow records, different hydraulic variables across multiple cross-sections, and quantitative biophysical figures of the flow- and habitat-related requirements of the biota and ecosystem components. A commensurately high degree of expertise in advanced hydrological and hydraulic habitat modelling, and in the ecology of the ecosystem components, is required. The most advanced, highly flexible approaches utilise several tools from hydrological, hydraulic rating and habitat simulation EFMs, within a modular framework, for establishing EFRs, and may also incorporate social (flow related ecosystem goods and services for dependent livelihoods) and economic data. The most advanced holistic EFMs are applied in cases of medium/large-scale WRDs involving rivers of high conservation and/or strategic importance, and/or with complex, negotiated water use tradeoffs. Simpler approaches (e.g. expert panel assessments, intermediate determinations) are appropriate for lower profile cases involving limited tradeoffs. Holistic EFMs have been applied in developed and developing countries.

5.5.1.5. Comparison of environmental flow assessment methodologies

Main features of the described methods are summarized in Table 5.2, to facilitate their comparison.

	Duration (months)	**Major advantages**	**Major disadvantages**
Hydrological	0.5	Low cost, rapid to use	Not site-specific, ecological links assumed
Hydraulic	2-4	Low cost, site specific	Ecological links assumed
Habitat	6-18	Ecological links included	Extensive data collection and use of experts, high cost
Holistic	12-36	Covers most aspects	Requires very large scientific expertise, very high cost, not operational

Table 5.2. Main characteristics of the different environmental flow assessment methodologies (Source: GEFN, 2009)

5.6. Reference water bodies

The reference water bodies for each river type must be defined and the reference conditions assigned through the analysis of the biological, morphometric and physico-chemical quality. For this task, stretches of river must be sought out within each river type, which are very well preserved and natural, and almost no alteration by human activity (reference stretches of river), (Munné and Prat, 2000). Through the analysis of the natural conditions of the selected reference stretches, the quality objectives will be set for each river type which, in some cases and for some of the elements analysed, may be the same for two or more types.

The parameters for the establishment of type-specific reference conditions for surface water body types in the WFD is detailed in its Annex II (point 1.3).

5.7. Definition of the statuses of the river according the WFD.

Increasing water scarcity together with decreasing quality is forcing developing countries into remediation options of river water quality. The assessment and evaluation of human impacts on the quality of surface waters have become the main objectives in river basin management (Kannel et al., 2007). The problem of predicting chemical loads in a river system has remained a key issue in the determination of the impact of human activity on aquatic ecosystem environments (Sokolov and Black, 1996).

The contamination generated by human activity due to agricultural, municipal and industrial activities, introduces significant amount of nutrients and organic materials into the rivers and streams. It acccelererates eutrophication process and decreases dissolved oxygen below a threshold value, what apparently happens during low flow periods. The impacts of low dissolved oxygen (DO) concentrations or, at the extreme, anaerobic conditions are an unbalanced ecosystem with fish mortality, odors and aesthetic nuisances (Cox, 2003).

A water quality management policy, in general, should maintain the existing pollutions below certain threshold levels and ensure minimum DO concentrations depending upon aquatic animals, specifically fisheries.

To achieve a stated target of the water quality, the assimilative capacity of the river should remain sufficient all along the river. This goal can be achieved by (Campolo et al., 2002):

- controlling the river flow rates
- controlling the wastewater pollution loads, and
- applying oxygenators

Several objective statuses (OS) for the water bodies are defined in the Article 2 of the WFD. Normative definitions of ecological status classifications are given for three different aspects: biological, hydromorphological and physico-chemical. For each of these categories, three statuses are defined: high status, good status and moderate status. In Annex V, all the normative definitions of ecological status classifications can be found. The objectives are really different depending on the type of water considered: rivers (treated in this work), lakes, transitional waters, coastal waters and heavily modified or artificial water bodies.

An additional important aspect in the WFD is the comparability of monitoring results among the different Member States (*inter-calibration process*). They shall establish monitoring systems for the purpose of estimating the values of the biological quality elements specified for each surface water category or for heavily modified and artificial bodies of surface water. Such systems may utilise particular species or groups of species which are representative of the quality element as a whole. In order to ensure comparability of such monitoring systems, the results of the systems operated by each Member State shall be expressed as ecological quality ratios for the purposes of classification of ecological status. These ratios shall represent the relationship between the values of the biological parameters observed for a given body of surface water and the values for these parameters in the reference conditions applicable to that body (Borja et al., 2006).

In addition to that, the section 1.4.1 v) of the Annex V of the Directive, indicates that, as part of this exercise, the Commission shall facilitate an exchange of information between Members States leading to the identification of a range of sites in each ecoregion in the Community; these sites will form an intercalibration network. The network shall consist of sites selected from a range of surface water body types present within each ecoregion. For each selected surface water body type, the network shall consist of at least two sites corresponding to the boundary between the normative definitions of high and good status, and at least two sites corresponding to the boundary between the normative definitions of good and moderate status. The sites shall be selected by expert judgement based on joint inspections and all other available information.

The area covered by PH is, exclusively, the physico-chemical part of the quality component. Neither biological, nor hydromorpholgical aspects can be analyzed from an exergy perspective with the current development of the methodology.

Experts define the general limit characterization conditions for each area, attending to the guidelines given in the WFD. In the determination of the *ecological state* of a water body, similar steps indicated to the shown in Figure 5.2 are followed.

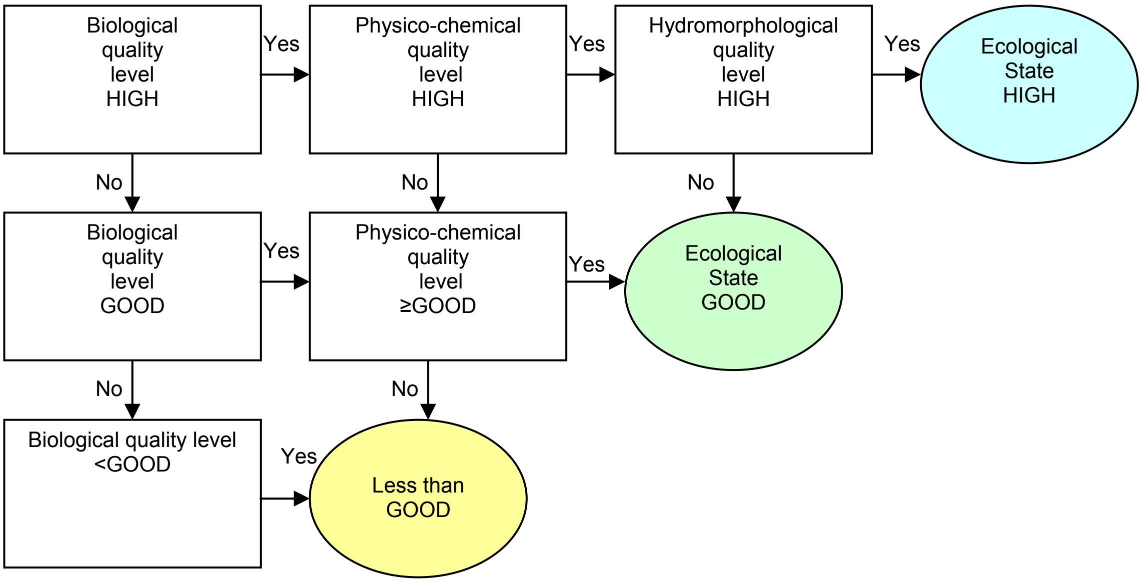


Figure 5.2. Determination of the ecological state of a water body. (Source: CWA, 2008c).

As previously indicated, the main interest of this work is focussed on the physico-chemical aspects defining the ecological state of a river.

The physico-chemical objectives fixed by the WFD are different depending on the water body type. When the water body under study is a reference water body, the pursued objective is *high status*. The same happened if the only pressure on the considered water is a derivation t o a hydroelectricity facility. However, for the rest of water bodies, the searched objective is the *good ecological state*. In many cases, there are no differences in objectives depending on if the water body is modified or not. As an example, Figure 5.3 shows the Catalonian rivers split on good and high (very good) states.

Figure 5.3. General objectives of physico-chemical quality for water in catalonian rivers. . (Source: CWA, 2008c).

The objectives can be lightly modified for some parameters related to salinity, according to the concrete natural conditions in the area .

Biological, hydro-morphological and physico-chemical aspects are treated in the WFD. The more relevant features defining the latter are shown in Table 5.3. Global aspects for the general conditions, specific synthetic pollutants and specific non-synthetic pollutants are given for the high, good and moderate status of the river waters.

Element	High status	Good status	Moderate status
General conditions	The values of the physico-chemical elements correspond totally or nearly totally to undisturbed conditions. Nutrient concentrations remain within the range normally associated with undisturbed conditions. Levels of salinity. pH. oxygen balance. acid neutralising capacity and temperature do not show signs of anthropogenic disturbance and remain within the range normally associated with undisturbed conditions.	Temperature, oxygen balance, pH, acid neutralising capacity and salinity do not reach levels outside the range established so as to ensure the functioning of the type specific ecosystem and the achievement of the values specified above for the biological quality elements. Nutrient concentrations do not exceed the levels established so as to ensure the functioning of the ecosystem and the achievement of the values specified above for the biological quality elements.	Conditions consistent with the achievement of the specified values for the biological quality elements.
Specific synthetic pollutants	Concentrations close to zero and at least below the limits of detection of the most advanced analytical techniques in general use.	Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6 without prejudice to Directive 91/414/EC and Directive 98/8/EC. (<EQS)	Conditions consistent with the achievement of the values specified above for the biological quality elements.
Specific non-synthetic Pollutants	Concentrations remain within the range normally associated with undisturbed conditions (background levels = bgl).	Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6 (2) without prejudice to Directive 91/414/EC and Directive 98/8/EC. (<EQS)	Conditions consistent with the achievement of the values specified above for the biological quality elements.

(1) The following abbreviations are used: bgl = background level. EQS = environmental quality standard.

(2) Application of the standards derived under this protocol shall not require reduction of pollutant concentrations below background levels: (EQS >bgl).

Table 5.3. Description of the physico-chemical quality elements (source: EU-WFD, 2000)

The physico-chemical state of a water body is, in a practical way, determined by following the schema shown in Figure 5.4. It is a though-procedure very similar to the one explained in Figure 5.2, but particularised to the physico-chemical quality parameters.

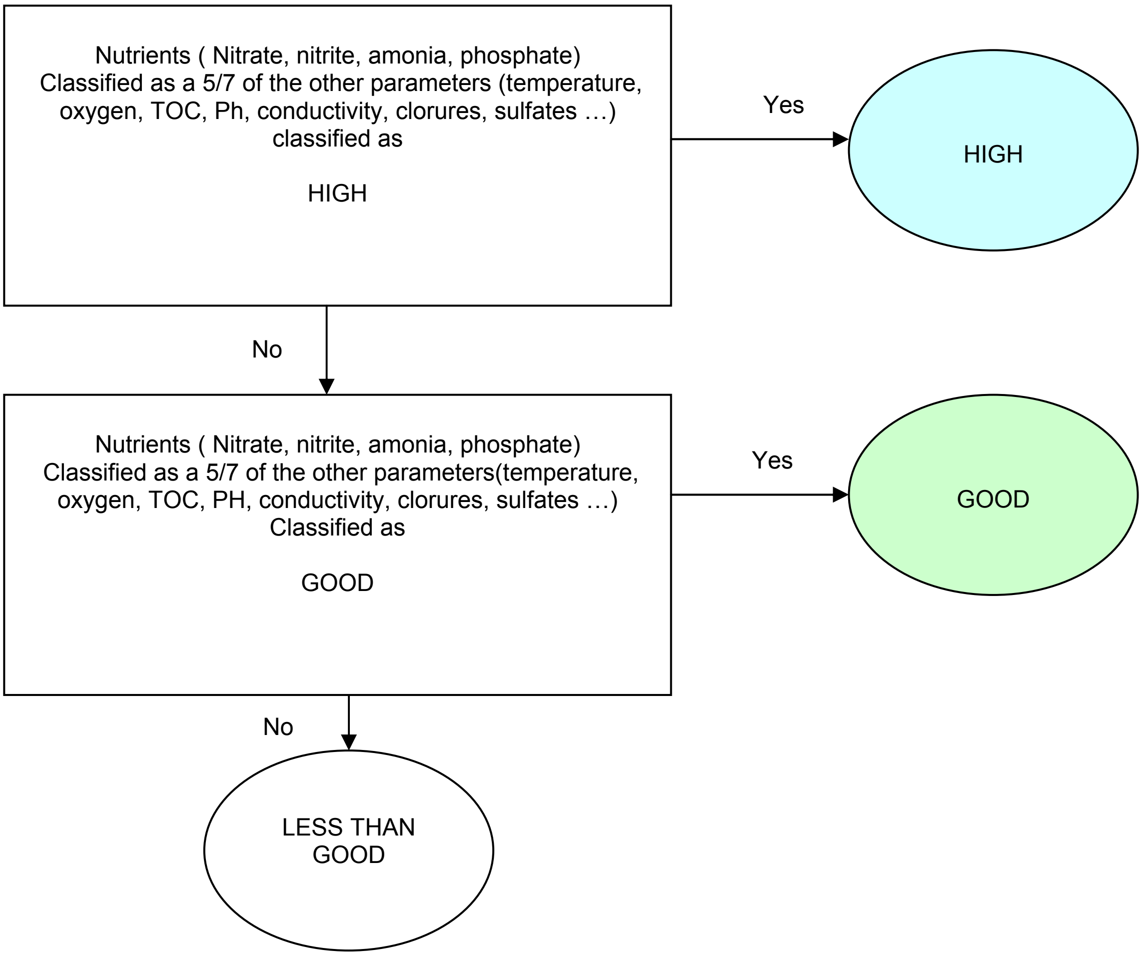


Figure 5.4. Determination of the physico-chemical quality in rivers. (Source: CWA, 2008c).

Following the WFD's guidelines, each watershed government unit is implementing the legislation and preparing its characterization of the different river statuses. As indicated in Chapter 1, several reports of very different scope have been presented after the WFD publication in 2000.

In this work, after carefully reviewing the WFD demands, both in statuses and costs definitions, several objective statuses (OS) for the water bodies have been defined:

Exploitation state (ES). It is a hypothetic state that represents water bodies without the existing sewage plants and, therefore, with higher degradation.

Present state (PS). It is the present state of the water body. The real data are known from sampling stations for specific points along the river. The simulation program gives then the information for each reach.

Natural state (NS). There is a natural status for each water body, characterized as if it were unaffected by human economic activities.

Future state (FS). It is understood as the future status of water bodies in 2015 by considering the increase of water consumption by diverse uses, according to the increase of pressures in the river basin. In the case of Catalonia, those future pressures are described in the IMPRESS document.

Objective state (OS). WFD establishes several objective statuses for the water bodies by 2015 (in flow and quality) according to the type of river or water mass that is being considered. In concrete, the good ecological status (GES) and the very good ecological status, designed as high status in the legislation (HS) are determined.

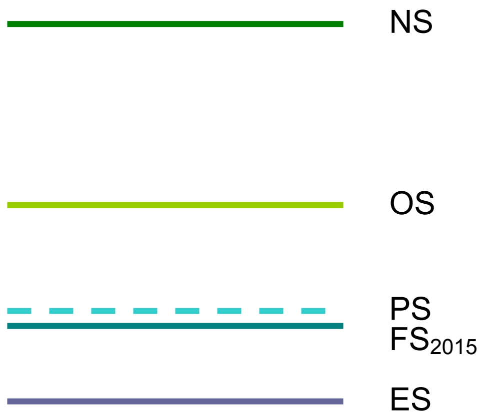


Figure 5.5. River states

5.7.1. States characterization:

Each river state has to be defined by means of its flow (m^3/s) and its quality (temperature, altitude, speed and chemical composition). WFD provides only general guidelines and every watershed management unit must properly define the water quantity and quality for each of the defined river statuses. In consequence, specific legal texts have to be consulted to define the exergy profile of each river, depending on its location and, therefore, on its district management.

The flows definition is an especially conflictive issue, since none reference appear in the WFD text regarding this issue. All its recommendations affect the quality parameters. However, it is clear that in order to reach the quality objectives, the existing flows have to be high enough. Then, the flow for each river state needed to be defined.

From Physical Hydronomics, once that information has been collected, the different statuses of a given river can be obtained. Table 5.4 summarizes the flow and quality designed for each conventioned state.

Present state is obtained from direct measurement in existing sampling and control stations. With more or less accuracy, they are present in every watershed, although usually. only a few real data are available along the river. They are not enough to build a river profile and flow simulation software is needed to implement the characterization of the water stream. This issue will be further developed in section 5.10 and in Annex E.

	ES	**FS$_{2015}$**	**PS**	**OS=GES**	**OS=HS**	**NS**
Flow	Q_{exp}	Q_{2015}	Q_{real}	$\max(Q_{MF}.\ Q_{2015})$	$\max(Q_{NF}.\ Q_{2015})$	Q_{NF}
Quality	b_{exp}	b_{2015}	b_{real}	b_{GES}	b_{HS}	b_{HW}

Table 5.4. Definition of flow and quality for each of the studied river statuses.

Exploitation state is obtained from the present status data, by simulating the same state but without any waste water treatment plant. Initially, the real state is calibrated and run; then, the WTP are deleted from the simulation.

Future state (2015) is simulated starting from the current situation and adding all the future pressures and their corresponding impacts. Those pressures are usually provided by competent official organisms, where studies are performed for those forecast future statuses.

Natural state is determined, in quantity, by means of flow restoration models to natural regime (from rainfall, ETP and consumption data). These kinds of studies are usually available for each watershed and provide natural flow values for several areas of the river within its basin. The quality for this natural state is taken as the quality of the existing reference sampling stations and from the reference quality values of the water bodies. Those reference points are usually headwaters without anthropic influence.

The two states to which special attention is devoted are the *good ecological* and the *high status* because their flows are not immediately defined. They have to be obtained as the maximum among the two indicated in Table 5.4. The flow in the GES is the maximum between the maintenance flow of the river and the flow existing in the analyzed moment –year 2015 in this case-. The reason is that if $Q_{2015}>Q_M$, there is no reason to say that the extra water has to disappear. Same reasoning is follow for the flow in the HS, comparing the natural flow of the river and the flow by 2015.

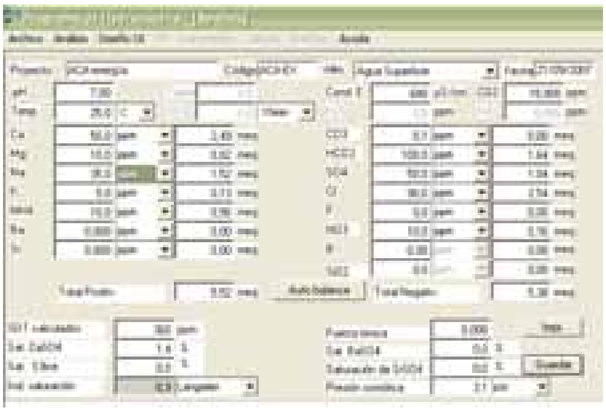


Figure 5.6. Main screen of the "Hydranautics" software to assure electrolytes equilibrium.

Some official data sources only provide partial information about the electrolytes generally present in water. In that case, the rest of ions and cations to reach the chemical equilibrium in the solution have to be estimated. Figure 5.6 shows the main screen of the software used in this work to define the missed concentrations. It is a software for the design of reverse osmosis desalination plants whose performance depends on the raw water quality. The program permits a maximum electrical disequilibrium of 10% for the positive and negative ions balance.

5.8. Costs definition

The cost concept first was mentioned in the third chapter, although its exergy definition was later given in Chapter 4. PH is aimed to use those calculated physical costs as a guide to allocate the environmental costs proposed by the WFD. Here, the cost definitions used in the PH methodology are defined.

As summary of the previous concepsts, there exist three basic conceptions about the cost:

- The minimum cost can be understood as the exergy gap among to given states of the river. In this context, they are noted with uppercase letters, X.
- The exergy cost is understood as the real cost needed to restore the degraded water. It is obtained after multiplying the exergy difference between the two states and the unit exergy cost. The notation is X^*.
- The economic cost derived from the exergy cost, obtained after multiplying the exergy cost times the energy price. It is designed as $ec\,X$.

5.8.1. Definition of WFD's costs in exergy terms.

Following the WFD and the WATECO group guidelines, together with our thermodynamic understanding, different costs are defined within Physical Hydronomics methodology, trying to meet the European demands.

Services Cost (SC) or Financial Cost (FC) is the costs associated to the already present measures that allow water bodies to be in the PS instead of being in the ES.

Environmental Cost (EC) ranges the gap between FS and OS.

Resource Cost (RRC) is the remaining cost, which assess the measures required to reach the NS starting from OS.

Finally, the *Integral Replacement Cost (IRC)* is the addition of the three referred costs. and it is associated to the measures needed to reach the NS, starting from the ES. Figure 5.7 shows these definitions.

The IRC defined in this way goes, in fact, further than the Principle of Full Cost Recovery marked by the WFD: the Directive marks the OS as final state. However, when the RRC is included, with the NS as final objective the project is more ambitious and the integral water cycle can be considered as covered. RRC accounts for the water consumption and the water degradation from its natural state. Then, all the required aspects (services, environment and resource) for PH are included in the proposed cost calculation.

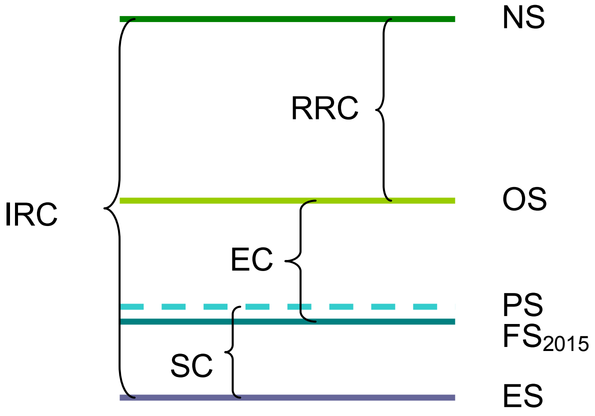


Figure 5.7. River states and cost required by the WFD to assess environmental costs.

From the analysis of the different states of the water bodies, it can be directly concluded that some of the costs can be understood as fixed because the are defined by fixed states. For example, the current state and the states of the river without WWTPs (ES) determine the SC and those river profiles determining this cost will be different depending on the features of the chosen study year. However, the RRC is defined by the OS (which is legally defined) and the NS (which is obtained from historical data series and considered as constant for each month). Then, the RRC comes from two constant exergy profiles and can be considered as fixed. In the EC a variable (FS) and a defined state (OS) intervene. In spite of this, it can be easily understood that an eventual change in some of the stated objectives would lead to a change in the corresponding cost.

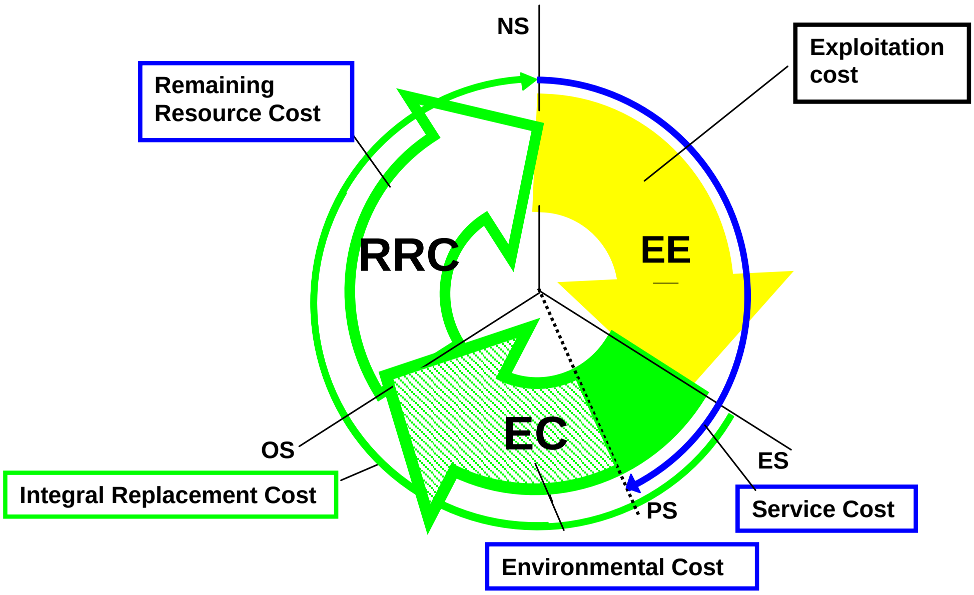


Figure 5.8. Representation of the costs of water (Source: Escriu. 2007).

Escriu (2007) proposed an alternative closed loop representation of the water costs define by the WFD. As it can be seen in Figure 5.8, the defined states for water bodies are identical to the ones considered by us, as well as the defined associated cost. The main difference is the inclusion of the exploitation cost as the difference between the natural and the exploitation state that is understood as the obtaining, distribution and return costs. i.e. and extended service costs concept (including hydrological cycle as well).

Once the states are established, the exergy gap can be calculated as the difference between two river profiles and this ΔB is understood, in a general sense, as the exergy cost (in energy units) provoked by human activities.

Eq. 5.1 and Eq. 5.2 synthesize the previous definitions:

Eq. 5.1.

$$\begin{aligned} RRC &= \Delta B_{NS-OS} = B_{NS} - B_{OS} \\ EC &= \Delta B_{OS-FS} = B_{OS} - B_{FS} \\ SC &= \Delta B_{FS-ES} = B_{FS} - B_{ES} \end{aligned}$$

Eq. 5.2.

$$IRC = SC + EC + RRC = \Delta B_{NS-ES} = B_{NS} - B_{ES}$$

Present and future states of the river by 2015 are two similar states, but they defined separately to fulfil the WFD requirements. When calculations are carried out, it can be observed that their difference is minimum and the overlap is negligible in terms of exergy cost.

Before going further, it is worth remembering the notation (Table 5.5):

	Minimum exergy cost	**Exergy cost**	**Economic cost**
Obtained as	*ΔB*	*k·ΔB*	*Energy price· exergy cost*
Noted as	*SC, EC, RRC and IRC*	*SC^*, EC^*, RRC^* and IRC^**	*ecSC, ecEC, ecRRC and ecIRC*

Table 5.5. Notation for the water costs

5.8.2. Quantity and Quality components of the exergy gap

In addition to the previous consideration, it is important to highlight that any exergy difference between to river states can be divided into its quantitative *(t)* and qualitative *(l)* terms, as shown in Eq. 5.3:

Eq. 5.3.

$$\begin{aligned} \Delta B &= \dot{m}_o \cdot b_o - \dot{m}_r \cdot b_r = (\dot{m}_r + \Delta \dot{m}) \cdot (b_r + \Delta b) - \dot{m}_r \cdot b_r = \\ &\approx \dot{m}_r \cdot \Delta b + \Delta \dot{m} \cdot b_r = \Delta B_l + \Delta B_t \end{aligned}$$

Where m is the flow and b is the specific exergy. Index *o* stands for the objective and *r* for the real state. The term *Δṁ·Δb* is negligible and therefore not included. They can also be considered as the initial and final state, since this reasoning is going to be repeatedly applied and initial and final state are going to change.

The change into a water body is due to the mass consumption, but also to the deterioration in its quality. Both contributions need to be present to describe accurately the water degradation.

A significant reason for separating ΔB in two parts is the difference nature of each of them. In a further step, this exergy gap has to be restored by means of the best available technology. The quantity and quality restoration procedures are different and, of course, they will have different cost.

The presented methodological development meets the WFD's spirit. The 34th point of its preamble establishes that *for the purposes of environmental protection there is a need for a greater integration of qualitative and quantitative aspects* of both surface waters and ground waters, taking into account the natural flow conditions of water within the hydrological cycle. As Eq. 5.3 indicates, quantity and quality components can be split if needed.

5.9. Calculation procedure.

Once the statuses of the river have been defined, the discrete exergy profile of the river for each of them can be obtained. Since there are several significant exergy components (b_{IM}.b_{OM}. b_p. b_t …), the corresponding exergy profiles can be presented for each state. Detail in the available information will be translated into detail in the exergy profile: the more available information, the more accuracy in the river exergy profile representation.

The ideal set of parameters to complete the exergy profile would be a continuous, but it is not feasible. The real sampling data, when exist, provide a discrete data base which lead to a discrete river profile defined by a given number of real data (Figure 5.9). Since real measurements are scarce, the already mentioned simulation software is used and the discrete profile is extended until the desired number of river reaches for the study.

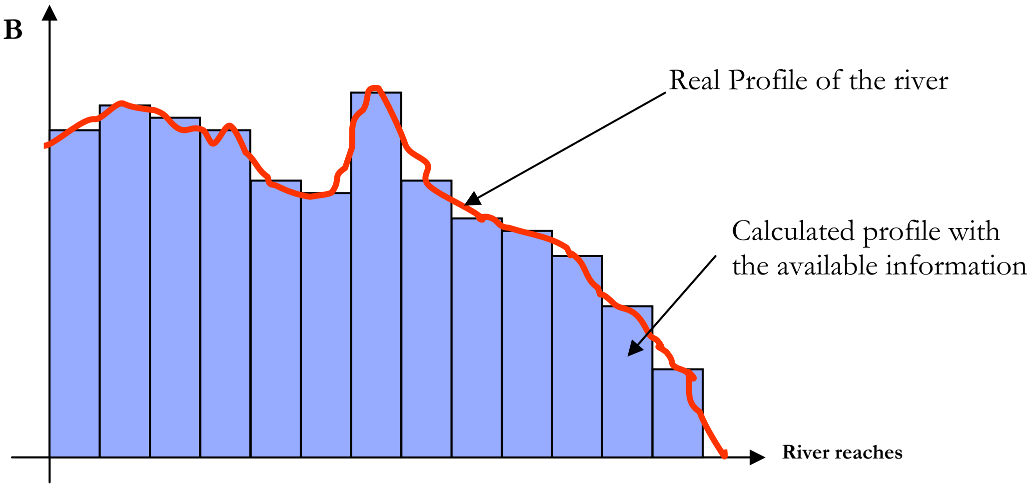


Figure 5.9. Theoretical real profile of the river and the calculated discrete profile

The conversion of the theoretically continuous river profile into a discrete profile is shown in the following equations, for the potential as well as the chemical component, as examples.

Potential component:

Eq. 5.4. $$B_p = \int gQ(h)dh \approx g\sum_i \left(Q(h)\cdot \Delta h\right)_i$$

Where g is the gravity constant, Q the river flow and h the altitude. The river flow changes with the altitude, that is, as long as the river is flowing from its source to its mouth.

Once the different profiles are obtained for the different river states, the exergy gap between two given states (denoted in general as objective, o, and real state, r), can be defined as indicated in Eq. 5.5.

Eq. 5.5. $$\begin{aligned} EC_{pot} &= \Delta B_p = g\left[\int Q_0(h)d(h) - \int Q_r(h)d(h)\right] = \\ & g\int \left[Q_0(h) - Q_r(h)\right]dh \cong g\sum_i \left(\Delta Q(h)\cdot \Delta h\right)_i \end{aligned}$$

Eq. 5.6. where $\Delta Q = Q_0 - Q_r$ and i =number of reaches in the river.

Since the topographical profile of the river is the same for all different statuses, ΔB is only a function of the flow fluctuations: $ExC_{pot} = \Delta B_p = f(\Delta Q)$.

The objective and real states are different depending on the costs to calculate (see Eq. 5.1). ΔB_{pot} will be identified with the corresponding (EC, SC or RRC) potential exergy cost, depending on the considered initial and final river states. In Eq. 5.5, it has been denoted as ExC_{pot}.

Chemical component:

Eq. 5.7. $$B_{ch} = \int Q(b)db \approx \sum_i \left(Q(b)\cdot \Delta b\right)$$

Where Q is the river flow and b stands for the chemical exergy component, which could be the chemical exergy of the inorganic matter, b_{IM}, or the chemical exergy of the organic matter, b_{OM}

As indicated in the potential component, the subtraction of two river profiles (Eq. 5.8) will lead to the exergy gap between them (Eq. 5.8).

Eq. 5.8. $$EC_{ch} = \Delta B_{ch} = \sum_i \left(Q_0(b)\Delta b_0 - Q_r(b)\Delta b_r\right)_i = \sum_i \left[\Delta Q\Delta b_0 + Q_r\left(\Delta b_0 - \Delta b_r\right)\right]_i$$

where $\Delta Q = Q_0 - Q_r$ and i =number of reaches in the river.

ΔB_{ch} will be identified with the corresponding (EC, SC or RRC) chemical exergy cost, depending on the considered initial and final river states. In Eq. 5.8, it has been denoted as ExC_{ch}. Correspondingly, it will be used for any of the chemical exergy components: IM, OM or NP.

5.9.1. Calculation example

A simple example is developed here to illustrate the calculation procedure to obtain the discrete exergy profile of a river and, afterwards, the three different exergy costs for the analyzed river.

Let's assume a seven-stretch river. The reaches labelled with *n'* are tributaries flowing into the *n* reach (Figure 5.10).

Figure 5.10. Schema of the theoretical river considered as example (reach 1 dies in the sea).

In this example, attention is focused on the potential and chemical exergy components, since they represent the higher exergy gaps among the river states. Therefore, the built exergy profiles are aimed to calculate EC, SC and RRC attending to those components.

It is important to bring at this point the already done reflexions about the convenience of adding all the chemical components. For the sake of clarity, the chemical exergy components are usually disaggregated in the following components:

- Inorganic matter, $b_{IM}=b_{salts}+b_{H2O}$
- Organic matter, b_{OM}
- Nitrogen and phosphor, b_{NP}

In this example, only the salts content (IM), and OM have been considered. In the real cases, nitrogen and phosphor are also analyzed, but they are usually omitted because the OM component follows similar pattern to the NP one.

In the following sections, the presentation of results will follow the same sequence: EC, SC and RRC. The calculation procedure is essentially the same, but the results will be quite different because of the intrinsic exergy distance of the river states coming into play.

5.9.1.1. Potential and inorganic matter components

Trying to summarize as much as possible the developed tables, the potential and inorganic components are presented together, where possible. Tables show, alternatively, the real data taken of the different river reaches and the exergy values obtained after calculations.

a. Environmental Cost calculation (from FS to OS)

The environmental cost due to the potential (altitude) component, EC_{pot}, and due to the IM (salinity) component, EC_{IM}, are calculated in this part of the example.

Table 5.6 presents the basic data needed for the profile construction, which represent the first and fundamental step in the cost calculation. Starting from left to right, it shows the number of the reach in the river, the objective and the real flows and their altitude and length. Then, the specific exergy value in both the objective and the real state are given, as well as the difference between two consecutive reaches, since these values are needed for the calculation.

No	Q_{OS}	Q_{FS}	h	L	b_{OS}	b_{FS}	dh	db_{OS}	db_{FS}
1	4	4	20	50	2.52	2.48	20	2.52	2.48
2	2.7	2.5	50	40	2.52	2.50	30	0.00	0.02
2'	0.8	0.8	60	10	2.52	2.40	10	0.00	-0.10
3	2.3	2	75	30	2.56	2.52	25	0.04	0.02
4	1	1	120	45	2.56	2.53	45	0.00	0.01
4'	0.3	0.3	130	15	2.56	2.55	10	0.00	0.02
5	0.6	0.6	150	20	2.56	2.54	30	0.00	0.01

Table 5.6. Basic data of the OS and the FS, needed for the EC_{IM} and EC_{pot} calculation.

In detail:

- dh: altitude difference between to consecutive river
- db_{OS}: exergy (salts, IM) difference between to consecutive river reaches in the objective state.
- db_{FS}: exergy (salts, IM) difference between to consecutive river reaches in the future state.

Following the Environmental Cost (EC) definition given in Eq. 5.5 and Eq. 5.8, the EC can be expressed as Eq. 5.9 and Eq. 5.10 indicate, for the potential and the salinity components respectively.

Eq. 5.9.
$$EC_{pot} = \sum_i \rho \cdot g \cdot (Q_{OS}(h) - Q_{FS}(h))_i \cdot \Delta h$$

Eq. 5.10.
$$EC_{IM} = \sum_i (Q_{OS}(h) \cdot \Delta b_{OS} - Q_{FS}(h) \cdot \Delta b_{FS})_i$$

Attending to the different nature of the exergy degradation (quantity and quality), Eq. 5.9 and Eq. 5.10 can be expressed in these two different components as:

Eq. 5.11.
$$EC_{pot} = \sum_i \rho \cdot (\Delta Q \cdot \Delta h)_i$$

Eq. 5.12.
$$EC_{IM} = \sum_i \left(Q_{OS}(h)\Delta b_{OS} - Q_{FS}(h)\Delta b_{FS}\right)_i = \sum_i \left[\Delta Q \Delta b_{OS} + Q_{FS}\left(\Delta b_{OS} - \Delta b_{FS}\right)\right]_i$$

These equations will be used next.

i) Potential exergy calculation

The potential exergy profile of the river is shown in Figure 5.11. The term h remains constant independently of the considered state of the river (ES, PS, OS, NS), and they will differ because of their flow (Q). Then, the variation of the specific potential exergy within a river reach will be always zero and the differences will be due to the quantity component. That is (Eq. 5.13):

Eq. 5.13. $$\Delta b_{EC,pot} = b_{OS,pot} - b_{FS,pot} = g \cdot (h_{OS} - h_{FS}) = 0$$

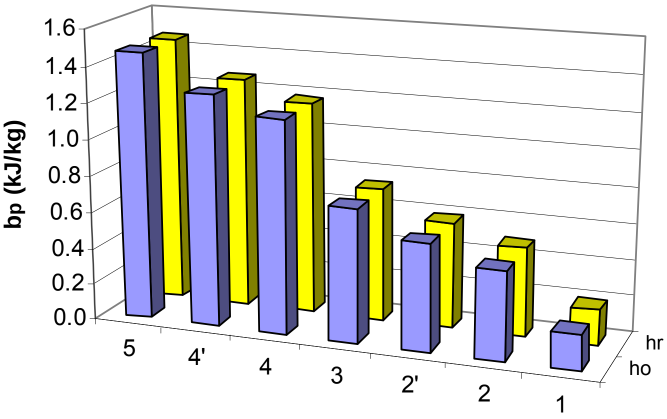


Figure 5.11. Potential exergy values for each river reach. This magnitude remains constant in both real r and objective o states.

The difference between the river profiles is obtained by applying Eq. 5.11 and has been graphically presented in Figure 5.12. The shady area corresponds to the different components (by reaches) of the EC_{pot}.

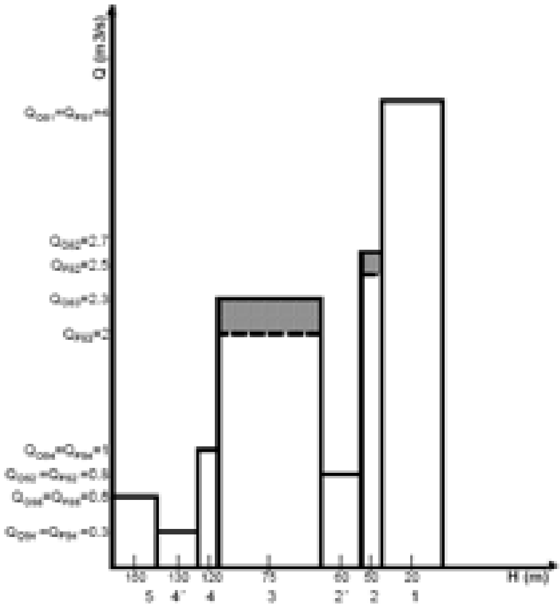


Figure 5.12. Flow vs. altitude for the real and objective states, for the sever reaches in the river.

Detailed calculations reach by reach are presented in Table 5.7:

No	$\Delta Bp_{,OS}$	$\Delta Bp_{,FS}$	dQ·dh
1	784.80	784.80	0
2	794.61	735.75	58.86
2'	78.48	78.48	0
3	564.08	490.50	73.58
4	441.45	441.45	0
4'	29.43	29.43	0
5	176.58	176.58	0
Sum	2869.43	2736.99	132.4
$EC_p=\Delta B_p$	132.4		132.4

Table 5.7. Potential exergy differences and EC_p.

Final results for ΔB_p can be obtained by two different ways:

a. Calculation procedure a (real and objective river profiles are independently calculated and then finally subtracted). Here, Eq. 5.9 has been applied (second and third columns)

b. Calculation procedure b (the gap of the diverse river profiles is added by reach). This time, Eq. 5.11 has been used (fourth column).

In the case of ΔB_p, there is no difference between proceeding as Eq. 5.9 indicates, or calculate the EC as the product *dQ·dh* (Eq. 5.11). The reason is that the magnitude h remains constant for each reach in the different river statuses, since it is a geographic feature, as indicated in Eq. 5.13.

However, it is not the case for the rest of exergy components, since both parameters, quantity and quality, vary from the real to the objective states.

ii) Chemical (IM) exergy calculation

The evolution of the chemical exergy component for the real and the objective states are shown in Figure 5.13. It can be observed that, in this example, the real quality of the river is lower than the desired quality in the objective in each river stretch state, because the exergy values are lower. This is a common situation in river basins, when salinity increases as the river flows down. In addition to that, the tendency follows the expected behaviour: higher specific exergy in the river headings and a decrease along the river due to the natural effects and to the human's water uses. A significant gap is observed in reach number 2'. It could mean that an important spill out is taking place in that area.

Detailed calculations for the chemical component, reach by reach, are presented in Table 5.8. On the left side, the calculation has been done according to Eq. 5.10, as difference of the two exergy profiles of the river. In the right side of the table, it can be seen that the final result is the same, although the integration has been done separating the quantity and the quality components.

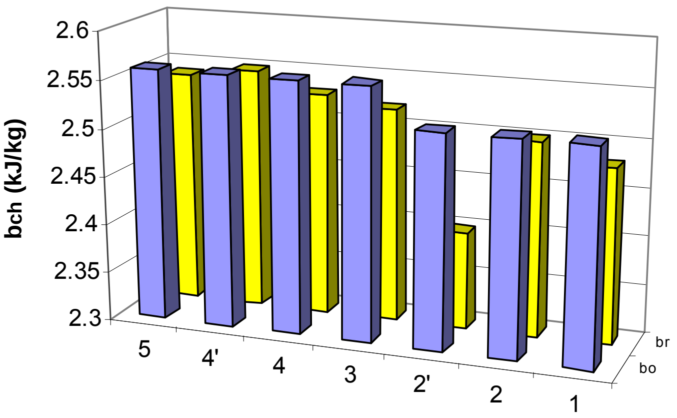


Figure 5.13. Chemical exergy values for each river reach. in the real r and the objective o states.

(a)

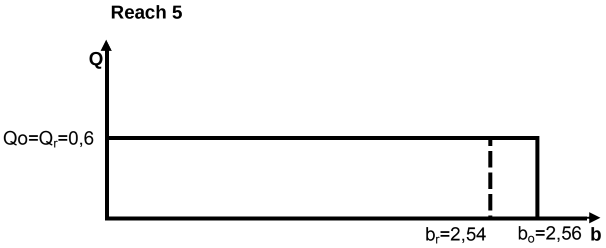
No	**$Q_{OS}\cdot\Delta b_{OS}$**	**$Q_{FS}\cdot\Delta b_{FS}$**	**ΔB_{IM}**
1	10.08	9.92	0.16
2	0	0.05	-0.05
2'	0	-0.08	0.08
3	0.092	0.04	0.052
4	0	0.01	-0.01
4'	0	0.006	-0.006
5	0	0.006	-0.006
Sum	10.172	9.952	0.22
$EC_{IM}=\Delta B_{ch,IM}$	**0.22**		**0.22**

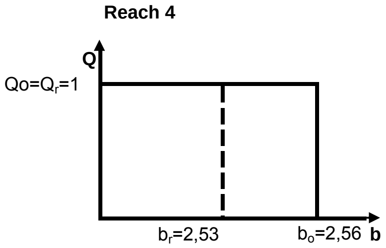
(b)

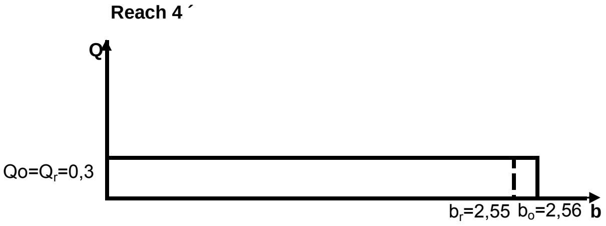
No	**$\Delta Q\cdot\Delta b_{OS}$**	**$Q_{FS}\cdot(\Delta b_{OS}-\Delta b_{FS})$**
1	0	0.16
2	0	-0.05
2'	0	0.08
3	0.012	0.04
4	0	-0.01
4'	0	-0.006
5	0	-0.006
Sum	0.012	0.21
$EC_{IM}=\Delta B_{ch,IM}$		**0.22**

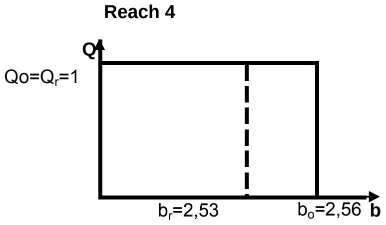
Table 5.8. Chemical exergy differences calculated as profiles differences (a), and as addition of the quantity and quality components (b).

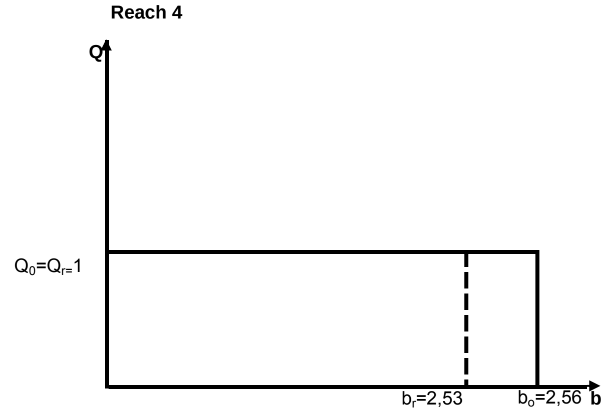
The nature of the b_{ch} component (values comprised in a very narrow stripe and repeated values along the river) makes it difficult to represent the change in an only graph. Therefore, the consecutive river reaches are presented in Figure 5.14. The flow change can be observed in the ordinal axis, while the quality for the real and objective states are showed in the cardinal axis.

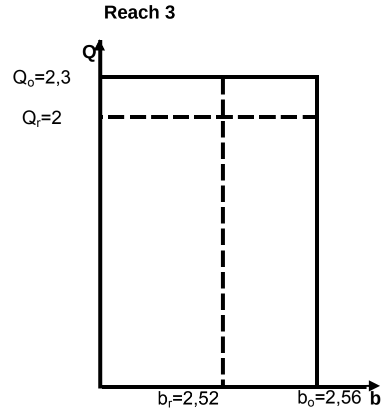

Reach 5


Reach 4


Reach 4´


Reach 4


Reach 4


Reach 3

For the step between the reaches 5 and 4, it can be directly seen that:

Eq. 5.14. $$Q_{os}\cdot db_{os} = 0.6\cdot(2.56-2.56) = 0$$

Eq. 5.15. $$Q_{FS}\cdot db_{FS} = 0.6\cdot(2.54-2.53) = 0.006$$

Eq. 5.16. $$dQ\cdot db_{os} = 0.4\cdot(2.56-2.56) = 0$$

Eq. 5.17. $$Q_{FS}(db_{OS} - db_{FS}) = 0.6[(2.56-2.56)-(2.54-2.53)] = 0.006$$

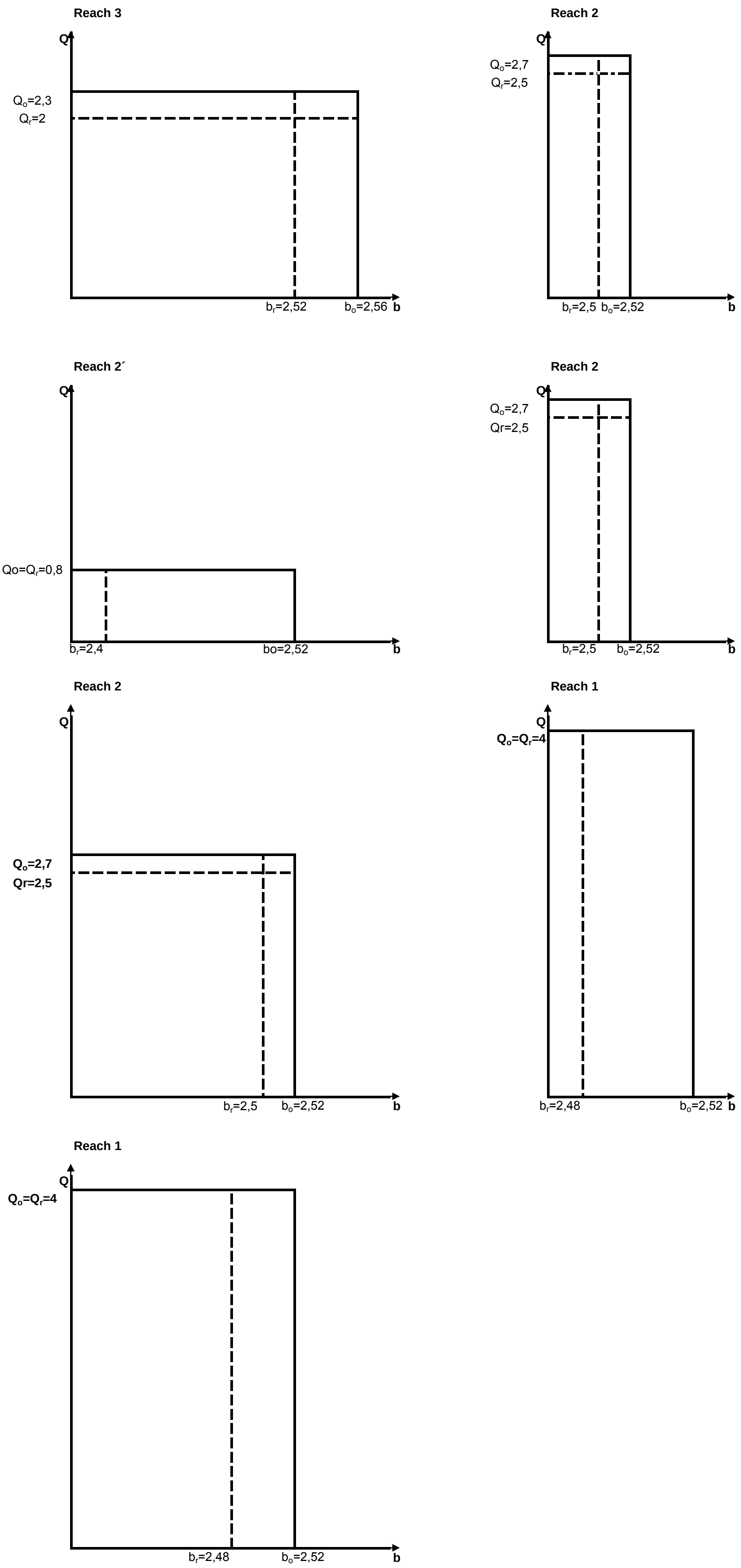


Figure 5.14. Flow vs. chemical exergies for the different river reaches.

b. Service Cost calculation (from ES to PS)

The service cost due to the potential (altitude) component, SC_{pot}, and the IM (salinity) component, EC_{IM}, were calculated in this section.

The procedure is the same as in the EC calculation, but the exergy values are different. Table 5.9 presents the basic data needed for the profile construction. Its structure is similar to the Table 5.6 one, but the values are quite different because the considered states are different: the present state of the river (PS) and the hypothetical state without WWTPs (ES). The column with the altitude values has been eliminated because it is the same as in Table 5.6, but the *dh* column is maintained by the sake of clarity.

No	Q_{PS}	Q_{ES}	b_{PS}	b_{ES}	Δh	Δb_{PS}	Δb_{ES}
1	4	4	2.5	2.5	20	2.5	2.5
2	2.5	2.5	2.5	2.5	30	0	0
2'	0.8	0.8	2.4	2.3	10	-0.1	-0.2
3	2	2	2.5	2.5	25	0	0
4	1	1	2.5	2.5	45	0	0
4'	0.3	0.3	2.6	2.5	10	0	0
5	0.6	0.6	2.5	2.5	30	0	0

Table 5.9. Basic data of the FS and the ES, needed for the SC_{IM} and the SC_p calculation.

i) Potential exergy calculation

As it was already explained, there is no difference between the qualities attending to the altitude, so the quality exergy component is zero. In addition to that, in the case of the SC,. the quantity component is also zero because it is assumed that in the WWTPs there is not water consumption, and therefore Q_{PS} and Q_{ES} coincides. Table 5.10 shows the obtained figures for the example.

No	$\Delta B_{p,PS}$	$\Delta B_{p,ES}$	$dQ \cdot dh$
1	784.8	784.8	0
2	735.8	735.75	0
2'	78.48	78.48	0
3	490.5	490.5	0
4	441.5	441.45	0
4'	29.43	29.43	0
5	176.6	176.58	0
Sum	2737	2737	**0**
$SC_p=\Delta Bp$	**0**		**0**

Table 5.10. Potential exergy differences for the SC_p calculation

Columns $\Delta B_{p.FS}$ and $\Delta B_{p.ES}$ account for the potential exergy profiles of the present and the exploitation states respectively and, at the bottom, they are subtracted as a whole (SC_{pot}=0). On the other hand, the last column shows the same calculation, but it has been made reach to reach; in consequence, since values of the present and exploitation states coincide for each reach, result is constantly zero and $SC_p=0$.

ii) Chemical (IM) exergy calculation

Following identical reasoning as in the EC determination, results for the inorganic matter component of the service cost SC_{IM} are presented in Table 5.11.

(a)

No	$Q_{PS}\cdot\Delta b_{PS}$	$Q_{ES}\cdot\Delta b_{ES}$	ΔB_{ch}
1	9.92	9.8	0.12
2	0.05	0.075	-0.025
2'	-0.08	-0.144	0.064
3	0.04	0.04	0
4	0.01	0.02	-0.01
4'	0.006	0.003	0.003
5	0.006	0.006	3E-16
Sum	9.952	9.8	0.152
$SC_{IM}=\Delta Bp$	**0.152**		**0.152**

(b)

No	$\Delta Q\cdot\Delta b_{PS}$	$Q_{ES}\cdot(\Delta b_{PS}-\Delta b_{ES})$
1	0	0.12
2	0	-0.025
2'	0	0.064
3	0	0
4	0	-0.01
4'	0	0.003
5	0	2E-16
Sum	0	0.152
$SC_{RO}=\Delta Bp$		**0.152**

Table 5.11. Chemical exergy differences calculated as profiles differences (a), and as addition of the quantity and quality components (b), obtained value for SC_{IM}.

c. Remaining Resource Cost calculation (from OS to NS)

For the RRC calculation, the procedure is the same as in EC and SC. The initial and final river states are the objective and the natural state respectively. In this case, significant differences can appear between the water flows at some reaches. Table 5.12 shows the initial data required for the calculation.

No	Q_{NS}	Q_{OS}	b_{NS}	b_{OS}	dh	db_{NS}	db_{OS}
1	4.5	4	2.58	2.52	20	2.58	2.52
2	3	2.7	2.58	2.52	30	0	0
2'	1	0.8	2.58	2.52	10	0	0
3	2.5	2.3	2.6	2.56	25	0.02	0.04
4	1.1	1	2.6	2.56	45	0	0
4'	0.5	0.3	2.6	2.56	10	0	0
5	0.6	0.6	2.6	2.56	30	0	0

Table 5.12. Basic data of the OS and the NS, needed for the RRC_{RO} and the RRC_p calculation.

i) Potential exergy calculation

Table 5.13 summarizes the results obtained for the RRC associated to the potential component. As in the previous calculations, it has been calculated in two different ways. They are both shown, just to check their equivalence.

No	**$\Delta B_{p.NS}$**	**$\Delta B_{p.OS}$**	**$dQ \cdot dH$**
1	882.9	784.8	98.1
2	882.9	794.61	88.29
2'	98.1	78.48	19.62
3	613.1	564.075	49.05
4	485.5	441.45	44.145
4'	49.05	29.43	19.62
5	176.58	176.58	0
Sum	3188.25	2869.425	**318.83**
$RRC_p=\Delta B_p$	**318.83**		**318.83**

Table 5.13. Potential exergy differences and RRC_p.

ii) Chemical (IM) exergy calculation

(a)

No	**$Q_{NS} \cdot db_{NS}$**	**$Q_{OS} \cdot db_{OS}$**	**$\Delta B_{ch.IM}$**
1	11.61	10.08	1.53
2	0	0	0
2'	0	0	0
3	0.05	0.092	-0.042
4	0	0	0
4'	0	0	0
5	0	0	0
Sum	11.66	10.172	**1.49**
$RRC_{IM}=\Delta B_{IM}$	**1.49**		**1.49**

(b)

No	**$dQ \cdot db_{NS}$**	**$Q_{OS} \cdot (db_{NS}-db_{OS})$**
1	1.29	0.24
2	0	0
2'	0	0
3	0.004	-0.046
4	0	0
4'	0	0
5	0	0
Sum	1.294	0.194
$RRC_{IM}=\Delta B_{IM}$		**1.49**

Table 5.14. Chemical exergy differences calculated as profiles differences (a), and as addition of the quantity and quality components (b), obtained value for RRC_{RO}.

Again, both procedures give identical results for the RRC_{IM} component.

5.9.1.2. Organic Matter component

A part of the chemical exergy has been analyzed in this example, through the salts (IM) component: In addition to that, the organic matter component (OM) and the nitrogen and phosphor component (NP) are also important contributions to the chemical exergy of a river. In this section, the exergy costs associated to OM are calculated: $EC_{OM.}$ SC_{OM} and RRC_{OM} are sequentially obtained.

a. Environmental Cost calculation (from FS to OS)

Main characteristics of the river reaches are shown in Table 5.15. The parameters b_{OS} and b_{FS} indicate the chemical exergy due to the organic matter contents in those postulated states of future and objective.

No	Q_{OS}	Q_{FS}	b_{OS}	b_{FS}	db_{OS}	db_{FS}
1	4	4	0.01	0.02	0.01	0.02
2	2.7	2.5	0.01	0.025	0	0.005
2'	0.8	0.8	0.01	0.03	0	0.005
3	2.3	2	0.05	0.08	0.04	0.055
4	1	1	0.05	0.07	0	-0.01
4'	0.3	0.3	0.05	0.06	0	-0.01
5	0.6	0.6	0.05	0.065	0	-0.005

Table 5.15. Basic data of the PS and the OS, needed for the EC_{OM} calculation.

The EC associated to OM is calculated, as in the previous section, in the two explained ways (procedure *a* and procedure *b* detailed in 5.9.1.1). Results are presented in Table 5.16

(a)

No	$Q_{OS}\cdot db_{OS}$	$Q_{FS}\cdot db_{FS}$	ΔB_{ch}
1	0.04	0.08	-0.04
2	0	0.013	-0.013
2'	0	0.004	-0.004
3	0.092	0.11	-0.018
4	0	-0.01	0.01
4'	0	-0.003	0.003
5	0	-0.003	0.003
Sum	0.132	0.191	-0.059
$EC_{OM}=\Delta B_{ch.OM}$	**-0.059**		**-0.059**

(b)

No	$dQ\cdot db_{OS}$	$Q_{FS}\cdot(db_{OS}-db_{FS})$
1	0	-0.04
2	0	-0.0125
2'	0	-0.004
3	0.012	-0.03
4	0	0.01
4'	0	0.003
5	0	0.003
Sum	0.012	-0.0705
$EC_{OM}=\Delta B_{ch.OM}$		**-0.059**

Table 5.16. Chemical exergy differences calculated as profiles differences (a) and as addition of the quantity and quality components (b). Obtained value for EC_{OM}.

It is relevant to remember that negative values of the ΔB_{OM} component mean that restoration measurements will be required.

b. Service Cost calculation (from ES to PS)

In this case, the OM content in the ES is very high with respect to the PS due to the lack of WWTPs. Then, a high value of the ΔB_{OM} is expected. Effectively, those values can be seen in Table 5.18.

No	Q_{PS}	Q_{ES}	b_{PS}	b_{ES}	db_{PS}	db_{ES}
1	4	4	0.02	0.1	0.02	0.1
2	2.5	2.5	0.03	0.05	0.01	-0.1
2'	0.8	0.8	0.03	0.15	0.01	0.1
3	2	2	0.08	0.12	0.06	0.07
4	1	1	0.07	0.09	-0	-0
4'	0.3	0.3	0.06	0.07	-0	-0
5	0.6	0.6	0.07	0.8	-0	0.71

Table 5.17. Basic data of the ES and the PS, needed for the SC_{OM} calculation.

(a)

No	$Q_{PS}\cdot db_{PS}$	$Q_{ES}\cdot db_{ES}$	ΔB_{ch}
1	0.08	0.4	-0.32
2	0.0125	-0.125	0.1375
2'	0.004	0.08	-0.076
3	0.11	0.14	-0.03
4	-0.01	-0.03	0.02
4'	-0.003	-0.006	0.003
5	-0.003	0.426	-0.429
Sum	0.1905	0.885	-0.695
$SC_{OM}=\Delta B_{ch.OM}$	**-0.6945**		**-0.695**

(b)

No	$dQ\cdot db_{PS}$	$Q_{ES}\cdot(db_{PS}-db_{ES})$
1	0	-0.32
2	0	0.1375
2'	0	-0.076
3	0	-0.03
4	0	0.02
4'	0	0.003
5	0	-0.429
Sum	0	-0.6945
$SC_{OM}=\Delta B_{ch.OM}$		**-0.6945**

Table 5.18. Chemical exergy differences calculated as profiles differences (a) and as addition of the quantity and quality components (b). Obtained value for SC_{OM}.

c. Remaining Resource Cost calculation (from OS to NS)

In general, the OM content in the Ns will be a bit lower than in the OS. Therefore, ΔB_{OM} will be negative. But in some stretches, if the water body is found in a poor state, it could be possible that no measurement will be required.

No	Q_{NS}	Q_{OS}	dQ	b_{NS}	b_{OS}	db_{NS}	db_{OS}
1	4.5	4	0.5	0.005	0.01	0.005	0.01
2	3	2.7	0.3	0.005	0.01	0	0
2'	1	0.8	0.2	0.005	0.01	0	0
3	2.5	2.3	0.2	0.02	0.05	0.015	0.04
4	1.1	1	0.1	0.02	0.05	0	0
4'	0.5	0.3	0.2	0.02	0.05	0	0
5	0.6	0.6	0	0.02	0.05	0	0

Table 5.19. Basic data of the OS and the NS needed for the RRC_{OM} calculation

No	$Q_{NS}\cdot db_{NS}$	$Q_{OS}\cdot db_{OS}$	ΔB_{ch}
1	0.0225	0.04	-0.018
2	0	0	0
2'	0	0	0
3	0.0375	0.092	-0.055
4	0	0	0
4'	0	0	0
5	0	0	0
Sum	0.06	0.132	-0.072
$RRC_{OM}=\Delta B_{chOM}$		**-0.072**	**-0.072**

No	$dQ\cdot db_{NS}$	$Q_{OS}\cdot(db_{NS}-dbr_{OS})$
1	0.0025	-0.02
2	0	0
2'	0	0
3	0.003	-0.0575
4	0	0
4'	0	0
5	0	0
Sum	0.0055	-0.0775
$RRC_{OM}=\Delta B_{chOM}$		**-0.072**

Table 5.20. Chemical exergy differences calculated as profiles differences (a), and as addition of the quantity and quality components (b), obtained value for RRC_{OM}.

5.9.1.3. Summary of results

Table 5.21 summarizes the obtained results for the whole developed example. These results are due to the variations in quantity and quality among the different states considered for the example river.

SC_{pot} is zero because both the quantiy and quality characterization for the ES and PS are equal. SC_{IM} (0.15 kJ/kg) and SC_{OM} (-0.69 kJ/kg) are due to the salinity and organic matter differences between the mentioned states. PS contains less dissolved salts than the ES, so it has higher exergy and the sign of the SC_{IM} is positive. Since the ES lacks of WTPs, its OM content is higher than in the PS and therefore a negative value is obtained for SC_{OM}.

EC_{pot} and RRC_{pot} clearly account for the flow difference between the PS and the OS on the one hand, and between the OS and the NS on the other hand. RRC_{pot} is higher than EC_{pot} because the flow gap is considerably higher. Although the flow differences remain constant, EC_{IM}(0.22 kJ/kg), RRC_{IM} (1.49 kJ/kg), EC_{OM} (-0.06 kJ/kg) and RRC_{OM} (-0.07 kJ/kg) are lower than the EC_{pot} (132.43 kJ/kg) and the RRC_{pot} (318.83 kJ/kg) because the chemical exergy differences and lower than the potential exergy ones.

	SC	EC	RRC	IRC
Pot	0.00	132.43	318.83	451.26
IM	0.15	0.22	1.49	1.86
OM	-0.69	-0.06	-0.07	-0.83

units: kJ/kg

Table 5.21. Summary of results for the example.

The EC gives idea of the exergy difference between the OS and the FS (≈ PS). The common situation is that both the salinity and the OM content are higher in the PS than in the OS and, therefore, the positive and negative sings for the IM and the OM components, respectively. The RRC is almost always the higher cost in module for the pot and the IM components because of the difference between the OS and the NS, in quantity as well as in quality. The IRC is the sum of the three costs for each component, pot, IM and OM. It accounts for the exergy difference between the natural and the exploitation states.

To sum up, it is important to highlight that this example has been developed with simple numbers in order to illustrate the difference between quantiy and quality for each of the defined water costs. Then, from the results, it can be appreciated that the EC is characterized by a small ΔQ and a high Δb. The SC is always zero in quantity because there is not any ΔQ, while the exergy variation Δb is considerable high because of the wastes in the exploitation state, mainly coming from urban water use. The RRC presents almost always a very high ΔQ due to the difference between the real rivers situation and their natural flow regime.

5.9.2. Cost calculation. Excel sheets organization.

The explained calculation procedure is then applied to real river basins. The complexity is obviously higher and much more unexpected behaviours can appear.

Data treatment is a hard task that has to be carefully planned. In this work, input data have been monthly organised in excel sheets.

The initial and final states have to be clearly defined, both in quantity and quality, in order to correctly operate. The quantity component is explained in detail in Table 5.22. In general, the flow of the initial state is written directly and the flow of the final state is expressed as that initial flow plus additional flow that separates both states ($Q_{initial}+\Delta Q$ where $\Delta Q = Q_{final}-Q_{initial}$). This technique allows a better structure and results' organization. The quality component is obtained from the simulations (Qual2k) or from the legal references.

River state	$Q_{initial}$	Q_{final}	$b_{initial}$	b_{final}
SC	Q_{ES}	$Q_{ES}+(Q_{PS}-Q_{ES})$	b_{ES}	b_{PS}
	FS	OS		
EC (OS=GEE)	Q_{FS}	$Q_{GEE}=Q_{FS}+\Delta Q$ where $\Delta Q=0$ if $Q_{FS}>Q_{MF}$ $\Delta Q=Q_{MF}-Q_{FS}$ if $Q_{FS}<Q_{MF}$	b_{FS}	b_{GEE}
EC (OS=HS)	Q_{FS}	$Q_{HS}=Q_{GEE}+\Delta Q$ where $\Delta Q=Q_{NF}-Q_{GEE}$	b_{FS}	b_{HS}
RRC	Q_{GEE} or Q_{HS}	Q_{NF}	b_{OS}	b_{NF}

Table 5.22. Correspondence of real and objective state for each cost

For the SC calculation, in general, $Q_{real}=Q_{exp}$ because only a quality change is assumed and there is not a physical consumption in the water treatment plants. If it were exist, $Q_{PS}<Q_{ES}$ and, in consequence a negative value would appear ($\Delta Q<0$). Quality parameters are obtained from the river simulation program.

Upon the EC calculation, objective flows and qualities are obtained from GEE and HS definitions. Regarding ΔQ, $Q_{2015}>Q_{man}$ in general because Q_{man} is defined as a minimum required flow. Quality parameters for 2015 are simulated by the Qual2k software and the quantity for the maintenance flow is legally determined.

The RRC is a fixed cost. Q_{NF} is obtained from flow restoration to natural regime studies (Sacramento. Nolte or Sato Method), and the quality of this natural flow is determined by the competent organism, depending on the type or river, and observing always the stablished objectives by 2015.

The presence of ΔQ in calculations allows considering separately the quantity and quality components. if needed. This feature will be especially important when, in an ulterior step, pollution abatement measurements will be proposed.

5.10. Sign analysis for water costs

The expected signs for the calculated water costs are analyzed in this section. For each cost, its potential and chemical component is considered. Their corresponding quantity and quality components are considered separately, keeping in mind that diverse measurement plans will be applied. The following expression, used for the analysis, is followed from Eq. 5.3. The subindex *r* and *o* state for the initial (real) and final (objective) states in each case.

Eq. 5.18.
$$\Delta B = \Delta B_t + \Delta B_l = m_r(db_o - db_r) + (m_r - m_o)\cdot db_r$$

In the cases where the resulted sign is clear, the expected result (positive, negative, null) has been marked with a square in the diagram. Where the final sign cannot be immediately predicted, all the possibilities are shown without any special mark. Options in red are impossible.

5.10.1. Sign analysis for the Service Cost

The flow has been assumed equal for the exploitation and present states of the river, so the quantity component of the service exergy cost does exist, neither for the potential nor for the chemical component.

The quality component coming from the potential component of the service cost is also zero because the altitude is maintained. However, the IM is usually lightly lower in the present than in the exploitation state and, in consequence the $SC_{l,IM}$ is positive (although not high in magnitude). The OM in the exploitation state (ES) is much higher than in the present state because, as indicated in the ES definition, the river suffers from the absence of WWTPs. Then, the sign for the $SC_{l,OM}$ is negative in most cases.

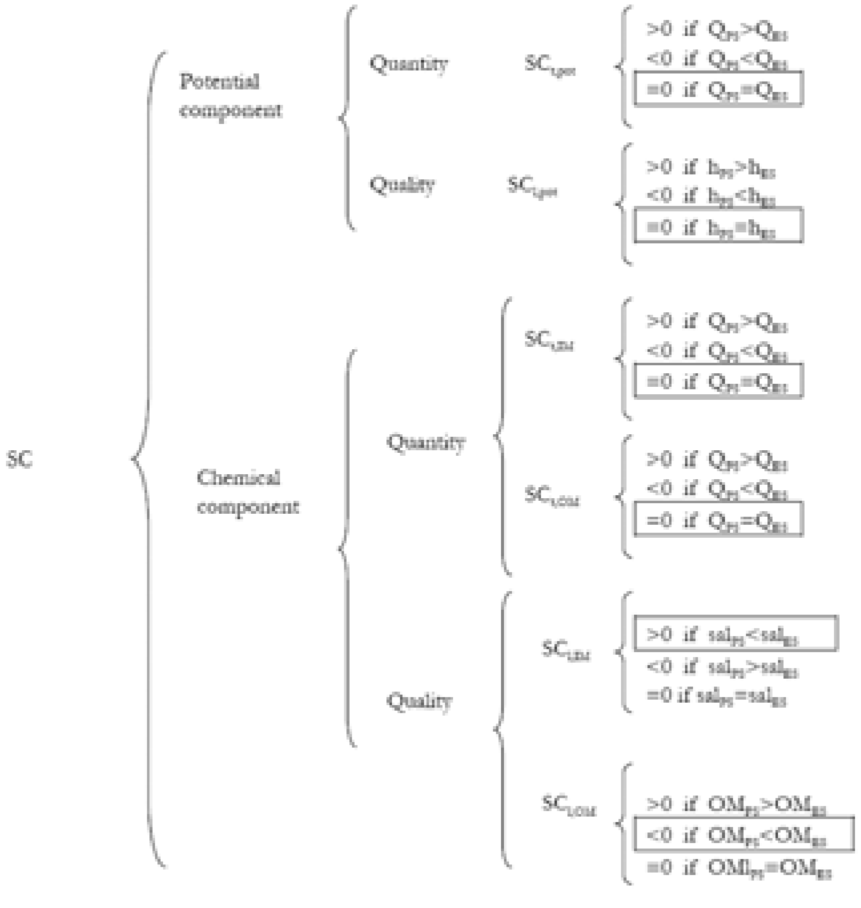


Figure 5.15. Signs analysis for the Service Cost

5.10.2. Sign analysis for the Environmental Cost

The flow in the OS is usually higher than the flow in the FS ($Q_{OS}>Q_{FS}$). Consequently, the quantity components of the EC are expected to result positive. However, it may happen that the river, in its current state (FS) receives many artificial tributaries (from other watersheds, from aquifers…), having in some reaches of its courses a flow higher than its natural flow regime and also higher than the OS: $Q_{OS}<Q_{FS}$ and the quantity component of the EC will result negative.

The quality of the potential component, $EC_{l,pot}$, is zero because of the constant altitude in each reach. However, the most common result of the EC for the other quality components can not be directly defined. It will depend on the values of the IM and the OM in the future state of the river and in the objective state. If the river is not polluted and the values derived from its chemical are lower than the marked objectives, no restoration measurements will be needed. Then, the EC_l is zero (in fact, negative, but it is understood as zero). If the situation is the contrary, the chemical quality of the future state is lower than the demanded by the legislation (OS), the EC_l will be positive and some kind of measurements will need to be implemented.

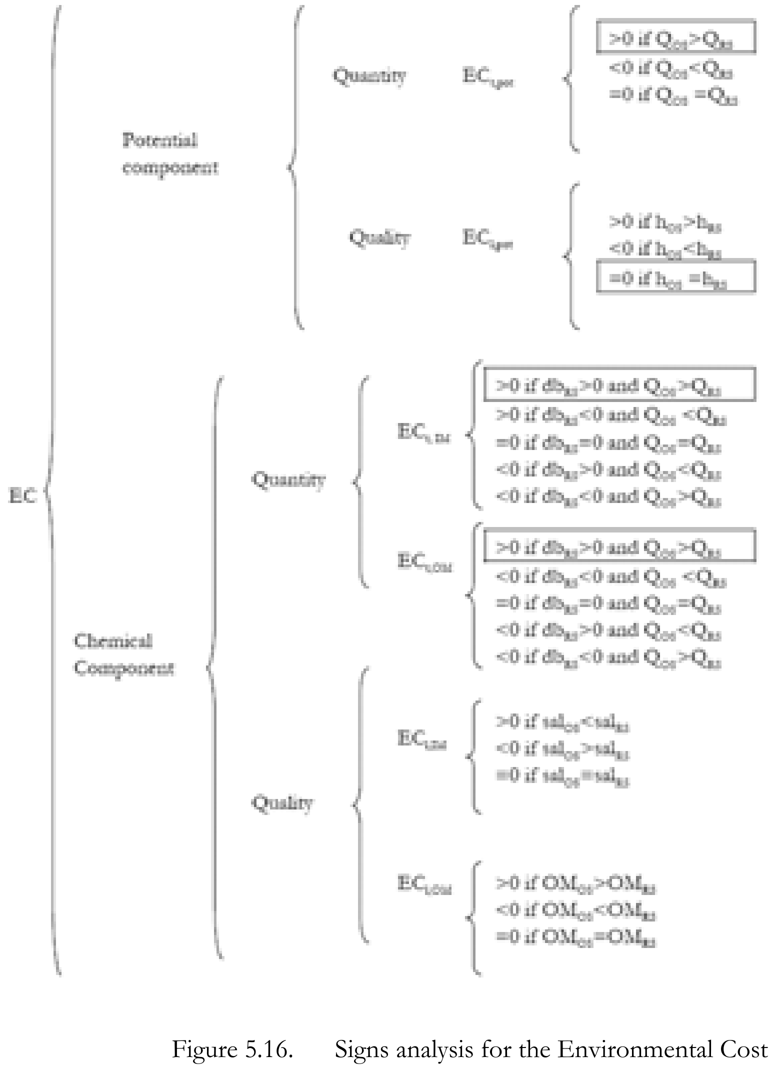


Figure 5.16. Signs analysis for the Environmental Cost

5.10.3. Sign analysis for the Remaining Resource Cost

The RRC represents the highest exergy gap in most cases. It accounts for the exergy distance between the objective (OS) and the natural state (NS) of the river and, in the first instance, it is expected that the flow and the quality were both higher in the NS than in the OS. Accordingly, their quantity components are usually positive and their quality components will follow the regular tendency: $RRC_{l,pot}=0$, $RRC_{l,IM}>0$ and $RRC_{l,OM}<0$.

In some few and particular situations, it may happen that the flow in the NS is lower than in the OS. Undoubtedly, it should lead to the conclusion that there exist some kind of mistake in the definition of the flow for the OS or, maybe, that an important modification of the original situation of the river has been performed in a permanent way.

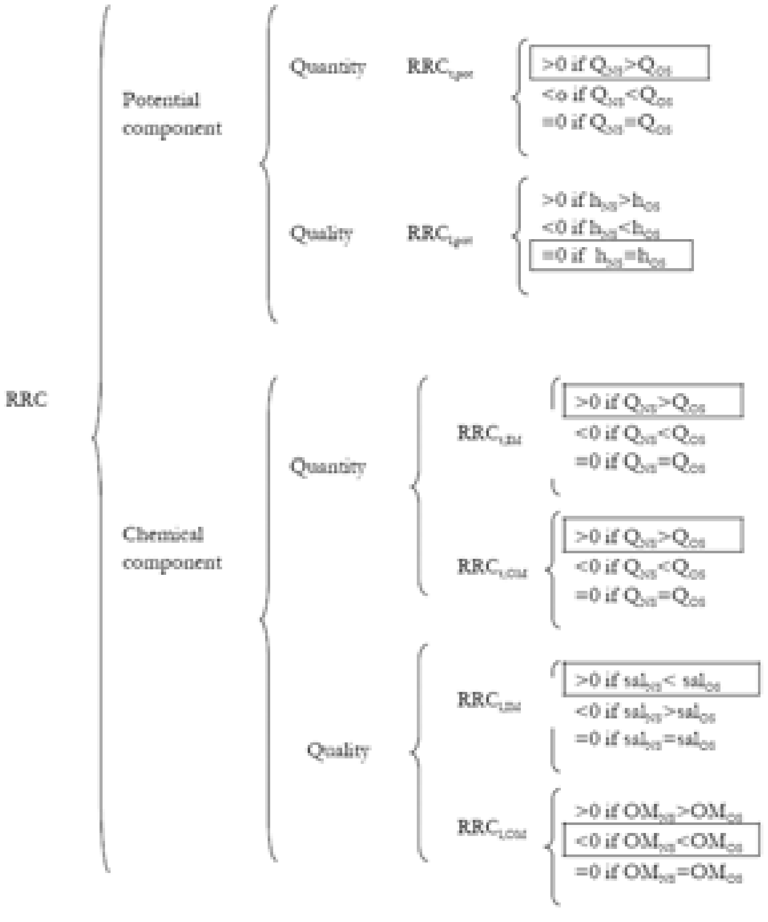


Figure 5.17. Signs analysis for the Remaining Resource Cost

5.10.4. Interpretation of the water cost signs from the Thermoeconomics perspective. River indices definition.

From the previous analysis, and keeping in mind the exergy cost background given in Chapter 4, the considered water flow can be interpreted as an exergy flow carrying some valuable exergy, the fuel F, and some exergy that needs to be eliminate, the residue R.

The PH's final objective is eliminating that R. In order to do it, external exergy sources need to be implemented, F_R, i.e., the measures planning that has to be proposed. In particular, the idea can be summarized as Figure 5.18 indicates.

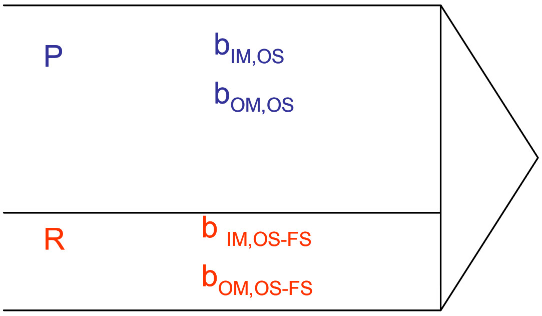


Figure 5.18. Water stream as an exergy flow

The residue R can present a negative or a positive value depending on the considered parameter, but it does not affect the concept of being a residue that needs to be eliminated from the water flow. The irreversibility in the system is then given by the residue and the exergy that is needed to invest in order to eliminate it (Eq. 5.19). In the considered water flow, a part of the residue to be eliminated is OM and the other one is IM (Eq. 5.20).

Eq. 5.19. $$R + F_R^* \rightarrow I_R$$

Eq. 5.20. $$R_{OM} + R_{IM} + F_{R,OM}^* + F_{R,IM}^* \rightarrow I_R$$

Going further in this idea, some pure thermoeconomics index can be defined. First of all, it is worth to remember that there exist two basic exergy values within the river: the potential and the chemical potential. Currently, only the potential component is exploited in hydro-electrical utilities. The chemical potential, although important and existing, is commonly ignored.

In consequence, the index of potential use of the river (PURI, Eq. 5.21) and the index of chemical use of the river (CURI, Eq. 5.22) can be defined. They can be both understood as index of the productive process.

Eq. 5.21. $$PURI = \frac{P_{pot}}{F_{pot}}$$

Where P_{pot} represents the energy obtained from the facilities along the river course, in MWh/yr, and F_{pot} stands for the existing potential in the watershed. This index, therefore, gives idea about how much of the potential is being used.

Eq. 5.22. $$CURI = \frac{P_{ch}}{F_{ch}}$$

Where P_{chem} is the energy obtained from the facilities using the chemical potential of the water and F_{chem} stands for the existing potential in the watershed. Currently, there is not any utility able to take advantage of the chemical exergy of the river and, in consequence, P_{chem} is equal to cero in any river. Then, the chemical use index of rivers is, at the current technology state, null.

In addition, an index related to de dissipative process can be defined, the ratio on the residue R parameters. The residue in the river index (RRI) is the ratio between the residue and the fuel used to eliminate that residue (Eq. 5.23). Nowadays, the OM is the factor determining the value of this index because it is the most representative parameter being eliminated in the WWTPs.

Eq. 5.23.
$$RRI = -\frac{R}{F_R}$$

A secondary index can be additionally defined in order to obtain information about the fuel consumed to keep clean the river waters, in relation to the chemical potential in the river. That is the fuel-residue river index (FRRI), as Eq. 5.24 indicates.

Eq. 5.24.
$$F_R RI = \frac{F_R}{F_{chem}}$$

5.11. Water quality modelling-River basin simulators

The water quality management strategy involves a series of complex inter-disciplinary decisions based on speculated responses of water quality to changing controls (McIntyre and Wheater, 2004). The complex relationships between waste loads from different sources

and the resulting water qualities of the receiving waters are best described with mathematical models (Deksissa et al., 2004).

5.11.1. The necessity of a pressure-impacts model

Article 36 of the WFD indicates that *it is necessary to undertake analyses of the characteristics of a river basin and the impacts of human activity as well as an economic analysis of water use. The development in water status should be monitored by Member States on a systematic and comparable basis throughout the Community. This information is necessary in order to provide a sound basis for Member States to develop programmes of measures aimed at achieving the objectives established under this Directive.*

According to that section, in order to be able to determine the measurements that would allow to reach the WFD's objectives by 2015, and to include them in the Management Plan of the watershed, a previous analysis has to be performed. The consequences of the human activity (anthropic pressures) affecting the environment (impacts) and possible measurements devoted to reduce them should be proposed and studied.

The necessity of developing a model able to analyze the provoked impacts due to different pressures is clear: the watershed Management Plan has to be totally developed by December 2009 and, obviously, the pressure-impacts analysis should be ready in advance.

5.11.2. Available pressure-impact softwares (Water Quality Models)

Water Quality Models (WQM) simulates the fate of pollutants and the state of selected water quality variables in water bodies. They incorporate a variety of physical. Chemical, and biological processes that control the transport and transformation of these variables, Water quality models are driven by hydrodynamics, point and nonpoint source loadings, and key environmental forcing functions, such as temperature, solar radiation, wind speed, pH, and light attenuation coefficients. The external drivers may be specified from observed data bases, or simulated using specialized models describing, for example, the water body hydrodynamics or the watershed pollutant loading. The internal forcing functions may also be specified from databases. or calculated within the water quality model using a range of empirical to mechanistic process formulations. Examples include temperature, pH, and light attenuation.

Some water quality models are quite general (e.g. WASP7 or QUAL2K), and can be used to simulate different water quality problems, such us eutrophication, phosphorus loading, nutrients, organic loadings, toxic chemicals, temperature. Depending on the model, one can be simulated one, two or three dimensional systems. Some of these models (e.g Aquatox, WAM, LSPC), have a particular environment of simulation such as PC-based ecosystem model, grid cell representation, road map, or streamlined hydrologic simulation -simplified stream transport model-. Some examples are included later in group 1 (see Annex E).

Other water quality models are specialized in a particular problem (e.g. oil spills, organic contaminants or atmospheric phenomena). Some examples are included later in group 2 (see Annex E)

In the following, the softwares that were considered as real alternatives for Qual2k in this Ph.D. Thesis are summarized. They are AQUATOOL, SWAT and WEAP.

5.11.2.1. AQUATOOL

AQUATOOLDMA is a new global watershed simulation graphics editor, developed by the Water Resources Engineering Group, which forms a part of the department of Hydraulic engineering and Environment of the *Universidad Politécnica de Valencia* (Spain). This interface provides a quality and organization watershed simulation support in the framework of hydrological programs. Its installation can be downloaded in <http://www.iiama.upv.es:8080/aquatool/aquatooldma>. The SIMGES.EXE (the module where the flows regime is implemented) and GESCAL.EXE (module of quality) files can be downloaded, but a previously installed program licence is necessary. Work interface is similar to the Microsoft Word one. Due to the water systems and the necessary solutions to relieve the existing problems in them, increase the necessary utilization of tools technologically advanced for the analysis of the systems of integrated form and to bear in mind classic uncertainties related to uses, demands, or resources, as well as new uncertainties, as for example impacts of climatic change.

Then, Aqua-tool is a decision support system, and interface to use different programs, including GESCAL, specific to water quality studies. Different scenarios can be saved and defined for the same project, in the same field.

Additionally, GIS data fields can be used in *.shp* format, by means of some approximations between conductions and water masses, and edited. The tools include pipes, withdrawals, nodes, aquifers, hydroelectric plants, infiltrations return, and dumps. Geographical location in facilitated.

The hydrological simulation can be calculated in detail. Main considerations to highlight are the availability of interchange between aquifers definition, the redistribution of storage excess water volumes, or the possibility of both constant and punctual water inputs data introduction from external text files. Demand points, and withdrawals are considered, taking into account infiltration coefficients. Industrial, urban, hydroelectric and irrigation are included as main water uses. Maximum monthly and yearly water withdrawals are taken into account. Demands priority, and different kinds of aquifers can be simulated. Additionally, as mentioned previously, infiltrations return coefficient can be simulated as the remaining one, when withdrawal and infiltration are know.

Application to real cases of planning in Spanish basins (Júcar, Segura, Tajo) and foreigners (Argentina, Brazil, Italy) assure the soundness of the model and its flexibility to shape great variety of systems. Permanent improvement and addition of utilities assure continue leading of the state of the art in this area of the knowledge.

GESCAL

AquaTool results, previously or simultaneously obtained, can be introduced in this program. Dissolved oxygen, nitrogen, phytoplankton, conductivity, solids, and organic matter in DBO_5, are considered in simulations, in both storage and water conductions. On the other hand, pathogens and pH are not considered.

Inclination, wide, manning coefficient, dispersion and salinity data are necessary for aquifers simulation. In relation with radiation values, only the average ones are introduced. Additionally, Water Treatment Plants can be modelled by two methods, both of them are right, they are, as returns or withdrawals, considering only the parameters which are modified by the treatment.

Results, divided by elements and themes, can be shown in graphics, tables, or can be exported to work in Excel dynamic tables. Finally, monthly data (but not diary) can be obtained.

5.11.2.2. SWAT

The Soil and Water Assessment Tool (SWAT) is a interdisciplinary watershed modelling tool which has been developed since the early 1990´s by the United States Department of Agriculture Research Service. Main distributed versions of the model include SWRRB, SWAT94.2, SWAT96.2, SWAT98.1, and SWAT99 .2. It can be freely downloaded from <http://www.brc.tamus.edu/swat/soft_model.html>.

This program consists on a basin-scale continuous model, which operates in a daily time step. It mainly predicts the impact of management on water, sediment and agricultural chemical yields. The model is capable of continuous simulation during large periods. Additionally, it is computationally efficient and physically based. Model works weather, hydrology, soil temperatures and properties, plant growth, nutrients, pesticides, bacteria, pathogens, and land management. It is divided in hydrologic response units (which are not spatially located), with homogeneous land use, soil and characteristics. They are grouped in subwatersheds which are grouped in watersheds. The overall hydrologic balance is simulated for each of those hydrologic response units. Main climatic inputs are daily precipitation, maximum and minimum temperatures, solar radiation, relative humidity, and wind speed data. These data can be measured or generated. Additionally, redistribution of water in soil layers in the soil profile can be calculated.

On the other hand, biomass and/or yields can be estimated with the crop grown model, for a wide range of crops rotation, grassland/pasture systems, and trees. Simulation of specific processes, focussed, in some cases, on specific regions, which includes percolation, hydraulic conductivity, or interflow functions, to simulate typical conditions in low mountain range in Germany.

In relation with applications, one of the main of them is the Hydrologic Unit Model modelling system of the United States, which consists on simulation of hydrologic and /or pollutants loss impacts of agricultural and municipal water use, tillage and cropping. Other applications allow quantifying environmental benefits of conservation practices, at national and watershed scales of varying sizes, representative of different regional conditions and mixes of regional practices (Conservation Effects Assessment Project). Swat is, additionally, used to perform analysis for impaired waters, by the different states. In Europe, SWAT is extensively used as support by various European Commission agencies. Climate Change, nonpoint source nitrogen and phosphorous losses, or intermittent stream conditions, are important studied issues. Finally, calibration and sensibility analysis, GIS interface descriptions, Variation on configuration or data input effects, comparison it other models or techniques, interfaces and pollutant assessment, such as pesticide, are groups of specific SWAT applications. Main interfaces of SWAT with other models are Modflow, surface water models, environmental models, genetic algorithms, economics and environmental, or ecological models. An effective watershed management is possible by using this program. More accurate simulations, incorporated advancements in scientific knowledge, are possible, too. Nevertheless, some problems are found, related to the accuracy, because of enough monitoring data, inadecuate data needed to characterize input parameters, or insufficient scientific understanding.

5.11.2.3. WEAP

Water Evaluation and Planning System (WEAP) is a software tool that takes an integrated approach to water resources planning, including main freshwater management challenges such as allocation of limited water resources between agricultural, municipal and environmental uses, integration of means of supply, demand, water quality and ecological considerations. WEAP was developed by the Stockholm Environment Institute's Boston Center at the Tellus Institute. This SEI Center is now independent of Tellus, and known as the Stockholm Environment Institute U.S. Center. WEAP was created in 1988, with the aim to be a flexible, integrated, and transparent planning tool for evaluating the sustainability of current water demand and supply patterns and exploring alternative long-range scenarios.

A number of agencies, including the UN, World Bank, USAID, US EPA, IWMI, Water Research Foundation (formerly AwwaRF) and the Global Infrastructure Fund of Japan have provided project support. WEAP has been applied in water assessments in dozens of countries, including the United States, Mexico, Brazil, Germany, Ghana, Burkina Faso, Kenya, South Africa, Mozambique, Egypt, Israel, Oman, Central Asia, India, Sri Lanka, Nepal, China, South Korea, and Thailand. Then, WEAP is available in English, French, Greek and Korean, with Chinese, Spanish and Portuguese versions nearly completed.

Conventional supply-oriented simulation models are not always adequate for exploring the full range of management options. WEAP has emerged over the last decade, as an integrated approach to water development in the context of demand-side management, and water quality and ecosystem preservation and protection, mainly, in developing countries. Main characteristics are a unique approach for conducting integrated water resources planning assessments, a transparent structure to facilitate engagement of diverse stakeholders in an open process and a database maintains water demand and supply information to drive mass balance model on a link-node architecture, calculating water demand, supply, runoff, infiltration, crop requirements, flows, and storage, hydropower, and pollution generation, treatment, discharge and instream water quality under varying hydrologic and policy scenarios. The program evaluates a full range of water development and management options, and takes account of multiple and competing uses of water systems. A financial analysis module also allows the user to investigate cost-benefit comparisons for projects, taking into account multiple and competing uses of water systems, are considered. A graphical GIS-based interface with flexible model output as maps, charts and tables completes the program description. Its integrated approach to simulating both the natural and engineered components of water systems, allows a more comprehensive view of the broad range of factors that must be considered in managing water resources. The result is an effective tool for examining alternative water development and management options. The analyst represents the system in terms of its various supply sources.

Different scenarios are simulated, such as population growth and economic development patterns, reservoir operating rules, groundwater exploitation, water conservation, ecosystem requirements, storing excess surface water in underground aquifers, water recycling program implementation, more efficient irrigation, mix of agricultural crops changes, climate change, pollution upstream affection in downstream water quality, or the relation between land use changes and runoff.

The registration and participation in the WEAP User Forum is mandatory to obtain the licence, necessary to activate it, which can be downloaded in <http://www.weap21.org/>. License fee varies according to the type of user. Each license is for a 2 year period, and can be used simultaneously by an unlimited number of users at one site. During the 2 year license period, licensed users are entitled to free upgrades and to limited technical support. Non-profit, governmental or academic organizations based on a developing country are free of taxes. All the collected money in WEAP license fees goes to supporting developing country users or in further developing the software and documentation.

QUAL2K and WEAP are compatible in their general approach to water quality modelling, but they do some things differently. Main differences are: QUAL2K measures distance along a reach from the tail of the reach, while WEAP measures distance from the head; QUAL2K allows for diurnal variations in water quality and climate, while WEAP applies the same value to all times of day; WEAP is more tolerant of zero or missing values than is QUAL2K; QUAL2K and WEAP use different climate parameters: for example, QUAL2K uses dew point, while WEAP uses humidity. Finally, QUAL2K models many more constituents in much more detail, including two separate CBOD constituents, ammonia, nitrate, organic and inorganic phosphorous, algae, sediment, pH and pathogens. Both programs treats a river as a sequence of reaches, not necessarily of equal lengths. However, the reach boundaries as defined in QUAL2K and in WEAP need not match. Where reach boundaries do not match, WEAP handles the task of mapping water quality and climate variables, based on distance markers. WEAP includes reservoirs, but not for water quality, while QUAL2K includes weirs, but they are not operated. It is recommended that rivers with reservoirs not be linked to QUAL2K, or that they be modelled in two sections—above the reservoir and below the reservoir.

Finally, WEAP was ruled out because of its mentioned limitations in the quality parameters. It only provides TSS, salinity, DBO and DQO. For the exergy analysis, it is much more convenient having some higher electrolytes disaggregation.

5.11.3. Description of the chosen pressure-impacts model: Qual2Kw

The most widely used mathematical model for conventional pollutant impact evaluation is QUAL2E (Brown and Barnwell, 1987) developed by United States Environmental Protection Agency (US EPA).

Park and Lee (2002) developed QUAL2K after modification of QUAL2E. The modifications include the expansion of computational structures and addition of new constituent interactions: algal BOD, de-nitrification and DO change caused by fixed plants. Pelletier and Chapra (2006) developed a model QUAL2Kw, by modifying QUAL2K. 2003 originally developed by Chapra and Pelletier (2003), which is intended to represent a modernized version of QUAL2E.

QUAL2kW is one-dimensional, steady state stream water quality model and is implemented in the Microsoft Windows environment. It is well documented and is freely available (http://www.epa.gov/). The model can simulate a number of constituents including temperature, pH, carbonaceous biochemical demand, sediment oxygen demand, dissolved oxygen, organic nitrogen, ammonia nitrogen, nitrite and nitrate nitrogen, organic phosphorus, inorganic phosphorus, total nitrogen, total phosphorus, phytoplankton and bottom algae.

QUAL2kW includes many new elements (Pelletier et al., 2006). It uses two forms of carbonaceous biochemical oxygen demand to represent organic carbon: slowly and rapidly oxidizing forms. It accommodates anoxia by reducing oxidation reactions to zero at low oxygen levels. It simulates attached bottom algae explicitly. It models sediment-water fluxes of dissolved oxygen and nutrients internally. In addition, its simulation includes de-nitrification, pH and sediment pore water quality.

In spite of the given characteristics, several limitations of the QUAL2E have been reported (Kannel et al., 2007). One of the major inadequacies is the lack of provision for conversion of algal death to carbonaceous biochemical oxygen demand (Park and Uchrin, 1997).

Because of its general field and easy simulation environment, its feasible external linkages, and its free distribution, QUAL2kW was chosen by the Catalan Water Agency to simulate the watersheds within the IBC. Since this work is somehow linked to the Agency, specially, in the data provision area, that software was decided to be used in the dissertation. Detailed information about the modelling tool can be found in Annex E.

5.12. Exergy degradation by diverse uses

Water uses by humankind are the main pressure influencing the rivers courses. Those uses are including in the simulation programs as point or diffuse sources. After running the program, it is possible to obtain the quality features of each river reach and, in consequence, to treat them from an exergetic perspective. In this section, starting from the information already provided in Chapter 2, a proper exergy characterization of the different water uses is carried out.

Society uses water in a range of domestic and productive endeavours. Over the past three centuries, the Industrial and Green revolutions and the growth of cities have brought about a transformation in the distribution and use of water on an unprecedented scale. The rate of water withdrawal rose steeply at the start of the past Century, and even further at mid-century. The volume of river water polluted to some degree by wastewater discharges has increased in a similar pattern (Groombridge, 1998). Human exploitation of the world's water resources occurs at a number of interacting scales, including the individual. household and society.

The mentioned general aspects about water uses by humans were already considered in Chapter 2. Consumptive and not consumptive water uses from a global perspective were summarized in section 2.3.2.1. In addition to that, the most representative sectors were analyzed and their effects on water quality were detailed.

At this point, the interest lies on the quantity and quality degradation that the water uses produce along the river flow.

In the domestic water use the originated Δb increases as the impact goes higher. Therefore, when the domestic use is classified as low, the quality variation (defined as difference between the catchment and return) is 0.03 kJ/kg for the inorganic matter and -1.78 kJ/kg for the organic matter and rises until 0.17 and -6.73 kJ/kg respectively, when the use is considered as intensive. The signs respond to the expected situation: more salts and more organic matter after the use. The higher magnitude of the organic matter correspond to the already explained circumstance of the chosen references environment in the analysis (see Chapter 4).

		b_{IM} (kJ/kg)	b_{OM} (kJ/kg)	Δb_{IM} (kJ/kg)	Δb_{OM} (kJ/kg)
1	Dom.Low.in	2.6695	0.6902	0.03	-1.78
2	Dom.Low.out	2.6383	2.473		
3	Dom. Medium in	2.6695	0.6902	0.07	-4.25
4	Dom. Medium out	2.5987	4.945		
5	Dom. High in	2.6695	0.6902	0.17	-6.73
6	Dom.High out	2.4986	7.418		
7	Irrig. None in	2.5147	0.4641	0.57	-0.37
8	Irrig. None out	1.9439	0.8308		
9	Irrig. Moderate in	2.36	0.4641	0.92	-0.37
10	Irrig. moderate out	1.4395	0.8308		
11	Irrig. Severe in	2.1491	0.4641	1.34	-0.37
12	Irrig. Severe out	0.8105	0.8308		
13	Energetic in	2.1491	1.904	0.06	-1.26
14	Energetic out	2.0841	3.165		
15	Ind. Salt extract. in	2.3703	0.6902	-0.25	-147.71
16	Ind. Salt extract. out	2.6179	148.4		
17	Ind. Gas product. in	2.3703	0.6902	-0.0027	-3.0198
18	Ind. Gas product. out	2.371	3.71		
19	Ind. Plastic in	2.3703	0.6902	-0.29	0.07
20	Ind. Plastic out	2.6606	0.6172		
21	Ind. Wash-mach. in	2.3703	0.6902	1.05	-98.22
22	Ind. Wash.-mach.out	1.3198	98.91		
23	Paper Industry in	2.3703	0.6902	-0.31	0.34
24	Paper Industry out	2.6758	0.3462		
25	Fruits and veget. in	2.6695	0.6902	0.53	0.62
26	Fruits and veget. out	2.1441	0.07418		
27	Animal waste in	2.3703	0.6902	0.01	-79.66
28	Animal waste out	2.36	80.35		
29	Ind. soap in	2.3703	0.6902	-0.18	-81.76
30	Ind. soap out	2.5519	82.45		

Table 5.23. Exergy of the input and out flows for different water uses and originated Δb, separated in inorganic and organic matter.

Salinity increase provoked by irrigation is higher than by domestic uses, but it depends on the type of soil and on the electrolytes equilibrium. But it does not occur the same in the case of organic matter, as logically expected. The change in OM is not representative and it has been taken equal for the different irrigation grades (low, medium, high).

The exergy variations produced by industrial uses cannot be characterized in general terms, since it greatly depends on the type of activity in the industry. Nine different production processes have been detailed in Table 5.23. Lowest alterations in quality are found in the energetic use. An important pollution due to OM is observed in wash-machinery industry, animal waste industry and soap industry.

5.13. Relationship between the IRC and the degradation due to water uses.

The IRC (SC+EC+RRC) accounts for the existing distance between the natural state of the river and the state that it would present if none water treatment after the use were considered. Then, it represents the complete degradation along the river course.

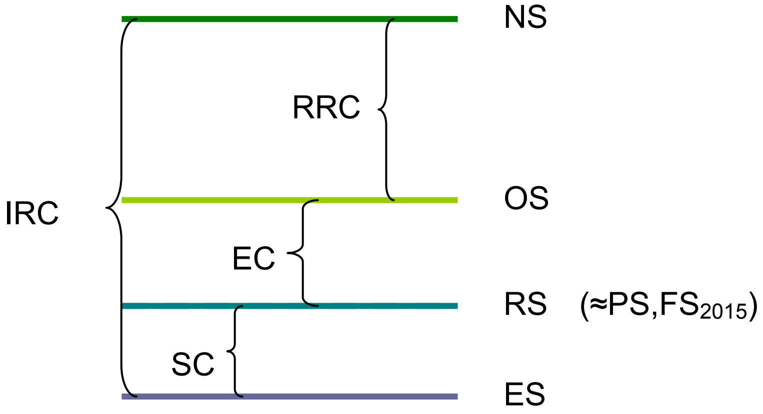


Figure 5.19. Defined costs according to the WFD.

On the other hand, it is easy to agree on thinking that the total exergy loss along that river flow is mainly originated by the human water uses, although the natural degradation could also have a small contribution, as indicated in Figure 5.20: water is originally taken from the river in its natural state (NS) and, after being used, is return to the river. If there are not any WWTP, the final state in the river is the defined exploitation state (ES).

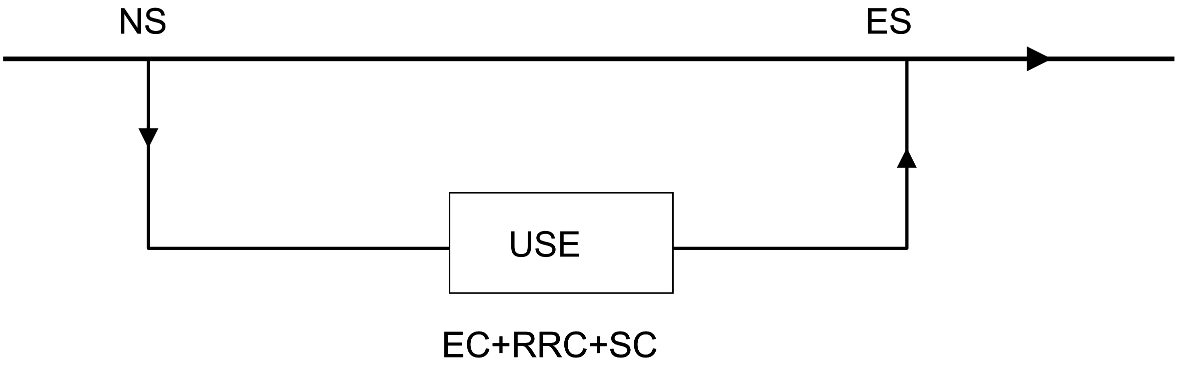


Figure 5.20. Conceptual diagramming: human uses along river flow degrade it from its natural state (NS) to its exploitation state (ES)

The alternative situation would be the existence of WWTP after those water uses. Then, the degradation would account for the EC and RRC, as illustrated in Figure 5.21.

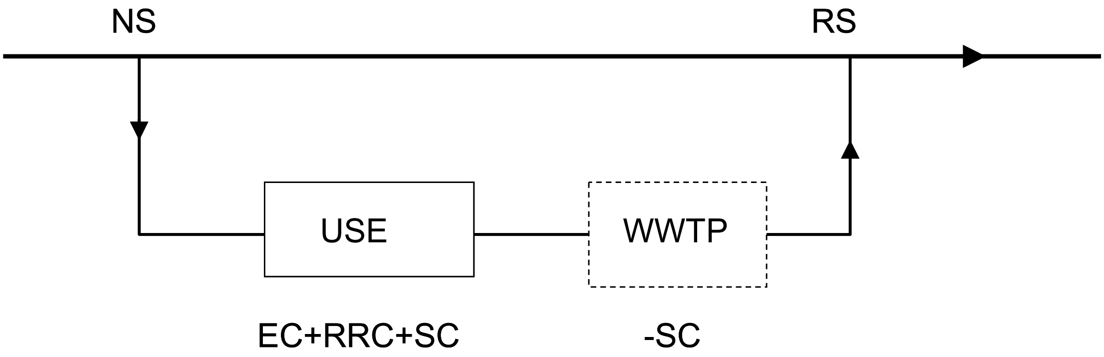


Figure 5.21. Conceptual diagramming: human uses along river flow degrade it from its natural state (NS) to its exploitation state (RS), when the existing WWTPs are included in the analysis.

In this connection, in theory, the IRC could be compared with the costs associated to restore the water body deterioration provoked by the diverse water uses and the relation could be represented by Eq. 5.25.

Eq. 5.25. $$\Delta B_{IRC} \approx \Delta B_{use}$$

The eventual small difference between both values is due to the exergy lost due to the salts dilution along the river, and to the natural self-depuration of the river course.

The proposed hypothesis postulates that the existing degradation in the river, the difference between the NS and the ES (i.e., the IRC), can be directly related to water uses. Going back to the WFD guidelines, this idea can be immediately linked to the Polluter Pays Principle: if PH is able to calculate de degradation (ΔB) provoked by each water user, the associated exergy cost and consequently the allocation of the monetary costs could be performed.

Eq. 5.26. $$\Delta B_{use} = \Delta B_{use\_households} + \Delta B_{use\_industry} + \Delta B_{use\_agriculture} + \Delta B_{use\_external}$$

To summarize, the IRC can be used to check that the ΔB_{use} has been properly calculated. Then, the cost allocation is done proportionally to the degradation produce by each water user (in exergy terms).

5.13.1. Study of the different water use cases

The hypothesis established in Eq. 5.25 is going to be studied in this section, where different simplified case studies are developed and analyzed. Since different situations may happen for a water use, the examples below have been structured trying to summarize those diverse hypotheses.

First, the usual water catchment and return of water along the same water flow is considered for an only use (section 5.13.1.1) as well as for several consecutive water uses (section 5.13.1.4). Secondly, a flow input from an external water source after being used and returned to the river, is shown (section 5.13.1.2), what usually means an increase in the water flow downstream, provoking the real flow to be higher than the natural flow. Subsequently, the water catchment in the studied river to be used and dumped in a different place is presented in section 5.13.1.3.

In each case, the degradation of the river is calculated as the difference of minimum and maximum characteristic profiles (IRC) and as the degradation provoked by the water uses (ΔB_{use}), always in exergy terms. Then, both procedures are proved to be equivalent and, finally, results and detailed dissagregation in quantity and quality are sequentially presented.

5.13.1.1. Catchment and return in different river reaches

A frequent situation in rivers is catching water at some point of the water course and giving it back downstream. The general schema is presented in Figure 5.22 and it has been considered in this section. However, the catchment and return of a given use can happen in the same river reach. This situation has been observed in the real case studies during their simulation and means a difficulty for identifying the degradation due to the water use because the software only provides one value for the flow and for the quality parameters (at the end of the reach). The corresponding figure and explanation can be found at the end of this section.

Coming back to the former situation, the river has been sectioned (in different reaches) in order to simulate the fractions in which water courses are usually studied. A water inflow or outflow, or any substantial change in the river determines a new reach.

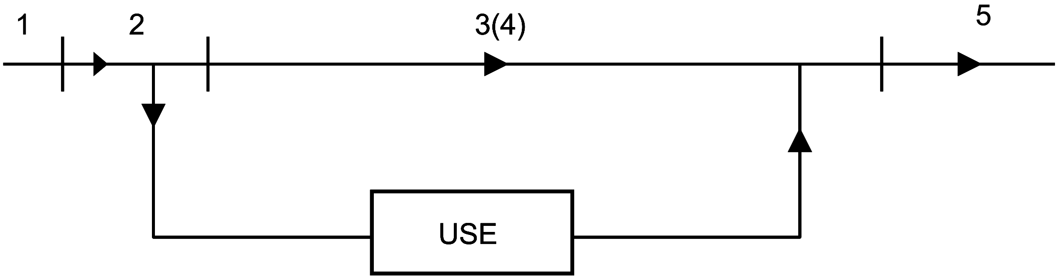


Figure 5.22. Catchment and return in different river reaches.

The river flow is Q_1 in reach 1. A certain amount of water, yQ_1, is taken from the river to be used by a determined sector (domestic, industrial, agriculture or energy; $0<y<1$). After being used, it is returned to the river. The factor α represents the possible water consumption in the use ($0<\alpha<1$). The quality of the water coming into the use is represented by its exergy, b_1, and after used, that quality becomes b_1'. These quality variations due to different water uses were carefully analyzed in Chapter 2, and their associated Δb were calculated in Table 5.23.

To develop the example, Table 5.24 summarizes the main inputs for the river profiles calculation. For each river state (natural –NS-, objective –OS-, real –RS- and exploitation –ES-), the main features (flow, salinity, organic matter and altitude) are given. RS is the same as PS: real and present states are used as synonyms.

Reach	Q_{NS}	Q_{OS}	Q_{RS}	Q_{ES}	C_{NS}	C_{OS}	C_{RS}	C_{ES}	TOC_{NS}	TOC_{OS}	TOC_{RS}	TOC_{ES}	h
1	0.4	0.4	0.4	0.4	400	300	400	400	0.4	0.4	0.4	0.4	300
2	0.5	0.45	0.4	0.4	450	300	450	450	0.55	0.4	0.55	0.55	120
3	0.7	0.6	0.6	0.6	480	400	480	480	0.7	1	0.7	0.70	50
4	0.7	0.68	0.68	0.68	480	400	488	488	0.7	1	5	12.45	50

Table 5.24. Main physical and chemical features for the example river reaches. Units: Q (m^3/s), C (mg/l), TOC (mg/l) and h (m).

Reaches 3 and 4 are an only river part, in fact. The use return reach (3), has been divided in two in order to include all the physical and chemical variations due to the water returns. In a first step the natural flow, salinity and TOC increase is included and, in a second step, the returned flow and its corresponding mixture with the water in the river.

In order to get an immediate vision of the flows behaviour, they have been represented in Figure 5.23: flows in the real and exploitation states are equal, the flow of the objective state is higher than the real flow in some stretches and it is reached in the last part of the river.

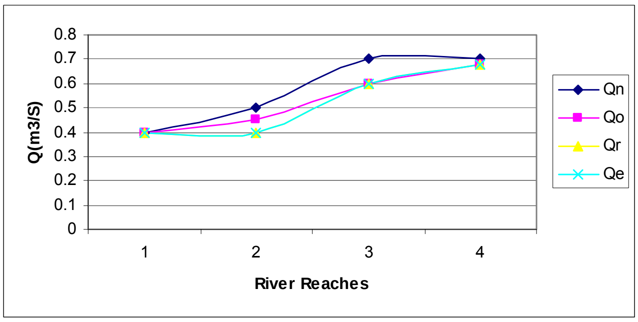


Figure 5.23. Flows along the river.

pot				IM				OM			
$B_{p,NS}$	$B_{p,OS}$	$B_{p,RS}$	$B_{p,ES}$	$B_{IM,NS}$	$B_{IM,OS}$	$B_{IM,RS}$	$B_{IM,ES}$	$B_{OM,NS}$	$B_{OM,OS}$	$B_{OM,RS}$	$B_{OM,ES}$
706.3	706	706	706	6.4	0.0	6.4	6.4	-2.6	0.0	-2.6	-2.6
343.4	309	275	275	4.6	14.9	3.7	3.7	-3.2	-11.7	-2.6	-2.6
0.0	0	0	0	0.0	0.0	1.4	1.4	0.0	0.0	-111.4	-304.4
343.4	334	334	334	1753	1720	1701	1701	21.2	29.4	146.8	365.5
1,393	1,349	1,315	1,315	1,764	1,735	1,713	1,713	15.3	17.7	30.2	56.0

Table 5.25. Results for the potential, inorganic matter (IM) and organic matter (OM) components. Units: kJ/yr.

The calculated exergy components are shown in Table 5.25. Last row indicates the exergy degradation along the river course for each of the river states. For example, the potential exergy loss along the river in its natural state is 1,393 kJ/l, while the same magnitude for the real state is 1,315 kJ/l (the same value than for the exploitation state, since both the flow and the altitude are equal in the real and exploitation states). Similar situation is found when the IM is studied: the inorganic matter exergy component lost along the river is 1,764 kJ/l for the natural state and lightly lower for the other states However, exergy degradation due to OM is much higher in the exploitation state, because of its high TOC content.

These values are used to obtain the previously defined water costs (SC, EC and RRC) according to the procedure explained in section 5.9. The obtained IRC is compared to the degradation due to water uses, as proposed in Eq. 5.25.

In this paragraph, the mentioned degradation due to water uses is presented. An only use is considered in this first case study. The demanded water, Q_{catch}=0.1 m^3/s, is taken from reach number 2 and is returned at the end of reach 3 (Q_{ret}=0.08 m^3/s). The use means an increase of 100 mg/l in the salinity and 100 mg/l in the TOC, corresponding to a conventional domestic use. The background data and the results for the degradation provoked by the water use in exergy terms are shown in Table 5.26; where the subindex *cat* stands for catchment and *ret* for return. H_{cat} and H_{ret} are defined by the point where water is taken from and returned to the river; C_{cat} and TOC_{cat} are determined by the catchment position as well. Finally, C_{ret} and TOC_{ret} depend on the variation of the quality defined by the given water use.

	pot					IM						OM						
Reach	H_{cat}	H_{ret}	$B_{p,cat}$	$B_{p,ret}$	dB_p	C_{cat}	C_{ret}	$b_{IM,cat}$	$b_{IM,ret}$	$B_{IM,cat}$	$B_{IM,ret}$	dB_{IM}	TOC_{cat}	TOC_{ret}	$b_{OM,cat}$	$b_{OM,ret}$	$B_{OM,cat}$	$B_{OM,ret}$	dB_{OM}
2-3(4)	120	50	117.7	39.2	78	450	488	2.51	2.5	251	200	51.2	0.55	12.45	0.024	0.538	2.375	43	-41

Table 5.26. Water uses characterization and results for the degradation due to water use (catchment and return in two different water reaches). Units: kJ/yr.

Table 5.27 summarizes the water costs derived from Table 5.25. The three components (potential, salts and organic matter) and the three costs (SC, EC and RRC) conforming the IRC are given separately. According to Eq. 5.25, the degradation of the river calculated from the uses effect should be equivalent to the IRC. Same table shows that the results coincide.

	SC	**EC**	**RRC**	**IRC**	**ΔB_{use}**
pot.	0.0	34.3	44.1	**78.48**	**78.48**
salts	0.00	22.14	29.07	**51.22**	**51.22**
OM	-25.73	-12.52	-2.38	**-40.63**	**-40.63**

Table 5.27. Results of SC, EC and RRC and their addition, the IRC, for the river in the analyzed uses situation and comparison of results: IRC and ΔB_{use}.

The validity of the starting hypothesis, postulating the equivalence between the IRC and the degradation due to water uses has been proved for this case study where only one water use is considered.

In addition to that, it has been considered interesting to show the desegregation of the obtained degradation values into their quantity and quality component. In the following, tables are structured to show such that detail for each component, the separation into quantity and quality has been carried out. First, in the river profiles procedure and, secondly, in the effect produced by the water uses:

$$\text{Pot/IM/OM component}\begin{cases}\text{Quantity and Quality for the river profile (SC, EC, RRC)}\\ \text{Quantity and Quality for the use}\end{cases}$$

The split equation for quantity and quality was already introduced in section 5.8 (Eq. 5.3). For the sake of clarity, it is rewritten here (Eq. 5.27). Depending on the calculated cost, the considered initial and final states are different.

Eq. 5.27. $$\Delta\mathrm{B} = \Delta\mathrm{B}_{\mathrm{t}} + \Delta\mathrm{B}_{\mathrm{l}} = (Q_{final} - Q_{initial})\cdot\Delta\mathrm{b}_{\mathrm{final}} + \mathrm{Q}_{initial}(\Delta\mathrm{b}_{\mathrm{final}} - \Delta\mathrm{b}_{\mathrm{initial}})$$

Results for the potential, IM and OM components are shown in the following tables. The IRC calculated by means of the river profiles, and the ΔB produced by water uses are alternatively shown.

a. Potential component

For each of the defined water cost (SC, EC and RRC), its quantity and quality components are presented in consecutive columns, adapting Eq. 5.27 to the proper exergy gap.

POTENTIAL COMPONENT

River profile

	SC		EC		RRC	
	Quantity $dQ_{RS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{RS}-db_{ES})$	Quantity $dQ_{OS-RS}\,db_{RS}$	Quality $Q_{RS}\cdot(db_{OS}-db_{RS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0	0.00	0	0.00	0
2	0	0	3.50	0	3.50	0
3	0	0	0.00	0	0.00	0
4	0	0	0.00	0	1.00	0
	0	0	34.34	0	44.15	0
	0		34.34		44.15	

Quantity	Quality
78.48	0
IRC_{pot}=	78.48

Table 5.28. Disaggregation in quantity and quality for the water costs calculated for the potential component, by means of the river profiles procedure.

Uses

Quantity	Quality
b·dQ	Q·db
23.54	54.936
$\Delta B_{use,pot}$=	78.48

Table 5.29. Degradation provoked by water uses.

The quality component of the SC_{pot} is zero for all the IRC components (as it is well known). The mass loss implies a quantity component of 78.48 kJ/l, due to the EC and the RRC, whose contributions are quite similar in this case. Table 5.28 shows the river profile calculations.

Degradation along the river provoked by the water use (Table 5.29) and whose characteristics are shown in Table 5.26, has been calculated applying Eq. 5.28

Eq. 5.28. $$\Delta B_{uses} = \Delta B_{uses,t} + \Delta B_{uses,l} = b_{cat} \cdot (Q_{cat} - Q_{ret}) + Q_{ret} \cdot (b_{cat} - b_{ret})$$

Where *cat* stands for "catchment" and *ret* for "return".

It can be observer that, IRC_{pot}, and $\Delta B_{use,pot}$ are equal, although their quantity and quality components are not. The quantity component is not zero in this case because there exits a physical water consumption in the use.

b. Inorganic matter component

The structure of the table is the same as in point a, where the potential component was studied. Table 5.30 shows the disaggregation in quantity and quality for the water costs calculated for the inorganic matter component, by means of the river profiles procedure; Table 5.31 presents the disaggregation in quantity and quality of the potential component, for the degradation provoked by water uses (inorganic matter component). Units are kJ/l.

CHEMICAL (IM) COMPONENT

River profile

	SC		EC		RRC	
	Quantity $dQ_{RS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{RS}-db_{ES})$	Quantity $dQ_{OS-RS}\, db_{RS}$	Quality $Q_{RS}\cdot(db_{OS}-db_{RS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0	0.0000	-0.0064	0.0000	0.0064
2	0	0	0.0017	0.0095	0.0005	-0.0107
3	0	0	0.0000	-0.0014	0.0000	0.0000
4	0	0	0.0000	0.0188	0.0501	-0.0171
	0.00	0.00	1.66	20.49	50.56	-21.49
	0.00		22.14		29.07	

Quantity	Quality
52.21	-1.00
IRC_{IM}=	51.22

Table 5.30. Water costs calculated for the inorganic matter component, by means of the river profiles procedure.

Uses

Quantity	Quality
b·dQ	Q·db
50.28	0.936
$\Delta B_{use,IM}$=	51.22

Table 5.31. Degradation provoked by water uses.

It can be clearly observed a different quantity-quality distribution between the two followed procedures.

c. Organic matter component

It can be observed that, although the final result is the same (see Table 5.27) the quality and quality contributions are different depending on the calculation procedure (IRC or ΔB_{use}), as indicated in Table 5.32 and Table 5.33.

An alternative situation that could happen is the catchment and return of the used water in the same river reach. It is represented in Figure 5.24. In this case, the effect of the use can not be observed because Qual2kW provides only an average flow and quality values for the reach, which correspond to the end of the reach. This is one of the main disadvantages for PH: if not enough stretches are considering in each water use, the provoked effects by the use cannot be appreciated in the exergy river profiles.

CHEMICAL (OM) COMPONENT

River profile

	SC		EC		RRC	
	Quantity $dQ_{RS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{RS}-db_{ES})$	Quantity $dQ_{OS-RS}\,db_{RS}$	Quality $Q_{RS}\cdot(db_{OS}-db_{RS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0.0000	0.0000	0.0026	0.0000	-0,0026
2	0	0.0000	-0.0013	-0.0078	-0.0003	0,0087
3	0	0.1930	0.0000	0.1114	0.0000	0,0000
4	0	-0.2187	0.0000	-0.1175	0.0006	-0,0088
	0.00	-25.73	-1.30	-11.23	0.28	-2,66
	-25.73		-12.52		-2.38	

Quantity	Quality
-1.01	-39.61
IRC_{OM}=	-40.63

Table 5.32. Dissagregation in quantity and quality for the water costs calculated for the inorganic matter component, by means of the river profiles procedure.

Uses

Quantity	Quality
b·dQ	Q·db
0.48	-41.10
$\Delta B_{use,OM}$=	-40.63

Table 5.33. Degradation provoked by water uses.

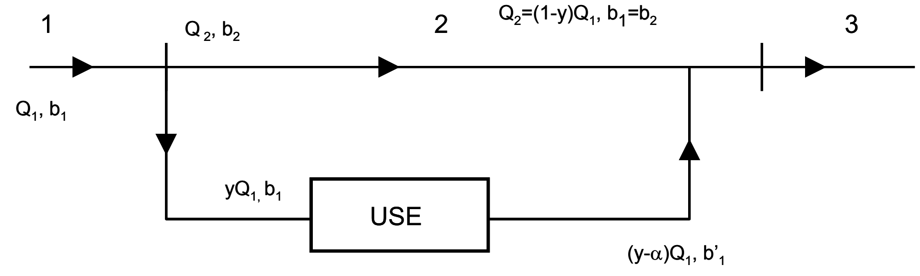


Figure 5.24. Catchment and return in the same river reach (y represents the catchment fraction and α stands for the return fraction).

5.13.1.2. Flow input from a different source, after being used.

A relatively common situation is the contribution to a river of a return flow coming from a foreign source (Figure 5.25). It happens, for example when an urban nucleus takes water from aquifers or from a water transfer and, after its treatment in a local

WWTP, water is dumped into a given watershed. In consequence, the real flow of the river is higher than the natural expected flow. This circumstance could be observed when the exergy profiles of the river present an anomalous behaviour.

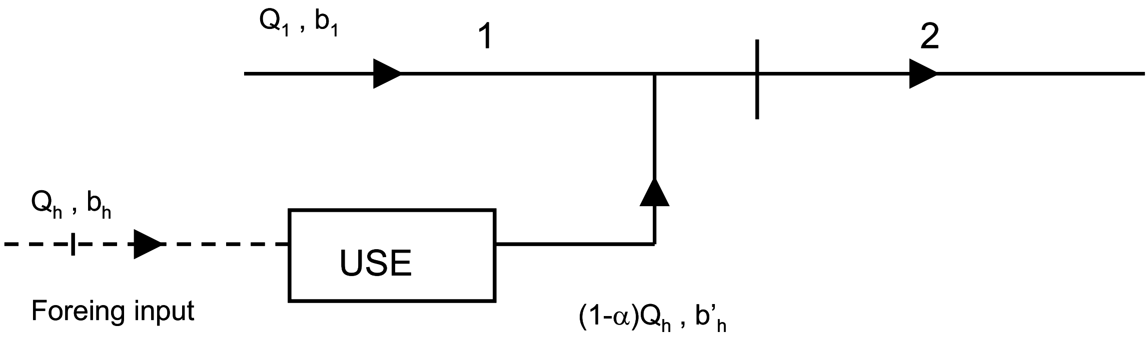


Figure 5.25. Flow input from a different source (other headwater) after being used.

A certain amount of water is taken from a foreign source. Whatever its origin, the important point for this analysis is the knowledge of its amount and quality when it arrives at the considered river. In this example, an input flow of 0.08 m^3/s is considered, with the quality described in Table 5.36.

Tramo	Qn	Qo	Qr	Qe	Cn	Co	Cr	Ce	TOCn	TOCo	TOCr	TOCe	dH	H
1	0.4	0.4	0.4	0.4	400	300	400	400	0.4	0.4	0.4	0.4	180	300
2	0.5	0.55	0.5	0.5	450	300	450	450	0.55	0.4	0.55	0.55	70	120
3	0.7	0.7	0.7	0.7	480	400	480	480	0.7	1	0.7	0.70	0	50
4	0.7	0.78	0.78	0.78	480	400	487	487	0.7	1	5	10.94	50	50

Table 5.34. Main physical and chemical features for the example river reaches. Units: Q (m^3/s), C (mg/l), TOC (mg/l) and H (m).

pot				IM				OM			
Bpn	Bpo	Bpr	Bpe	Bsn	Bso	Bsr	Bse	Bon	Boo	Bor	Boe
706.3	706.3	706.3	706.3	6.360	0.000	6.360	6.360	-2.591	0.000	-2.591	-2.591
343.4	377.7	343.4	343.4	4.650	18.205	4.650	4.650	-3.239	-14.252	-3.239	-3.239
0.0	0.0	0.0	0.0	0.00	0.00	1.68	1.68	0.000	0.000	-129.994	-309.599
343.4	382.6	382.6	382.6	1753.29	1973.32	1951.79	1951.79	21.162	33.686	168.431	368.562
1.393	1.467	1.432	1.432	1764.30	1991.53	1964.48	1964.48	15.33	19.43	32.61	53.13

Table 5.35. Results for the potential, inorganic matter (IM) and organic matter (OM) components. Units: kJ/yr.

	pot					IM							OM						
Reach	Hc	Hr	Bpc	Bpr	dBp	Cc	Cr	bsc	bsr	Bsc	Bsr	dBs	TOCc	TOCr	boc	bor	Boc	Bor	dBo
2-3	120	50	0.00	39.24	-39.24	450	487	2.514	2.502	0.00	200.2	-200.2	0.55	10.94	0.024	0.473	0	37.80	-37.80

Table 5.36. Water uses characterization and results for the degradation due to water use (catchment and return in two different water reaches). Units: kJ/yr.

It can be observed that, in this situation, the results for the different exergy components are always negative, since the flow in the catchment (from the considered watershed perspective) is zero.

IRC is calculated as addition of the different costs and results are shown in Table 5.37.

	SC	EC	RRC	IRC	ΔB_{use}
pot.	0.0	-527.4	655.3	127.92	127.9
IM	-4.70	-2088.96	2196.99	103.32	103.32
OM	202	-387.93	34.44	-151.57	-151.57

Table 5.37. Results of SC, EC and RRC and their addition, the IRC, for the river in the analyzed uses situation and comparison of results: IRC and $\Delta B_{use.}$

a. Potential component

As in the previous examples, the potential quantity component in the river is zero, but it has a value when the analysis is focussed on the degradation due to water use because the catchment and return points are different. The potential IRC is usually positive, since water is taken upstream. In this case, on the contrary, it presents a negative value because the input of potential exergy is taken as zero –see Table 5.36- . The reason is that it is out of the area of study, the watershed.

	POTENTIAL COMPONENT					
	SC		EC		RRC	
	Quantity $dQ_{RS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{RS}-db_{ES})$	Quantity $dQ_{OS-RS}\,db_{RS}$	Quality $Q_{RS}\cdot(db_{OS}-db_{RS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0	0.0000	0	0,0000	0
2	0	0	3.5000	0	-3,5000	0
3	0	0	0.0000	0	0,0000	0
4	0	0	0.0000	0	-4,0000	0
	0.00	0.00	34.34	0.00	-73,58	0,00
	0.00		34.34		-73.58	
		Quantity		Quality		
		-39.24		0.00		
		IRCpot=		-39.24		

Table 5.38. Disaggregation in quantity and quality for the water costs calculated for the potential component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
-94.18	54.936
$\Delta \mathbf{B}_{\mathbf{use,pot}}$	-39.24

Table 5.39. Degradation provoked by water uses.

b. Inorganic matter component

As well as in the potential component, the exergy of the input flow is zero. In consequence, the resulting IRC is clearly negative and, correspondingly, the main contribution corresponds to the quantity component (high importance of the Q factor).

	INORGANIC MATTER					
	SC		EC		RRC	
	Quantity $dQ_{RS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{RS}-db_{ES})$	Quantity $dQ_{OS-RS}\,db_{RS}$	Quality $Q_{RS}\cdot(db_{OS}-db_{RS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0	0.0000	-0.0064	0,0000	0,0064
2	0	0	0.0017	0.0119	-0,0005	-0,0131
3	0	0	0.0000	-0.0017	0,0000	0,0000
4	0	0	0.0000	0.0215	-0,2004	-0,0197
	0.00	0.00	1.66	25.39	-200,84	-26,39
	0.00		27.04		-227.23	

Quantity	Quality
-199.19	-1.00
IRC_{IM}=	-200.18

Table 5.40. Disaggregation in quantity and quality for the water costs calculate for the potential component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
-201.12	0.94
$\Delta B_{use,IM}$	-200.18

Table 5.41. Degradation provoked by water uses.

c. Organic matter component

Input exergy keeps being cero, so it leads to a negative final value of the IRC and the ΔB provoked by the use. The quality component, however, is the most important one in this case. It is due to the high exergy content of the organic matter that can be specially appreciated in the third (and its added fourth) reaches.

	ORGANIC MATTER COMPONENT					
	SC		EC		RRC	
	Quantity $dQ_{RS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{RS}-db_{ES})$	Quantity $dQ_{OS-RS}\,db_{RS}$	Quality $Q_{RS}\cdot(db_{OS}-db_{RS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0.0000	0.0000	0.0026	0,0000	-0,0026
2	0	0.0000	-0.0013	-0.0097	0,0003	0,0107
3	0	0.1796	0.0000	0.1300	0,0000	0,0000
4	0	-0.2001	0.0000	-0.1347	-0,0024	-0,0101
	0.00	-20.53	-1.30	-11.88	-2,09	-2,01
	-20.53		-13.17		-4.10	

Quantity	Quality
-3.39	-34.41
IRC_{IM}=	-37.80

Table 5.42. Dissagregation in quantity and quality for the water costs calculated for the potential component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
-1.90	-35.90
$\Delta B_{use,OM}$	-37.80

Table 5.43. Degradation provoked by water uses.

The situation of a flow being taken from an external source and returned afterwards to the studied river, also fits with the hypothesis of equal degradation attending to the river course on the one hand, and to de degradation provoked by the use on the other hand.

5.13.1.3. Catchment in the river and return (after used) to a different watershed

The opposite situation –the catchment of water in a given river to be moved to a different watershed- has also to be considered. In this situation, as shown in Figure 5.26, all the exergy contained in caught water is lost by the origin basin.

In the calculation procedure, the final exergy assigned to the missed flow is zero because it goes out of the studied watershed.

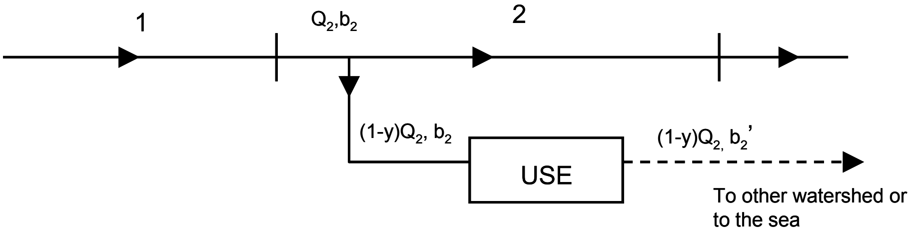


Figure 5.26. Catchment in the river and return (after used) in a different watershed.

Summary of the example data are presented in Table 5.44, and their corresponding exergy values can be seen in Table 5.45 for the potential, the inorganic and the organic contents.

Tramo	Qn	Qo	Qr	Qe	Cn	Co	Cr	Ce	TOCn	TOCo	TOCr	TOCe	dH	H
1	0.4	0.4	0.4	0.4	400	300	400	400	0.4	0.4	0.4	0.4	180	300
2	0.5	0.45	0.4	0.4	450	300	450	450	0.55	0.4	0.55	0.55	70	120
3	0.7	0.6	0.6	0.6	480	400	480	480	0.7	1	0.7	0.70	0	50
4	0.7	0.6	0.6	0.6	480	400	480	480	0.7	1	5	0.70	50	50

Table 5.44. Main physical and chemical features for the example river reaches. Units: Q (m^3/s), C (mg/l), TOC (mg/l) and H (m).

pot				IM				OM			
Bpn	Bpo	Bpr	Bpe	Bsn	Bso	Bsr	Bse	Bon	Boo	Bor	Boe
706.3	706.3	706.3	706.3	6.360	0.000	6.360	6.360	-2.591	0.000	-2.591	-2.591
343.4	309.0	274.7	274.7	4.650	14.895	3.720	3.720	-3.239	-11.661	-2.591	-2.591
0.0	0.0	0.0	0.0	0.00	0.00	1.44	1.44	0.000	0.000	-111.424	0.000
343.4	294.3	294.3	294.3	1753.29	1517.94	1501.38	1501.38	21.162	25.913	129.563	18.139

Table 5.45. Results for the potential, inorganic matter (IM) and organic matter (OM) components. Units: kJ/l.

Regarding the water use, in this example, it is assumed that 0.1 m^3/s are taken from the river course and, after being used, they are released out of the area of study. In consequence, as mentioned, the output exergies are ignored. That is, it can be understood as exergy lost in the watershed. Figures defining the water use are given in Table 5.46. As a clear difference with the previous case, it can be seen in Table 5.46 that all the exergy differences are positive

	pot					IM							OM						
Reach	Hc	Hr	Bpc	Bpr	dBp	Cc	Cr	bsc	bsr	Bsc	Bsr	dBs	TOCc	TOCr	boc	bor	Boc	Bor	dBo
2-3	120	50	117.7	0.00	117.7	450	480	2.51	2.5	251.4	0.000	251.4	0.550	0.700	0.0	0.030	2.375	0.00	2.38

Table 5.46. Water uses characterization and results for the degradation due to water use (catchment and return in two different water reaches). Units: kJ/yr.

The summary of results is given in Table 5.47, where it can be seen that the hypothesis of equivalence among the two calculation ways is precise, as well. The detailed calculation of the exergy variation along the river can be found in next tables.

	SC	**EC**	**RRC**	**IRC**	**ΔB_{use}**
pot.	0.0	34.3	83.4	**117.72**	**117.72**
salts	0.00	19.94	231.47	**251.40**	**251.40**
OM	0.00	1.30	1.08	**2.38**	**2.38**

Table 5.47. Results of SC, EC and RRC and their addition, the IRC, for the river in the analyzed uses situation and comparison of results: IRC and ΔB_{use}.

Figures for the potential, salts and organic matter component are given separately, as it was done in the previous cases.

a. Potential component

Flow lost will always mean positive value of the exergy, since exergy assigned to the return is zero. Effectively, it can be seen in the obtained result: 117.72 kJ/l (see Table 5.48 and Table 5.49). The quality contribution is clearly zero because the potential component is considered (h constant).

b. Inorganic matter component

As above explained, the high quantity positive contribution is due to the lost flow; and the quality factor in the use (Table 5.51) comes also from the lack of returned flow. The positive obtained value would mean, in a real situation, that restoration measures will be needed to meet the established objectives.

In the river stream calculation, Table 5.50, the small value of the quality component, is due to the small defined salinity increase.

	POTENTIAL COMPONENT					
	SC		EC		RRC	
	Quantity $dQ_{PS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{PS}-db_{ES})$	Quantity dQ_{OS-FS} db_{FS}	Quality $Q_{FS}\cdot(db_{OS}-db_{FS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0	0	0	0	0
2	0	0	3.5	0	3.5	0
3	0	0	0	0	0	0
4	0	0	0	0	5	0
	0	0	34.33	0	83.38	0
	0		34.335		83.39	

Quantity	Quality
117.72	0
IRC_{pot}=	117.72

Table 5.48. Disaggregation in quantity and quality for the water costs calculated for the potential component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
117.72	0
ΔBuse,pot	117.72

Table 5.49. Degradation provoked by water uses.

	INORGANIC MATTER					
	SC		EC		RRC	
	Quantity $dQ_{PS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{PS}-db_{ES})$	Quantity dQ_{OS-FS} db_{FS}	Quality $Q_{FS}\cdot(db_{OS}-db_{FS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0	0	-0.00636	0	000636
2	0	0	0.001655	0.00952	0.000465	-0.01071
3	0	0	0	-0.00144	0	0
4	0	0	0	0.01656	0.25047	-0.01512
	0	0	1.655	18.28	250,935	-19,47
	0		19.935		231.47	

Quantity	Quality
252.59	-1.19
IRC_{IM}=	251.40

Table 5.50. Water costs calculated for the potential component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
251.40	0
$\Delta B_{use,IM}$	251.40

Table 5.51. Degradati on provoked by water uses.

c. Organic matter component

The organic matter component present, as expected, the same behaviour as the previous studied components. Results for the river stream are given in Table 5.52. Final exergy variation is 2.38 kJ/l, which in the use calculation (Table 5.53) completely comes from the quantity component, as expected because of the lost flow.

	ORGANIC MATTER COMPONENT					
	SC		EC		RRC	
	Quantity $dQ_{PS-ES} \cdot db_{ES}$	Quality $Q_{ES} \cdot (db_{PS}-db_{ES})$	Quantity dQ_{OS-FS} db_{FS}	Quality $Q_{FS} \cdot (db_{OS}-db_{FS})$	Quantity $dQ_{NS-OS} \cdot db_{OS}$	Quality $Q_{OS} \cdot (db_{NS}-db_{OS})$
1	0	0	0	0.00259	0	-0.00259125
2	0	0	-0.00129	-0.00777	-0.0003239	0.008745469
3	0	-0.11142	0	0.11142	0	0
4	0	0.11142	0	-0.10365	0.00302312	-0.00777375
	0	0	-1.30	2.59	2.70	-1.62
	0		1.29		1.08	

Quantity	Quality
1.40	0.97
IRC$_{OM}$=	2.38

Table 5.52. Water costs calculated for the potential component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
2.38	0
ΔB$_{use,OM}$	2.38

Table 5.53. Degradation provoked by water uses.

5.13.1.4. Several water uses along the river flow.

In a wider analysis, attending to real situation in rivers, different uses happening along the river have to be considered (Figure 5.27).

The catchment corresponding use 1 is taken from reach 2. Return is calculated in two steps: first, the natural flow, salinity and organic matter variation is introduced and, secondly, the returned flow with its corresponding mixture with the river (reaches 3 and 4 for the first use and reaches 7 and 8 for the second use).

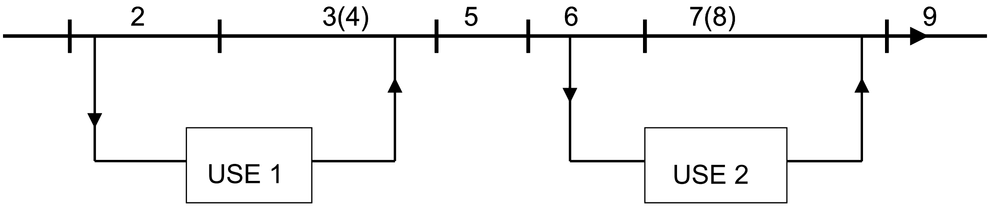


Figure 5.27. Successive catchment and return along the river

Data considered in this example are shown in Table 5.54. Two water catchment and their corresponding returns are considered. First catchment is 0.1 m^3/s and the return is 0.08 m^3/s. In the second one, 0.2 m^3/s are taken and 0.18 m^3/s is the return.

Tramo	Qn	Qo	Qr	Qe	Cn	Co	Cr	Ce	TOCn	TOCo	TOCr	TOCe	dH	H
1	0.4	0.4	0.4	0.4	400	300	400	400	0.4	0.4	0.4	0.4	90	300
2	0.5	0.45	0.4	0.4	450	300	450	450	0.55	0.4	0.55	0.55	20	210
3	0.7	0.6	0.6	0.6	480	400	480	480	0.7	1	0.7	0.70	0	190
4	0.7	0.68	0.68	0.68	480	400	488.2	488.2	0.7	1	5	12.45	40	190
5	0.8	0.8	0.78	0.78	520	400	528.2	520.0	0.8	1	5.1	0.80	40	150
6	1	0.8	0.78	0.78	550	450	558.2	550.0	0.9	1	5.2	0.90	28	110
7	1.3	0.85	1.08	1.08	570	450	578.2	570.0	1	1.25	5.3	1.00	0	82
8	1.3	0.85	1.26	1.26	570	450	595.7	595.7	1	1.25	10.0	15.27	32	82
9	1.8	0.9	1.76	1.76	610	500	635.7	610.0	1.1	1.5	10.1	1.10	50	50

Table 5.54. Main physical and chemical features for the example river reaches. Units: Q (m^3/s), C (mg/l), TOC (mg/l) and H (m).

A very important issue about the Table 5.54 are the numbers in bold. They informed about the characteristics of the water taken for the second use. In other to get the equivalence between both calculation procedures (river degradation and degradation due to water use), the parameters defining the water for the second use, must be the natural state ones. It means, without any previous pollution, i.e., omitting the existence of the first water use.

Although, as it will be seen in the following, the equivalence will be proved, the inclusion of the natural state parameters in the exploitation state, ignoring the first water use, needs a further consideration. Water catchments, whatever the point they are taken from, account for all the previous upstream contamination. In order to observe the real stream behavior, considering any water use as starting from the natural river has none sense.

Spite of the explanation, for the sake of completeness, the example is going to be completely explained. 0 summarizes the obtained results for the exergy, by components.

pot				IM				OM			
Bpn	Bpo	Bpr	Bpe	Bsn	Bso	Bsr	Bse	Bon	Boo	Bor	Boe
353.2	353.2	353.2	353.2	6.360	0.000	6.360	6.360	-2.591	0.000	-2.591	-2.591
98.1	88.3	78.5	78.5	4.650	14.895	3.720	3.720	-3.239	-11.661	-2.591	-2.591
0.0	0.0	0.0	0.0	0.00	0.00	1.50	1.50	0.000	0.000	-111.424	-304.396
274.7	266.8	266.8	266.8	8.54	0.00	8.30	6.60	-3.023	0.000	-2.937	342.045
313.9	313.9	306.1	306.1	7.20	12.72	6.94	7.02	-3.455	0.000	-3.369	-3.369
274.7	219.7	214.3	214.3	5.90	0.00	4.68	4.60	-4.319	-8.638	-3.369	-3.369
0.0	0.0	0.0	0.0	0.00	0.00	5.51	8.21	0.000	0.000	-219.220	-665.655
408.1	266.8	395.5	395.5	15.34	13.09	14.62	5.29	-5.614	-9.177	-5.442	771.156
882.9	441.5	863.3	863.3	4438.44	2248.74	4326.78	4339.81	85.511	58.303	767.701	83.611
2606	1950	2478	2478	4486.4	2289.4	4378.4	4383.1	63.26969	28.82766	416.7594	214.8415

Table 5.55. Results for the potential, inorganic matter (IM) and organic matter (OM) components. Units: kJ/yr.

	POT					IM							OM						
Reach	Hc	Hr	Bpc	Bpr	dBp	Cc	Cr	bsc	bsr	Bsc	Bsr	dBs	TOCc	TOCr	boc	bor	Boc	Bor	dBo
2-3(4)	210	190	206.01	149.11	56.90	450	488.2	2.5140	2.5022	251.40	200.18	51.22	0.55	12.45	0.0238	0.5376	2.375	43.00	-40.63

Reach	Hc	Hr	Bpc	Bpr	dBp	Cc	Cr	bsc	bsr	Bsc	Bsr	dBs	TOCc	TOCr	boc	bor	Boc	Bor	dBo
6-7(8)	110	82	215.82	144.80	71.02	550.0	595.7	2.4835	2.4700	496.70	444.60	52.10	0.90	15.27	0.0389	0.7	7.774	118.72	-110.94

Table 5.56. Water uses characterization and results for the degradation due to water use (consecutive water uses). Units: kJ/yr.

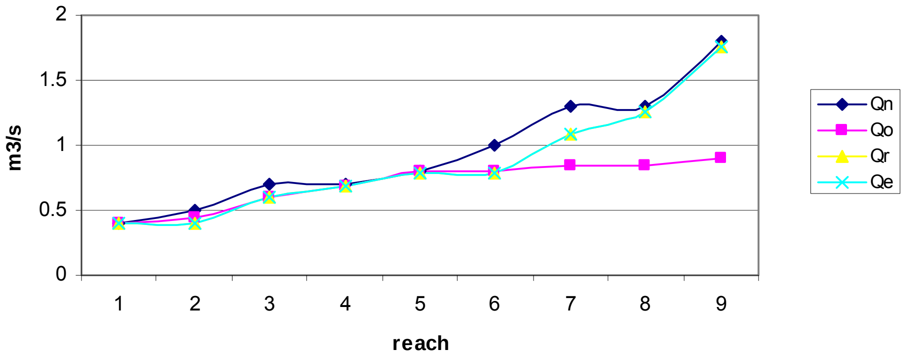


Figure 5.28. Flows along the river.

The IRC, calculated by means of river profiles. is detailed in Table 5.57. As in the previous case, potential, salts and organic matter component are given separately.

The inclusion of a second water use following the first one should lead to higher exergy gaps and, in consequence, to higher degradation.

	SC	EC	RRC	IRC	ΔB_{use}
pot.	0.0	-527.4	655.3	127.92	127.9
salts	-4.70	-2088.96	2196.99	103.32	103.32
OM	202	-387.93	34.44	-151.57	-151.57

Table 5.57. Results of SC, EC and RRC and their addition, the IRC, for the river in the analyzed uses situation.

Same degradation along the river has been calculated in terms of ΔB originated by the use of water and, same results are obtained.

a. Potential component

As it can be seen in Table 5.58, the main exergy variation appears in the last reach of the river, when it flows into the sea: -43 kJ/l in the EC and 45 kJ/l in the RRC (quantity components of the costs). The sign minus in the EC means that $Q_{RS}>Q_{OS}$, so no restoration measurements will be needed. As repeteadly indicated, the quality component is zero because Δh=0.

The real loss due to the use because of the altitude differences between the catchment and the return points, is reproduced in Table 5.59, a water catchment that is not returned again to the basin.

	POTENTIAL COMPONENT					
	SC		EC		RRC	
	Quantity $dQ_{RS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{RS}-db_{ES})$	Quantity $dQ_{OS-RS}\,db_{RS}$	Quality $Q_{RS}\cdot(db_{OS}-db_{RS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0	0.00	0	0.00	0
2	0	0	1.00	0	1.00	0
3	0	0	0.00	0	0.00	0
4	0	0	0.00	0	0.80	0
5	0	0	0.80	0	0.00	0
6	0	0	0.56	0	5.60	0
7	0	0	0.00	0	0.00	0
8	0	0	-13.12	0	14.40	0
9	0	0	-43.00	0	45.00	0
	0	0	-527.39	0	655.31	0
	0				655.31	

Quantity	Quality
127.92	0
IRC_{pot}=	127.92

Table 5.58. Dissagregation in quantity and quality for the water costs calculated for the inorganic matter component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
62.78	65.14
$\Delta B_{use,pot}$	127.92

Table 5.59. Degradation provoked by water uses.

b. Inorganic matter component

In the inorganic matter component comparison, it can be appreciated that the main exergy variation is due to the quantity component (73.28 versus 30.04 kJ/l in the river -Table 5.60-; and 99.95 versus 3.37 kJ/l in the use, Table 5.61). The final degradation is -151.57 kJ/l, whatever the chosen evaluation way. This result corresponds to a couple of uses defined with a non-elevated degradation in salinity. As indicated in Table 5.56, water is taken with 450 ppm and returned with 488.2 ppm in the first used; and it has 550 ppm when it enters in the second use, which returns it with 595.7 ppm.

	INORGANIC MATTER					
	SC		EC		RRC	
	Quantity $dQ_{PS-ES} \cdot db_{ES}$	Quality $Q_{ES} \cdot (db_{PS}-db_{ES})$	Quantity dQ_{OS-FS} db_{FS}	Quality $Q_{FS} \cdot (db_{OS}-db_{FS})$	Quantity $dQ_{NS-OS} \cdot db_{OS}$	Quality $Q_{OS} \cdot (db_{NS}-db_{OS})$
1	0	0.0000	0.0000	-0.0064	0.0000	0.0064
2	0	0.0000	0.0017	0.0095	0.0005	-0.0107
3	0	0.0000	0.0000	-0.0015	0.0000	0.0000
4	0	0.0017	0.0000	-0.0083	0.0002	0.0083
5	0	-0.0001	0.0003	0.0055	0.0000	-0.0055
6	0	0.0001	0.0000	-0.0047	0.0012	0.0047
7	0	-0.0027	0.0000	-0.0055	0.0000	0.0000
8	0	0.0093	-0.0063	0.0048	0.0053	-0.0031
9	0	-0.0130	-2.1488	0.0708	2.2192	-0.0295
	0	-4.70	-2153.14	64.18	2226.42	-29.43
	-4.70		-2088.96		2196.99	

Quantity	Quality
73.28	30.04
IRCim=	103.32

Table 5.60. Dissagregation in quantity and quality for the water costs calculated for the potential component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
99.95	3.37
$\Delta B_{use,IM}$	103.32

Table 5.61. Degradation due to water uses.

c. Organic matter component

The quality component is the most important one in the organic matte analysis after the water use. In the river, the share quantity-quality is -13.6 versus -138.31 kJ/l; while in the use it is 1.25 kJ/l in quantity and -152.82 kJ/l in quality. The negative sign in the EC means that restoration measurements will be needed. However, the RRC is positive, so the OM values in the OS are good enough to reach the NS.

Until here, all the proposed examples have fit with the initial hypothesis about the equivalence between the use degradation and the corresponding exergy variation along the river. However, the case of two consecutive used need to be modified to meet the proposed equivalence.

An additional three-uses example was made and similar results with respect the two-uses case were obtained: each downstream use does not "see" the previous one. Only in that non-realistic case the equivalence between ΔB_{uses} and ΔB_{river} could be maintained. Thus, the initial hypothesis is not fulfilled and an alternative analysis (able to show the real situation on rivers) was required, since one of the main advantages of PH is that global degradation could be disaggregated among the different water users.

	ORGANIC MATTER COMPONENT					
	SC		EC		RRC	
	Quantity $dQ_{PS-ES}\cdot db_{ES}$	Quality $Q_{ES}\cdot(db_{PS}-db_{ES})$	Quantity $dQ_{OS-FS}\, db_{FS}$	Quality $Q_{FS}\cdot(db_{OS}-db_{FS})$	Quantity $dQ_{NS-OS}\cdot db_{OS}$	Quality $Q_{OS}\cdot(db_{NS}-db_{OS})$
1	0	0.0000	0.0000	0.0026	0.0000	-0.0026
2	0	0.0000	-0.0013	-0.0078	-0.0003	0.0087
3	0	0.1930	0.0000	0.1114	0.0000	0.0000
4	0	-0.3450	0.0000	0.0029	-0.0001	-0.0029
5	0	0.0000	0.0000	0.0034	0.0000	-0.0035
6	0	0.0000	-0.0002	-0.0051	-0.0009	0.0052
7	0	0.4464	0.0000	0.2192	0.0000	0.0000
8	0	-0.7766	0.0044	-0.0082	-0.0019	0.0055
9	0	0.6841	-0.0557	-0.6537	0.0428	-0.0155
	0	201.91	-52.79	-335.13	39.53	-5.09
	201.92		-387.93		34.44	

Quantity	Quality
-13.26	-138.31
IRC_{IM}=	-151.57

Table 5.62. Disaggregation in quantity and quality for the water costs calculated for the potential component, by means of the river profiles procedure.

Quantity	Quality
b·dQ	Q·db
1.25	-152.82
$\Delta B_{use,OM}$	-151.57

Table 5.63. Degradation provoked by water uses.

5.13.1.5. Summary of results and validity of the initial hypothesis.

In summary, after carefully analyze all the raising example cases, an important aspect (in addition to the particular aspects already explained in each situation) has been highlighted: the proposed hypothesis establishing the equivalence between the river profiles difference (IRC) and the degradation due to water uses (Eq. 5.25), has an important weakness. It can be only applied when the successive water uses are assumed to be independent one of the other, that is, as if the NS where always the catchment place without attending to the fact that the quality of the water taken from a downstream point is affected by the returns happened upstream.

The described situation is not feasible because water is always affected by upstream effect and this is the way in which watershed simulators work. After mature consideration, it was concluded that the initially proposed idea to allocate water costs among the user should be modified to get a proper tool for water costs allocation. However, the detailed analysis carried out is a crucial point to understand how the river-water uses dynamics works and to propose new costs allocation proposals able to meet the real available data (from sampling station or from the watersheds simulation models).

5.13.2. Water costs allocation among the different water users.

Focussing the analysis on the water uses system boundary, the degradation provoked by water uses can be defined as Eq. 5.29 shows.

Eq. 5.29.
$$\Delta B_{uses} = \sum_i \Delta B_i = \sum_i B_{i,cat} - \sum_i B_{i,ret}$$

Where *i* stands for the number of uses, and keeping in mind that it may happen that some uses can be just a return or just a catchment.

The ΔB has been defined in this way (cat-ret) because it is assumed that the quality in the return flow will be lower than the quality in the catchment ($\Delta b=b_{cat}-b_{ret}>0$). Same reasoning can be applied for the quality component in those uses where an amount of the catch flow is not returned to the same watershed ($\Delta Q=Q_{cat}-Q_{ret}>0$).

Then, Eq. 5.29 can be written and calculated by components, quantity and quality, and afterwards the contribution of each use to water quality degradation (or water loss – quality degradation-) can be used to divide the water costs among the users.

Eq. 5.30.
$$\Delta B_{uses} = \sum_i (\Delta Q \cdot b_{cat} + Q_{ret} \cdot \Delta b)_i + \sum_j (\Delta Q \cdot b_{cat} + Q_{ret} \cdot \Delta b)_j + \sum_z (\Delta Q \cdot b_{cat} + Q_{ret} \cdot \Delta b)_z$$

Where *i* represents the number of domestic water uses, *j* the number of industrial uses and *z* the number of agricultural uses.

As it can be seen in Eq. 5.30, the quantity and quality components can be independently calculated. In broad outline, the cost allocation for quantity and quality components will be different: uses that usually damage the water quality do not necessarily reduce the available amount of water.

Although the methodology for obtaining the economic cost from the exergy gaps has not been properly explained yet, a small example of economic cost allocation is develop here for the sake of completeness.

This example tries to illustrate the basic steps for the cost allocation, once the IRC has been calculated and the water uses in the area were analyzed. Table 5.64 shows the different water cost of a theoretical river basin. The cost that wants to be allocated is the EC, marked in bold.

	Economic Cost		
€/yr	t	I	tot
SC	0	15,000	15,000
EC	440,000	11,000	451,000
RRC	7,200,000	215,000	7,415,000
IRC	7,640,000	241,000	7,881,000

Table 5.64. Economic cost calculation for the IRC's components (obtained from ΔB_{river})

The exergy loss due to a water uses in the river has been calculated by applying Eq. 5.30, and that the degradation is shared as indicated in Table 5.65

	t	l
domestic	5.0%	80.0%
industry	4.0%	13.0%
agric	91.0%	7.0%

Table 5.65. Example of use degradation (obtained from ΔB_{use})

Then, the calculated economic cost could be allocated by multiplying them and their corresponding percentage. Results are shown in Table 5.66.

	EC allocation		
€/yr	t	l	tot
domestic	22,000	8,800	30,800
industry	17,600	1,430	19,030
agric	400,400	770	401,170
tot	440,000	11,000	451,000

Table 5.66. Economic EC allocation amont the different uses

Finally, it is concluded that the exergy analysis of the quantity and quality degradation due to water use can be use to allocate the calculated water cost.

5.14. Physical Hydronomics and the WFD

Again, let’s remember that the achievement of the Good Ecological State for the EU’s waters in one of the main objectives of the WFD. According to the Directive, such a GES is defined by a Chemical and an Ecological perspective, as detailed in Figure 5.29.

The approach proposed in this dissertation, as it has become apparent along this chapter, fits many of the aspects tackled by the WFD: the parameters defining the Chemical Good Ecological State (GES) on the one side, and the other physico-chemical and hydromorphological indicators, which partially define the Ecological GES, on the other side, can be analyzed from the PH perspective.

However, there are some other issues that have to be treated separately. The morphological conditions could be included in the PH analysis if they were translated into physical features, but the biological indicators need an additional study. At this development stage, PH can only consider them tangentially: for example, if a minimum amount of water flow is needed for fishes survival, such a level can be expressed as a minimum flow.

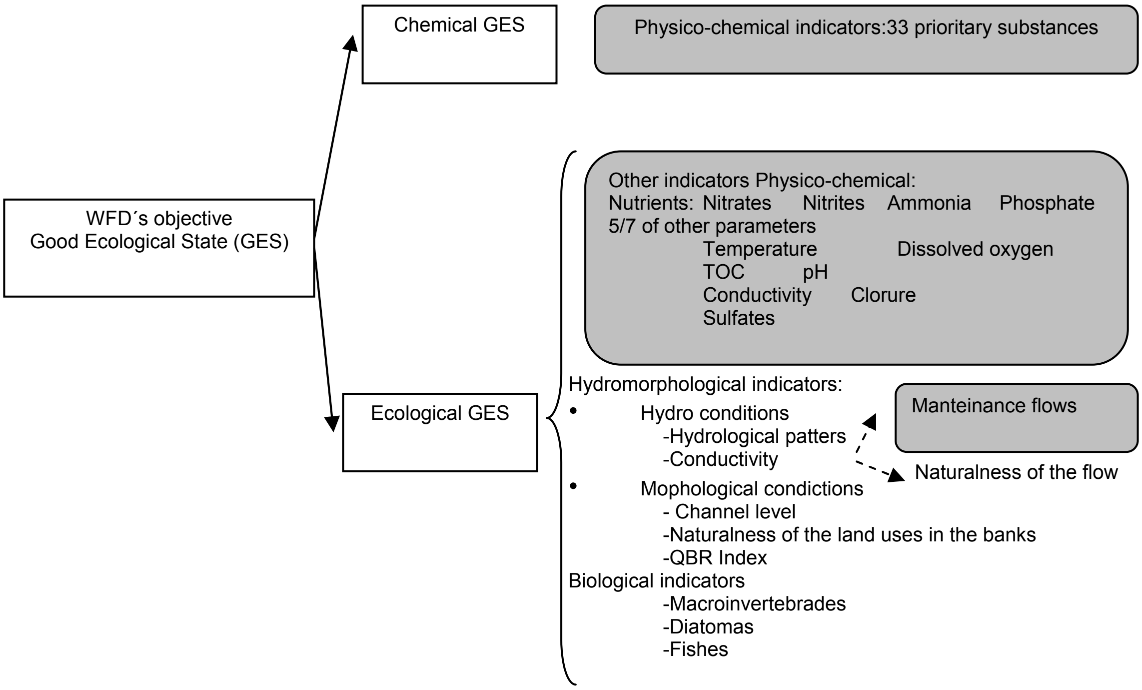


Figure 5.29. Definition of the GES required by the WFD.

5.15. Exergy cost

In the previous methodological explanation, the exergy cost has been considered from an strictly reversible thermodynamic perspective: the exergy gap between different river statuses has been calculated and, according to the definitions given for SC, EC and RRC, the minimum IRC for a watershed has been given in exergy terms.

However, as it was already indicated in Chapter 4 for the global fresh water resources analysis, the real performance of the restoration techniques has to be taken into account if the real exergy cost has to be calculated. Then, since the depuration processes that will transform a dirty river flow into a clean water course are not reversible, the extra exergy consumption of the process (due to the unavoidable irreversibility) has to be taken into account.

The proper theoretical background was given in Chapters 3 and Chapter 4. In addition to that, the unit exergy cost of desalination technologies was calculated and justified in section 4.3.2. Water desalination processes were used to calculate the exergy needed to replace the lost water within a watershed.

Aimed to a clear understanding, a schema of the PH methodology is presented in Figure 5.30

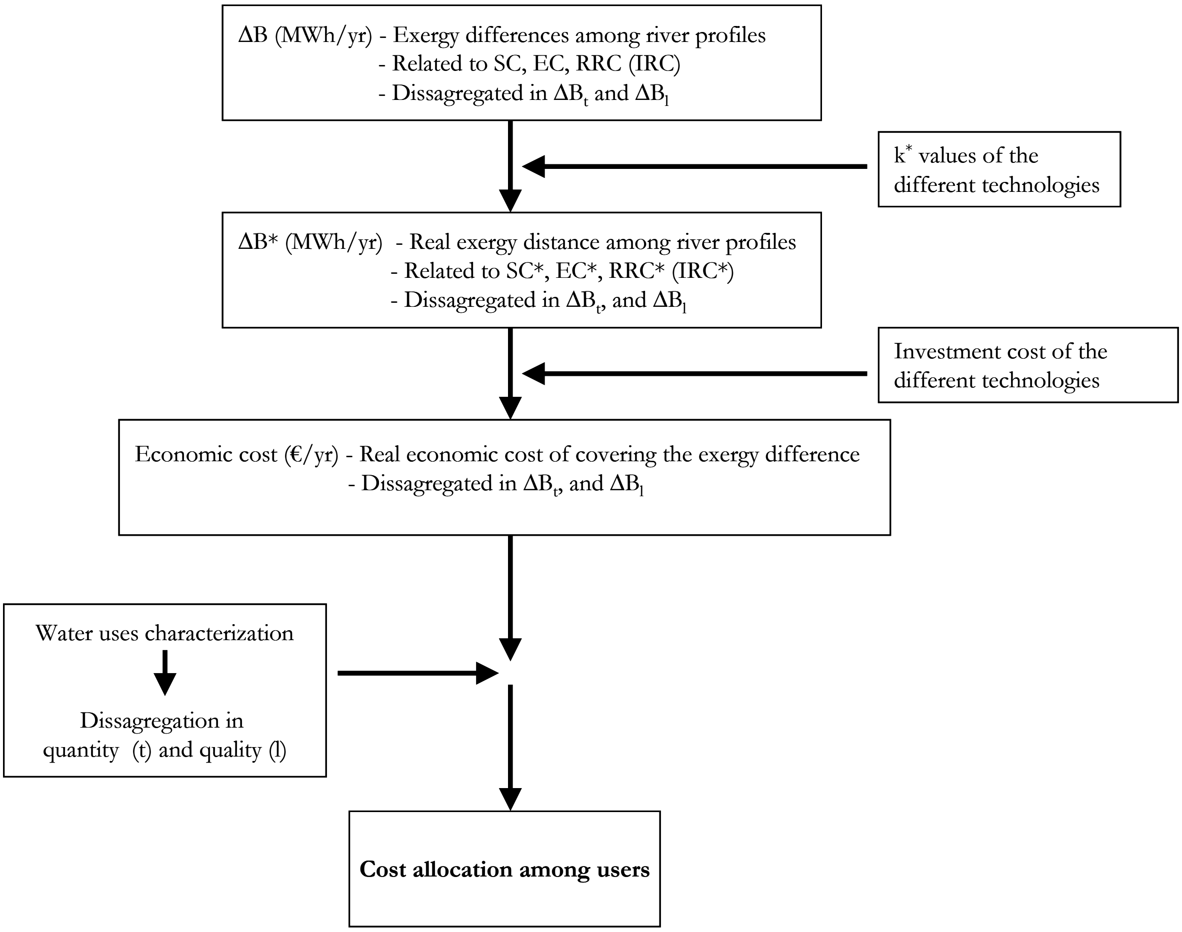


Figure 5.30. Steps of the PH methodology

Definition of the unit exergy costs of the different technologies is fundamental to obtain the real exergy restoration cost. Desalination costs were already presented in Chapter 4. At this point, the interest is focussed in calculating the replacement exergy cost to restore the water quality. Then, the depuration and cleaning water-related processes need to be considered.

Desalination technologies are needed because, in the proposed PH methodology, they are considered the base to restore the lack of water originated by its use. Where water is needed, the most suitable desalination technique is proposed to generate fresh water from the seawater. Depuration technologies are considered to restore the water quality lost due to the human uses of water. Depending on the quality of the input water and on the final requirements, WTP with more or less cleaning steps (see Chapter 2 for detail) are proposed.

The technologic process considered to treat or generate water has to be clearly defined in order to calculate its exergy cost. The boundaries of the system need to be establishes as first step. Then, any input and output flows are identified and translated into exergy units.

Energy consumption data from different real plants, as well as literature average data, have been studied in this work. Same considerations about the exergy cost of the product, $k_{product}$, and the exergy cost of the process, $k_{process}$, than in the study of the desalination processes are observed here.

5.15.1. Exergy cost of WTP

Water treatment energy requirement are driven principally by the characteristics of incoming raw water and by the distance and elevation of the treatment plant in relation to water sources and the distribution system. Lowest energy cost usually correspond to good-quality springs waters (Klein et al., 2005).

Most surface and groundwater sources require treatment to meet regulatory standards and the taste and odor preferences of the public. Some treatment plants also have unique requirements, such as the removal of industrial chemicals from well water that require more energy. In general, net energy demand is expected to change as more energy-intensive disinfection processes are used to address water quality concerns and meet increasingly stringent potable water rules under the applicable legal regulations.

In general, the available figures are always related to the investment cost of the WWTP. As an example, the data provided by the CWA regarding running plants in the region has been processed and organized to get four treatment categories:

- With waste stabilization ponds and physico-chemical in the primary, (S).
- Secondary and N-P elimination, (SN).
- Secondary and reuse, (SR).
- Secondary plus N-P elimination and reuse, (SNR).

About 100 plants have been analyzed and the obtained relations for the cost-capacity are shown in Figure 5.31.

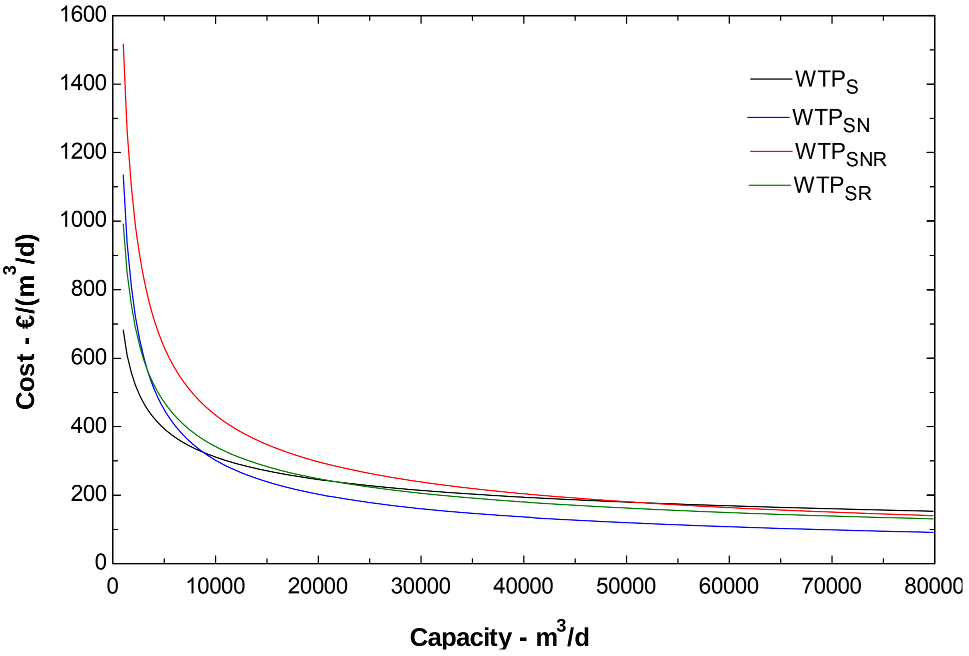


Figure 5.31. Cost vs. capacity for WWTP in Catalonia (Source: own elaboration from the data provided by the CWA, 2008c)

It can be seen that the plants with secondary treatment, N-P elimination and reuse (red line) are the most expensive ones, while the plants with secondary and N-P elimination are the cheapest when size is higher than 10,000 m^3/d. In lower sizes, the simplest installation, with waste stabilization ponds and physico-chemical in the primary, are the cheapest.

However, the data of the plants related to energy consumption are more difficult to find. Despite extensive data searches, it has been quite hard to find global studies about energy consumption in WTP. Only few studies that partially attempted to determine the exact electricity use for water treatment facilities were found. Table 5.67 summarizes average values of electricity consumption by plant size.

Plant Size (m^3/d)	**Electricity consumption (kWh/m^3)**
3,800	0.3918
19,000	0.3746
37,800	0.3714
75,700	0.3722
189,200	0.3720
378,500	0.3717

Table 5.67. Average electricity consumption by plant size (source: adapted from Klein et al., 2005).

Because of the mentioned heterogeneity in the existing WWTP, twelve real plants have been analyzed from the exergy point of view. Their operation parameters have been taken from historic running records, when available. If needed, literature values have been included in the study. It was considered as the most accurate calculation way, since each plant has different process parameters values and considering only an standard plant could be too generalist.

The process schemes of each of the studied WWTP are found in Annex F. Main treatment features are summarized in Table 5.68.

STATION	**TREATMENT**	
Begur	Active Sludge (N, P elim.)	secondary and reuse
Blanes	Active Sludge (N, P elim.)	secondary and reuse
Cadaqués	Active Sludge (N, P elim.)	tertiary
Castell d'Aro	Active Sludge (N, P elim.)	secondary
Colera	Active Sludge (N, P elim.)	tertiary
El Port de la Sel.	Active Sludge (N, P elim.)	tertiary
Empuriabrava	Natural Aireation	tertiary
L´Escala	Active Sludge (N, P elim.)	secondary and reuse
Llançà	Active Sludge (N, P elim.)	secondary and reuse
Lloret de mar	Active Sludge +Phisico-Chemical	secondary and reuse
Palamós	Active Sludge (N, P elim.)	secondary and reuse
Pals	Active Sludge (N, P elim.)	secondary and reuse

Table 5.68. Waste water treatment plant categories

It is important to highlight that the plant size (m^3 treated water/time) is independent of the percentage of substances elimination. The percentage of substances elimination depends not only on the plant performance, but also on the substances concentration of the raw water.

5.15.1.1. Flows analysis

Main flows in a WTP are drawn in Figure 5.32. Their respective exergies have to be calculated for obtaining the unit exergy cost.

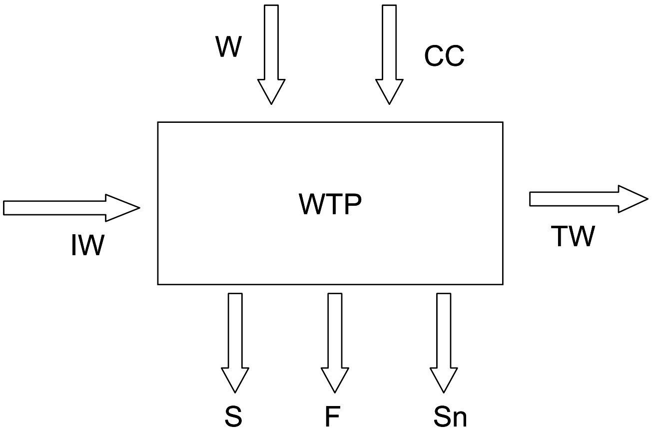


Figure 5.32. Main flows in a WTP

Input water (IW), together with the required electricity (W) and chemical components (CC) go into the plant. Once the treatment process takes place, the output flows are the treated water (TW) and some additional by-products: sludge (Slg), fat (Ft) and sand (Sn).

The untreated water flow with its specific composition is mainly described by C and COD and the dissolved sand. Chemicals, given in kg/m^3 treated water, are used in coagulation and flocculation processes. Electricity input runs the process.

Heat flows have not been included because most of the times it is generated within the plant in a closed cycle (the sludge treatment hot gaseous products are used as energy resource for the sludge gasification).

The solid material included in waste water, but which are stopped at the beginning of the treatment (solids handling), have not been included in the analysis. They are assumed to be out of the study control volume.

The input and output values of conductivity C (ppm) and carbon oxide demand, COD (mg/l) were taken from literature and, when available, from real figures (Qual2k).

Table 5.69 shows the input values for each of the plants and the corresponding exergy values.

	WWTP capacity (m^3/day)	C (ppm)	COD mg/l	W (kWh/m3*)	b_{IM} (kJ/kg*)	b_{OM} (kJ/kg *)	b_W (kJ/kg*)
Begur	2,190	1,184	600	0.567	2.3142	8.16	2.0412
Blanes	23,500	883	640	0.377	2.3903	8.704	1.3572
Cadaqués	4,000	1,612	1,041	0.557	2.215	14.16	2.0052
Castell d'Aro	35,000	1,555	540	0.483	2.2278	7.344	1.7388
Colera	1,300	1,568	762	1.04	2.2249	10.36	3.744
El Port de la Sel.	2,625	1,081	421	1.033	2.3394	5.726	3.7188
Empuriabrava	16,750	2,566	505	0.679	2.0211	6.868	2.4444
L´Escala	21,000	2,182	573	0.792	2.0955	7.793	2.8512
Llançà	9,625	1,772	380	0.673	2.1802	5.168	2.4228
Lloret de mar	20,000	908	719	0.283	2.3836	9.778	1.0188
Palamós	33,000	851	574	0.017	2.3988	7.806	0.0612
Pals	6,750	1,356	509	0.595	2.2731	6.922	2.142

Table 5.69. Waste Water Treatment Plants Inputs.

The output flows included in the analysis are the flow of recovered water (m^3/m^3 treated water), the fat, the sand and the sludge. The last three measurements, in kg/m^3 treated water.

	Rc	C (ppm)	COD mg/l	Sn (kg/m^3*)	Slg (kg/m^3*)	b_{IM} (kJ/kg*)	b_{OM} (kJ/kg*)	b_{Sn} (kJ/kg*)	b_{Slg} (kJ/kg*)
Begur	0.999968053	1139.2	48	0.0883177	0.368232	2.325	0.653	0.601	3.643
Blanes	0.999998171	755.2	29	0.0957378	0.226216	2.425	0.3943	0.618	2.225
Cadaqués	0.999990504	1075.2	70	0.0880009	0.199906	2.341	0.952	0.621	1.98
Castell d'Aro	0.999998615	640	49	-0.092552	0.255166	2.457	0.6663	0.615	2.525
Colera	0.999972827	1337.6	57	0.0981408	0.185922	2.278	0.7753	0.623	1.842
El Port de la Sel.	0.999982909	1132.8	54	0.0976388	0.236123	2.327	0.7343	0.617	2.337
Empuriabrava	0.999996947	2636.8	55	0.0973084	0.269159	2.008	0.748	0.613	2.663
L´Escala	0.999998279	1939.2	57	0.0980982	0.19018	2.145	0.7753	0.622	1.881
Llançà	0.999997657	1529.6	53	0.0988129	0.118708	2.233	0.721	0.631	1.178
Lloret de mar	0.999998207	832	42	0.0981122	0.188782	2.404	0.571	0.622	1.871
Palamós	0.999999133	1542.4	72	0.0984937	0.150629	2.231	0.98	0.627	1.486
Pals	0.999994255	1139.2	43	0.0979588	0.204116	2.325	0.585	0.621	2.02

Table 5.70. Waste Water Treatment Plants outputs. Adapted from "Consorci de la Costa Brava" (2008); Metcalf and Eddy (2003).

It is important to note that the values corresponding with chemical compounds and dissolved sand are not included in Table 5.70, since they have been taken constant (0.04083 kg/m^3 -as the addition of coaguler and flocculer quantitites- and 0.1008 ppm of sand, respectively). Fat and recovered sand flows have also been taken as constant. These features are detailed in next paragraphs.

To maintain the parallelism with the study of the desalination plants and also to check the performance of the water treatment plant regarding mass consumption, the recovery ratio R_c has been calculated as the ratio of the TW respect the IW. As it can be appreciated in the second raw of the Table 5.70, mass loss is insignificant and can be neglected.

Next, the way of calculation for the exergy of the involved flows is detailed: chemical compounds, sand (dissolved in the input and in the output water flow), organic matter content, sludge and fat.

Chemical compounds

Aluminium sulphate, $Al_2(SO_4)_3$, is a main coaguler in most of the WWTP processes. It was not possible to found separate values for the coaguler and flocculer composition in the studied plants. This compound was considered to calculate the specific exergy of the chemical compounds intervening in the depuration process because the coaguler fraction is much more important than the polyelectrolyte (flocculer) fraction.

The exergy of the real substance acting as flocculer, a polymer with an unknown composition, is difficult to estimate accurately. Polyelectrolyte usually can be considered polyacrilamide. As an example, sodium polyacrilate, a commonly used polyelectrolyte, has an average molecular mass of 14,000 g/mol (about 17,000 monomers/molecule), accoding to Vargas et al (2005). However, it seems to be almost impossible to find polymeric specific exergy tables or empirical correlations to calculate the exergy of liquid substances –considerer combustible- without sulphur (Kotas, 1985; Ikumi et al., 1982). Mora and De Oliveira (2006) include some interesting parameters values for such exergies, but they units are referred to the mol number, and it seems to be less accurate for exergies calculation.

In consequence, the assumption of considering the aluminium sulphate can be done without including much error. An adequate average input for chemicals can be taken as 0.04083 kg/m^3 (as the addition of coaguler and flocculer), and a chemical compounds molecular mass of 342 g/mol (Kotas, 1985).

Finally, an exergy value of the added chemical compounds ($b_{ch,cc}$), in kJ of the chemical compounds per kg of treated water is obtained from the exergy value in kJ/mol (Eq. 5.31).

Eq. 5.31. $$b_{ch,CC} = \bar{b}_{ch,CC} \cdot \frac{CC}{M_{cc}}$$

Where $\bar{b}_{ch,cc}$ is the molar coaguler and flocculer specific chemical exergy, and CC stands for the ratio between the kg of chemical compounds and the kg of treated water. M_{cc} represents the above-mentioned chemical compounds molecular mass.

Sand

Sand is present in the input water flow and in the out water flow. After the treatment, the output recovered sand flow has been considered to be about 8 mg/l of treated water (Martínez et al., 2009). The remaining sand in the output water flow, as well as the contained sand in the sludge, have been also accounted for. In the sludge, the amount of sand is obtained from its composition and a empirical equation (which is function of C,H,N, and O composition and the sludge Net Calorific Value). Then, it can be said that the sand is leaving the WTP in three different ways: dissolved in the clean treated water, recovered sand, and sand included in the sludge.

The sand concentration in the input water has been taken as $x_{Sn,in}$ = 0.1008 mg/l, a typical value for Catalonian rivers. The sand specific concentration exergy for the input is calculated as a function of the sand input and reference concentrations ratio because it is an inorganic compound included in the Reference Environment (RE), the sea water. Then, sand concentration exergy was calculated using Eq. 5.32

Eq. 5.32. $$b_{Sn} = R \cdot T_0 \cdot (\bar{x}_{Sn} \ln \frac{\bar{x}_{Sn}}{\bar{x}_{0,Sn}})$$

Where R is the gas constant, 8.314 kJ/kgK, T_0 is the reference temperature and x is the molar fraction in the water (x_{Sn}) and in the reference ($x_{0,Sn}$). Sand is represented by SiO_2, 60.09 g/mol. The reference values are the same as in all the previous calculations. The exergy is obtained in kJ/kg of treated water.

Eq. 5.33 has been used to calculate the molar fraction of the sand in the output water. The mass fraction was obtained applying Eq. 5.34.

Eq. 5.33. $$\bar{x}_{Sn} = \frac{x_{Sn}}{1000 M_{Sn}}$$

Eq. 5.34. $$x_{Sn,out} = x_{Sn,in} - \frac{m_{Sn,S\lg}}{m_{tTW}} - m_{Sn}$$

Where $x_{Sn,in}$, $x_{Sn,out}$ and $x_{Sn,sludge}$ are the input and output dissolved sand mass fractions, and the sludge sand mass fraction, respectively (in ppm). The terms m_{TW} and $m_{Sn,Slg}$ represent the total mass of treated water and the mass of the sand in the sludge; m_{Sn} represents the sand mass recovered per m^3 of treated water

Organic matter

The organic matter is not included in the reference environment, and its exergy contribution was determined by their formation chemical exergy, applying the relation obtained by Tai et al. (1986), already considered in Chapter 4 (Eq. 4.19, section 4.2.3). Because of the explanations given in Chapter 2, in this case, the TOD and COD can be indistinctly used.

Eq. 5.35. $$b_{ch} = 13.6 \cdot COD$$

Eq. 5.35 is applied both for the input and output water flow. COD value represents the Chemical Organic Demand (mg/l) and b_{ch} represents the specific OM exergy (J/l).

Sludge

Kotas (1985) related empirically the dry combustion material exergy and its calorific value by the Eq. 5.36

Eq. 5.36. $$b_{sludge} = coef \cdot PC_{sludge}$$

And the coef definition is given in Eq. 5.36

Eq. 5.37. $$coef = 1.0437 + (0.1882 x_H / x_c) + (0.0610 x_O / x_C) + (0.0404 x_N / x_C)$$

Where x_C, x_H, x_O and x_N, represents the average mass fractions of carbon, hydrogen, oxygen, and nitrogen, respectively (dimensionless)

Finally, the sludge specific chemical exergy*(kJ/kg treated water)* was calculated taking into account this correlation, using Eq. 5.38

Eq. 5.38. $$b_{sludge} = coef \cdot HV_{S\lg} \cdot \frac{S\lg}{1000}$$

Where the HV_{Slg} is equal to 19,451 kJ/kg dry sludge (Castells and Cadavid, 2005) and the Slg represent the kg of obtained sludge per m^3 of treated water

Other authors (Ikumi et al., 1982), consider a moisture percent in the organic material, and the water exergy, which is not the study case because of the dry organic sludge collected data.

Fat

Because of their similar nature, to calculate the fat specific exergy, the same method as for the sludge one was used (Eq. 5.36). A procedure similar to the one described for the sludge flow was applied in this section. Fat was all considered as the C18H32O2 molecule, one of the most common fat acid molecule in the environment. The used net calorific value was 38.874 kJ/kg (considering a 9.3 cal/g of nutritional fat acid standard calorific value).

Finally, taking into account the ratio between the kg of generated fat per kg of treated water, the fat specific chemical exergy value (in kJ/kg of treated water) was finally obtained.

A study about the possible sludge treatment processes to obtain electricity was also carried out (see Annex F). From it, the most adequate alternative for this WTPs study seems to be considering a net electricity input flow (Eq. 5.39) in order to reduce the input work exergy.

Eq. 5.39. $$W_{net} = W_{biogas} - W_{consumed}$$

On the other hand, anaerobically dry digested sludge output flow specific exergy is empirically calculated (Plaza and Garralón, -2008; Kotas, 1985).

5.15.1.2. Unit exergy cost in WTPs

Finally, the calculated exergy flows were introduced in the definitions given in Chapter 3 to obtain the unit exergy costs of the considered WTP, which appear summarized in Table 5.71.

	k process	k product
Begur	1.83	4.46
Blanes	2.32	4.69
Cadaqués	3.23	5.81
Castell d'Aro	1.92	3.87
Colera	3.08	5.60
El Port de la Sel.	2.07	4.10
Empuriabrava	1.99	4.39
L´Escala	2.47	4.62
Llançà	2.19	3.57
Lloret de mar	2.53	4.69
Palamós	2.06	3.44
Pals	2.17	4.16
k (average)	**2.32**	**4.45**

Table 5.71. Exergy costs for specific WWTP in Catalonia.

A relatively narrow range is obtained for the unit exergy values, what means a similar behaviour of the plants.

Nowadays, because of the rising water scarcity, some alternatives to restore quality and quantity will be necessary. Thus, the appropriate measurement of its cost by means of applying physical parameters (given by Thermodynamics) could be one of the tools to evaluate its environmental consequences. In this way, the Unit Exergy Cost has been used to calculate the cost of restoring the quality (WTPs in this Chapter and pumping in Chapter 4) and quantity (desalination in Chapter 4) of water resources. Desalination and pumping k* values are reproduced in Table 5.72 to facilitate the comparison.

	k^*_{proc}	k^*_{prod}
MSF	3.8	21.4
MED	3.8	8.3
RO	2.5	5.5
ED	1.2	8.0
Pumping	_	1.43

Table 5.72. Exergy unit costs for desalination and pumping technologies

In general, the unit exergy cost of the product (k^*_{prod}) is obviously higher than the exergy cost of the process (k^*_{proc}) since some outputs has available energy (exergy) that is not used by any other activities or processes. In relation with desalination, as the diverse outflows of the process are getting valuable for any other process or final user, they can be considered as products (co-products of the desired clean water) and the cost of the process could be reconsidered.

Regarding the obtained results, minimum k^* value is about 1.5 (corresponds to pumping unit exergy). Traditionally, thermal desalination or distillation has been the most commonly used technology for producing large quantities of freshwater from seawater. Different thermal desalination processes require different magnitudes and combinations of heat and electricity. Because of it, their unit exergy cost varies, fluctuating in a wide range. RO, as known, is the most efficient desalination technology. MSF presents the higher value when the attention is focused in the products, since this technology provides an important amount of released heat. MED and ED have also a relatively low unit exergy cost; however the latter is only applicable to brackish waters, not to seawater.

Finally, it is important to highlight that in WTP the plant size (m^3 treated water/day) is independent of the percentage of substances elimination in the studied examples. This percentage of substances elimination depends not only on the plant performance, but also on the substances concentration of the input wastewater. It is also noticeable that in order to calculate accurate k^* for the WTP, chemical composition of main outputs is essential.

5.16. Summary of the chapter

The whole PH methodology in river basins has been developed in this chapter. In the first part of the chapter, the exergy of water and, in particular, the exergy profiles of a river are explained, highlighting that they are always composed by a quantity (flow) and a quality (quality parameters) components. The expected ideal exergy profile of a river has a characteristic curved appearance, with initial and final null exergy points. Secondly, some fundamental concepts are summarized: environmental flows and reference water bodies need to be defined in order to apply PH. In a third step, the PH's interpretation of the WFD is done, what allows to translate the WFD's costs terminology in exergy magnitudes: the exergy difference between the ES and the PS is defined as the SC; the difference between the FS and the OS as the EC, and the exergy gap between the OS and the NS is named RRC.

Next, in the section 5.10, the calculation procedure is explained and a very simple calculation example is developed to clarify the exergy profiles obtaining, attending to their quantity and quality components. It is important to separately calculate those two components, quantity and quality, because if the river wants to be restore, the techniques will be different. Then, a sign analysis is carried out in order to avoid confusion with the results. A negative value can mean (or not) the necessity of restoration measurements. It always depend on the studied parameter (OM, IM or potential components).

The next section covers the simulation softwares needed to get complete information about the area of study. Real gauging stations provide periodical data, but they are usually not enough to correctly run the PH methodology. Then, a simulation of the watershed is required. Qual2k is the programm that has been used in this dissertation, but an overview of the existing softwares was done in the twelfth part of this chapter and in the Annex E.

A very important issue within PH, the cost allocation methodology, is the next issue in the chapter. The degradation of the river stream due to the water uses is considered and analyzed, applying the uses characterization carried out in Chapter 2. The search of a proper water costs allocation among water users leads to consider different alternatives. The first proposed equivalence between the degradation along the river and the degradation due to water uses has to be rejected. It does not allow considering the upstream water uses. A second alternative, taking the percentages of degradation due to each water use sector, provides the adequate tool for that cost allocation and this is the one that is applied in the latter example.

Finally, once the minimum exergy cost (SC, EC and RRC) are clearly defined and the cost allocation method has been established, it is needed to include the irreversibility of restoration processes in the analysis. Then, the unit exergy cost of the restoration technologies needs to be defined. As mentioned, quantity and quality restoration measures will be defined. The quantity can be restores by desalination technologies, already reviewed and calculated in Chapter 4. Here, diverse types of WTP were included to restore the water quality. The heterogeneity of the existing WTP makes difficult defining average values for them. In consequence, twelve real WTP have been studied (Annex F) and their unit exergy cost have been calculated in section 5.16.

After this chapter, which is the basis of the PH application, two river basins are analyzed: the Muga Basin and the Foix Basin. They present quite different features, as it will be immediately seen.

Chapter 6

Application of Physical Hydronomics

Physical Hydronomics methodology has been applied to two watersheds within the Inland Basins of Catalonia (IBC). In this chapter, a general description of the IBC from the perspective of the WFD implementation is done. Most of the input data have been collected from different documents published or directly provided by the Catalan Water Agency (CWA). The different data types required for the PH application were explained: real and projected figures on the one hand, and legally defined figures on the other hand.

Afterwards, detailed descriptions of the Muga and the Foix watersheds are provided. In each case, a socio-geographical description is done: main characteristics such as area, population and water uses are needed.

Then, available real data on quantity and quality are analyzed and each river has to be divided into several stretches to start with the simulation modelling of the watershed. In addition to the geo-morphological figures, water uses are allocated and characterized in the software. Final output of the simulation model in Qual2k allow to construct the searched river profiles. Then, the different water costs are calculated, both in energy and economic units. Next step is the comparison between the IRC and the exergy degradation provoked by water users in the area.

Finally, that mentioned equivalence makes possible to allocate the environmental cost of water among users.

6.1. Introduction

Catalonia, from a topographical point of view, is a region (*Autonomous Community* according to the Spanish designation) of great contrasts. With an extension of 31,896 km², it includes very diverse geological formations and a highly marked relief. There is also a great imbalance in the occupation of the territory and a significant limitation of its water resources, which are, in addition, distributed irregularly, as in any other Mediterranean area. The hydrographical network of Catalonia has two great slopes: the western slope, which mainly covers the tributary waters of the Ebro basin and the eastern slope, made up of rivers that have their source and mouth in Catalonia, designed as Inland Basins of Catalonia (IBC).

The Catalan Water Agency (CWA), the administrative body responsible of water issues in Catalonia, is a pioneering Agency working towards the gradual implementation of the WFD since 2001. As already pointed in Chapter 1, one of the first steps in the WFD application is the redaction of the corresponding impacts-pressures report. In 2005, the CWA published its *IMPRESS Document* (CWA, 2005a), which includes the categorisation and definition of water masses (unit of management to be governed by the Programme of Measures for compliance with the WFD objectives), and the risk of non-compliance with WFD objectives. It also responds to the Article 5 (economic analysis that includes an assessment of the current costs of water-related services) of the Directive. This analysis is essential for the subsequent viability of the Programme of Measures and fulfilment of the Cost Recovery Principle (including environmental recovery costs) in integrated, sustainable management of water and its associated area.

In the IBC, as in other parts of Spain, different players (public and private institutions) contribute to giving or adding value to natural water resources. The mere fact of administering and policing the public domain involves an added value, as does the fact of collecting wastewater or controlling rainwater to prevent flooding (CWA, 2005b). These different players can exchange services for economic consideration, either between themselves or with end users. All players can be involved in the value chain (Chain 5 in Figure 6.1).

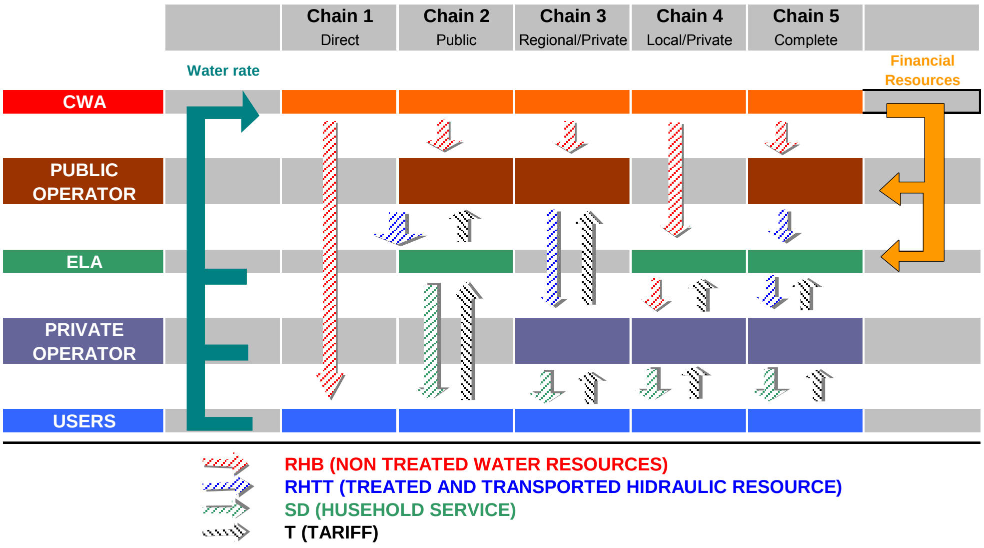


Figure 6.1. Water-related services in Catalonia. Diagram of the value chain and financial-economic flows (Source: CWA, 2005b)

The entity covering the whole process is the CWA, and the final fate of water are the users. Public and private operators are present at different stages of the process.

The local water entities, ELA (*Entidades Locales del Agua*) are, according to the Legislative Royal Decree RLD 3/2003, the local entities with their own legal personality and the ability to manage one or more public wastewater treatment systems, as well as the upstream and downstream water supply systems of the municipalities that make them up. This legal figure has undergone significant development in recent years, as a part of a process of decentralisation and increasing the effectiveness of actions.

The CWA provides with founds both to the public operator and to the ELA. The different water provision possibilities are represented by the chains in Figure 6.1

6.1.1. Current recovery water costs and water imbalance

The current water costs recovery system in Cataluña presents two main problems. On the one hand, it allows recovering 100% of supply costs, but only 50% of internal CWA costs and 25% of sewage costs. On the other hand, the water tariff structure (which supposes the 95% of the CWA incomes) is outdated because it has not been adapted to the real current services that are being provided to fulfil the legislation. In fact, the water price is defined by the city councils and they are not interested in increasing the price of water because it would be an unpopular measure. However, unavoidably, the new environmental objectives coming from the WFD will mean an important increase of the current cost in a very close future, that politicians do not want to tackle.

The management of water resources in Catalonia is conditioned by their availability, defined by regional meteorological, land relief and geological characteristics, and by the needs distribution. Both variables, supply and demand, are polarised in accordance with the two hydrological and administrative units which divide the Catalan territory (Figure 6.2): the Inland River Basins and the Ebro Basin. Although each one supplies water to approximately half of the Catalan territory, these two basins have significantly different features in terms of resources and demands. As in other Mediterranean countries with restricted availability because of the meteorological and geological conditioning factors, examples of water management intended to underwrite demand generated by different activities are very frequent.

In addition, the canals for distributing irrigation water, weirs and ditches inherited from past centuries, and the modern water conveyances from the Ter to Barcelona area or from the Ebro to Tarragona area, are a sample of this management in terms of the quantity of the resource that needs to be distributed. As an example, the water management of the River Llobregat is characterised by the intensive use of water and by the deterioration in its quality caused by the salinity added in discharges and, also, by the contributions of salts from the accumulation of mining activity in the *Cardona Region* and other industrial regions (Cantó, 1999). These salt contributions affect the quality of the water supplied in Barcelona and have made necessary to build various collectors in order to pick up contributions and discharge them in the final stretch of the river, beyond the point where it is massively abstracted for urban supply. The case of the Llobregat is one example of the importance of the quality of the resource and the efforts made to ensure that the supply is appropriate for the needs. This river proporcionates an important part of the domestic supply for the Barcelona area.

6.1.2. Two well-defined areas

The Internal River Basins, made up of river basins located entirely on Catalan territory, occupy 15% of the surface water resources available and approximately 92% of the population. The Ebro Basin includes the final stretch of this river and its tributaries (mainly the Segre) on Catalan territory, with 85% of surface water resources and only 8% of the population (CWA, 2005a).

Figure 6.2. Inland River Basins and the Ebro Basin

This difference is basically due to the hydrological typology of the rivers in each basin. The average annual contribution from the Segre River, restored to the natural regime, is 6,183 hm^3, which is more than the total contributions of all rivers of the IBC. Moreover, the regulation of river flow by dams is notably different; the capacity of the reservoirs in the internal basins is around 760 hm^3, while that in the Ebro basin is 2,280 hm^3 (although the last one is not a relevant figure when the down part of the Ebro river is considered, because *Mequinenza* and *Ribagorza Dams* are reservoirs with multiple functions within the Ebro Basin: hydropower, cooling, flooding …). Groundwater resources are not included in this accounting, as their characterisation is limited only to certain aquifers and existing figures do not show all the available groundwater. This fact is also important, as 40% of the potable use in the IBC is obtained from underground resources (CWA, 2005a).

The type of demand from human activities is also different in the two hydrological zones. Thus, the majority of urban demand (domestic and industrial) is concentrated in the inland river basins, whilst the Ebro basin caters for farming demands. Globally, a little over 72% of water demand in Catalonia corresponds to farming, despite the fact that in the Inland River Basins, this percentage drops to 35%.

In particular, in the internal basins, demand is basically domestic (43.7%). Industrial (21.2%) and agriculture (35.1%) uses are not so great. In addition, this demand is concentrated in the metropolitan area of Barcelona (approximately 50% of total demand) and along the coast (due to the seasonal nature of domestic in relation to tourism), and agricultural uses are particularly relevant. On the contrary, in the Ebro Basin, 95.6% of demand is agricultural, 2.8% urban and 1.6% industrial (CWA, 2005a).

Finally, the relationship between demand and annual estimated surface contributions under the natural regime is 43% in the internal river basins and 10% in the Ebro basin.

Plana and Castelvi (2004) presented a complete study about the water consumption in the IBC with special interest on the resources (both surface waters and aquifers) and its evolution along the time. The last part of the study is devoted to the dams, eventual desalination plants and consumption analysis.

6.2. WFD in Catalonia: a long and visionary project

The WFD's works in the fluvial Catalonia Basins started with the physical characterization of each of the water bodies in the territory (continental surface and deep waters, coastal waters and transitional waters). Then, the characterization is completed with two issues: on the one hand, the risk of non compliance of the WFD's objectives and, on the other hand, the economic analysis of water, focused on the economic characterization of the water uses and of the anthropic pressures on each of the water bodies. In addition to that, a projection of the pressures by 2015 is required, as well as the recovery water costs analysis of the water services in Catalonia. From those defined reports, the quality objectives for the Catalonia water bodies are established: good ecological status (GES) and high status (HS), which are a compendium of biological, hidro-morphological and physico-chemical objectives.

Once the described works were finished, a clear working methodology needed to be defined in order to achieve three immediate challenges:

- The analysis of the exerted pressures in the water bodies provoked by the human activity and the characterization of the contribution of each pressure in the current deterioration of the quality parameters (biological, hydro-morphological and physico-chemical) for each water body. That is, analyzing the impact on the environment of each pressure. Without this precise characterization, it would not be possible to set out a measures program with real effect on the pressures and, therefore, on the environment.

- The analysis of the pressures acting on the hydro-morphological parameters that degrade the physico-chemical quality and the biological indicators. It is important to consider that the hydro-morphological and physico-chemical modifications are the cause of the habitat variations and the biotic indicators worsening.

- The interrelations among the different water bodies and how the upstream pressures influence the ecological quality downstream or in other connected water bodies. In the same way, the measures applied in a given river reach would have a beneficial effect downstream, what would mean stricter or laxer measurements in the rest of the river zones.

To solve these matters, a systemic working methodology, based on a simulation, was established, where the environmental pressures (both point and diffuse sources) on the different water bodies are included. The methodology is identified as *Pressure-Impact* model (P-I model).

By including the projected pressures by 2015, the simulation software allows comparing the water state by 2015 with the WFD's environmental objectives for each water body (or river reach). When the output values of the 2015 simulation exceed the limits of the objective values, restoration measurements are required in order to reduce the pressures and, in consequence, their derived impacts.

The WFD also states the necessity of developing a cost-efficiency analysis of the proposed measurements to reach the WFD objectives (a set of measures obtained from the P-I model). Each of the measures has to be analyzed and those with a lower cost have to be chosen, that is, the most cost-efficient measures.

According to the point 38 of the WFD's preamble, …*the use of economic instruments by Member States may be appropriate as part of a programme of measures. The principle of recovery of the costs of water services (…) should be taken into account in accordance with, in particular, the polluter-pays principle. An economic analysis of water services based on long-term forecasts of supply and demand for water in the river basin district will be necessary for this purpose.* From the cited article, it is deduced the necessity of a sensitivity analysis of the program of measures in which the cost and eventual environmental damages of the proposed measures are also analyzed. The Directive clearly establishes that, once the measurements are identified, a mechanism to allocate water cost among the different agents acting in the water cycle has to be designed. One of the main contributions of PH is framed in this issue: cost allocation.

Figure 6.3 shows the WFD's works carried out in Catalonia with is logic sequence. Grey area contents the already done issues, while the yellow one presents the works that are currently being developed and those that still need to be set off.

As it is established in the Preamble of the Water Framework Directive, European water resources are subjected to the pressure of the constantly increasing demand for good quality water in sufficient amounts for all uses. This increasing demand justifies the need to establish measures for the protection of community water supplies, both in terms of quantity and quality.

Therefore, and as far as Catalonia is concerned, it was considered important to determine, at least in general terms, the main characteristics of the water demand and its probable evolution as these tendencies will give an idea of the pressure being put on the quality and quantity of this resource, now and in the future.

WFD does not present any definition of water demand. Nevertheless, it does differentiate between possible categories such as agriculture, industry and households.

Acting on the demand, through various management measures, it is essential to ensuring compliance with most of the stipulations of the Framework Directive, especially in regard to the chemical and ecological quality of our aquatic ecosystems. In any case, management and control of demand are not easy tasks to carry out in Catalonia. First, because it is extremely difficult for the main user of water, irrigation farming, to assume some instruments such as higher prices, and second, because on the level of domestic consumption, certain structural factors such as improved well-being, changes in the models of urban growth and life styles, could be spurring water demand and make more complicated its control.

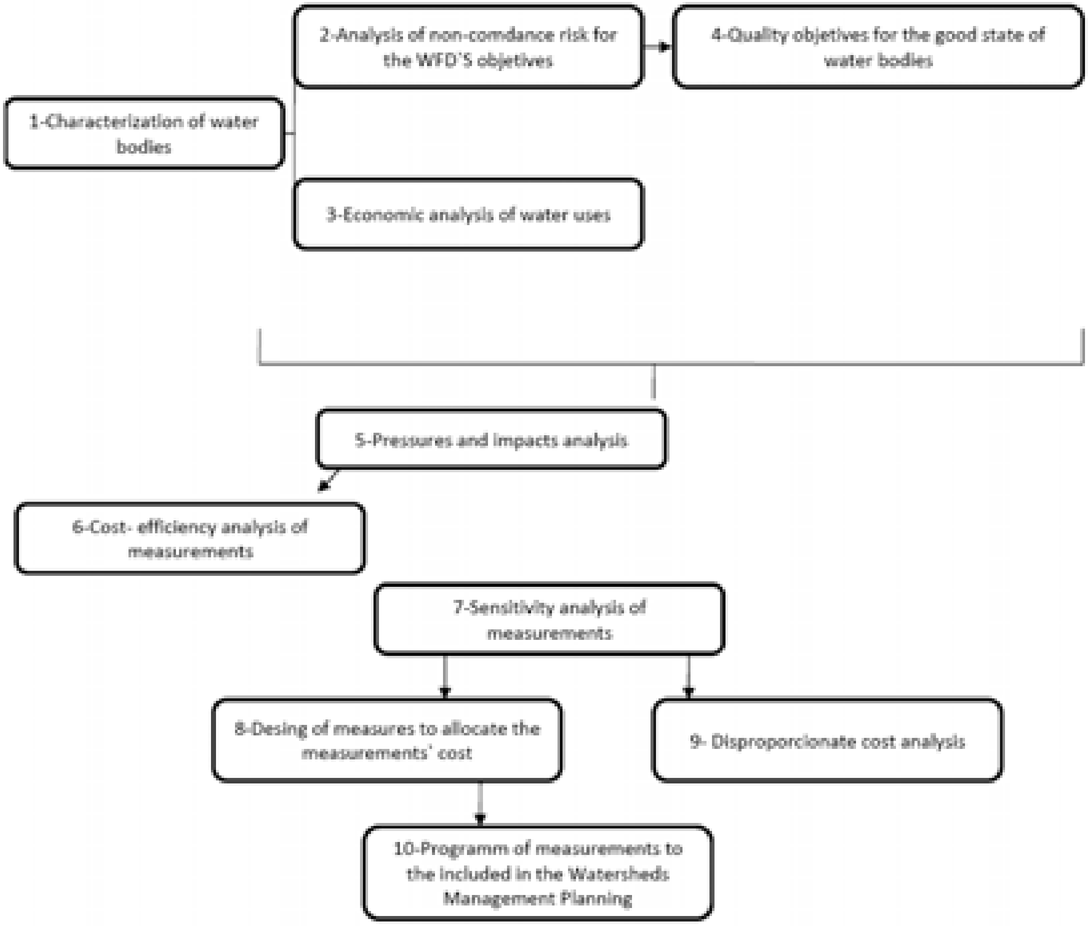


Figure 6.3. Schema of the work procedure in Catalonia in relation the WFD implementation

6.2.1. Catalan Inland Basins (IBC) characterization

Before 22nd December 2003, several technical studies gave the background for the CWA to delimitate the hydrologic demarcations of the IBC, as it was required by the WFD. A land digital model (15x15m), from the *Instituto Cartográfico de Cataluña* was used. In this hydrologic network, in addition to review the surface basins, the coastal waters were added (from the coast line until one nautical mile). Figure 6.4 shows the Basins forming the IBC.

Figure 6.4. Detail of river basins in the IBC. (Source: CWA, 2005a)

According to the criteria established in Appendix II of the WFD, the first step that must be taken is to characterise the water bodies in each hydrographical demarcation and group them, depending on whether they are rivers, lakes (including wetlands), transition waters, coastal waters, highly modified waters or artificial waters. Once included in a category, the different water bodies are subdivided into types according to the natural characteristics that might condition the structure and operation of the ecosystem and, consequently, the management model and diagnosis protocol.

A hierarchical approach must therefore be taken, firstly establishing the categories of water bodies (rivers, lakes, etc.), and then classifying them into types. Finally, the water bodies (belonging to a type within a category) are defined as the functional and management unit, taking into account:

- the geographical and hydro-morphological characteristics;
- human pressures;
- their ecological status; or
- the fact that they have a particular protection status.

The ultimate objective of this process is to mark out the appropriate management units (water bodies) to achieve the environment objectives of good status (or potential). For each type of water body, the CWA, following Directive's requirements, has established specific reference conditions that must correspond with the hydro-morphological, physico-chemical and biological status of an undisturbed water body (or one little affected by humans) in order to adapt the diagnosis as an element of reference for the management of resources. WFD's quality references (objectives) are provided by each river subtype

6.2.1.1 Surface Water

In the case of river systems, the environmental heterogeneity of Catalonia and the availability of reliable data representing this condition make it possible to adapt the level of discrimination while, at the same time, maintaining coherent spatial interpretation and justification. So, using multivariant analysis methodologies to classify and organise the different river stretches through the analysis of environmental variables unaltered by human activity or restored to their natural state (where and when possible): hydrological, morphometric, geological and climatic variables (Munné and Prat, 2004). Thus, twelve "river types" were defined in Catalonia within a European contextual framework useful in the sphere of river basin management and operating at the level of a river basin body (the Catalan Water Agency) (table 3.2 and Figure 6.5).

	River types
1a	Wet mountain rivers on silica
1b	Wet mountain rivers on limestone
2a	Mediterranean mountain rivers on silica
2b	Mediterranean mountain rivers on limestone
2c	High-flow Mediterranean mountain rivers
3a	Lowland Mediterranean rivers (variable flow)
3b	Mediterranean lowland rivers on silica
3c	Rivers with karstic influence
4a	Major rivers
5a	Coastal torrents
6a	Large rivers with low mineralization
7a	Great Mediterranean rivers (low stretch of the Ebre)

Table 6.1. Fluvial types in the Internal River Basins of Catalonia (Munné i Prat, 2002; Munné i Prat, 2004), and in the Catalan Basins of the Ebre and Garona rivers (Munné i Prat, 2000).

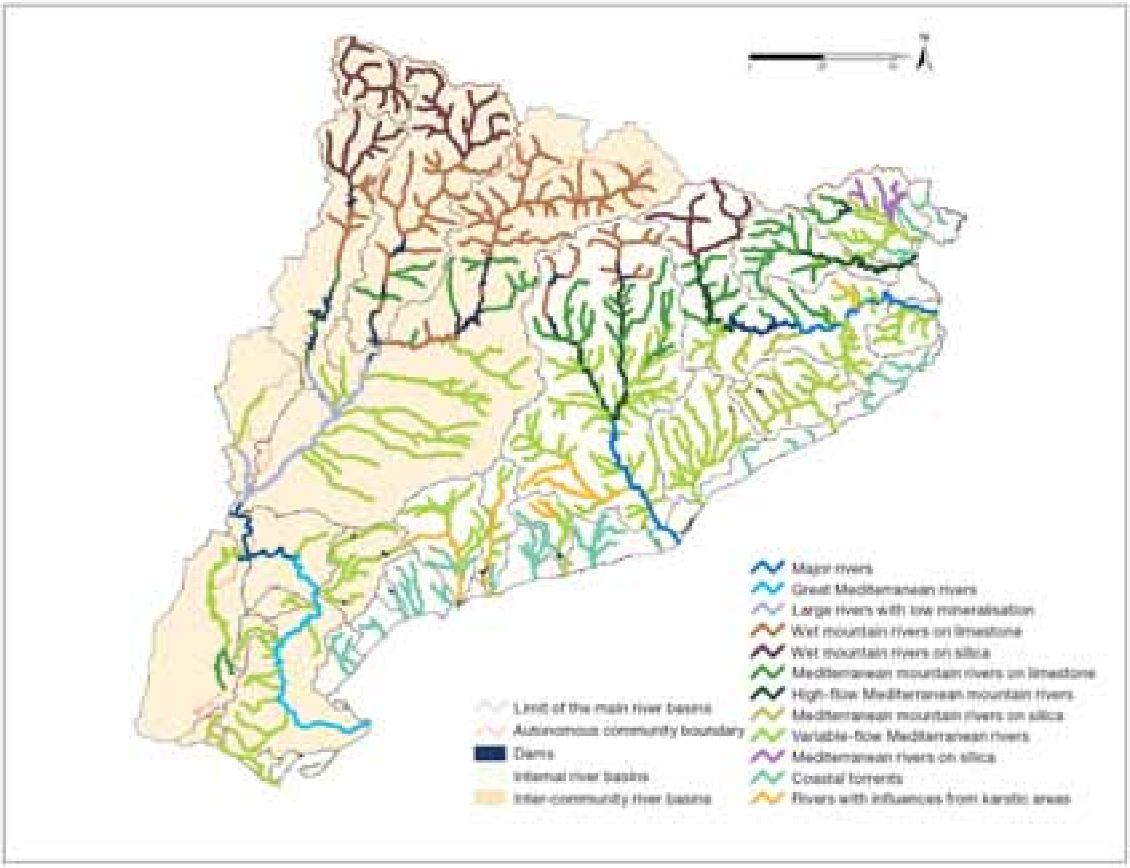


Figure 6.5. River types

For each of these types of water systems, following the WFD requirements, objective quality values are provided. Those values are reproduced in Table 6.2, according to the river type. The parameters to define those states are mentioned in the WFD, although they are definitely adapted by the competent organism.

	Objective	**T (ºC)**	**O (min)**	**O (max)**	**TOC**	**Cond**	**Cl^-**	**pH (min)**	**pH (max)**	**NO_3^-**	**NO_2^-**	**NH_3**	**PO_4^-**	**SO_4^{-2}**
Major rivers	HS	25	9	15	4	600	50	6.5	9	3	0.05	0.2	0.1	50
Great Mediterranean rivers	HS	25	9	15	4	600	50	6.5	9	3	0.05	0.2	0.1	50
Large rivers with low mineralisation	HS	25	9	15	3	500	25	6.5	9	3	0.05	0.2	0.1	50
Wet mountain rivers on limestone	HS	22	9	15	1.5	300	25	6.5	9	3	0.05	0.2	0.1	50
Wet mountain rivers on silica	HS	22	9	15	1.5	150	25	6.5	9	3	0.05	0.2	0.1	50
Mediterranean mountain rivers on limestone	HS	25	9	15	3	500	50	6.5	9	3	0.05	0.2	0.1	50
High-flow Mediterranean mountain rivers	HS	25	9	15	3	600	50	6.5	9	3	0.05	0.2	0.1	50
Mediterranean mountain rivers on silica	HS	22	9	15	3	150	50	6.5	9	3	0.05	0.2	0.1	50
Lowland Mediterranean rivers with variable flow	HS	25	9	15	3	500	50	6.5	9	3	0.05	0.2	0.1	50
Mediterranean lowland rivers on silica	HS	22	9	15	3	150	25	6.5	9	3	0.05	0.2	0.1	50
Coastal torrents	HS	25	9	15	3	700	25	6.5	9	3	0.05	0.2	0.1	50
Rivers with karstic influence	HS	25	9	15	3	1,300	50	6.5	9	3	0.05	0.2	0.1	50
Major rivers	GES	25	7	15	6	1,000	100	6.5	9	10	0.5	0.5	0.25	100
Great Mediterranean rivers	GES	25	7	15	6	1,000	100	6.5	9	10	0.5	0.5	0.25	100
Large rivers with low mineralisation	GES	25	7	15	5	800	50	6.5	9	10	0.5	0.5	0.25	100
Wet mountain rivers on limestone	GES	22	7	15	3	500	50	6.5	9	10	0.5	0.5	0.25	100
Wet mountain rivers on silica	GES	22	7	15	3	250	50	6.5	9	10	0.5	0.5	0.25	100
Mediterranean mountain rivers on limestone	GES	25	7	15	5	750	100	6.5	9	10	0.5	0.5	0.25	100
High-flow Mediterranean mountain rivers	GES	25	7	15	5	1,000	100	6.5	9	10	0.5	0.5	0.25	100
Mediterranean mountain rivers on silica	GES	22	7	15	5	250	100	6.5	9	10	0.5	0.5	0.25	100
Lowland Mediterranean rivers with variable flow	GES	25	7	15	5	750	100	6.5	9	10	0.5	0.5	0.25	100

Mediterranean lowland rivers on silica	GES	22	7	15	5	250	50	6.5	9	10	0.5	0.5	0.25	100
Coastal torrents	GES	25	7	15	5	1,000	50	6.5	9	10	0.5	0.5	0.25	100
Rivers with karstic influence	GES	25	7	15	5	1,700	100	6.5	9	10	0.5	0.5	0.25	100

Table 6.2. Quality objectives fixed by the Catalonian Water Agency. Units: mg/l. (source: CWA, 2008c)

6.2.1.2 Deep water masses

According to the WFD, an aquifer is understood as a subsurface layer or layers of rock or other geological strata with enough porosity and permeability to allow either a significant flow of groundwater or the abstraction of significant volumes of groundwater. Therefore, the groundwater term refers to all water which is below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil.

The quantitative and qualitative status of a body of groundwater may have an impact on the ecological quality of surface waters and terrestrial ecosystems associated with that groundwater body.

Groundwater may provide significant base flows in some rivers and supposes the direct sustain of some land-based ecosystems such as wetlands. An alteration to this contribution would involve a reduction of the chemical or ecological quality of the associated ecosystems (Castañón et al., 2007). With this definition, the Directive recognises the unity of the water cycle through the importance of the river-aquifer relationship. This relationship is especially important on alluvial plains which, because of their characteristics, have become preferred areas for often intensive exploitation of underground water resources.

However, deep aquifers do not show such a direct relationship with ecosystems, so ecological quality cannot be a reference for their preservation. The Directive therefore recognises the bodies of groundwater that are currently being used, or that could be used in the future for extraction of a volume equal to or greater than 10 m^3 per day for drinking water, or for demand of 50 people or more.

The aquifers identified in Catalonia and their denominations are showed in Figure 6.6.

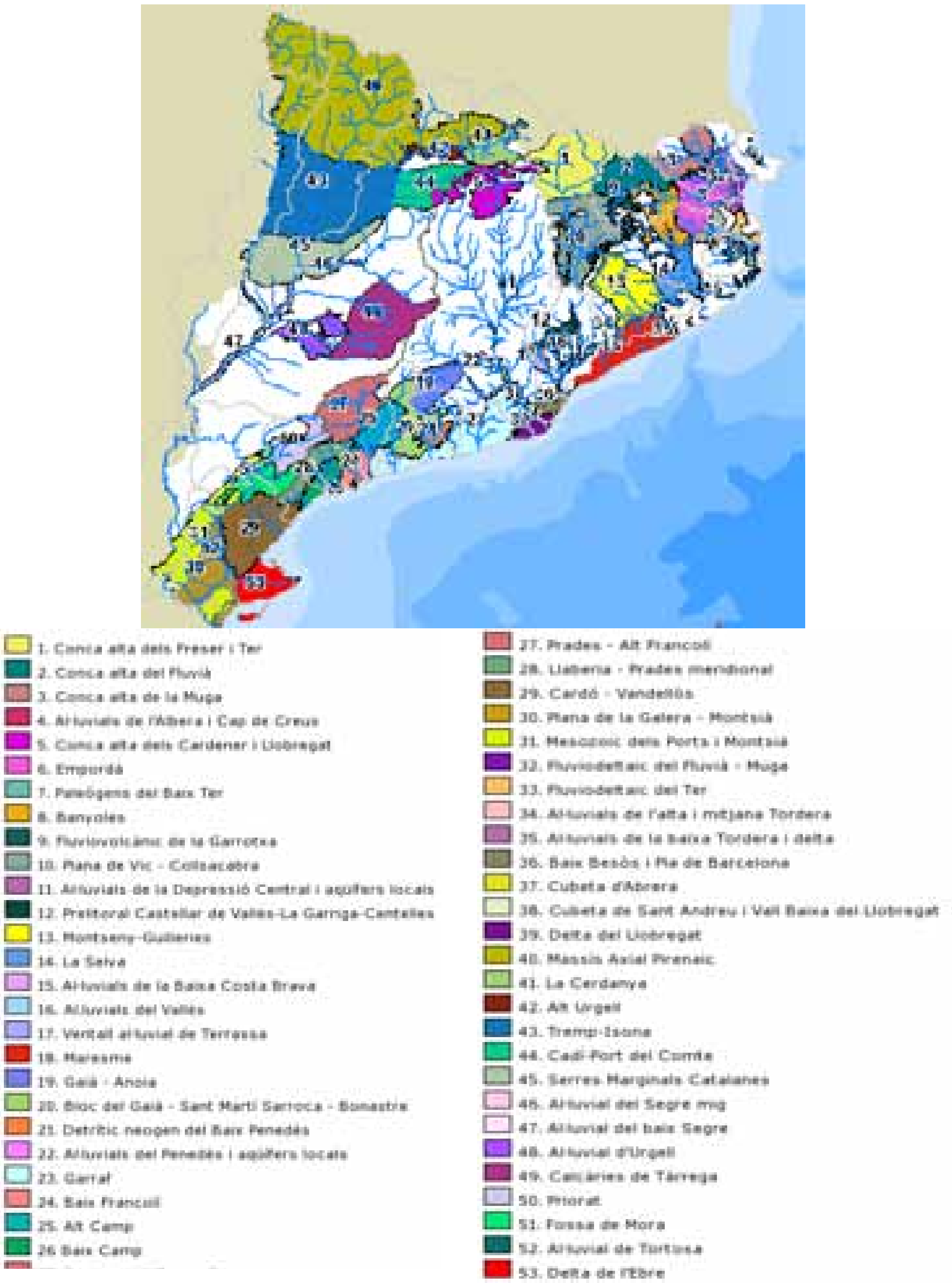


Figure 6.6. Catalonian aquifers (Source: CWA, 2005a)

6.2.2. Reference water bodies in Catalonia

The definition of the reference water bodies was already given in section 5.7. At this point, reference water bodies in Catalonia are presented.

In the case of the internal river basins of Catalonia, the search for reference stretches of river is quite complex. Above all, some river types have strong human presence on their banks or in their drainage basins: this is the case of the major rivers (lower stretches greatly affected by human action) or the high-flow Mediterranean mountain rivers (with many industrial activities on their banks).

As already mentioned, the state of the surface water bodies is evaluated by combining chemical and ecological features. Depending on the current situation of each water body, it will be classified as reference, not reference or highly-modified water (Figure 6.7). The objective state to be achieved for each water body in Catalonia by 2015 will depend on its starting point: reference waters will need to reach the high status, while non-reference waters will apply for the *good ecological status*. On the other hand, highly-modified water bodies are only required to reach the *good ecological potential* (a less restrictive state).

Figure 6.7. Ecologic state of the Catalonian surface waters.

	State	O	TOC	Cond	NO_3^-	NO_2^-	NH_3	PO_4^-	SO_4^{-2}
Major rivers	R	9.5	3	500	0.5	0.05	0.1	0.05	35
Great Mediterranean rivers	R	9.5	3	500	0.5	0.05	0.1	0.05	35
Large rivers with low mineralisation	R	9.5	1.5	300	0.5	0.05	0.1	0.05	35
Wet mountain rivers on limestone	R	9.5	1	300	0.5	0.05	0.1	0.05	35
Wet mountain rivers on silica	R	9.5	1	100	0.5	0.05	0.1	0.05	35
Mediterranean mountain rivers on limestone	R	9.5	1.5	450	0.5	0.05	0.1	0.05	35
High-flow Mediterranean mountain rivers	R	9.5	1.5	500	0.5	0.05	0.1	0.05	35
Mediterranean mountain rivers on silica	R	9.5	1.5	100	0.5	0.05	0.1	0.05	35
Lowland Mediterranean rivers with variable flow	R	9.5	1.5	400	0.5	0.05	0.1	0.05	35
Mediterranean lowland rivers on silica	R	9.5	1.5	100	0.5	0.05	0.1	0.05	35
Coastal torrents	R	9.5	1.5	600	0.5	0.05	0.1	0.05	35
Rivers with karstic influence	R	9.5	1.5	800	0.5	0.05	0.1	0.05	35

Table 6.3. Quality values for the reference water bodies of each type of river. (Source: CWA, 2006)

In addition to the objective values, the reference values are also provided by the CWA and they have been collected in Table 6.3. The number of parameters defining this reference state (R) are lower than in the previous case (13 parameters define the objective states, while only 8 are available for the reference –see Table 6.2 and Table 6.3, respectively-). In consequence, to the complete PH application, lacked parameters have been completed by taking averaged and coherent values for the reference (such as temperature, clorurs in the headwater).

These values can vary if the considered area is immersed in special territory (e.g., areas with natural high salinity). Extra values for those cases are also given in the CWA's literature. Figure 6.8 shows the areas with high salinity (measured in chlorides content). In Figure 6.9, the areas with sulphates affection are also represented.

Figure 6.8. Areas affected by special chlorides concentration. (Source: CWA, 2006)

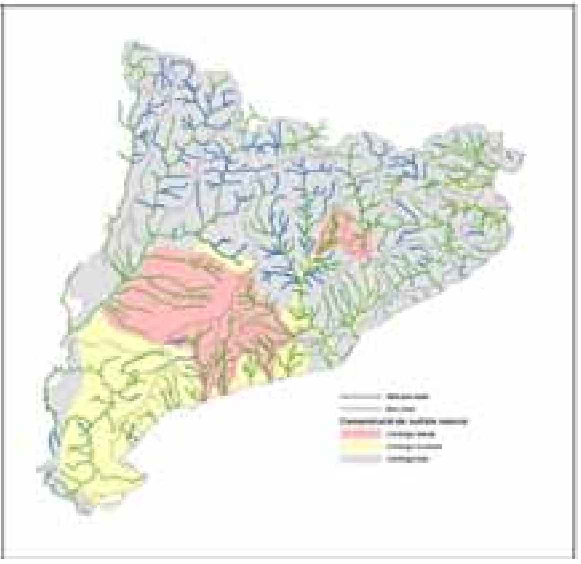


Figure 6.9. Areas affected by special sulphates concentration. (Source: CWA, 2006)

The two studied areas in this PhD are not affected by the chlorides, but the Foix watershed is immersed in the high-sulphates zone and a value of 200 mg/l was therefore taken, instead of 35 mg/l for the reference (assigned to that type of water).

The typification of rivers and the analysis of their reference conditions are the basis that make possible to adapt the Sectorial Plans and Action Programmes to the specific characteristics of the river areas of the internal river basins of Catalonia. Some examples are the *Sanitation Plan* (PSARU, 2005 and 2010) and its future revisions, *Restoration and Hydromorphological Recovery and Riparian Woodland Plans* or specific Zonal Plans for the implementation of environmental flows.

6.2.3. Maintenance Flows in Catalonia.

Although the maintenance flows are not a specific objective of the WFD, a relevant condition for a water body is having a flow as close as possible to its natural flow. An abundant and constant flow would allow an adequate quality.

Thus, the Sector Plan for Maintenance Flows of the Inland Basins of Catalonia (*Pla Sectorial de Cabals de Manteniment de les conques internes de Catalunya*- CWA, 2005c) defines a system of minimum flows below which piscicultural life and the operation of the river ecosystems could become difficult to maintain. It was approved on 3 November 2005 by the Catalan Water Agency. This Plan sets out a system of monthly maintenance flows at 320 points of the rivers network of Inland Basins of Catalonia (about 2,000 km of river) and provides the methodology for calculating the flows of the other river sections (small headwaters and streams between the above mentioned points).

The setting of a system of maintenance flows arises from the need to account for industrial or agricultural uses, human consumption and/or energy generation, with the maintenance in good condition of the water systems where the resource is extracted from. This system is a prior restriction to the water uses, which permits, and intends to maintain, minimum acceptable environmental conditions, and it is a useful tool for regulating new water concessions and for adapting existing ones (specially the non-used ones).

The Sector Plan for Maintenance Flows complements the forecasts of the current Hydrological Plan of the Inland Basins of Catalonia. The setting of the ecological flows must take place within the hydrological plans of the basin, and the Basin Authority is responsible for specifying them through specific studies for each river section.

The maintenance flows defined in the Plan are not guaranteed in any case. The maintenance flow is a threshold below which the river system enters a critical state and thus below this threshold it is not recommended to extract more water from the system. The circulating flows, naturally and temporarily, could be below the flows defined in the Plan as environmental flows. A very different problem are those river sections where the maintenance flow does not circulate because of the high level of consumption of the limited resources of the basin.

Its introduction will take place under the operating rules (with regard to the reservoirs) and the Local Introduction Plans for the homogeneous river sections with specific problems. The Operating Rules and the local plans will specify the flows to circulate through the existing operations and with current concessions, and taking into account the strategic uses and the social perception. For this introduction, there will be a public participation process involving the users, organisations and institutions affected or closely linked (operators, environmental groups, ecologists, fishermen, local councils, etc.).

Upon drought periods, maintenance flows will be temporarily lower defined. This aspect will be detailed in the Drought Management Plan, which will form part of the Basin Management Plan.

6.2.3.1 Ecological flow definition

The following sequential criteria, with hydrological methods (see section 5.6.1.5), have been considered for defining the environmental flow (EF) in the different river basins of the IBC (CWA, 2005c):

1. Environmental flows (basic flows) have been assigned in certain points, starting from specific studies. Those studies have been carried out by diverse competent organisms, administrations and research centres and have previously been examined and validated. Used data have been contrasted with results from

hydrologic methodologies (CWA, 2004) calculated for different reaches of the IBC.

2. If there does not exist any specific study properly contrasted and validated, the protocols of analysis of ecological state (biological, hydromorphological and physico-chemical quality), which have been developed by the CWA and different Catalonian research centres, have been analyzed. Where a good structure of fitobentonique communities, macroinvertebrates, fishes fauna and a good hydro-morphological quality are detected, the flowing streams previous to the sampling period are analyzed, and the results of some hydrological methods (QBM and several statistics based on daily-classified flows) applied is adjusted in each river stretch.

3. In the river stretches where there does not exist specific studies, and environment quality figures and the good ecological state is not reached, the QBM method is applied to calculate the basic flow (Q_b) with a value not higher than Q_{330} (value higher or equal flow for 90% of days in the hydrology series 1940-2000 restored to natural flow) and it is taken as a reference the Q_{347} and the 7Q2 for the adjustment of the basic flow in each river reach.

4. In the river stretches where do no exist specific studies, evidences of a good ecological status or an optimum series of daily flows restored to natural flows for the application of the QBM method and classified flows analyses are not found, the QPV method for variable percentages is then applied.

The QBM method was developed at the University of Lleida, and is a way of interpret the flows information obtained as a flows series, with the objective of getting a minimum flow (Palau, 2006). It is a sequential, pulse-based hydrologic model designed to search sudden changes within the low flow regimes.

The QPV method, uses a variable percentage (20-15-20%) of the average annual flow. It is based on the yearly contribution in the considered river reach and fixes a gradual maintenance flow according to averaged interannual flows:

The classified flows method uses the following parameters: Q347, Q330 and 7Q2. It is based on statistics figures obtained from historical hydrologic studies. Q347 is the flow which is matched or exceeded 347 days per year. It has been calculated for the complete 60 year serie (1940-2000), corresponding to the Q95 (flow which is equalled or exceeded 95% of the time along one year) of the daily classified flows curve. The same definition is applied for the Q330, corresponding to the Q90 (flow which is matched or exceeded 90% of the timer) of the daily classified flows curve. Finally, 7Q2 is calculated as a moving average of seven consecutive days for each year in a given record (two years discharge).

As a result of the application of the defined criteria, a Q_b is obtained. It is modulated for the determination of the *maintenance flows regime*, which follows the hydrology patterns of the hydro regions defined in the third point of the Annex 2 of the mentioned Plan (CWA, 2005c). For drought periods, a flow corresponding to the 80% of the Q_b is determined. Summing up, the maintenance flow regime in each of the fluvial points is obtained from a Q_b fixation in each of them, applying the following temporal function (Table 6.4), depending on the hydrological type:

Hydrologic type	**Monthly variation on the calculated Qb**											
	Oct	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Abr**	**May**	**Jun**	**Jul**	**Ago**	**Sep**
A1	**Qb**			**0,8Qb**		**Qb**	**1,5Qb**			**Qb**		
A2	**Qb**						**1,3Qb**		**Qb**	**0,8Qb**		
A3	**Qb**		**1,2 Qb**						**Qb**	**0,8Qb**		
B1	**1,1 Qb**								**Qb**	**0,8Qb**		
B2	**Qb**		**1,2 Qb**				**Qb**			**0,8Qb**		

Table 6.4. Monthly variation on the calculated Qb. (Source: CWA, 2005c)

According to their hydrologic regime, main rivers have been classified in six types:

A1: snow regime
A2: snow-rainfall regime
A3: humid Mediterranean regime
B1: plugged Mediterranean regime
B2: low Mediterranean zone
B3: temporal regime

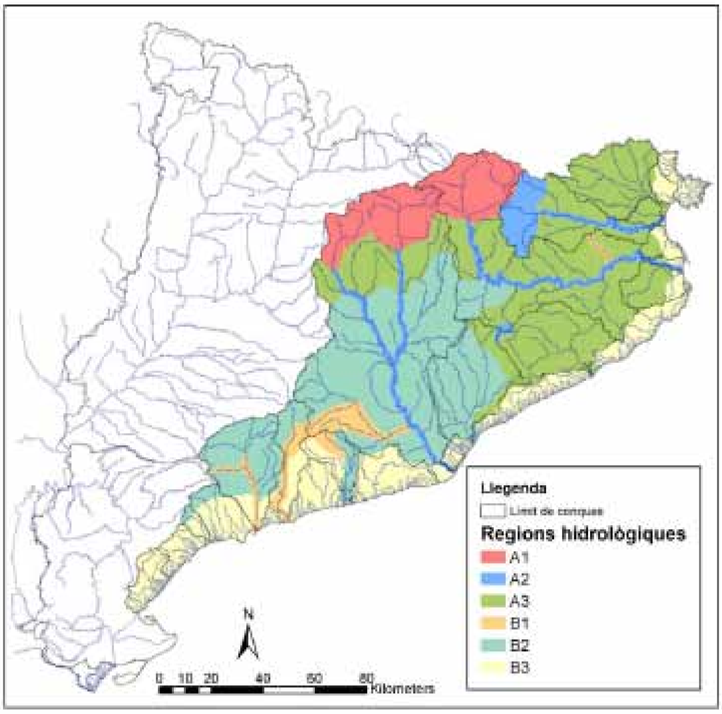
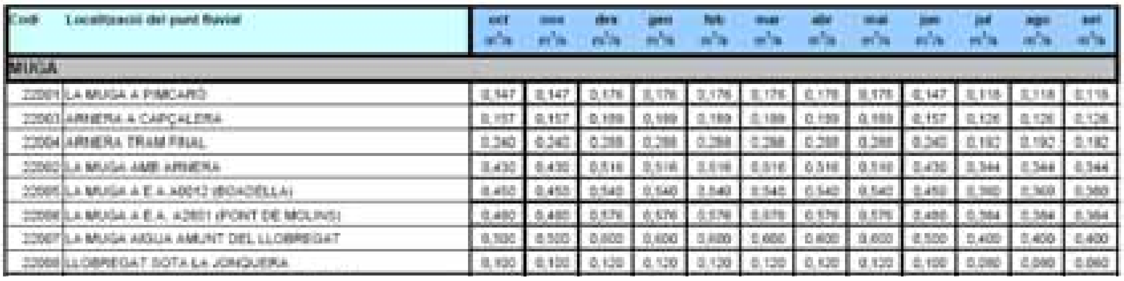


Figura 2. Tipus de variabilitat del règim hidrològic natural catalogats a partir de dades restituïdes al règim natural de 320 estacions de les conques internes de Catalunya.

Figure 6.10. Hydro-regions in IBC. (Source: CWA, 2005c)

Tables showing the maintenance flows (320 points covering 2,788 km of river courses) can be found in the document *Pla Sectorial de Cablas de Manteniment de les conques internes de Catalunya*, CWA (2005), as well as in the *Resolució MAH/2465/2006* of the Environment and Habitat Department (*Departament de Medi Ambien i Habitatge*) of the Catalonian

Government (*Generalitat de Catalunya*), (GC, 2006) . As an example, some of the Muga's EF values are showed in Table 6.5.



Codi	Localització del punt fluvial	oct m³/s	nov m³/s	des m³/s	gen m³/s	feb m³/s	mar m³/s	abr m³/s	mai m³/s	jun m³/s	jul m³/s	ago m³/s	set m³/s
MUGA													
22001	LA MUGA A PIMCARÓ	0,147	0,147	0,176	0,176	0,176	0,176	0,176	0,176	0,147	0,118	0,118	0,118
22003	ARNERA A CAPÇALERA	0,157	0,157	0,189	0,189	0,189	0,189	0,189	0,189	0,157	0,126	0,126	0,126
22004	ARNERA TRAM FINAL	0,240	0,240	0,288	0,288	0,288	0,288	0,288	0,288	0,240	0,192	0,192	0,192
22002	LA MUGA AMB ARNERA	0,430	0,430	0,516	0,516	0,516	0,516	0,516	0,516	0,430	0,344	0,344	0,344
22005	LA MUGA A E.A. A0012 (BOADELLA)	0,450	0,450	0,540	0,540	0,540	0,540	0,540	0,540	0,450	0,360	0,360	0,360
22006	LA MUGA A E.A. A2001 (PONT DE MOLINS)	0,480	0,480	0,576	0,576	0,576	0,576	0,576	0,576	0,480	0,384	0,384	0,384
22007	LA MUGA AIGUA AMUNT DEL LLOBREGAT	0,500	0,500	0,600	0,600	0,600	0,600	0,600	0,600	0,500	0,400	0,400	0,400
22008	LLOBREGAT SOTA LA JONQUERA	0,100	0,100	0,120	0,120	0,120	0,120	0,120	0,120	0,100	0,080	0,080	0,080

Table 6.5. Maintenance flows (source: Pla Sectorial de Cablas de Manteniment de les conques internes de Catalunya, CWA, 2005)

6.2.3.2 Procedure to determine the maintenance flow in the Rivers network of the IBC

In order to determine the mainteimance flow in any desired point of the river network simulating the river basin, the following criteria have to be observed:

- If the point appears in the mentioned tables (a gauging point), it is directly assigned.

- If the point is located between two points showed in tables, the Q_b of the upstream point is assigned (only if the difference with the downstream point was less than 10%). If the difference is higher than 10% of the first value, $Q_b(x)$ is calculated with the lineal interpolation showed in Eq. 4.1.

Eq. 4.1. $$Q_b(x) = \frac{Q_{b,av} \cdot (S_x - S_{am})}{S_{av} - S_{am}} - \frac{Q_{b,am} \cdot (S_x - S_{av})}{S_{av} - S_{am}}$$

Where:

S_{av} : Watershed surface for the downstream stretch.
S_{am} : Watershed surface for the upstream stretch
$Q_{b,av}$: Basic flow of the downstream stretch
$Q_{b,am}$: Basic flow of the upstream stretch
S_x : Watershed surface of the considered stretch
$Q_b(x)$: Basic flow of the stretch to be calculated

- If the point is located upstream the studied points or in a non-studied area, the QPV method about the average interannual flow will be applied to calculate Q_b.

Remember that the maintenance flows regime is monthly modulated, starting from the hydroregion where the river reach belongs.

6.2.4. Real quality values

As indicated in Chapter 5, the quality values for the different river states are needed to apply PH. Some of them can be designed as *real* values (PS, FS), and some others as *established* or *legally defined* values (GES, HS). The PS accounts for the river quality measurements and the FS includes the projected new pressures starting from the PS as reference. However, the GES and the HS, as it happened for the EF, are defined by the competent organism (the CWA in this case), following the WFD guidelines. In addition to them, the quality of the NS of the river is assumed to have the reference quality values for the different river types.

For real quality values in Catalonian Rivers, it exists an on-line data base (Figure 6.11) available at the CWA website (CWA, 2008a). An important amount data regarding water quality can be downloaded. A deep analysis of the available data for the IBC and, in particular, for the Muga and the Foix Basins, was carried out. The sampling stations with complete data sets were chosen. The basic criterion was having, at least, monthly values of the considered parameters. In addition to that, it was highly recommended that the quality gauging stations were located as close as possible to the corresponding flow gauging stations.

La qualitat de les aigües superficials

Consulta i descàrrega de resultats de la qualitat de les aigües superficials a Catalunya

Trieu una de les dues opcions:

Figure 6.11. Sample of the web interface to download quality data (Source: CWA, 2008a)

6.2.5. Geographic characterization: GIS and LDM

The watershed representation provided by GIS (Geographic Information System) layers provides a huge amount of information in a quick way, and it facilitates a realistic simulation of the watershed. The accurate definition of the watershed is needed in order to determine what villages and, in consequence, what drainages and municipal catchments have to be included in the simulation analysis. Therefore, the area was delimited taking the available topography information as one of the starting points.

The land digital model (LDM) plays a fundamental role in the watershed simulation because it provides needed information about the terrain maximum and minimum elevation, air temperature, wind speed, slopes, river basin width and distances, among others (Figure 6.12). It is clear that as much information as possible about the basin's physical reality has to be translated into the model.

Figure 6.12. Land digital model for the Muga Watershed (Source: CWA, 2008c)

As an example, the LDM for the Muga Watershed is reproduced in Figure 6.12. Darker colours are use for the upland areas. The purple line is used to establish the limits of the watershed, that is, the boundaries of the studied system.

The LDM implemented in the watershed simulation developed in this PhD was provided by the CWA, since its elaboration is out of the scope of this work.

6.2.6. General aspects about water demand in Catalonia

In order to find out the problems suffered by our river ecosystems and improve the design and creation of the appropriate corrective measures to achieve the objectives of the Water Framework Directive before the end of 2015, the 5th article of the WFD has to be observed. It establishes that, for each hydrographical demarcation, an analysis of the pressures and impacts on water bodies, and an assessment of the risk of not achieving the objectives set by the WFD, should be drawn up.

The analysis of pressures and impacts on internal river basins in Catalonia has been carried out following the recommendations of Guidance Document No. 3 (CIS, 2003) and is shown in the WFD IMPRESS document (CWA, 2005a).

In this way, the risk faced by certain river stretches, based on the pressures assessed as significant, taking account of the magnitude of the pressure and the susceptibility or vulnerability of the receiving environment (the river type and its capacity to withstand pressure) has been evaluated. Then, through an analysis of the impacts measured in the environment (using biological, hydromorphological and physiochemical indicators), the effect of the pressures on the ecosystem can be specified.

In Catalonia, the water demand involves three large sectors: agriculture (irrigation), industry and domestic. The latter also includes the uses by commerce as well as public uses such as streets cleaning and sewers and watering gardens. Other classifications also include the use for livestock, as well as the so-called *ecological demand*, which is the minimum amount of water with certain quality that must flow along a river so that it complies with its inherent environmental functions (see EF definition). In this way, the CWA does not consider ecological or environmental flows as water demand as they form part of the resources that can not be used (Castañón et al., 2006). The analysis of the *ecological demand* constitutes a basic part of the Framework Directive.

Important organisms are claiming for the direct inclusion of environment as a water user. As an example, the World Bank (WB, 2003) stated that being integral to overall water resources management, the environment is voiceless when other water using sectors have distinct voices. As a consequence, representatives of these other water using sectors need to be fully aware of the importance of environmental aspects of water resources management for the development of their particular interests.

National organizations have also included this issue in their communications. For example, the COAGRET's report on the criteria for implementing the environmental flow also defines the EFR as a key point in the water bodies analyses (COAGRET, 2007).

Traditional studies published by the CWA basically differentiate between agricultural demand (irrigation and livestock demand) and urban demand (domestic plus industrial demand). It is also frequent to differentiate between consumptive demands and non-consumptive demands.

Consumptive demands are all those that effectively use all or part of the required water . CWA includes the following categories in this group:

a) Irrigation demand (crops and golf courses),
b) Domestic demand (homes, commercial and public uses),
c) Industrial demand (industrial uses),
d) Livestock demand (cattle raising).

Non-consumptive demands are those which do not imply a tangible use of an amount of water (although they may vary its quality). The main non-consumptive uses are the production of hydroelectric energy, the use of water for cooling systems in conventional or nuclear power stations, or fish-farming.

The CWA uses various methods to estimate the water demand of different sectors. The agricultural demand is determined by considering the irrigated area, the type of crop and the irrigation techniques used, as well as the type of livestock. Urban demand is considered to be the same as the actual consumption (plus system losses) without considering any pre-established provisions. This definition differs from those used in the past, where these projections were defined. As these pre-defined provisions were normally far higher than the real consumption, the calculations of urban demand tended to be overestimate. The current method is considered to provide data that are closer to reality.

Finally, in the analysis of the water demand is very common to speak of *quotas*, corresponding to the unit demands per person and day for urban uses; per head of cattle and day for livestock uses, and per hectare and year for irrigation uses. It is important to note that the quotas are identified with the amounts of water that enter a system, for example the water that feeds the supply network of a town or the water that feeds an irrigation network. The real consumption is always lower than the corresponding supply since, among others, there are losses in distribution networks once the water has entered the corresponding system.

In Catalonia, the urban demand can be satisfied using local resources or, more and more frequently, through public regional supply networks. The *Ter-Llobregat Water Board* (ATLL) is a regional supply network that covers 74% of the population and 64% of the urban consumption of the IBC (Barcelona metropolis). It collects water from Llobregat Basin, and a water canal from the *Susqueda Dam* (Ter River) with a main flow of 6 m^3/s. Other important regional networks are the private company Tarragona Water Consortium (CAT), which serves at the majority of Tarragona townships of the IBC, with water provided by the Lower Ebro River by means of an small transfer of 4 m^3/s; and the Costa Brava Consortium (CCB), which also supplies the majority of townships in the Girona province, also connecting water from the *Ter River*. During the last few years, and especially as a result of the increase of demand and/or degradation of local resources (mainly aquifers), many municipalities of the IBC have asked to be connected to these large regional networks. ATLL and CCB are connected by the Ter river through two channels.

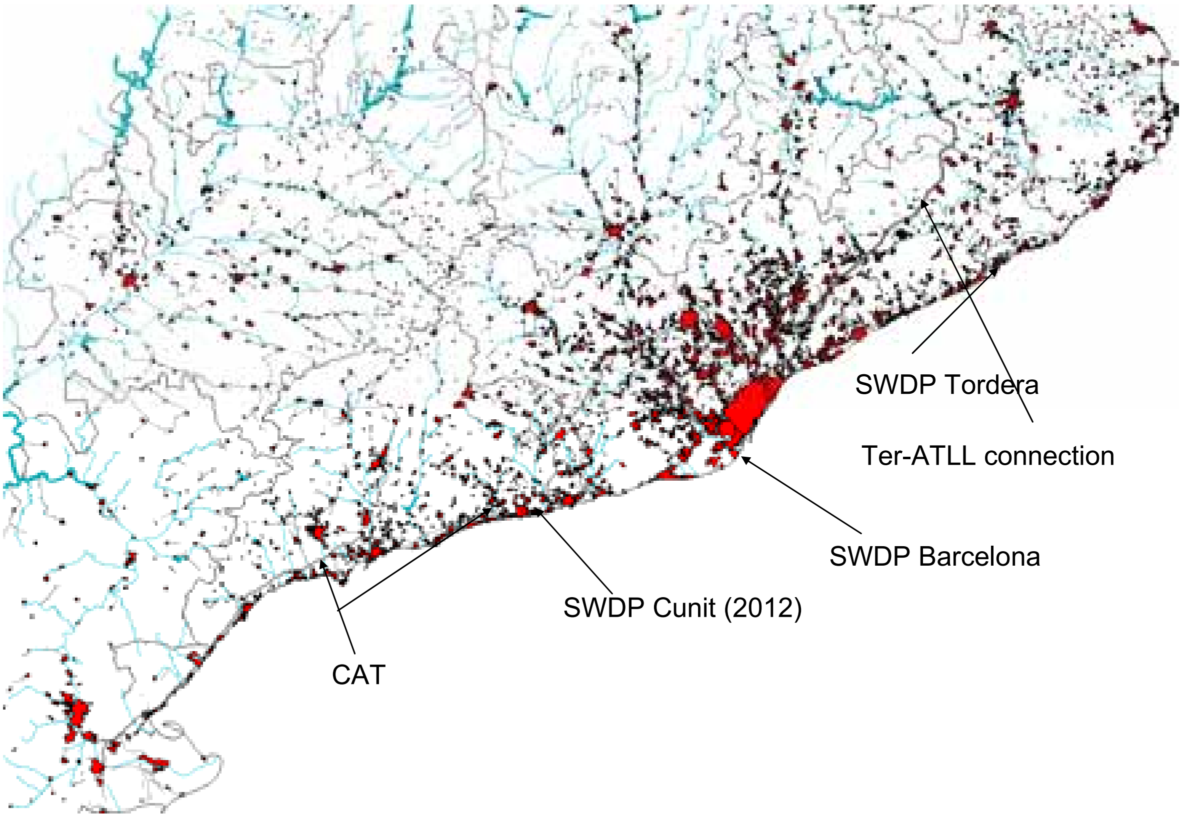


Figure 6.13. Location of the CAT and the Ter-ATLL connexion, in addition to the most important SWDP. Urban areas in red.

However, the ATLL and CAT are still not connected (Figure 6.13). IBC's reserves failed dramatically up to 20% in April 2008. Thus, an emergency plan with a new pipe connecting ATLL and CAT water network systems was approved by Law. Surprisingly, spring period of that 2008 year presented the highest rainfall in the records and, consequently, works were not definitely carried out. At present, the new SWDP of *Barcelona* incorporates new 60 hm^3/yr to the ATLL system, partially avoiding the vulnerability of surface water resources in the area. Furthermore, by the year 2012, the *Cunit* SWDP is projected, with a capacity of more than 50 hm^3/yr, first in the interface between the existing CAT and ATLL water network systems.

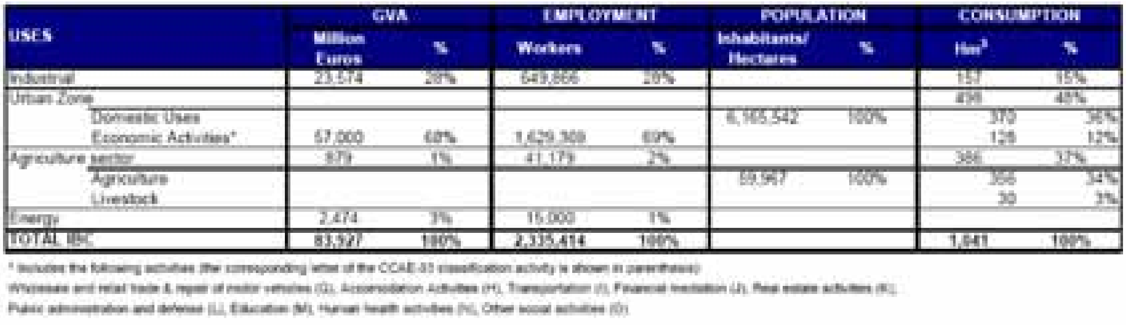
Farming demand is mainly satisfied by large irrigation works that obtain water from reservoirs, even though irrigation with ground water is also important in some areas, for example in *the Baix Camp (Tarragona)* or certain areas of the *Girona* province.

6.2.7. Economic characterization of water use and trend analysis

As indicated, the economic characterization of water uses was also compulsory to fulfil the WFD's requirements. Chapter 5 of the repeatedly mentioned IMPRESS document published by the CWA collected relevant information about the economics of water uses in Catalonia (CWA, 2005a). Main aspects have been summarized in this section in order to provide a glance of the current economic importance of water in that area.

CWA's total financial costs in 2003 was about 360 million euros, from which 23 million euros correspond to the *Foix, Gaia, Francolí* area, and 6.5 million euros to the *Muga, Fluviá, Costa Brava Nord* observation system (CWA, 2005b).

The Table 6.6 shows, on the one hand, the relative economic importance of each water use, in an economic sense (characterized by their gross added value -GAV- and the jobs associated by each of them) and, on the other, the importance of each use in terms of its demand with respect to water resources. As it can be seen from this table, industrial and urban uses (the later covering domestic usage and the use of water by economic activities carried on in an urban setting) create the 96% of the GAV and 97% of jobs in the IBCs, and create a demand for water that represents 63% of the total for the IBCs, while the agricultural sector demand for water represents the remaining 37%.



USES	GVA		EMPLOYMENT		POPULATION		CONSUMPTION	
	Million Euros	%	Workers	%	Inhabitants/ Hectares	%	Hm^3	%
Industrial	23,574	28%	649,866	28%			157	15%
Urban Zone							498	48%
Domestic Uses					6,165,542	100%	370	36%
Economic Activities*	57,000	68%	1,629,369	69%			128	12%
Agriculture sector	879	1%	41,179	2%			386	37%
Agriculture					59,967	100%	356	34%
Livestock							30	3%
Energy	2,474	3%	15,000	1%				
TOTAL IBC	83,927	100%	2,335,414	100%			1,041	100%

* Includes the following activities (the corresponding letter of the CCAE-93 classification activity is shown in parenthesis):
Wholesale and retail trade & repair of motor vehicles (G), Accommodation Activities (H), Transportation (I), Financial mediation (J), Real estate activities (K),
Public administration and defense (L), Education (M), Human health activities (N), Other social activities (O)

Table 6.6. Relative importance of water uses in the internal basins of Catalonia (source: CWA, 2005b)

Gross Value Added or GVA is a measure in economics of the value of goods and services produced in an area or sector of an economy (ONS, 2009). It is primarily used to monitor the performance of the national economy and is now the measure preferred by many institutions to measure the overall economic well-being of an area.

Both GVA and GDP are output measures. They both measure the value of the goods and services produced in the Economy. However, GVA differs from GDP in that GVA excludes taxes and subsidies.

GVA + taxes on products - subsidies on products = GDP

As the total aggregates of taxes on products and subsidies on products are only available at whole economy level, GVA is used for measuring Gross Regional Domestic Product and other measures of the output of entities smaller than a whole Economy (an example of this circumstance will be explained in Chapter 7, with the Emergy accounting).

The economic characterization of water uses is based on the overview of productive activities in the three IBCs provinces (Barcelona, Girona and Tarragona), in which the evolution of the GVA, employment and apparent productivity of labour for the period between 1995 and 2002 was analyzed. This analysis has been based on the tables for GVA at current prices and employment in the three IBC provinces published in the yearbook *Spanish Regional Accounting* by the National Institute of Statistics (CWA, 2005b). To estimate 1995 GVA at constant prices, data of GVA at current prices has been updated with 1995's general accumulated inflation.

The evolution of the GVA at constant prices in the three IBCs mentioned provinces shows an upward trend, growing from 75 billion euros in 1995 to 88 billion euros in 2002 (an increase of 17% in 7 years).

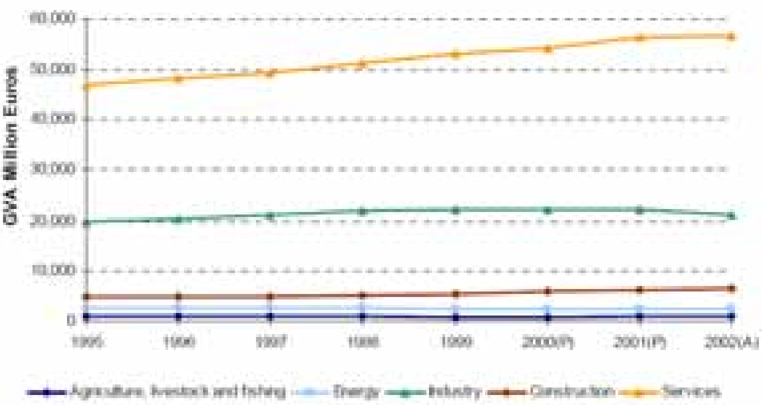


Figure 6.14. Evolution of GVA at constant prices in IBC provinces by sector. (Source: CWA, 2005b)

The sector that most contributes to the GVA is the services sector (according to the forecast for 2002, it contributes 64% to the GVA in the three IBC provinces). Particularly important within this sector is tourism, with a GVA of 4 billion euros, representing the 20% of the GVA generated by tourism in Spain.

Industrial activity, with 28% of the GVA, is the second most important activity, followed by construction (7% of the GVA), energy (3%), and agriculture, livestock and fishing (1%).

The IBCs working population for a total of 2.6 million people in 2002 and the trend in recent years has been towards a small increase in employment.

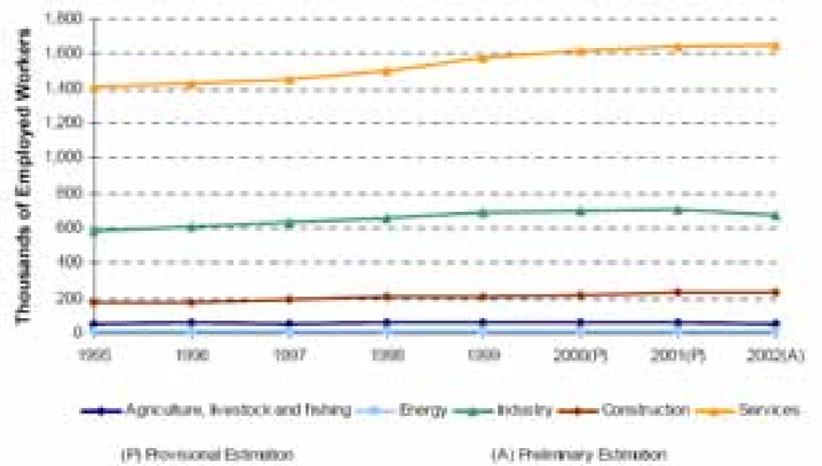


Figure 6.15. Evolution of GVA at constant prices in IBC provinces by sector. . (Source: CWA, 2005b).

Sectors with the highest employment rate are services (60% of total employment in the three provinces) and industry (28%). The other sectors, which have a lower weight as regards employment and job creation, are construction (9% of total employment), agriculture (2%) and energy (1%).

The sector with the highest growth in employment during the analysed period was construction, which grew up to 32%, followed by industry (20% growth) and services (17% growth). Employment in agriculture, livestock and fishing and energy fell by 11% and 1%, respectively.

In order to measure the general productivity of each of the sectors analysed, the GVA at constant prices / employment ratio has been calculated.

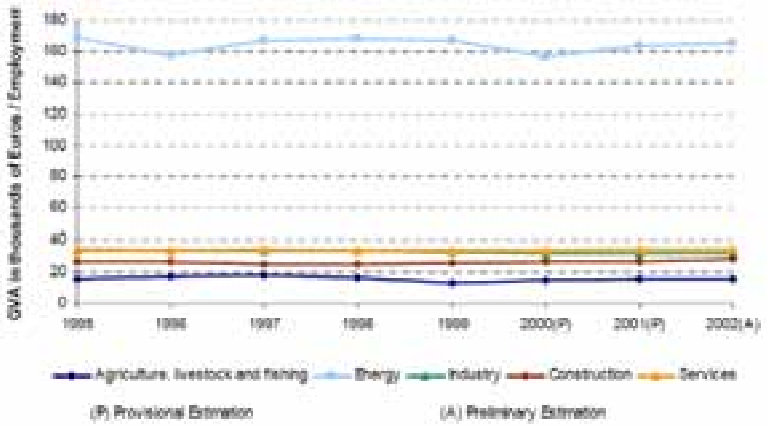


Figure 6.16. Evolution of productivity (GVA at constant prices/employment) by sectors in IBC provinces). (Source: CWA, 2005b)

As expected, highest productivity goes to the energy sector, whose productivity levels are considerably above the others. Nonetheless, energy productivity in the IBCs shows a slight decrease in the period between 1995 and 2002. Industry and the agriculture, livestock and fishing sector show similar trends. Productivity growth in the services sector and in construction reveals an upward trend.

6.3. Case studies: PH's procedure for the Muga and the Foix Watersheds.

Two basins within the IBC have been taken as case studies for this work. The first one, the Muga basin is a seemly clean river, born in the Pyrenees, and no significant pollution sources. The second one, however, is the Foix basin, which is affected by an important environmental damage due to its low flow, the important contaminant charges, and the groundwater overexploitation.

Of course, the applied PH methodology was the same for both rivers. After characterizing the geography and physical issues, a pressures inventory is done. Then the regular PH steps are implemented to get the river exergy profiles in each state (ES, PS, FS, OS and NS). The working steps to proceed with PH for both basins are synthesized in Figure 6.17. It summarized all the details about the procedure given in Chapter 5.

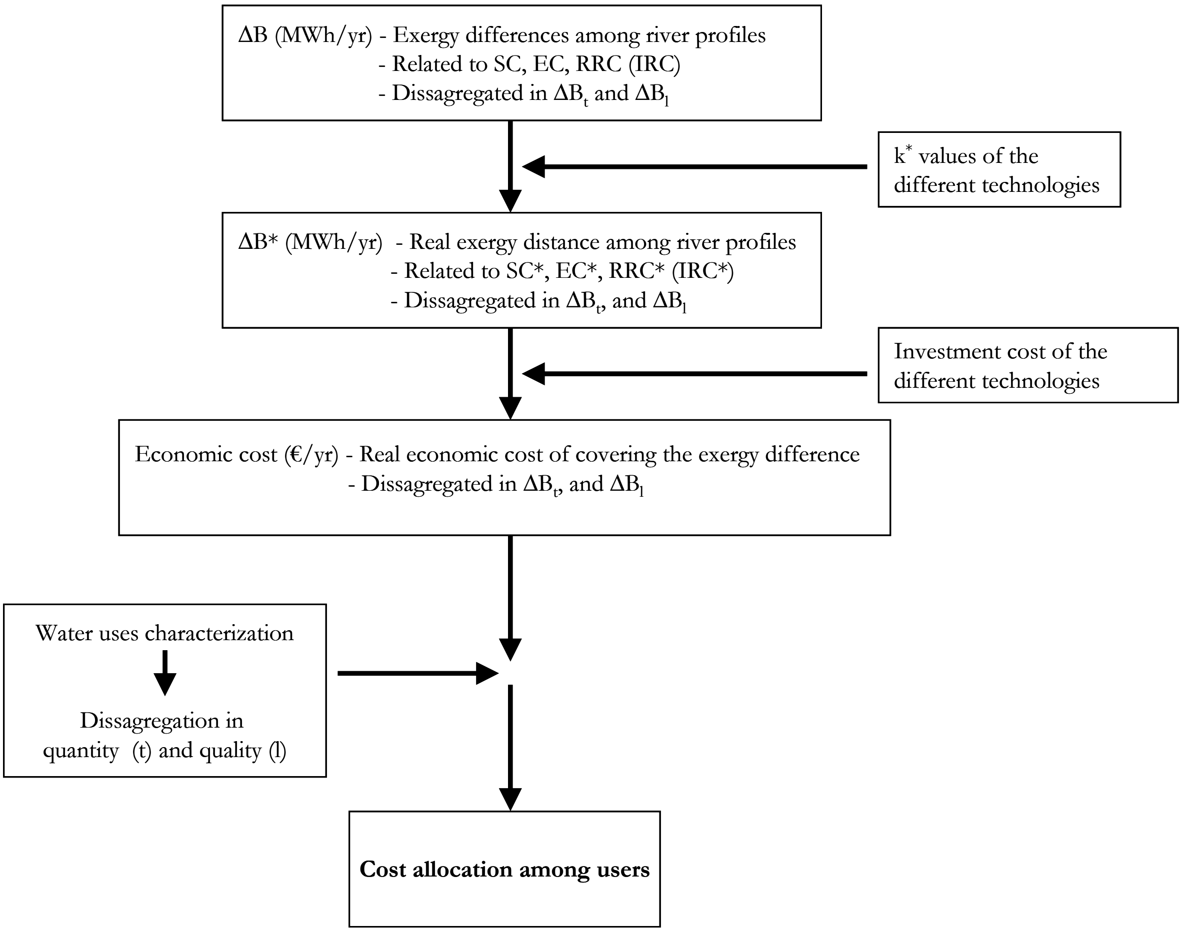


Figure 6.17. Main steps of the PH methodology

There is not much specific information about those watersheds. General data about them have been obtained after reviewing different sources. The most relevant data have been taken from the numerous CWA's documents cited along the chapter, and specific external studies. In addition to that, Ventura et al. (2000) carried out a wide study about the water conflicts in the Muga basin. She made a complete description on the water uses in the Muga river and their consequences. The most relevant aspects on this issue have been reproduced here. About the Foix watershed, several specific works have been reviewed: García (1997) published a paper about the water supply problem in the housing developments located in this area. Marcé et al. (2000, 2005) studied the limnology of the Foix reservoir.

6.4. Case study 1: Muga Basin

6.4.1. Muga Basin: physical description

The Muga Watershed (Figure 6.18) is located in the l'Alt Empordà region, northeast Catalonia. Its surface is 758 km^2 (2.3% of Catalonia), with an average annual rainfall of 612 hm^3 (807 mm) and an average yearly contribution under natural regime conditions of 147.76 hm^3 (CWA, 2004). There are 34 villages in the watershed area and the population rise to 65,756 inhabitants.

Figure 6.18. Location of the Muga Basin (Source: CWA, 2008c)

The *Muga* river is born in the junction of the mountain ranges *Roda* and *l'Abera* and it flows through the region along 65 km until its mouth close to the Natural Park *Aiguamolls de l'Empordà*, after receiving the main contributions of the *Llobregat de la Muga* and the *Manol*, as well as *Figueres* tributaries.

The upper stretch of the Muga river, upstream of the Boadella reservoir, flows trough a mountainous area where several particular spurious irrigation lands are located (the most important are: *Albanyà, Sant Llorenç de la Muga* and *Maçanet de Cabrenys*), covering an approximate area of 40 ha (CWA, 2008).

Figure 6.19. La Muga Basin (Source: Institut CArtogràfic de Catalunya, 1995)

The *Boadella* reservoir also collects water coming from the *Arnera* river and its tributaries, the *Frausa* river and the *Garravera* river (see Figure 6.19). Different irrigation lands are found along the *Frausa* bed, some of them placed in small derivation channels. The *Maçanet de Cabrenys* supply catchment is found in this reservoir as well.

The Darnius' catchment supply is located down waters from the junction of the Frausa and Arnera rivers. This catchment is found in the supply channel of a mini hydropower plant already in disuse, which joins the derivation channel and the Arnera River.

The Boadella Dam is devoted to supply water to Figueres and to irrigate wide agricultural lands downstream through three canals in Pont de Molins (*Boadella d'Empordà, MD, E –Derivació Canal de la Dreta and Derivació Canal de l'Esquerra-*). It has also permission for nautical sailing activities (without engine). In the dam there is also a hydroelectric power plant. The abstraction for Figueres supply is a conduction flowing in the right bank of the reservoir.

In drought periods, *Figueres* has taken water from the *canal del'Esquerra*, which raises from the *Pont de Molins* canal, 16 km downstream the dam.

Hydropower generation is subordinated to the irrigation demands, that is, only the water flowing to irrigation canals is turbinated, starting in *Pont de Molins*. So, *Figueres* supply catchment and the maintenance flow are independent from the central derivation and those flows are not turbined.

At the beginning, the power plant had an only turbine, but it was substituted by two smaller ones in order to optimize energy and irrigation demand. Downstream the dam there is a canal to regulate the drainage from the hydropower and, in this way, to be able to favour the plant operation: when the irrigation demand decreases, a water volume higher than the demand is turbined and regulated in that canal.

In the stretch between *Boadella* and *Pont de Molins*, there were found several non-operative mini-hydroelectric power plant and some private irrigation lands using surface water. Main catchments are located in the crib dam of*Pont de Molins*: the right canal (*Canal de la dreta*) and the left canal (*Canal de l'esquerra*); they do not receive any additional water contribution along their course.

Down water the convergence of the *Llobregat de la Muga* and *la Muga* rivers there is a new diversion dam deviating water to *Rec del Molí*, close to *Castelló d'Empuries*. The CCB takes water from this canal, but just in emergency situations. *Cabanes* municipality is supplied with local wells and the possibility of using the Figueres network is being studied.

The rivers *Orlina* and *Llobregat de la Muga* join in the city of *Peralada*. The *Anyet* river is a contributor of the *Orlina* river in its right side and several private irrigation lands take water from it.

Close to *Peralada*, there are some wells that provide water supply to a set of urban areas. On the one side, water is leaded to *La Jonquera, Capmany, Espolla, San Climent Sescebes, Mollet de Peralada* and *Masarac*. In the future, Agullana will be included in this distribution network though a branch pipe at the beginning between Capmany and La Jonquera.

The regular water supply in the CCB Nord (*Roses, Cadaqués* and *Llança)* is based on wells, but in peak demand periods, some water is also taken from the *Canal de l'Esquerra* and, in emergency situations, from the *Rec de Molí* in *Castelló d'Empuries* as well, as it has been already said. Rec de Molí dies in *la Mugueta* (the Muga's Delta).

WWTP in *Figueres* pours in the *Riera de Figueres* and merge downstream the Muga river. Afterwards, *Muga river* joins to *Manol* river. From this river and its contributor, the *Alguema*, the water for the small private lands is being taken. A pond to collect water from the *Canal de la Dreta* coming from *Pont de Molins* is planned to be built. Several channels from that pond to the different irrigation zones are in project in order to extend the irrigable land in the right bank, but none of them are under construction at this moment. The confluence with *la Mugueta* is found downstream the *Manol* confluence. This contributor has an especial operation because the *canal de l'Esquerre* and the *Rec del Molí* return there. At the end of the *Rec del Moli*, a part of the water goes to the Muga and other part, together with the flow coming from the *canal de l'Esquerra*, goes into the sea at *Santa Margarida*.

6.4.1.1 Water availability in the Muga Basin

The main water supply in the Muga river basin comes from the Boadella dam reserves and from the rich aquifers in the *altoampurdanés* subsoil. The water capacity of the reservoir is 62 hm^3. Its construction finished in 1969, with a triple purpose: laminating the frequent freshets and flooding episodes of the Muga river, water supplying for the city of Figueres and the conversion of 12,270 ha within an ambitious irrigation plan still uncompleted today (Ventura et al., 2000).

Regarding aquifers, the most important are the one in the middle course of the Muga river, with abstractions in *Peralada* area, and the aquifer in the low Muga, whose exploitation in Castelló d'Empúries registered, before 1987, a decrease up to 11 m in the freatic level (CWA, 2008a).

In addition to this two basic supply sources, the offer has been amplified by means of secondary sources such as the water catchment in the river bed and its contributors, or the reuse of treated wastewaters from the plant in Empúriabrava.

The surface water catchments are a common practice in the Muga basin, although they are not always done in a regulated way (IADEN, 1998). The river flow greatly fluctuates along the year (on average, from 1.9 to 11.9 m^3/s) according to the typical flow regime of the Mediterranean area.

In relation to the reuse of depurated waste water, the *Empúriabrava* facility treated in 2007 a water volume of 1,032,785 m^3 – the equivalent to 35,000 inhabitants- (CCB, 2008). This sewage treatment plant was, at its building moment in 1995, pioneer in Spain since its biological treatment derivates depurated water to the *Natural Park Aiguamolls de l´Empordà*, devoted to maintain the *Cortalet wetland* levels. This environmental reuses project meant multiple benefits at the zone. In addition, it provides sufficient water of high quality to the *Cortalet lagoon* to avoid its desiccation in summer and/or to flood the wet meadows in the surrounding area, to restore the healthy ecological condition of the area's flora and fauna to achieve biodiversity similar to that of natural ecosystems. Ammonia is an important steering parameter: if the ammonia content of the effluent of the WTP is below 5 mg/l, it is allowed to divert it in the constructed wetland. Next, all the nitrogen is oxidized. Once oxidation has finished, other processes happen spontaneously, improving the effluent and upgrading the nature reserve.

Finally, it is important to highlight that, in scarcity moments, some municipalities such as *Capmany, Sant Climent Sescebes* or *Lladó*, obtained up to 240,000 liters of water per day, transported from *Figueres*.

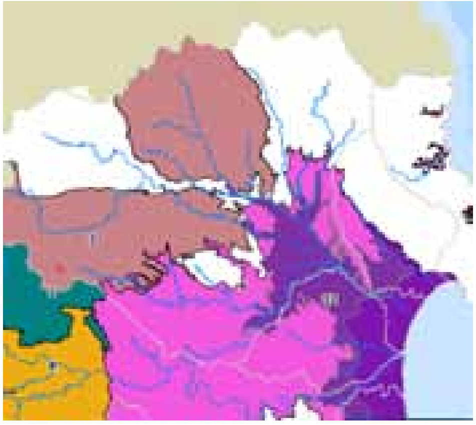


Figure 6.20. Subterranean water bodies in the Muga river basin. (Source: CWA, 2008a)

6.4.1.2 Main water uses in the Muga Basin

Because of their proximity and groundwater connections, water demands in the Muga basin are usually given aggregated to the Fluvia basin, under the denomination Muga-

Fluviá system. The global consumption in that area was 110.4 hm^3/yr (CWA, 2005a), distributed as follows:

a. Urban: 27 hm^3/yr (24%)
b. Industry: 2 hm^3/yr (2%)
c. Livestock: 4.6 hm^3/yr (4%)
d. Irrigation: 76.8 hm^3/yr (70%)

Water supply for *Figueres* and *Roses* are the most representatives in urban demand. They are strongly affected by the increase of population in summer time.

In general, there is no specific figures for the water demand for industrial uses because most of the industries are connected to urban networks. So, they are accounted for in the urban water demand. In spite of that, because of the scarce industrial activity in the area, it is possible to affirm that the industrial water uses are low and that they are concentrated in the most industrialized cities: *Figueres, Vilasacra, Vilamalla.*

Main pressures in the area are represented in Figure 6.21. These are the locations considered in this work. They will be further developed in next section.

Figure 6.21. Main pressures in the Muga watershed.

6.4.2. Application of the pressure-impacts model to the Muga Watershed.

The construction of the P-I model using the Qual2k simulation software implies a set of stages that need to be sequentially followed. Each of them has their associated information requirements. Total input data required by the model means a wide and varied information. The main phases of the work are:

- the identification and ramification of the river,
- the headwaters characterization, the description and
- introduction of the main anthropic pressures and the model calibration.

6.4.2.1 Identification and sliceage

The geographical location of the river within Catalonia defines the type of river that is being considered. Looking at the Figure 6.7, the river features are defined and the river headwaters, as well as all the stretches. Then, the objective for any of them can be chemically characterized.

By following the general criteria for river fragmentation (relevant catchments or returns define a new reach) and the IMPRESS guidelines, the Muga Basin has been divided intro 54 reaches, with 12 headwaters. The river types are given in Table 6.7

Headwater name	**River type**
Muga (1); Arnera (3)	Mediterranean mountain rivers on limestone
Ricardell (26); Merdàs (28); Manol (42); Riera d'Alguema (46); Riera de Figueres (50)	Lowland Mediterranean rivers with variable flow
Llobregat de la Muga 1 (15); Llobregat de la Muga 2 (20); Anyet (30); Merdança (32); Reguerada (34); Orlina (36)	Mediterranean lowland rivers on silica

Table 6.7. Types of river for the Muga's headwaters.

The 54 reaches forming the Muga general schema are shown in Figure 6.22. The 12 headwaters are marked, as well as the most representative pressures points. An enlarged version of this figure can be found in Annex A.

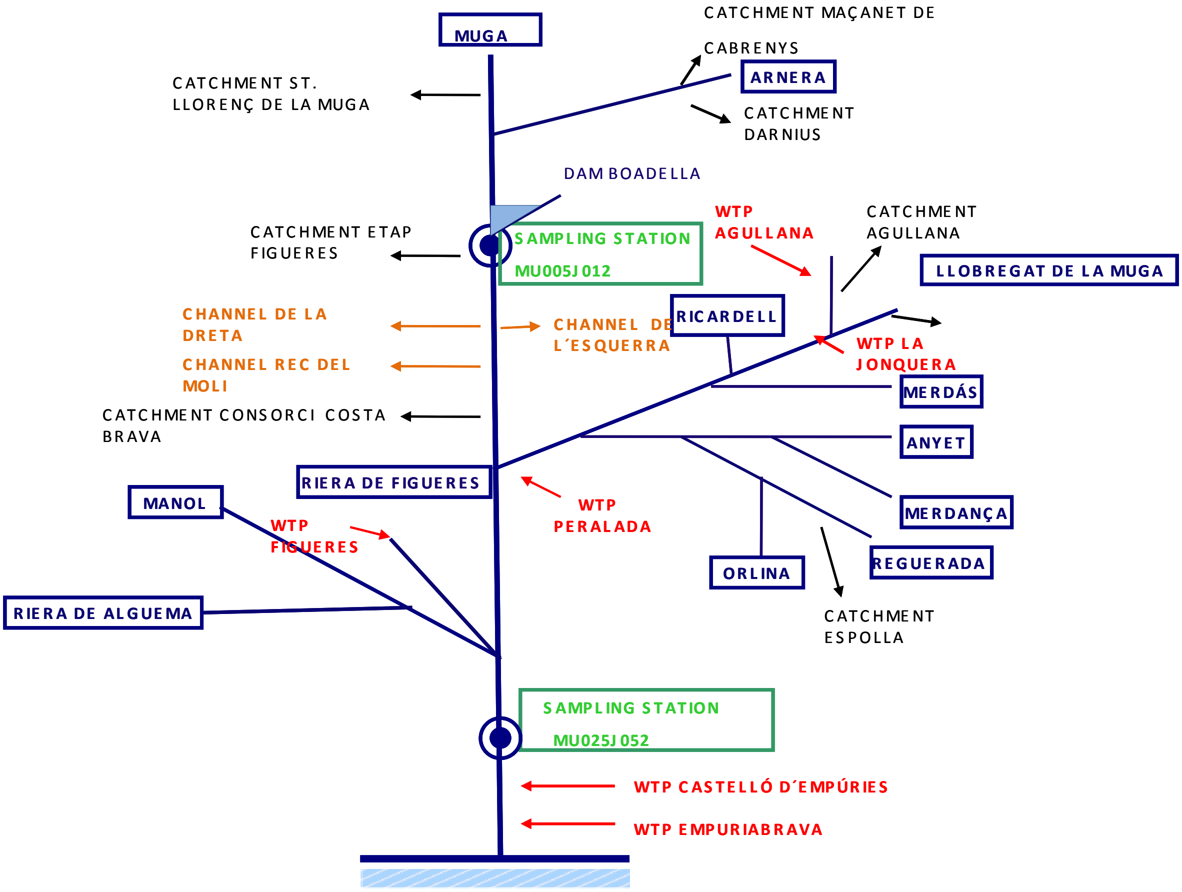


Figure 6.22. Muga basin schema, with the most important uses.

6.4.2.2 Headwaters characterization

Muga's headwaters are showed in Table 6.8. Special attention has to be devoted to the reaches forming each water course or tributary.

	Name	Reaches
HW#1	Muga	1, 2, 3, 4, 8, 9, 10, 11, 12, 13, 14, 41, 49, 51, 52, 53, 54
HW#2	Arnera	5, 6, 7
HW#3	Llobregat de la Muga (1)	15, 16, 17, 18, 19, 23, 24, 25, 27, 29, 39, 40, 41
HW#4	Llobregat de la Muga (2)	20, 21, 22
HW#5	Ricardell	26
HW#6	Merdàs	28
HW#7	Anyet	30, 31, 33, 38
HW#8	Merdança	32
HW#9	Reguerada	34, 35, 37
HW#10	Orlina	36
HW#11	Manol	42, 43, 44, 45, 48
HW#12	Riera de Alguema	46, 47
HW#13	Riera de Figueres	50

Table 6.8. Headwaters' names and reaches contained in each headwater

For each headwater of the main water courses, quantity and quality figures in their source point have to be introduced in the simulator:

For those river sources, quantity and quality parameters are required. Flows are obtained from CWA (2004), where the natural flows of the IBC were restored from 1940 to 2000. Quality parameters in those headwaters are defined by CWA (2006) according to the river type.

6.4.2.3 Description of the anthropic pressures in the watershed

Domestic, urban and agricultural water uses were collected to simulate the current pressures in the Muga river. Table 6.9 reports the location and geographical features of the water uses. However, detailed information about the abstracted water for each of them along the year is also required. In the following sections, agricultural, urban and industrial uses are given and graphically represented.

Name	Headwater	Location	Upstream	Downstream
	ID*	km	Reach	Reach
CAPT. FIGUERES	1	35.24	4	8
REG ALBANYÀ	1	57.42	1	2
REG BOADELLA D'EMPORDÀ	1	30.44	10	11
REG SANT LLORENÇ DE LA MUGA	1	45.58	2	3
REGS MD	1	23.02	12	13
REGS ME	1	23.02	12	13
REGS MOLÍ	1	19.48	13	14
URBÀ CCB (out of the basin)	1	26.27	11	12
URBÀ SANT LLORENÇ DE LA MUGA	1	45.14	3	4

REG MAÇANET DE CABRENYS	2	11.64	5	6
URBÀ MAÇANET DE CABRENYS	2	9.95	6	7
REG BIURE	3	11.51	24	25
REG CAPMANY	3	15.46	23	24
REG JONQUERA, LA	3	21.64	15	16
REG AGULLANA	4	5.17	20	21
URBÀ AGULLANA	4	5.17	20	21
URBÀ DARNIUS	5	9.23	26	26
REG SANT CLIMENT SESCEBES	7	12.66	30	31
URBÀ ESPOLLA	9	6.48	35	37
REG LLADÓ	11	32.81	42	46
REG BORRASSÀ	12	6.03	46	47
ALBANYA	1	51.50	2	--
BOADELLA D'EMPORDA	1	26.27	11	12
LLERS	1	21.25	13	13
TERRADES	11	17.29	44	45
MAÇANET DE CABRENYS	2	7.46	7	7
CAPMANY	3	13.49	24	24
BIURE	5	3.08	26	26
DARNIUS	5	9.23	26	26
SANT CLIMENT DE SESCEBES	7	8.01	31	31
MOLLET DE PERALADA	8	4.29	32	32
RABOS	10	2.09	36	36
CABANELLES	12	13.84	46	46
CISTELLA	11	27.78	43	43
BORRASSA	12	3.02	47	47
NAVATA	11	24.02	43	43
ORDIS	12	9.76	46	46
SANTA LLOGAIA D'ALGUEMA	12	6.03	46	47
VILABERTRAN	13	4.47	50	50
EDAR Agullana	4	3.29	21	22
EDAR La Jonquera	3	19.01	17	18
EDAR Figueres	13	5.96	50	--
EDAR Peralada	3	0.73	39	40
EDAR Castelló d'Empúries	1	4.11	52	53
EDAR Empuriabrava	1	2.06	53	54
Embassament de Boadella	1	35.24	4	8
Ind. Figueres	13	5.00	50	50

Table 6.9. Location of the anthropic pressures in the watershed

Agricultural uses.

Main agricultural catchments along the muga watershed are represented in Figure 6.23. It can be easily noticed that the main ones are those in the left and right canals (*Derivació canal de la Dreta y derivació canal de l'Esquerra*).

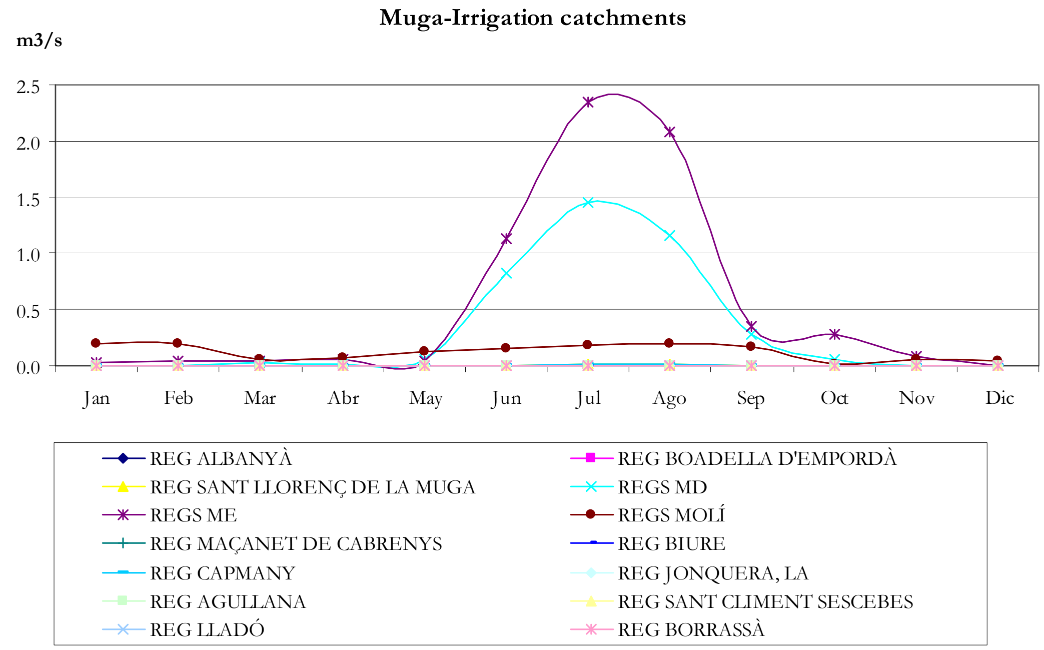


Figure 6.23. Agricultural catchments in the Muga river.

There are important amount of catchments devoted to irrigation (*REG*), which are very small compared to the right and left canals (ME and MD). For the shake of clarity, the smaller catchments have been represented separately in Figure 6.24.

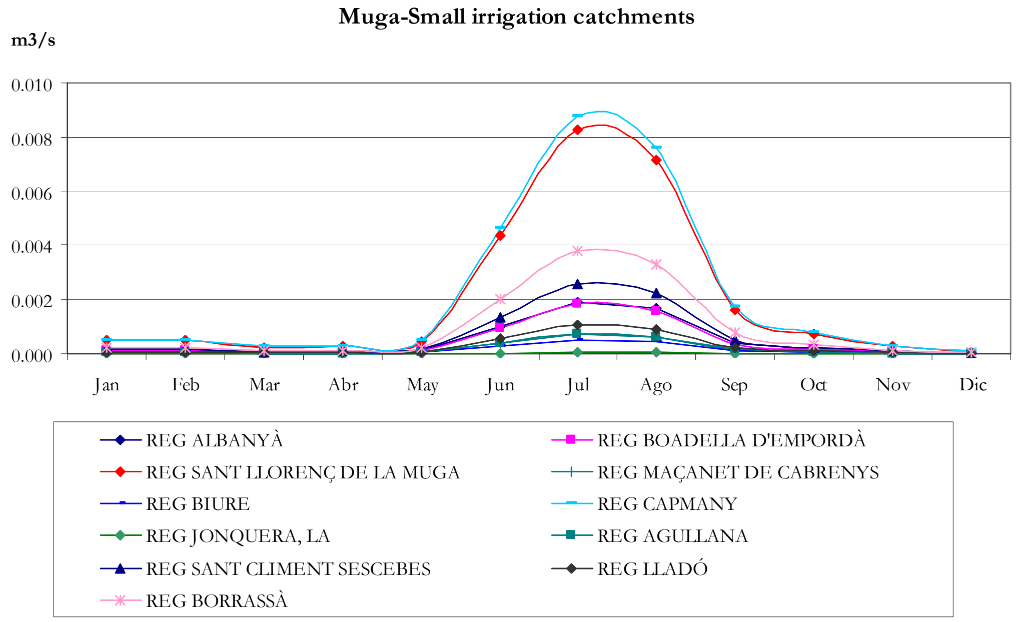


Figure 6.24. Muga-Small irrigation catchments

There are several irrigated lands along the river, as they have been described in previous section. The catchments are considered as punctual abstraction sources, but their returns are in a diffuse way (10% is the return rate considered in this work). When this information is integrated in the simulation, diffuse return is assumed to happen along the reaches 13 to 54, to main headwater (Muga course).

	Quantity	**Quality**	**Location**
Catchment	Q_{irr}	Quality of the abstraction point	Corresponding reach
Return	$10\%Q_{irr}$	Input quality plus degradation produced by the use	Reaches from 13 to 54

Table 6.10. Summary of the data required for the irrigation use characterization

Urban uses

There are an important amount of surface water catchments for urban uses although, as it has been explained, groundwater has also a very representative contribution. Figure 6.25 shows main urban surface water sources in the basin.

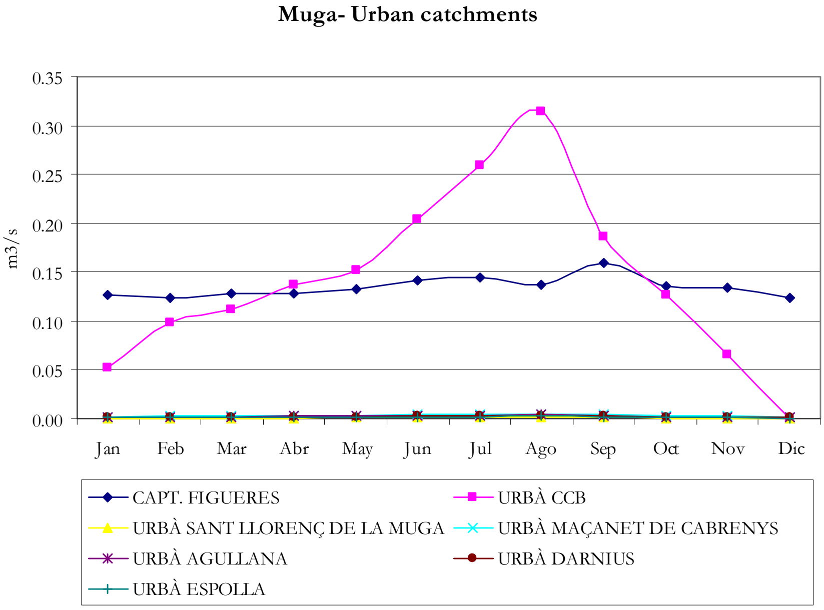


Figure 6.25. Muga-Urban catchments

As it was already done for the irrigation uses, in order to appreciate the smaller catchments, they have been separately represented in Figure 6.26.

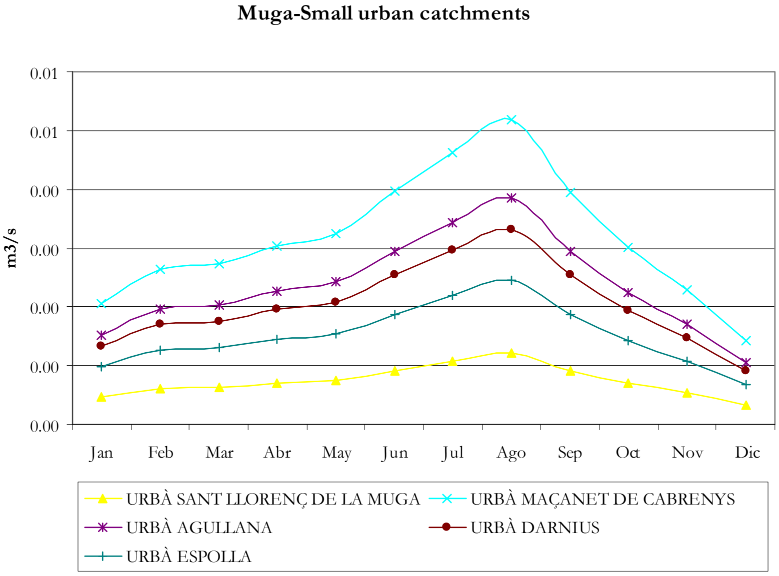


Figure 6.26. Muga-Small urban catchments

Muga Dam

Regulation of the *Boadella Dam* is represented in the simulator as an additional flow, positive in winter months and negative in summer, as it can be seen in Figure 6.27. The negative sign represent water releasing the dam, to be used in irrigation, after being turbined. This is the reason why hydroelectricity production is usually higher in summer than in any other time, independently on the rainfall period.

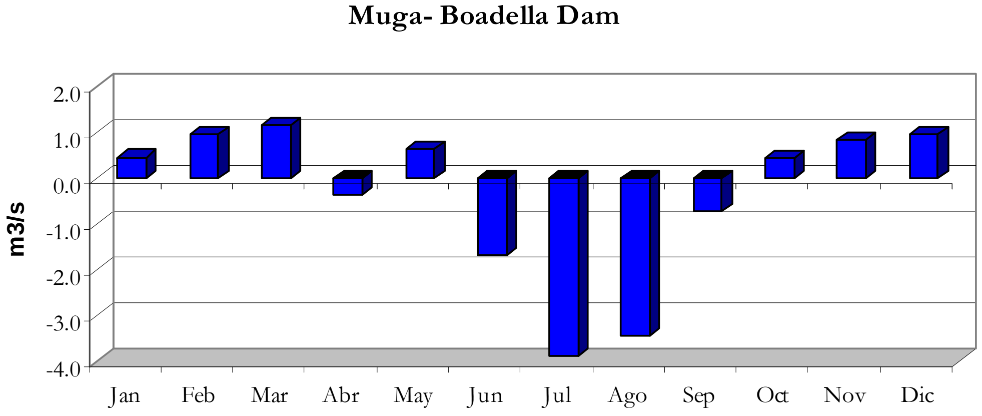


Figure 6.27. Muga-Boadella Dam

6.4.2.4 Diffuse sources

There are two different types of diffuse sources included in the simulation. On the one hand, rainfall contribution along the river basin and, on the other hand, irrigation returns. The general characterization of the diffuse sources in the Muga basin is shown in Table 6.11, and their variation along the year can be seen in Figure 6.28. Table 6.11 indicates the headwater where the diffuse source is located and its up and down location in km. When de down location is cero, it means that the main headwater has been reached (see Annex E for further details).

Name	**Headwater ID**	**Location Up km**	**Down km**
Muga	1	62.91	35.24
Arnera	2	16.22	0.00
Riera de Alguema	12	6.03	0.00
Riera de Figueres	13	5.96	0.00
Llobregat de la Muga	3	22.82	9.75
Llobregat de la Muga_part final	3	6.27	0.00
Anyet	7	19.79	0.00
Reguerada	9	16.81	0.00
Manol	11	32.81	0.00
Irrigation returns	1	23.02	8.85

Table 6.11. Diffuse sources location of the Muga watershed.

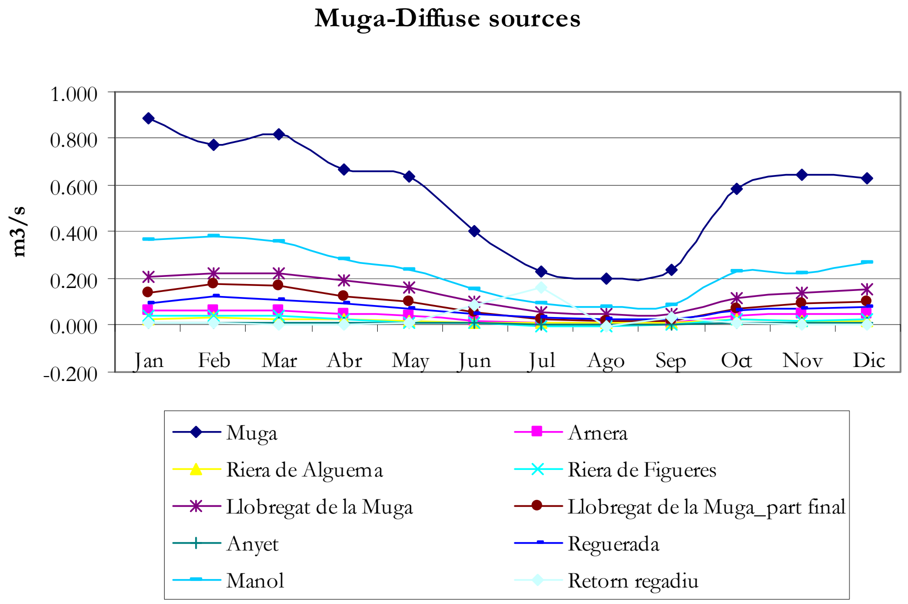


Figure 6.28. Muga- Diffuse Sources

Diffuse sources are demarcated in the simulator by its starting and ending kilometer points. The flow is distributed to or from each reach in a length-weighted fashion.

6.4.2.5 Quality data

As it has been explained, flow, temperature, geographical figures, conductivity and the rest of quality data are given by real data and the watershed simulator (In particular, the parameters directly taken from the simulator for the exergy assessment are: Q, T, TOC, Cond, NO_3, NH_4, PO_4 and SS –see exergy results tables in Annex A-). The quality data not provided by the software, but needed for the exergy assessment, were extrapolated from real sampling data and weighted according to the conductivity in each reach. These adjusted parameters are: Cl, SO_4, NO_2, Ca, HCO_3, K, Mg and Na (see exergy results tables in Annex A). The sampling station assigned to each reach is chosen according to its proximity. In Table 6.12, the assignments are detailed.

Sampling station name (CWA's denomination)	**Reference reach**	**Used to reaches:**
QLSup - Riu Arnera aigües amunt de Boadella	6	1 to 7
MU000L001	8	8
MU055J012 (Peralada)	9	9 to 14
QLSup - Capçalera del Llobregat de la Muga fins al Ricardell	23	15 to 33 (except 26)
QLSup - Riu Ricardell	26	26
QLSup - Conca de l'Orlina	37	34 to 37
MU010J100	40	38 to 40
MU015J067	41	41
QLSup - Riu Manol i riera d'Àlguema	45	42 to 45
QLSup - Santa Llogaia D'alguema - Riu Muga	47	46 to 47
MU0251052	51	48 to 54 (except 50)
MU020J101	50	50

Table 6.12. Sampling stations and reaches where they are used to define the quality data not provided by the software

Remaining the data characterization given in Chapter 5, lets analyze the reality for the Muga Watershed.

	ES	FS_{2015}	PS	OS=GES	OS=HS	NS
Flow	Q_{ES}	Q_{FS}	Q_{PSI}	$\max(Q_{MF}, Q_{FS})$	$\max(Q_{NF}, Q_{FS})$	Q_{NF}
Quality	b_{ES}	b_{FS}	b_{PS}	b_{OS}	b_{HS}	b_{HW}

Table 6.13. River states characterization in quantity and quality.

Both the flow and the quality parameters for the ES, FS and PS are given by the simulation software (starting from real collected figures). The flow for the NS is the natural flow obtaining from historical hydrological studies. The quality values for the objective states and for the NS are legally defined from areas characterization.

By analyzing the GES, it can be observed that Q_{GES} ($=Q_{2015}$) is higher than Q_{MF} in almost all the river stretches. Only two exceptions are found: reach 28 and reach 32. Both of them are headwaters. Since Q_{MF} is defined according to minimum needed flow to ensure biological life and not attending the flow pattern in its source (even totally dry at some periods of the year), these misunderstandings can be then explained.

6.4.2.6 Calibration

The Qual2k model has an auto calibration module based on an genetic algorithm (Pikaia –see Appendix E for details-). The calibration is done on the main course of the river, modelling the different tributaries of the basin as point contributions. In this task, it is considered that the initial and final points of the calibrated stretch coincides with the control stations located as much upstream and downstream as possible. Both the extreme points and the point sources have to be quantitatively and qualitatively characterized.

Before executing the calibration, an adjustment formula regarding the goodness of the model (*fitness*) is introduced, in order to compare its outputs with the real parameters measured in the sampling stations. In this case, the default formula in the software has been used (the inverse root mean squared error).

After the auto calibration process, the model outputs some taxes for the physico-chemical parameters defined as *rates*. These *rates* have to be introduced in the program to run the different river states.

The representation of the Muga river calibration is presented in Figure 6.29. The initial point is the control station MU005J012 and the gauging in the *Boadella Dam*; and the final point is the control station MU025J052, located in *Castelló d' Empúries*. When more than one contribution coincides in the same point source, the introduced quality is the volume-weighted average.

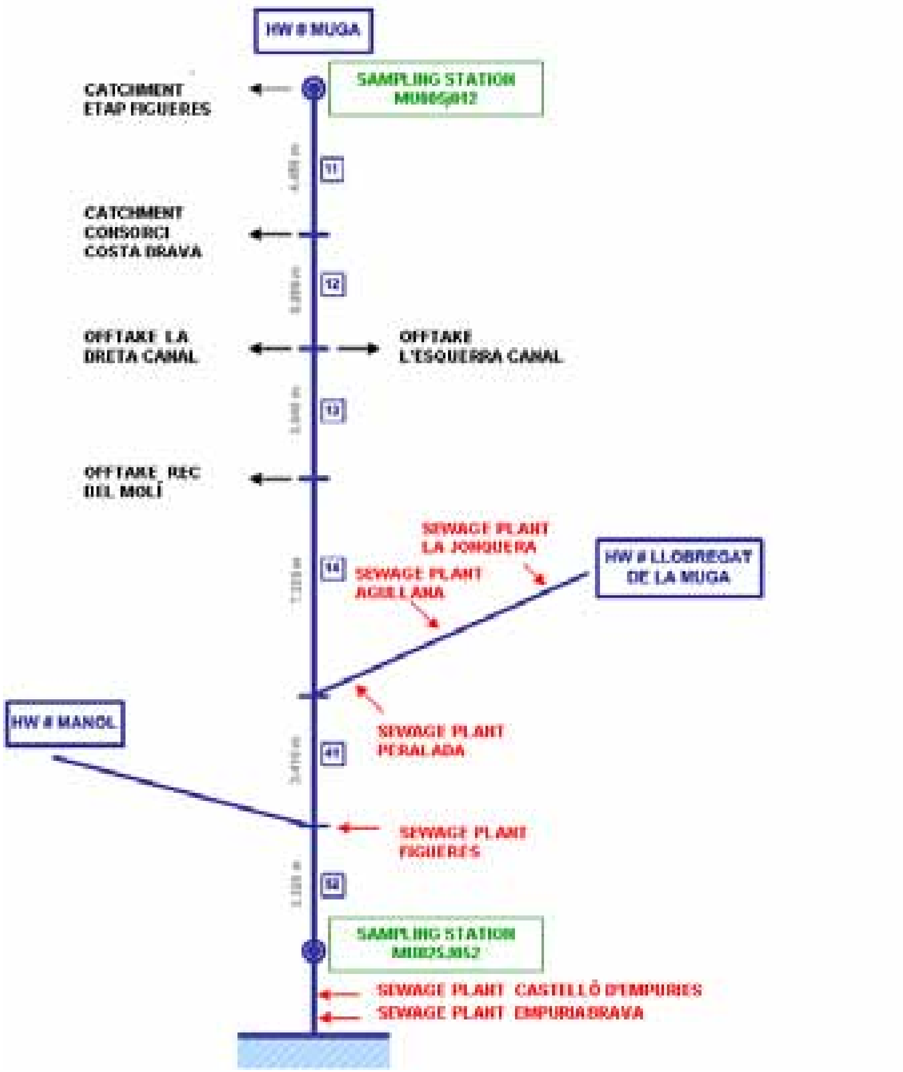


Figure 6.29. Muga calibration schema

In general, the required information to calibrate the model is the same as in a regular simulation. The magnitude of the work is lower because the hydraulic schema is simpler and, therefore, less information is required. In any case, geomorphological information for each river, as well as knowledge about the existing catchments and returns, are needed.

6.4.3. Results of Physical Hydronomics in the Muga Watershed

The PH methodology described in Chapter 5, together with the input required data described along this Chapter, merge here to study the exergy profiles, exergy costs and WFD's costs allocation in the Muga watershed. The most representative final values are given in this section. Additional tables and figures can be found in Annex A.

First of all, the most relevant values for the river flow in January (as an example) are given in Figure 6.30. If all the 54 reaches of the river were represented, it would lead to a confusing interpretation of the B curves presented in Chapter 5 (well-shaped figures) because of the particular tributaries behaviour. In consequence, only the main course of the river has been drawn. The monthly graphs corresponding to the whole year can be found in Annex A.

As it can be easily understood, the final reaches of the river carry more water due to the received contributions from tributaries. Natural flow is almost always higher than the real flow, since it accounts for the original situation of the river, without antrophic influence. NF is only similar to the real flow in the reaches located close to the source, where no human effect is still detected. For each month, the maintenance flows are lower than the two previous flows, as it corresponds to its definition (see Chapter 5).

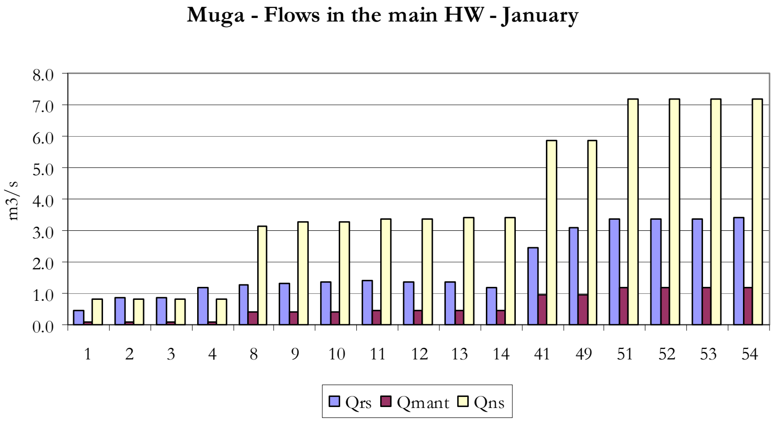


Figure 6.30. Flows (real, maintenance and natural) in the main course of the Muga river in January.

6.4.3.1 Global exergy value of the Muga watershed

Before going further with the PH's methodology steps, it has been considered as interesting to show some general global numbers about the exergy value of the Muga river.

As already indicated, the main value of the river comes from its potential and chemical features. The potential content of water is commonly used in hydroelectricity, what leads to the PURI index definition. Nowadays, the chemical content of the river is not used to produce energy and, as a result, the CURI index is always zero. In addition, two additional indices related to the fuel used to maintain clean the river waters are defined (see section 5.10.4 for details).

At this point, it is worth to remember that the chemical potential is defined by the exergy of water b_{H2O}. This value generally appears aggregated with the b_{salts} in the term b_{IM}. Because of the small value of the salts exergy, b_{H2O} and b_{IM} are similar (Table 6.14). However, the salts contribution is fundamental because the increase of salts dissolved in the river water indicates a decrease in the water exergy value.

B_{H2O}(MW)

	Min	Max
PS	2.30	8.78
OS	2.62	9.71
NS	2.51	9.40

B_{chem} (MW)

	Min	Max
PS	2.30	8.78
OS	2.36	8.85
NS	2.38	8.91

Table 6.14. Comparison of B_{H2O} and B_{IM} for the PS, OS and NS in the Muga river

Table 6.15 summarizes the results obtained for the potential and the IM component. The study was carried out for each month. Here, for the sake of clarity, only the values range (minimum and maximum), have been reproduced. The complete results, as well as the values for all the considered river states (PS, FS, ES, OS and NS) can be found in Annex A.

B_{pot} (MW)

	Min	Max
PS	2.37	7.15
OS	2.44	7.16
NS	2.64	8.05

B_{chem} (MW)

	Min	Max
PS	2.30	8.78
OS	2.36	8.85
NS	2.38	8.91

Table 6.15. Minimum and maximum exergy values of the Muga river

	$B_{av,pot}$ (MW)	$B_{av,chem}$ (MW)
PS	4.83	5.10
OS	4.97	5.58
NS	5.76	6.01

Table 6.16. Average exergy values of the Muga river

As it can be seen, the order of magnitude of the pot and IM components is the same. The potential of the NS is higher than the potential in the PS and in the OS. On average, the exergy value of the Muga river, is about 5 MW (potential) and 5 MW (chemical) in the PS. It perfectly fits with the known data of the hydroelectricity power installed in the Boadella Dam (close to the river source), which is 3.6 MW.

In addition to that, looking at the global results given in Annex A, the resulting power is higher in those months when the river flow is higher.

An additional interesting figure was obtained when these global exergy chemical values were compared with the power currently used to clean the Muga river waters. That power is about 4 MW, almost the same as the chemical exergy.

Finally, the indices related to the potential and chemical use of the river can be calculated:

P_{pot}	P_{chem}	F_{pot}	F_{chem}	R	F_R	PURI	CURI	RRI	F_RRI
3.60	0.00	4.83	5.10	0.71	3.92	0.75	0.00	0.18	0.77

Table 6.17. Index Refining the exergy value of the Muga river in its PS.

6.4.3.2 Exergy profiles in the Muga watershed

The characterization of each river state was done by the addition of the real data, the values obtained from the watershed simulation and the legally defined parameters. Then, each river state was always characterized by their corresponding pair quantity-quality. Next, the exergy of each river state was calculated using the equations explained in Chapter 5, by introducing them in the EES program as calculation tool. The obtained exergy profiles for the PS of the Muga river in January (hydrologic year 2003-04) are presented in the next figures (Figure 6.31 to Figure 6.36):

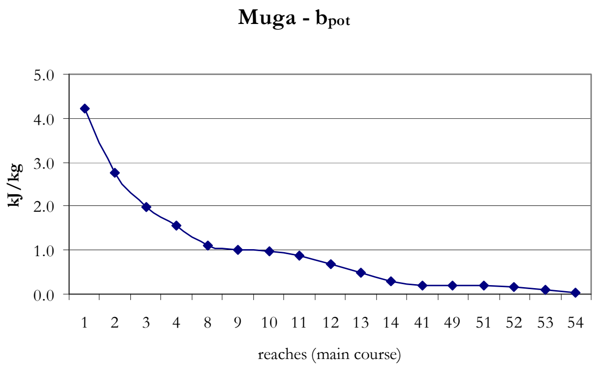


Figure 6.31. Specific exergy profile of the potential component (PS)

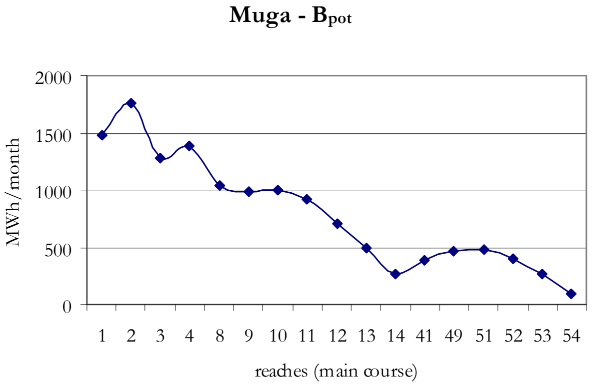


Figure 6.32. Exergy profile of the potential component (PS)

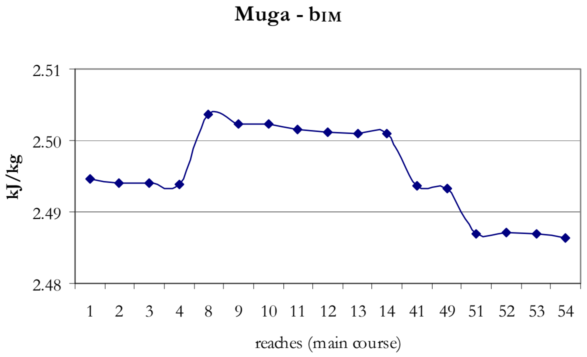


Figure 6.33. Specific exergy profile of the IM chemical component (PS)

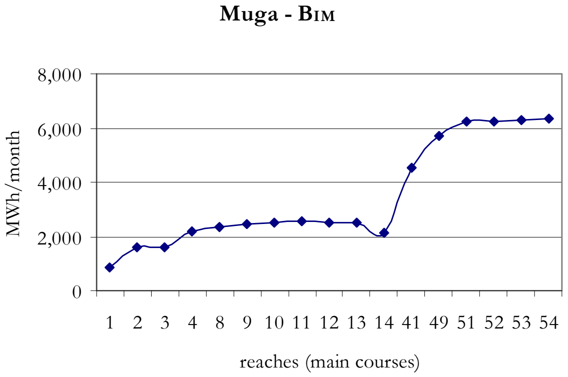


Figure 6.34. Exergy profile of the IM chemical component (PS)

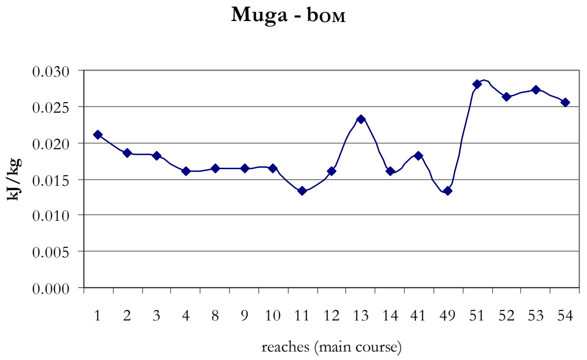


Figure 6.35. Specific exergy profile of the OM chemical component (PS)

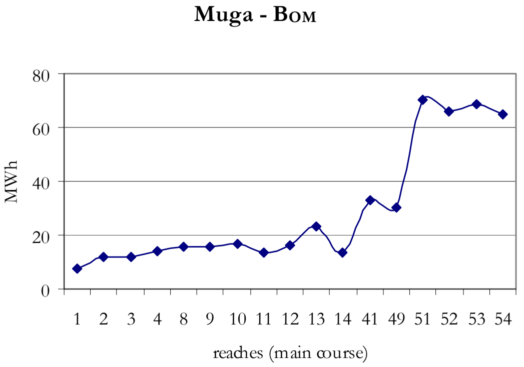


Figure 6.36. Exergy profile of the OM chemical component (PS)

The exergy profiles are the cornerstone of the methodology. In fact, they are the starting point for the PH application. As it can be seen, the specific potential component follows the expected behaviour (decreasing as the river flows to the sea), but ht IM and the OM component do not due to the human alterations on the river. In consequence, the total exergy does not represent a parabola. In the case of the OM, because of its special feature of increasing as the organic matter content in water increases, both the flow and the b_{OM} grow along the river.

In addition to the PS, the exergy profiles of the rest of river states were obtained. The most representative ones, PS, ES and OS, are jointly shown in the next figures, where the important differences from the real to the theoretical profiles can be easily appreciated. Figure 6.38 to Figure 6.43 present the specific and total exergy profiles and the corresponding flows are reproduced in Figure 6.37. There, it can be appreciated the equality between the Q_{PS} and Q_{ES}. As mentioned, no flow consumption in the WWTPs has been assumed in this study. In addition, the Q_{OS} in this case is very similar to the previous ones. In general, the flow rises up along the river course, as expected. This behaviour is different in other months, when the effect of the dam storage can be clearly observed (see, for instance, July and September in Annex A).

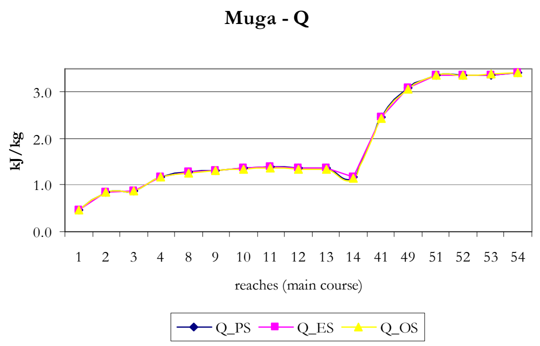

Muga - Q

Figure 6.37. Flows in the PS, ES and OS in the Muga river in January

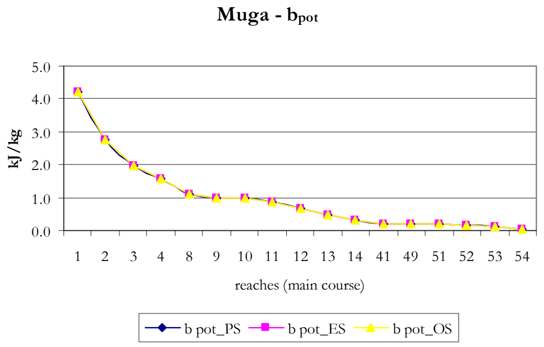

Muga - b_{pot}

Figure 6.38. Specific exergy profile of the potential component

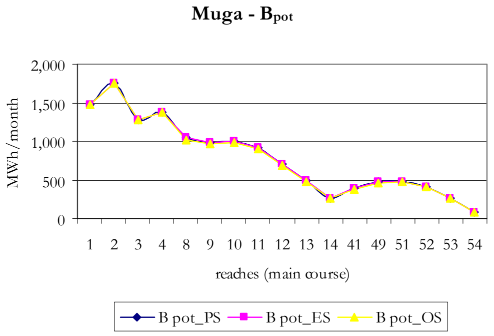

Muga - B_{pot}

Figure 6.39. Exergy profile of the potential component

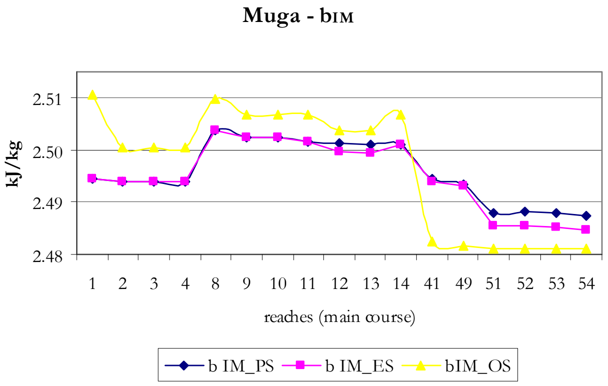

Muga - bIM

Figure 6.40. Specific exergy profile of the IM chemical component

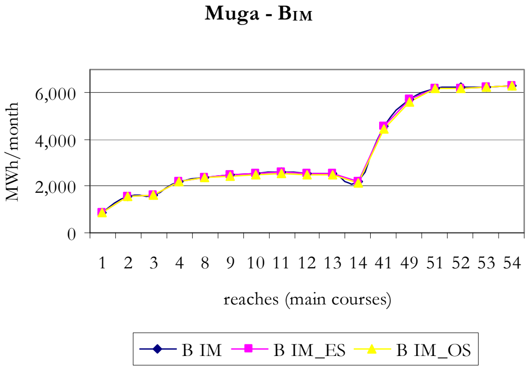

Muga - BIM

Figure 6.41. Exergy profile of the IM chemical component

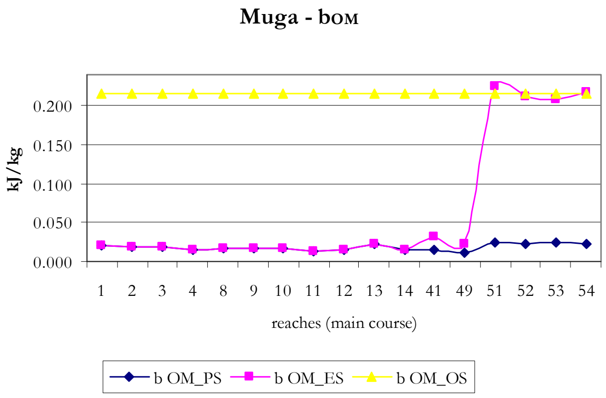


Figure 6.42. Specific exergy profile of the OM chemical component

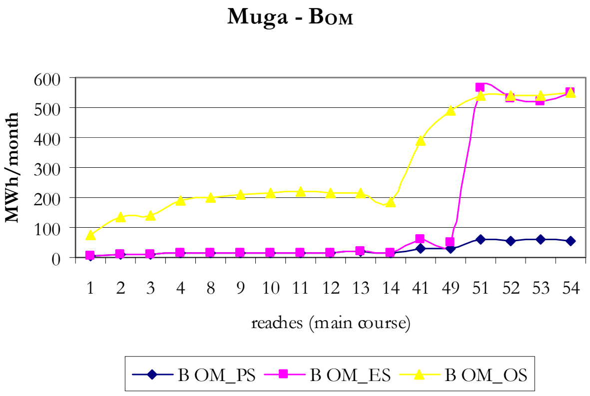


Figure 6.43. Exergy profile of the OM chemical component

Regarding the specific potential component (Figure 6.38), its decrease along the main river course corresponds to the theoretical proposal. The shapes of the specific chemical exergies, both IM and OM, are quite far from the idealistic curve described in Chapter 5. The water uses mean exergy variations along the river. Attending to the IM component, in those reaches were the OS present higher exergy values than the FS (which is extremely similar to PS), restoration measures are needed. In the last part of the Muga river, however, the current exergy values indicate that the river is good enough, i.e., the established OS already exists and, in consequence, no restoration measurements need to be proposed. Figure 6.42 represents the specific exergy profile of the OM. There, it can be appreciated that the OM value in the OS is almost constant. The important change in the ES between reaches 41 and 49 comes from the WWTP existing in the area (WWTP Figueres). In this case, because of the origin and exergy quantification of the OM component, if the B_{OM_OS} is higher than in the current state, it means that no measure is needed.

The graphs corresponding to March, July and September are reproduced in Annex A with the objective of complementing the information given here and of identifying the different variations along the year. As mentioned, of special relevance is the flow profile sift due to the reservoir.

The subtraction of those river profiles originates the minimum exergy costs. In particular:

- PS-ES will lead to the minimum SC
- OS-FS will lead to the minimum EC
- NS-OS will lead to the minimum RRC

Table 6.18 shows the results of those substractions for each month and the aggregated totals. Again, they are all disaggregated in quantity and quality and in their different components (potential, IM and OM). With those values, the exergy gaps among the river states have been obtained.

These exergy gaps can be somehow understood as the minimum exergy costs (SC, EC and RRC). Nevertheless, the minimum cost does not exactly correspond with the reproduced values. An adequate reasoning regarding their meaning has still to be done. In the following step, the unit exergy cost (k^*) of the corresponding restoration technologies (see sections 4.3 and 5.16) has to be introduced. It leads to the real exergy cost SC^*, EC^* and RRC^*, whose sum is the IRC^*. Finally, the economic costs in the Muga watershed are calculated by multiplying the real exergy restoration cost by the energy price.

MWh/month		**Quantity**			**Quality**		
		$\Delta B_{t,pot}$	**$\Delta B_{t,IM}$**	**$\Delta B_{t,OM}$**	**$\Delta B_{l,pot}$**	**$\Delta B_{l,IM}$**	**$\Delta B_{l,OM}$**
PS-ES	**Jan**	0.00	0.00	0.00	0.00	4.04	-796.25
	Feb	0.00	0.00	0.00	0.00	4.54	-1030.74
	Mar	0.00	0.00	0.00	0.00	3.09	-909.75
	Apr	0.00	0.00	0.00	0.00	3.27	-817.01
	May	0.00	0.00	0.00	0.00	1.72	-683.09
	Jun	0.00	0.00	0.00	0.00	3.59	-608.71
	Jul	0.00	0.00	0.00	0.00	5.58	-595.57
	Ago	0.00	0.00	0.00	0.00	8.32	-578.10
	Sep	0.00	0.00	0.00	0.00	4.19	-690.65
	Oct	0.00	0.00	0.00	0.00	1.42	-639.83
	Nov	0.00	0.00	0.00	0.00	2.17	-574.50
	Dec	0.00	0.00	0.00	0.00	2.34	-557.07
	Total	**0**	**0**	**0**	**0**	**44**	**-8,481**
OS(GEE)-FS	**Jan**	21.11	0.01	0.0000	0.00	-28.42	598.79
	Feb	24.81	1.38	0.0000	0.00	-33.19	468.02
	Mar	32.24	0.32	0.0000	0.00	-35.31	458.32
	Apr	21.11	0.01	0.0000	0.00	-29.39	600.62
	May	53.85	4.12	0.0000	0.00	-36.30	315.24
	Jun	60.40	-4.56	0.0000	0.00	-12.84	619.50
	Jul	99.47	-3.00	0.0000	0.00	19.84	141.58
	Ago	154.59	-1.21	0.0000	0.00	11.18	127.81
	Sep	99.07	3.34	0.0000	0.00	-3.71	131.82
	Oct	58.60	-0.08	0.0000	0.00	-17.02	268.95
	Nov	42.94	1.57	0.0000	0.00	-23.17	292.94
	Dec	124.60	2.40	0.0000	0.00	-24.06	346.47
	Total	**793**	**4**	**0**	**0**	**-212**	**4,370**
NS-OS(GEE)	**Jan**	897.01	-0.22	0.00	0.00	75.28	-296.32
	Feb	1,312.46	612.50	31.08	0.00	75.39	-244.09
	Mar	1,484.18	902.50	46.62	0.00	73.70	-238.66
	Apr	701.21	-5.70	0.00	0.00	70.62	-305.17
	May	1,337.70	1329.69	68.64	0.00	53.67	-175.20
	Jun	358.38	-2.06	0.00	0.00	54.77	-306.66
	Jul	206.38	-0.40	0.00	0.00	23.79	-94.49
	Ago	144.33	-1.08	0.00	0.00	28.76	-82.54
	Sep	198.61	1.28	0.00	0.00	30.48	-89.27
	Oct	744.17	381.11	19.43	0.00	46.46	-158.11
	Nov	1,052.31	782.04	40.15	0.00	50.52	-162.68
	Dec	1,039.32	607.58	31.08	0.00	54.58	-177.44
	Total	**9,476**	**4,607**	**237**	**0**	**638**	**-2,331**

Table 6.18. Exergy gaps among the different river states

Regarding the PS-ES difference, the exergy difference is only defined by the quality exergy gaps (IM, OM and NP components), since Q_{PS} and Q_{ES} are the same because no matter consumption was associated to the WWTPs (then, $\Delta B_t=0$) and $\Delta B_{l,pot}$ is clearly zero because the altitude of each reach is kept constant. On the other hand, high contribution of ΔB_{OM} is founds, since (PS-ES) meand the picture of present and total polluted river without WWTPs.

In the analysis of the gap between the OS and the FS, the flows are different, so the quantity (ΔB_t) component appears. Coming back to the description given in Chapter 5, it can be concluded that the null value of the $\Delta B_{t,OM}$ component is due to the OM objectives definition: two consecutive river reaches have the same OM objective and, in consequence, $db_{OM}=0$. Then, the product $\Delta Q \cdot db_{OM}$ is zero. The interpretation of the $\Delta B_{t,IM}$ component needs some wider explanation: first, it is clear that $\Delta Q>0$ because the potential component is positive. Then, the negative value of this component means that in some months (June, July, August and October) db_{IM} is negative (the IM exergy of the reach i-1 is lower than the exergy in the reach i –decrease of salinity-). In consequence, the gap OS-FS is negative. This fact is very important for the cost calculation because such a negative value means that is not needed to desalt waters. When the $EC_{IM,t}$ is calculated, the negative values must not be taken into account for further measures. On the other hand, the positive values of the $\Delta B_{t,IM}$ are consequence of a salinity increase along the river in some periods of the year, so restoring measures are needed.

Looking at the quality component of the OS-FS difference, the IM component presents both positive and negative values, while all the months are positive for the OM component. The later means that the OM content in the OS is higher than in the FS, so waters at 2015 are expected to fulfil the WFD objectives in this basin (therefore, this cost component will be zero). Regarding the IM, a negative value means that no restoration is needed. The positive value for the gap only happens in July and August, when irrigation returns increase the salinity in the river; all the other months present a negative value for $\Delta B_{l,IM}$ (which would not imply any environmental cost).

The exergy gap between the NS and the OS is clearly important, as it was explained in the river state definitions section. The flow in the NS is almost always higher than in the OS (with the exception of non-correctly defined Q_{OS}). Here, the quantity potential component $\Delta B_{t,pot}$ indicates that all the flows differences as positive. Then, it is immediately concluded that the small negative values of the $\Delta B_{t,IM}$ are due to the IM differences between consecutive river reaches, as explained above. The negative values are not considered for the RRC definition. The quality component does require restoration measurements in this case, since all the IM results are positive (of course, less salinity is imposed to NS with respect to OS), and all the OM ones are negative (again, OM content of pristine waters, NS, are lower than the objectives of the WFD, OS).

Values given in Table 6.18 are now presented in figures (Figure 6.44 to Figure 6.48) with the purpose of facilitate their interpretation.

The potential component is drawn in Figure 6.44. Since the potential quality component does not exist, that profile stands for both the quantity and the total potential component.

Results for the IM component are represented in Figure 6.45 (quantity) and Figure 6.46 (quality). The quantity component comprises by the ranges OS-FS and NS-OS. (The former is much lower in magnitude than the latter). Therefore, it can only hardly be appreciated in the graph. The same happens in the IM quality component reproduction: the gap PS-ES is low and can not be appreciated (values can be seen in Table 6.18.). The signs for the OS-FS and NS-OS are different. That is an important issue since, as explained in Chapter 5, the negative sign in the IM analysis means that no restoration measure is needed. This concept will be taken later on in order to correctly define the real exergy cost of the Muga watershed.

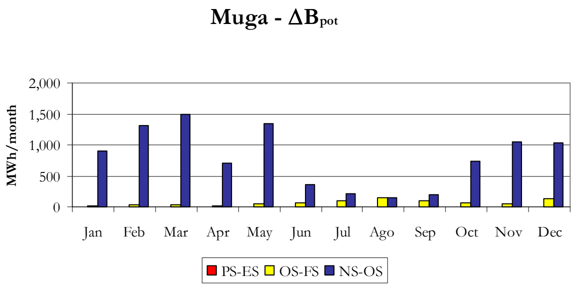


Figure 6.44. Potential exergy profile (here, $B_{pot}=B_{pot,t}$ because $B_{pot,l}=0$)

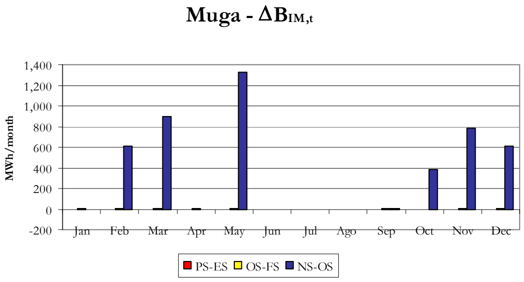


Figure 6.45. IM-chem exergy profile (quantity)

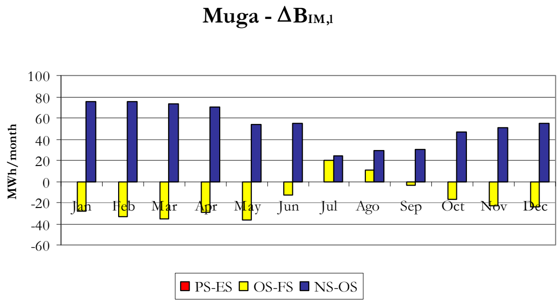


Figure 6.46. IM-chem exergy profile (quality)

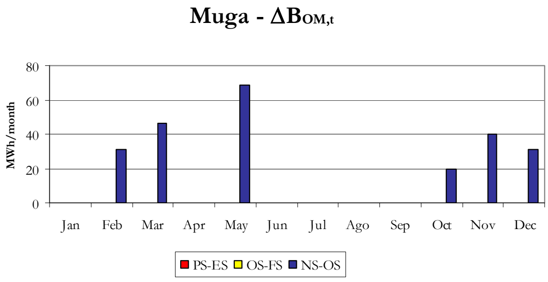


Figure 6.47. OM-chem exergy profile (quantity)

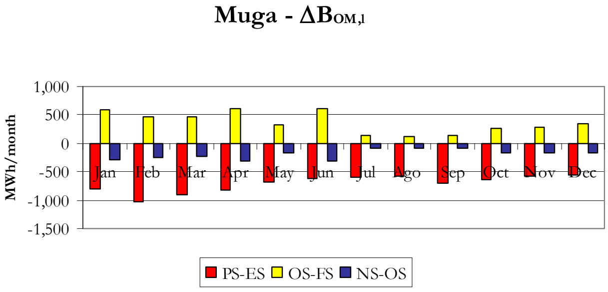


Figure 6.48. OM-chem exergy profile (quality)

Figure 6.47 and Figure 6.48 provide information about the OM component, quantity and quality respectively. The only contribution to the quantity is given by the gap NS-OS (the first difference PS-ES is cero because of their equal flow and the second, OS-FS, has resulted cero in this river because of the equal-defined objectives). The three different components do appear in the quality component. Again, the signs are important to be observed: contrary to the IM, a negative sign in the OM analysis is translated in the necessity of restoration measures.

It is also interesting to point out the proportionality between the IM and the OM profiles, since they are respectively obtained as the product of ΔQ times b_{IM} and b_{OM}. Thus, Figure 6.45 and Figure 6.47 have similar tendency, as well as Figure 6.46 in relation to Figure 6.48.

In summary, the gap NS-OS, as expected, presents the highest values because of the river water consumption, which is the gap between the flows associated to the OS and the NS. The difference (PS-ES) in the quantity component does not exist and, in the quality component, is only visible for the OM component. Its value for the IM is too small to be appreciated with the represented scale.

Until this point, the exergy profiles of the river and the subtraction of the states have been done. Table 6.18 presents the exergy gaps without any filter. At this point, it is needed to think about the meaning of the obtained figures.

		Quantity			**Quality**		
MWh/month		$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,pot}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
SC	**Jan**	0.00	0.00	0.00	0.00	4.04	-796.25
PS-ES	**Feb**	0.00	0.00	0.00	0.00	4.54	-1,030.74
	Mar	0.00	0.00	0.00	0.00	3.09	-909.75
	Apr	0.00	0.00	0.00	0.00	3.27	-817.01
	May	0.00	0.00	0.00	0.00	1.72	-683.09
	Jun	0.00	0.00	0.00	0.00	3.59	-608.71
	Jul	0.00	0.00	0.00	0.00	5.58	-595.57
	Ago	0.00	0.00	0.00	0.00	8.32	-578.10
	Sep	0.00	0.00	0.00	0.00	4.19	-690.65
	Oct	0.00	0.00	0.00	0.00	1.42	-639.83
	Nov	0.00	0.00	0.00	0.00	2.17	-574.50
	Dec	0.00	0.00	0.00	0.00	2.34	-557.07
	Total	**0.00**	**0.00**	**0.00**	**0.00**	**44.28**	**-8,481.27**
EC	**Jan**	21.11	0.01	0.00	0.00	-28.42	598.79
OS(GEE)-FS	**Feb**	24.81	1.38	0.00	0.00	-33.19	468.02
	Mar	32.24	0.32	0.00	0.00	-35.31	458.32
	Apr	21.11	0.01	0.00	0.00	-29.39	600.62
	May	53.85	4.12	0.00	0.00	-36.30	315.24
	Jun	60.40	-4.56	0.00	0.00	-12.84	619.50
	Jul	99.47	-3.00	0.00	0.00	19.84	141.58
	Ago	154.59	-1.21	0.00	0.00	11.18	127.81
	Sep	99.07	3.34	0.00	0.00	-3.71	131.82
	Oct	58.60	-0.08	0.00	0.00	-17.02	268.95
	Nov	42.94	1.57	0.00	0.00	-23.17	292.94
	Dec	124.60	2.40	0.00	0.00	-24.06	346.47
	Total	**792.79**	**13.15**	**0.00**	**0.00**	**31.02**	**0.00**
RRC	**Jan**	897.01	-0.22	0.00	0.00	75.28	-296.32
NS-OS(GEE)	**Feb**	1,312.46	612.50	31.08	0.00	75.39	-244.09
	Mar	1,484.18	902.50	46.62	0.00	73.70	-238.66
	Apr	701.21	-5.70	0.00	0.00	70.62	-305.17
	May	1,337.70	1,329.69	68.64	0.00	53.67	-175.20
	Jun	358.38	-2.06	0.00	0.00	54.77	-306.66
	Jul	206.38	-0.40	0.00	0.00	23.79	-94.49
	Ago	144.33	-1.08	0.00	0.00	28.76	-82.54
	Sep	198.61	1.28	0.00	0.00	30.48	-89.27
	Oct	744.17	381.11	19.43	0.00	46.46	-158.11
	Nov	1,052.31	782.04	40.15	0.00	50.52	-162.68
	Dec	1,039.32	607.58	31.08	0.00	54.58	-177.44
	Total	**9,476.05**	**4,616.70**	**236.99**	**0.00**	**638.03**	**-2,330.63**
IRC	**Total**	**10,269**	**4,630**	**237**	**0**	**713**	**-10,812**

Table 6.19. Minimum exergy cost for the Muga watershed

6.4.3.3 Exergy costs assessment in the Muga watershed

There are some figures appearing in Table 6.18 that, because of their sign, do not need to be included when the restoration measures are defined. Thus, they must not be added to the final minimum exergy costs (SC, EC and RRC). The corresponding data have been eliminated from the final sum in Table 6.19. Removed figures are enhanced in blue.

The minimum exergy costs have been therefore obtained in Table 6.19. Nevertheless, those results have none repercussion until the technologies efficiency is introduced. At this point, the unit exergy cost of the technologies used in the restoration measurements, are introduced to obtain the real exergy costs (SC^*, EC^* and RRC^*).

In particular, for the quantity components, desalination and pumping are the applied technology; and the quality restoration is done by other water treatments (depuration for the OM and brackish desalination for the IM). Corresponding k^*s were obtained in previous chapters. They are brought here to facilitate the understanding of the methodology (Table 6.20). The brackish desalination unit cost is assumed to be an ED procedure, which was studied in Chapter 4 together with the desalination technologies.

Technology	k*
Pumping (k^*_{pot})	1.43
Desalination, RO, (k^*_{des})	5.50
Water treatment (k^*_{dep})	4.45
Brackish desalination, ED, (k^*_{bdes})	8.00

Table 6.20. Unit exergy costs of the water restoration technologies

Afterwards, the economical cost can be immediately obtained by introducing the average energy price (80 M€/MWh). The step by step results can be summarized as Table 6.21 indicates. There, values are already given in absolute value.

In order to clarify the obtained PH's results for the Muga watershed, a set of graphs are presented in the following. Firstly, the objective is identifying the main quantity and quality components of the final cost and, secondly, the cost allocation among the water users.

Figure 6.49 shows the IRC (SC+EC+RRC) for each exergy component in economic units, keeping the separation between the quantity and quality terms of each component (pot, IM and OM). That difference disappears in the following figures, where the quality and quantity have been added in order to see the specific contribution of the pot, IM and OM exergy components.

The percentages of the values presented in Figure 6.49 are given in Table 6.22. The quality component of the potential exergy has been directly eliminated because it is zero by definition. The RRC is, for any of the components, the most important contribution. A exception is the $\Delta B_{l,OM}$, mainly defined by the SC contribution (78.4%).

(a) **Exergy gap**

MWh/yr	$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,pot}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
SC	0	0	0	0	44	8,481
EC	793	13	0	0	31	0
RRC	9,476	4,617	237	0	638	2,331
IRC	**10,269**	**4,630**	**237**	**0**	**713**	**10,812**

(b) **Exergy cost** *

MWh/yr	$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,pot}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
SC*	0	0	0	0	354	37,742
EC*	5,494	72	0	0	248	0
RRC*	65,669	25,392	1,303	0	5,104	10,371
IRC*	**71,163**	**25,464**	**1,303**	**0**	**5,707**	**48,113**

(c) **Economic cost**

€/yr	$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,pot}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
***ec*SC**	0	0	0	0	28,338	3,019,332
***ec*EC**	439,522	5,784	0	0	19,855	0
***ec*RRC**	5,253,521	2,031,349	104,273	0	408,339	829,705
***ec*IRC**	**5,693,043**	**2,037,134**	**104,273**	**0**	456,533	**3,849,037**

Table 6.21. IRC, IRC* and ecIRC for the Muga watershed, disaggregated by components.

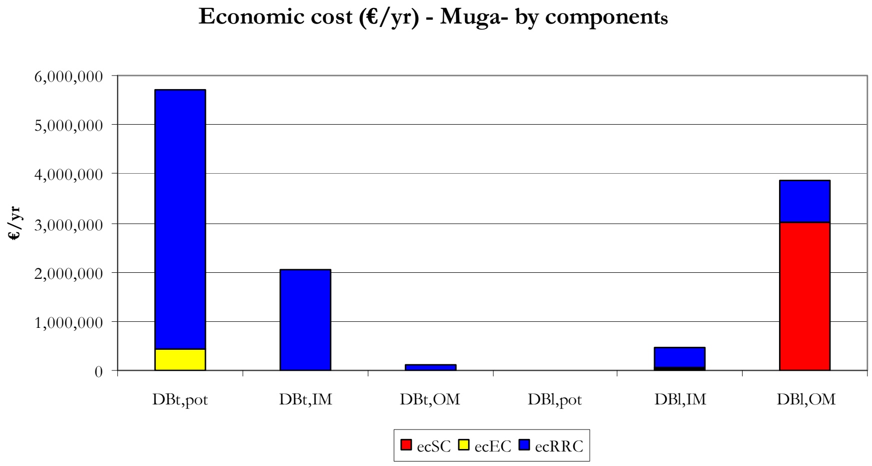


Figure 6.49. Components of the IRC (SC+EC+RRC) for each exergy component in economic terms (€/yr).

	$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
SC	0.0%	0.0%	0.0%	6.2%	78.4%
EC	7.7%	0.3%	0.0%	4.3%	0.0%
RRC	92.3%	99.7%	100.0%	89.4%	21.6%

Table 6.22. Percentages of the ecIRC components (ecSC, ecEC and ecRRC), by exergy components.

Because of its relevance, the exergy costs are separately presented in Figure 6.51 (minimum costs) and Figure 6.51 (real exergy cost). The same scale has been maintained in both graphs to facilitate the comparison. The difference between the bars for each component (pot, IM and OM) is due to the irreversibility of the water restoration techniques.

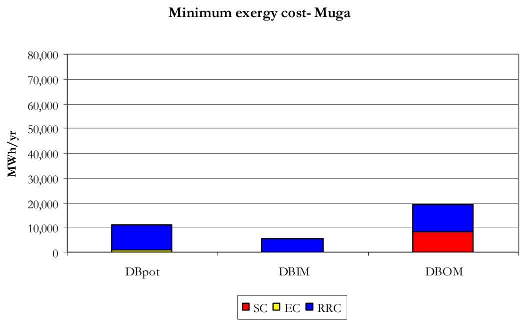


Figure 6.50. IRC$_{pot}$, IRC$_{IM}$ and IRC$_{OM}$ in the Muga watershed

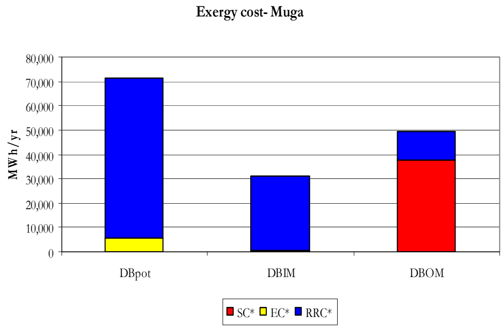


Figure 6.51. IRC$^{*}_{pot}$, IRC$^{*}_{IM}$ and IRC$^{*}_{OM}$ in the Muga watershed

The OM component comprises mainly the SC that accounts for the WWTPs (red bar). The IM component is only related to the different salts content between the FS and the OS. Attending to the EC, no additional cost comes then from this IM contribution. The potential component has a non negligible contribution due to the flow of the OS, which would need to be higher than the current flow (yellow bar).

As it has been seen, including at any time the quality aspects in the analysis, provide additional and fruitful information. The values given in Table 6.21 are aggregated in quantity and quality and presented in next figures: Figure 6.52 summarizes the minimum IRC as addition of the SC, EC and RRC, and disaggregated in quantity and quality; Figure 6.53 represents the exergy cost maintaining the same disaggregation; and finally the economic cost is given in Figure 6.54.

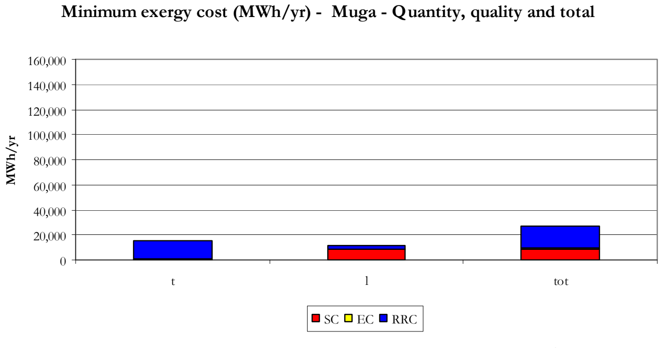


Figure 6.52. Components of the minimum IRC (SC+EC+RRC), disaggregated in quantity and quality

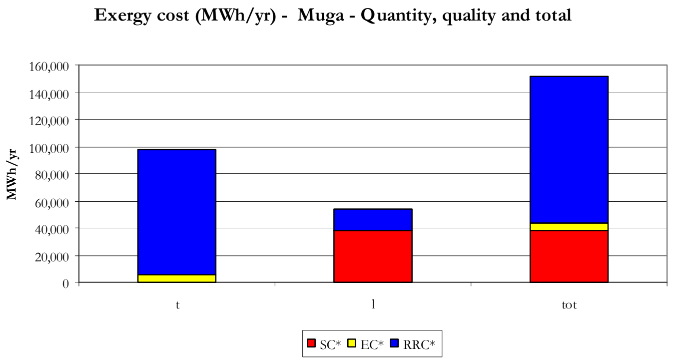


Figure 6.53. Components of the IRC* (SC*+EC*+RRC*), disaggregated in quantity and quality

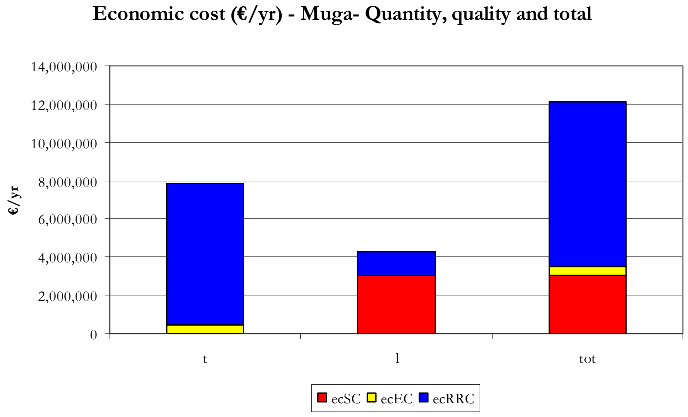


Figure 6.54. Components of the ecIRC (ecSC+ecEC+ecRRC), disaggregated in quantity and quality

The minimum costs are distributed as indicated in Table 6.23. In quantity, most of the degradation is due to the RRC, what was expectable due to the important flows difference between the FS and the OS. In the quality part, the service cost accounts for about the three quarters and the remaining quarter comes from the RRC. When the total IRC is analyzed, it becomes evident that the EC, the most important contribution to the IRC from the point of view of the WFD application, represents only the 3.1% of the cost of restoring the complete hydrological cycle. The EC contribution for each of the parameters is quite low (5.3% in quantity and 0.3% in quality).

	t	l	tot
SC	0.0%	74.0%	32.0%
EC	5.3%	0.3%	3.1%
RRC	94.7%	25.8%	64.9%

Table 6.23. IRC distribution in quantity, quality, and total

Once the technologies efficiencies are introduced in the analysis, these percentages slightly varied. The new distribution, which is valid from the IRC*and the ecIRC (the conversion factor is just the energy price) is shown in Table 6.24. None very high variation is found and the allocation cost is approximately the same.

	t	l	tot
SC*	0.0%	70.8%	25.1%
EC*	5.7%	0.5%	3.8%
RRC*	94.3%	28.8%	71.1%

Table 6.24. IRC* distribution in quantity, quality, and total

6.4.3.4 Service Cost in the Muga watershed

It can be useful to remind that the service cost accounts for the exergy differences among the ES and the PS of the river. In addition to that, the obtained sings for the cost can be checked with sign analysis presented in the section 5.11.

There is no contribution to the SC from the quantity component, since no flow variation exists between the ES and the PS. However, the quality component is really representative because of the important quality degradation between those river states (the difference is the existence of present WWTPs). The $SC_{l,IM}$ is 44 MWh/yr (6.2 % of the $IRC_{l,IM}$) and the $SC_{l,OM}$ is -8,481 MWh/yr (78.4 % of the $IRC_{l,OM}$). The potential component, $SC_{l,pot}$ is zero by definition. As expected, the OM component is much higher than the IM component. It is also due to the chosen RE, where no OM presence is considered (see Chapter 4).

After applying the corresponding k^*s, the $SC^*_{l,IM}$ and the $SC^*_{l,OM}$ are 354 MWh/yr and -37,742 MWh/yr, respectively.

When the corresponding k^*s are introduced to obtain the exergy restoration cost of the river, the percentage of each component in reference to its IRC remains constant since the technology proposed for restoring the specific component is equal for all cost (for instance, pumping and desalting for the potential component). However, due to the differences between the k^* of the different restoration technologies, the percentages among the SC, EC and RRC within the IRC in the quality component differ in the different consecutive steps (exergy gap and exergy cost). The percentages of the economic (only accounting for *physical*, maintenance part) cost are the same as in the exergy cost because only the money-energy conversion factor is introduced.

6.4.3.5 Environmental Cost in the Muga watershed

The flow difference between the desired flow in the OS and the expected flow by 2015 (FS) defines the EC_t. The obtained values for $EC_{t,pot}$ and $EC_{t,IM}$ are 793 MWh/yr (7.72% of the $IRC_{t,pot}$) and 13 MWh/yr (0.28% of the $IRC_{t,IM}$) respectively. The former results come from the product of the flow difference and the altitude; the latter is defined by that flow difference and the salts content in the river ($\Delta Q \cdot db_{IM}$). $EC_{t,OM}$ is zero because of the profiles features: $EC_{t,OM}$ is obtained as the product $\Delta Q \cdot db_{OM}$ and, in this case, db_{OM} leads to that null value.

The quanlity component, EC_l has only the IM contribution ($EC_{l,IM}$), 31 MWh/yr, because $EC_{l,OM}$ is zero due to the OM objectives (less restrictive than the future ones) and $EC_{l,pot}$ is zero, as always (constant altitude value of each reach). It represents 4.3% of the $IRC_{l,IM}$.

6.4.3.6 Remaining Resource Cost in the Muga watershed

As expected, the RRC represent the highest contribution to the IRC, both in quantity and quality. It account for the differences among the objective and the natural state of the river. All the components contribute to the IRC, except the $RRC_{l,pot}$, as it is null by convention.

The quantity components are all one or even two order of magnitude higher than in the SC and EC: $RRC_{t,pot}$ is 9,476 MWh/yr, $RRC_{t,IM}$ is 4,617 MWh/yr and $RRC_{t,OM}$ is 237 MWh/yr. They represent, respectively: 92.28% of the $IRC_{t,pot}$, 99.72% of the $IRC_{t,IM}$ and 100% of the $IRC_{t,OM}$. Obviously, the RRC is the highest contribution in the quality analysis because of the Q_{NS} value, which differs so much from the objective value, Q_{OS}. On the other hand, $RRC_{l,IM}$ is 638 MWh/yr (89% of the $IRC_{l,IM}$) and $RRC_{l,OM}$ is -2,331 MWh/yr (22% of the $IRC_{l,OM}$).

6.4.3.7 Economic cost of water in the Muga Watershed

The physical costs allocation calculated in the previous section are next used to allocate the total (energy plus investment) economic costs of the Muga watershed.

Only two types of costs were allocated here: the *energy (operation) costs*, defined by the exergy calculations carried out, and summarized in Table 6.21; and the *installation cost* of the utilities needed to perform the water restoration (WTPs, pumping stations and desalination units).

The installation costs have been taken as average figures, after consulting different sources. None specific plants size has been introduced, but those specific cost per capacity unit. A 25-years life-time period was taken for all the plants. The economic installation cost for each of them is reproduced in Table 6.25. Specific capacity is kept constant, independently of the plant capacity.

WTP		**Pumping**		**Desalination/Brackish Desalination**	
400	€/(m^3/d)	5	€/(m^3/d)	600	€/(m^3/d)

Table 6.25. Installation cost of the water-related technologies needed to restore the river flow

In consequence, by applying the previously calculated contributions in percentages, the final economic cost of water in the Muga Watershed is obtained (see Table 6.29). The searched EC is highlighted in bold. The EC in the Muga watershed rises to 9,587,419 € according to the PH methodology.

The investment cost was estimated attending to the specific costs indicated in Table 6.25 and to the amount of water being treated in each of the specified technologies. Following with the initial hypothesis, the river flow has to be treated in the WTP looking for a quality improvement; the flow is quantified from the yearly river natural contribution (404,822 m^3/d). Nevertheless, only the missed water needs to be obtained by desalination and then pumped to its original point; it is calculated by comparing the flow in the FS and in the OS and it results to be about 27% of the total flow.

Operation Cost (€/yr)		
Op (t)	**Op (l)**	**Op**
0	3,047,671	3,047,671
445,306	19,855	465,162
7,389,143	1,238,044	8,627,187
7,834,450	4,305,570	12,140,020

Investment Cost (€/yr)		
Pumping	**Desalination**	**WTP**
21,860	2,623,246	6,477,151

Economic Cost	**€/yr**
SC	12,169,928
EC	**9,587,419**
RRC	17,749,444
IRC	21,262,277

Table 6.26. Economic EC in the Muga watershed

Although the EC has been already calculated, the fundamental part about cost allocation can not be forgotten, since it is one of the main PH's strengths.

6.4.3.8 Cost distribution among water users

According to the theory given in section 5.11, the water uses in the Muga basin, studied in section 6.12.3 and included in the Qual2k simulation, were carefully analyzed. Their quantity and quality features were considered. The final aim was to get the percentage of water degradation coming from each of the water users. The polluters were grouped by economic sectors: domestic, industrial and agricultural (irrigation). As previously mentioned, many of the industries are included in the domestic use because they are connected to the same water network and there is no separate data for them.

Table 6.27 summarizes the calculations made for the obtaining of the degradation in exergy terms, separating IM and OM variations. The subscript *c* and *r* stand for catchment and return, respectively.

IM	**Quantity**			**Quality**		
type of water use	ΔQ_{c-r}	b_c	ΔB_t	Q_r	Δb_{c-r}	ΔB_l
domestic	0.33	2.6700	7,663.87	3.11	0.1714	4,669.44
industrial	0.01	2.6695	324.09	0.08	0.5254	361.46
irrigation	11.54	2.3600	238,484.19	0.33	0.3600	1,051.46

OM	**Quantity**			**Quality**		
type of water use	ΔQ_{c-r}	b_c	ΔB_t	Q_r	Δb_{c-r}	ΔB_l
domestic	0.33	0.6902	1,981.13	3.11	-6.7278	-183,285.03
industrial	0.01	1.9040	231.16	0.08	-1.2610	-867.53
irrigation	11.54	0.4641	46,898.52	0.33	-0.3667	-1,071.02

Table 6.27. Quantity and quality contribution to water degradation (IM and OM) by each water use

These data were used for allocating the costs of water pollution, in commitment to the Polluter Pays Principle stated by the WFD. Each use contribution is given in percentages, in Table 6.28.

IM

	t	l
domestic	3.1%	76.8%
industrial	0.1%	5.9%
irrigation	96.8%	17.3%

OM

	t	l
domestic	4.0%	99.0%
industrial	0.5%	0.5%
irrigation	95.5%	0.6%

Table 6.28. Contribution to water degradation (IM and OM) by each water use, in percentage, for quantity and quality.

As expected, the inorganic quality degradation, as well as the organic one, is mainly due to the domestic contribution (77% and 99% respectively). However, the quantity degradation has its origin in the irrigation demand (97% and 95% respectively).

Cost allocation procedure can be maybe better understood in Figure 6.55. There, the theoretical equivalence between the total cost of water (IRC) and the cost paid by the users (present cost recovery of water uses) is represented. The PH's proposal is allocating those water costs according to the Degrader Pays Principle, using the exergy decrease provoked by each water user sector as guideline, and avoiding the present use (and abuse) of subsidies for less cost-effective uses.

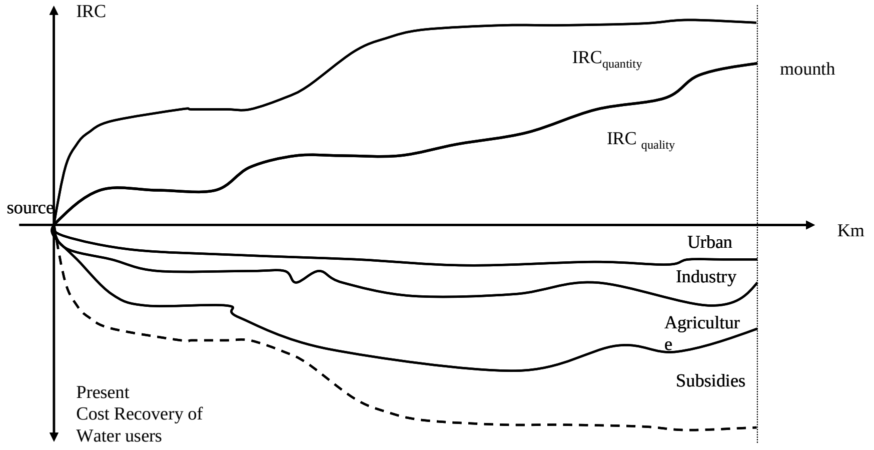


Figure 6.55. Cost sharing among the water users

On average, the degradation provoked by each water use present a quantity and a quality contribution, as it is shown in Figure 6.56. Results are really illustrative: main degradation of the agricultural sector comes from the amount of consumed water, while in the case of the domestic and the industry, the problem is the water pollution that they produce.

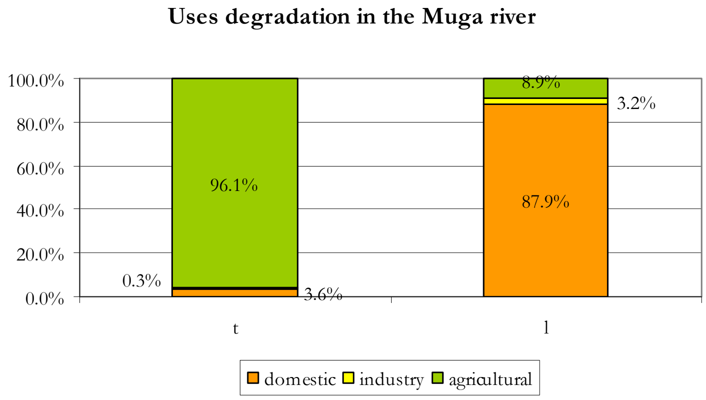
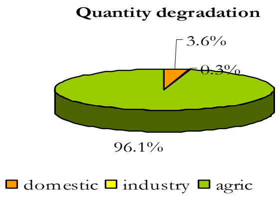


Figure 6.56. Quantity and quality allocation for the total degradation provoked by each water use.

In detail, the general user's contribution to the water degradation appears in Figure 6.57 (quantity degradation) and Figure 6.58 (quality degradation, commonly designed as *pollution*). If the cost allocation were carried out only attending to the information given in Figure 6.58; this is the conventional analysis based on the Polluter Pays Principle (88% due to households). However, following the Degrader Pays Principle and attending only to the EC, it charges 60% to the domestic use and 37% to the agricultural water use.



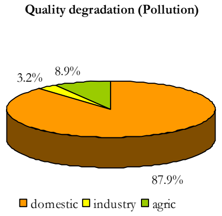
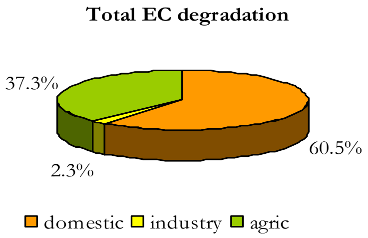


Figure 6.57. User's contribution to the general quantity degradation

Figure 6.58. User's contribution to the general quality degradation



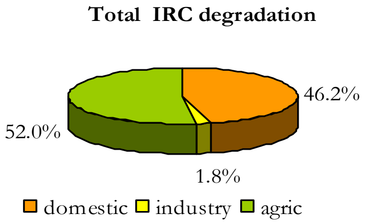


Figure 6.59. User's contribution to the EC in the Muga watershed

Figure 6.60. User's contribution to the IRC in the Muga watershed

Figure 6.59 accounts for the total degradation attending to the EC. It can be seen that the domestic sector is responsible for 60% of that total damage on waters. In fact, because of the already explained aggregation of industrial uses to the urban sewage system, it can be understood as domestic plus industry responsibility. Figure 6.60 accounts for the total degradation when the IRC, and not only the EC is considered. In that case, the energy cost is considerably higher. The consequence is that in this situation the major contributor to the water degradation is the agricultural sector, where important amounts of water are abstracted and latterly consumed.

From those four circular graphs, it is easily concluded that diverse interpretation of the cost allocation could be taken by the use of PH information. Even having use an objective methodology to determine the final cost allocation numbers, partial use of them can be done. This idea is further developed in the following and it becomes especially clear in figures from Figure 6.61 to Figure 6.66.

Op. Cost
(€/yr)

	EC_t	EC_l
domestic	15,905	17,445
industrial	1,341	636
irrigation	428,061	1,774

Inst. Cost
(€/yr)

	EC_t	EC_l
domestic	94,475	5,690,943
industrial	7,964	207,629
irrigation	2,542,667	578,579

Total
cost
€/yr

	EC_t	EC_l	EC
domestic	110,381	5,708,389	5,818,769
industrial	9,305	208,265	217,570
irrigation	2,970,727	580,352	3,551,080
			9,587,419

Table 6.29. EC in economic terms, distributed by sectors and disaggregated in quantity and quality, and total.

The 9,587,419 €/yr corresponding to the total EC of the Muga Watershed are distributed among the water users as 5,818,769 €/yr for the domestic sector, 217,570 €/yr for the industrial sector and 3,551,080 €/yr for the irrigation sector. The industrial is really low because of the mentioned fact about the aggregation with the domestic sector. Mainly, the quality degradation provoked by the domestic (and the included industrial) use of water means the higher contribution to water degradation and, in turn, the highest economic cost of restoration, about 60% of the total cost. The irrigation degradation, coming mainly from the quality component represents about 37% of the total cost and the remaining 3% (cost allocation described in Figure 6.59, corresponding to the Degrader Pays Principle, that is, including quantity and quality).

From the whole study, it can be concluded that the cost allocation highly depend on the interpretation given to the obtained results. It is not he same considering only the energy cost than attending to the whole costs, including the installation. In the same sense, the cost allocation will depend on the attention devoted to the quantity and the quality components, as well as to the cost component that is being considered: SC, EC, RRC or the total IRC. To clearly appreciate the difference, the most relevant costs within the WFD are graphed in next figures. Attending to the operation cost of the EC, the quantity contribution is clearly the most important and agricultural use is the responsible for it (Figure 6.61). A similar situation, although with higher values as it is logic, happens with the IRC (Figure 6.62). Since the water-treatment plants to be constructed are the same in both cases, the installation cost is equal for the EC and the IRC (Figure 6.63 and Figure 6.64). In this case, the costs of the demanded WWTP for cleaning the urban water pollution imply the highest cost. Finally, the total EC for the Muga watershed is given in Figure 6.65 and the importance of the urban uses are clearly identified. Figure 6.66 shows the same behaviour for the total IRC.

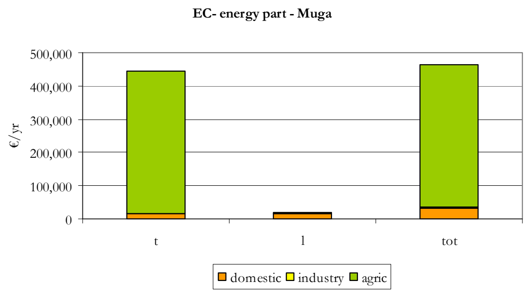


Figure 6.61. Quantity and quantity components of EC (operating cost)

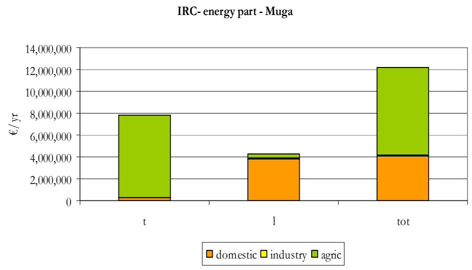


Figure 6.62. Quantity and quantity components of IRC (operating cost)

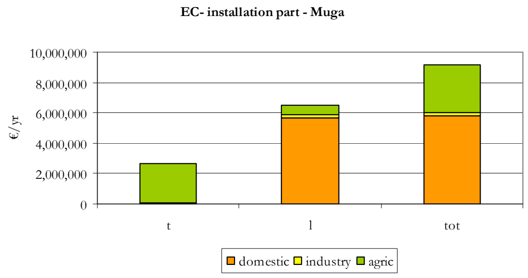


Figure 6.63. Quantity and quantity components of EC (installation cost)

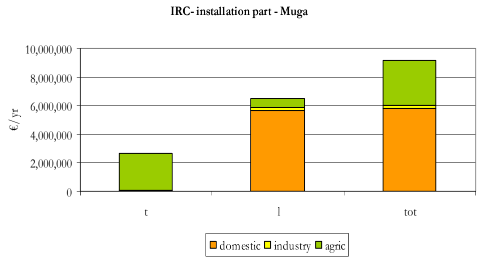


Figure 6.64. Quantity and quantity components of IRC (installation cost)

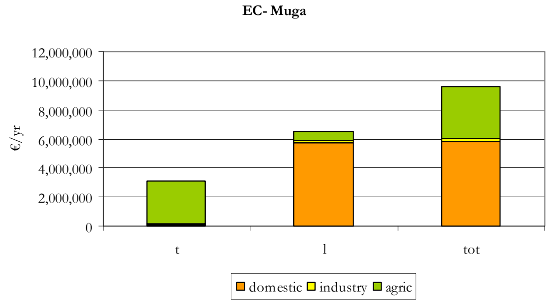


Figure 6.65. Quantity and quantity components of EC (total cost)

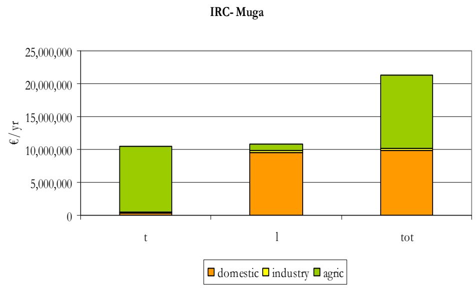


Figure 6.66. Quantity and quantity components of IRC (total cost)

To complement the information provided by the figures, the exact percentages are summarized in Table 6.30 and Table 6.31. The installation cost distribution is the same in both analysis, since the utilities calculated to correctly estimate the EC are assumed to be the same as those required for the IRC. The energy cost contribution, however, is higher for the domestic sector in the IRC allocation because more water needs to be cleaned to reach the objective flow requirements introduced by the RRC.

All the river water is supposed to flow through the WWTPs, while only a part of the final water has to be obtained by desalination. That is the reason by the desalination cost is not especially representative when it is compared with the depuration water units.

To sum up, it can be said than, as expected, the irrigation is the most water-consuming activity and the domestic the most water-polluter sector. The obtained results completely meet the extended ideas about the different responsibilities in water use.

	energy cost	installation cost	total EC
domestic	7.2%	63.2%	60.5%
industry	0.4%	2.4%	2.3%
agric	92.4%	34.5%	37.3%

Table 6.30. EC* allocation according to the DPP

	energy cost	installation cost	total IRC
domestic	33.5%	63.2%	46.2%
industry	1.3%	2.4%	1.8%
agric	65.2%	34.5%	52.0%

Table 6.31. IRC* allocation according to the DPP

6.4.3.9 Sensitivity analysis of the results

Because of the high uncertainty in some of the used parameters to develop the PH analysis of the watershed, a sensitivity analysis should be done. The parameters analyzed were the energy price, the installations life time, and the installation cost of the utilities needed for the water quantity and quality restoration.

The energy price was changed from free energy until 160 €/MWh (100% of energy price increase). It meant only a small variation in the EC: ±4.8% of variation (Figure 6.67), that is, in the range from 9,122,257 €/yr to 10,034,959 €/yr. It is due to the importance of the installation cost of the plants, which is higher than the O&M cost, the one affected by the energy prices.

The price of the WTP's installation cost taken for the study was 400 €/(m^3/d). It was varied from 0 to 800 €/(m^3/d). The EC suffered very important variations with these changes, since it is the highest installation cost in the study. Results range from 3,101,457 €/yr if the plant is given for free (a completely unrealistic situation), to 16,055,759 €/yr if the price would double (Figure 6.68), i.e., ±68% variation.

When the investment of desalination facilities (Figure 6.69) is varied, it also appears also representative changes, although not so high as in the previous analysis of WTP cost. The cost taken for the study was 600 €/(m^3/d); and it was varied from zero to 1,200 €/(m^3/d) for the sensitivity analysis, resulting 6,955,362 and 12,201,854 €/yr as limit values (±27%). So, this parameter has also an important specific weight for the EC determination.

The third varied installation cost was the pumping cost. As in the previous reported case, it was changed from cero to double its initial cost, stated as 5 €/(m^3/d). The sensitivity to this parameter (see Figure 6.70) is almost negligible (from 9,556,748 to 9,600,468 €/yr).

Finally, the life time estimated for the different plants was considered. The value taken for the study was 25 year. In Figure 6.71, the EC obtained varying the life-time between 7 and 50 years is shown. The most important changes in the EC is appreciated here, from 30,863,874 to 5,017,479 €/yr. In consequence, it is concluded that the operation time of the utilities, together with the installation cost of the WTP and desalination plants, are the most relevant factors in the EC calculation.

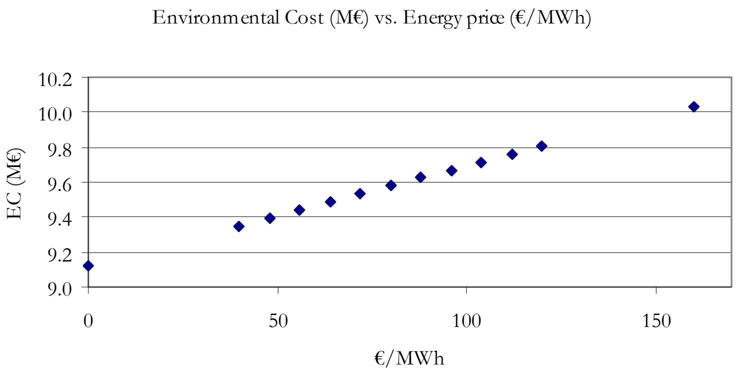


Figure 6.67. Sensitivity analysis: EC vs Energy price

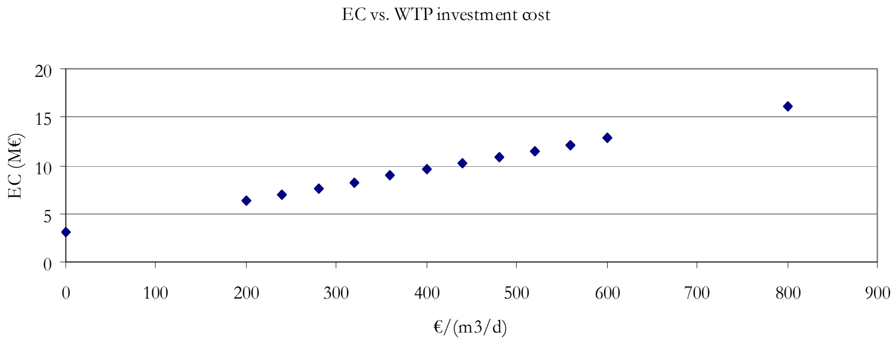


Figure 6.68. Sensitivity analysis: EC vs WTP investment cost

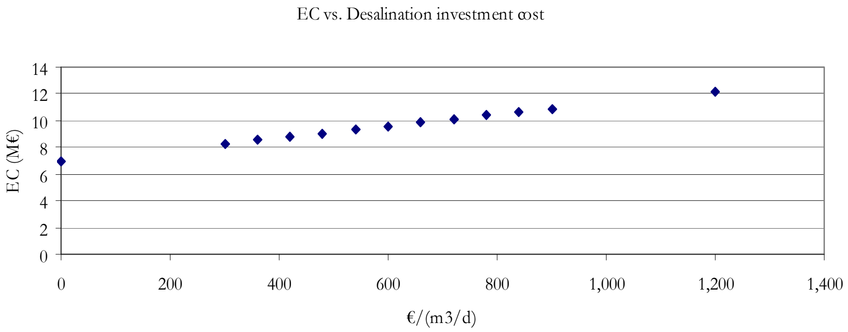


Figure 6.69. Sensitivity analysis: EC vs desalination plant investment cost

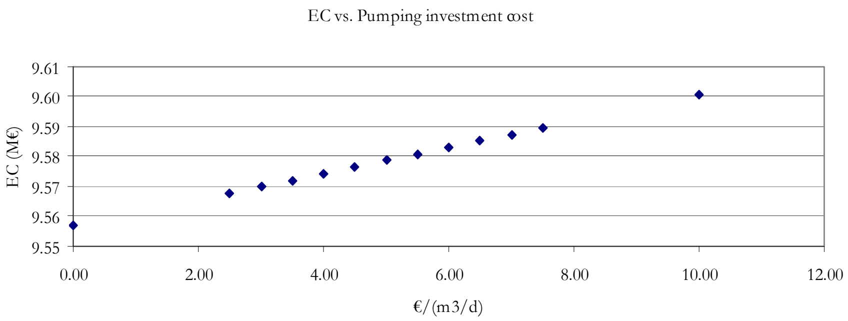


Figure 6.70. Sensitivity analysis: EC vs pumpling investment cost

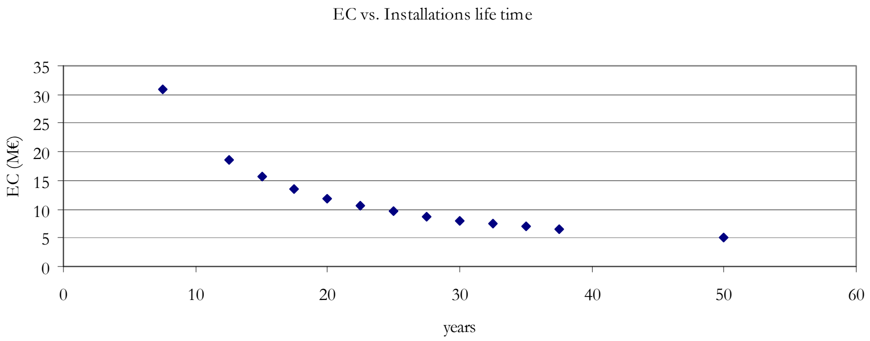


Figure 6.71. Sensitivity analysis: EC vs installations life time

6.4.4. Results comparison with previous studies

Muga basin was studied by Escriu (2007), who adapted some of the exergy concepts to its analysis. He obtained an environmental cost of 9,639,000 €, extremely close to the value presented in this study. According to his allocation, the quantity was responsible for 70% of the EC, and quality components for the remaining 30%.

With the PH methodology, the EC are shared as 32.5% for quantity and 67.5 % in quality when all the cost, also the installation costs of the required restoration technologies, are accounted for (see Table 6.32). The important differences between both studies come from the flows characterization. Escriu accounted for a huge external use considering that nothing from it returns to the Muga watershed.

		This study		
	Total (Escriu)	**Total**	**Energy cost**	**Installation cost**
Quantity	70%	32.50%	95.7%	29.3%
Quality	30%	67.50%	4.3%	70.7%

Table 6.32. Summary and comparison of results: quantity-quality distribution

If only the energy operating cost is considered, the distribution totally changes: 95.7% is quantity and 4.3% is quality. Such a big difference is due to the high cost of the required WTP, which are included in the analysis through the installation costs. From the previous considerations, the inclusion of all the cost represents a most adjusted value.

The cost allocation methodology followed by Escriu (2008) is not completely detailed in his publications, so a thorough comparison can not be done. In spite of this circumstance, the differences among the obtained results could come from the special treatment that exergy allows, by considering the water quality and its demanded restoration.

In addition to that, there exists a key factor to explain the diverse results: the CCB catchment. Escriu considers it as a transfer out to the watershed that represents 40% of the quantity loss (Escriu, 2008). However, that flow has been considered in this study as an additional urban use in the watershed, assuming a return rate of about 80%.

The cost among the water uses was allocated according to the percentages in Table 6.28. It led to a final sharing of the total cost distributed as 60% domestic use, 3% industrial use and 37% irrigation use in the area of study.

Escriu (2008) wrote that if the domestic and urban uses would pay attending to *degradation*, their part would be about 8% of the total cost. But if they would pay attending only to *pollution*, their importance would rise until almost 99% of the total cost. The comparison of results has been done in Table 6.33.

	PPP (this study)	**DPP (this study)**	**PPP (Escriu)**	**DPP (Escriu)**
domestic	87.9%	60.5%	99%	8%
industry	3.2%	2.3%		
agric	8.9%	37.3%	1%	92%

Table 6.33. Summary and comparison of results for the cost allocation

Concluding, the obtained results are accurate enough and the existing difference with the previous study can be reasonably explained.

6.5. Case study 2: Foix Basin

6.5.1. Foix Basin: physical description.

Foix watershed is a quite small basin (301,3 km^2) located at the northeast of the *Tarragona* province, southern the IBC (Figure 6.72). Its total length is 163.8 km, and has three main tributaries: *Marmellar, Pontons* and *Llitrá*. The population in the territory is about 100,000 inhabitants, with about 15 important villages, but with a very high population variation due to the numerous visitants during the vacation periods.

Its flow is scarce: the average annual contribution of the river is only 9.47 hm^3, corresponding to an average flow of 0.3 m^3/s, with an average annual rainfall of 182 hm^3 (586 mm). The river is born in a mountainous area named *Sierra de la Llacuna* and, forming a small delta, flows into the *Cubelles beach*, in the Barcelona province. Remember that the mentioned projected SWDP in *Cunit* is very close to its mouth.

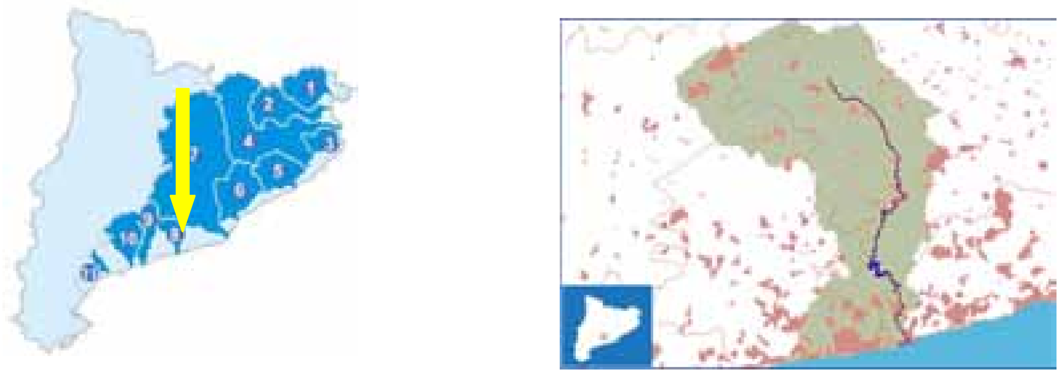


Figure 6.72. Location of the Foix Basin

There is a Dam in the area close to *Castellet i la Gornal*. It retains most of the water flowing into it. The Foix Dam is devoted to water storage, not to electricity production, as it happens in many others Dams in the IBC. The quality of the stored water is very low. This fact makes the competent authorities to close the fishing activity in the Dam along 2009.

The water amount in the Foix river is also due to the drought in the area, as well as to the few present tributaries.

6.5.1.1 Water availability in the Foix Basin

The Foix flow regime is typical from Mediterranean rivers, characterized by carrying little water volume all the year long, except in torrential rainfall episodes, mainly in autumn. The rain is clearly insufficient and they are irregularly allocated along the year, with important torrential episodes. This fact is manifested with the reduce river bed width.

The progressive depopulation of the inland mountain range has been compensated with the population increase in the coast area. Around 100,000 people travel from Barcelona and its metropolitan area. This massive exodus coincides in summer with the minimum hydrological availability

The high average temperature, lightly tinged in the inland, and the progressive decrease of the relative humidity, affect the evapotranspiration and, in consequence, in the available water volume for the aquifers recharge. The water deficit in the global balance is about 5 hm^3 per year (García i Ruiz, 1997).

Because of the limited availability of water in origin, there exist an important amount of subterranean catchments within the Foix Watershed. In fact, the mentioned urbanizations have been traditionally supplied by deep waters (see aquifers in the area in Figure 6.73), through extractions close to them. The depth and amount of those catchments have increased as the demands multiplied. However, these solutions do not completely solve the problem.

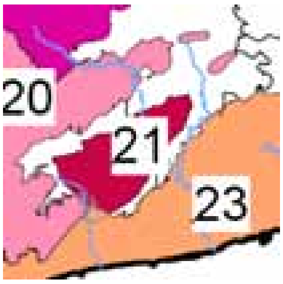


Figure 6.73. Aquifers in the Foix Watershed area.

García i Ruiz (1997) carried out a complete study about the difficulties of maintaining an adequate water supply in the second residence housing developments in the Foix Watershed. He pointed out that these particular forms of human settlement on the territory means a landscape transformation, and that they affect the amount of water demand as well as the water use types. Regarding the water shortage, the joint of the own aquifers supply, together with the import of water from other watersheds was seen as the best solution. Of course, a proper town-planning for the urbanizations was also demanded.

In the Mediterranean Catalonian System, the peculiar parallel disposal of the relief in relation to the coast, determines the existence of small drainage basins, as the Foix one. The Gaia Massif, the pre-coastal mountain range (Sierra Prelitoral) constitutes the watershed main headwater. The middle reach is the pre-coastal depression (Depresión Prelitoral penedesenca); and the final part, both the Garraf Massif and the river mouth are found.

The main headwater houses many gullies and torrents. They collect water from different slopes and feed the main river course, as well as the tributaries streams *Pontons, Vilobí* and *Marmelar*. In this area, there exist few courses with permanent flow; they always depend on the rainfall intensity. In direction to the coast line, the watershed altitude rapidly decreases. The middle course of the river is polluted by the waste domestic and industrial waters spill.

6.5.1.2 Main water uses in the Foix Basin

The area of study considered for data Collection by the CWA is the Foix-Gaia-Francolí system, covering 8.3% of the IBC territory and with an average population of 631,367 inhabitants (with maximums of more than 1 million people in vacation periods).

According to the IMPRESS document of the CWA (CWA, 2005a), the water demand is allocated as follows:

- Urban: 99.6 hm^3/yr (it includes 55 hm^3 form the low Ebro transfer (CAT) and it is shared among domestic, 51.7 hm^3, and industrial, 47.9 hm^3, uses).
- Livestock: 4 hm^3/yr
- Irrigation: 113 hm^3/yr (it is the theoretical value; currently, the real water use for irrigation is about 40 hm^3/yr)

Main pressures in the area are represented in Figure 6.74. These are the locations considered in this work. They will be further developed in next section.

6.5.2. Application of the pressure-impacts model to the Foix Watershed

As it was already explained in the previous case study, in order to apply the P-I model, it is necessary to define the river reaches. It was done by considering the fluvial types and the water bodies definition, as well as the existing point sources along the river.

Regarding the monitoring and control stations, only two sampling stations for quality data and four sampling stations for water flow were available in Foix watershed. Then, it is obliged to use hydrologic simulators of a River Basin. Qual2kw model, a well-know and free application developed by the EPA, was used to simulate the watershed. First, the figures (quantity and quality) for each stretch of the river at the present status were obtained.

Figure 6.74. Main pressures in the Foix watershed (this map is amplified in Annex A)

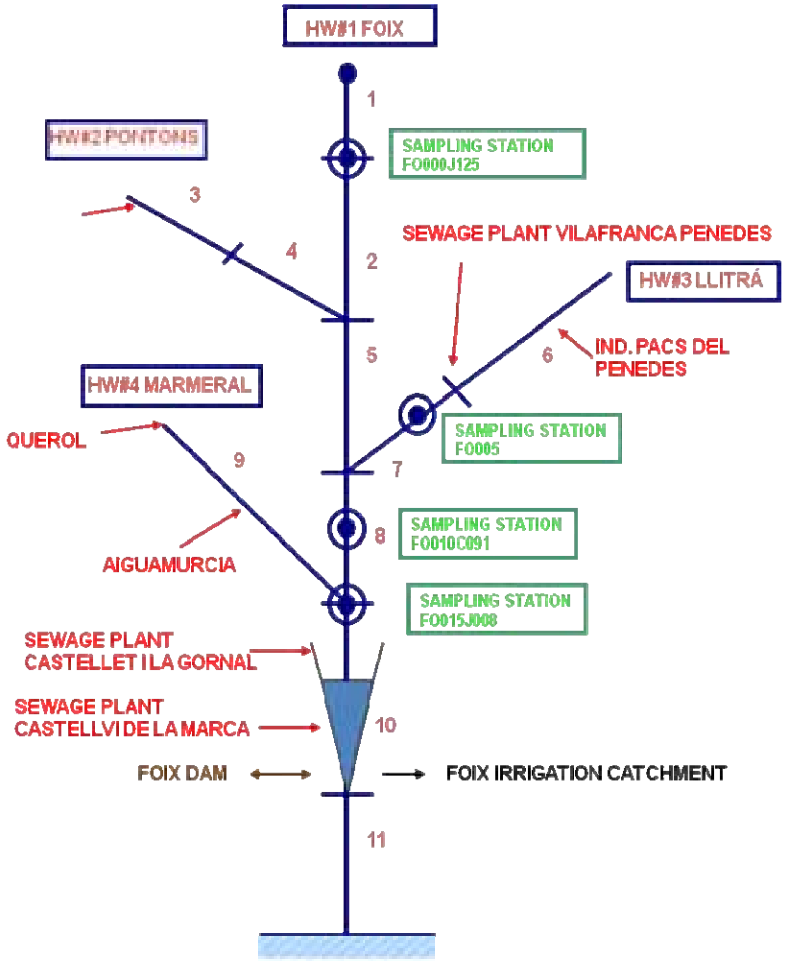


Figure 6.75. Foix basin schema, with its sampling stations and the most relevant water uses

6.5.2.1 Identification and sliceage

Foix basin was divided into 11 water stretches. The main course of the river comprises reaches 1, 2, 5, 7, 8, 10 and 11. The river types identified in the watershed are presented in Table 6.34.

Headwater name	River type
Foix (1), Pontons (3)	Rivers with karstic influence
Llitra (6)	Mediterranean mountain rivers on limestone
Marmelar (9)	Coastal torrents

Table 6.34. Types of river for the Foix's headwaters.

Figure 6.75 shows the general scheme for the Foix River Basin.

The exact location of each reach is shown in Table 6.35. Each headwater is computed independently and the main headwater is always the final aim. For example, the Marmelar (reach 9) start in its source, 35.49 km, and dies in the main headwater, so the downstream value is 0 km.

	Upstream (km)	Downstream (km)
1	46.69	35.33
2	35.33	31.11
3	18.08	5.65
4	5.65	0.00
5	31.11	23.94
6	18.68	1.67
7	1.67	0.00
8	23.94	14.58
9	35.49	0.00
10	14.58	10.48
11	10.48	0.00

Table 6.35. Location of the Foix's reaches

6.5.2.2 Headwaters characterization

There are four courses within the watershed (Table 6.36): main one is the Foix Headwater, formed, as already said, by stretches 1, 2, 5, 8, 10 and 11; the Pontons (reaches 3 and 4) is located east to the main headwater; the *Marmelar*, on the west side of the watershed, is only constituted by stretch 9 and it joins the main course before Foix Dam (stretch 10) and, finally, the *Llitra* is formed by stretches 6 and 7, in the east part of the watershed. It is noticeable that major population nucleus is *Villafranca del Penedés* whose supply water comes from another river basin (ATLL system), but incorporates its depurated waters throughout stretch 7.

	Name	Reaches
HW#1	Foix	1, 2, 5, 8, 10, 11
HW#2	Pontons	3, 4
HW#3	Llitrá	6, 7
HW#4	Marmelar	9

Table 6.36. Headwaters characterization

6.5.2.3 Description of the anthropic pressures in the watershed

From the general demand figures given in section 6.15, together with excel sheets data provided by the CWA, the particular water uses in the Foix watershed were identified. As in the Muga case study, domestic, industrial and agricultural uses were reported. Table 6.37 summarizes the included uses, both punctual and diffuse.

Name	***Headwater ID***	***Location km***	***Reach up stream***	***Reach down stream***
Captacio Reg E. Foix	1	10.476	10	11
EDAR Vilafranca del Penedès	3	2.17	6	6
EDAR Castellet i la Gornal (Sant Marçal)	4	0.82	9	9
EDAR Castellet i la Gornal (Torrelletes)	1	12.49	10	10
EDAR Castellet i la Gornal (Castellet)	1	13.76	10	10
EDAR Castellet i la Gornal (Clariana)	1	11.93	10	10
EDAR Castellet i la Gornal (Rocallisa)	1	11.93	10	10
EDAR Castellet i la Gornal (Les Casetes)	1	11.93	10	10
EDAR Castellví de la Marca (La munia)	1	19.03	8	8
EDAR Castellví de la Marca (El Maset del Cosí)	4	13.22	9	9
Querol	4	35.49	--	9
Pontons	2	18.08	--	3
Aiguamúrcia	4	26.62	9	9
Embassament del Foix	1	10.48	10	11
Industria Pacs del Penedes	3	6.10	6	6

Table 6.37. Description of the anthropic pressures in the watershed (EDAR stands for WWTP in the simulation)

The irrigation catchment *Captacio Reg E. Foix* is the only outflow registered in the whole watershed. It is actually a weird characteristic of this river. Almost any water catchment is from aquifers.

Embassament del Foix is the inflow or outflow of the reservoir. All the other analyzed pressures are WWTP (*EDARs*) and non connected urban uses. The water inflow coming from *Industria Pacs del Penedes* is a monthly constant inflow from an important industry in the Llitrá area.

Agricultural uses

Only a relevant catchment for irrigation is computed in the Foix watershed. No more data about this important water consumption was provided by the CWA. It is know that many non-registered water for irrigation is extracted from private wells. The variation of the irrigation use is shown in Figure 6.76.

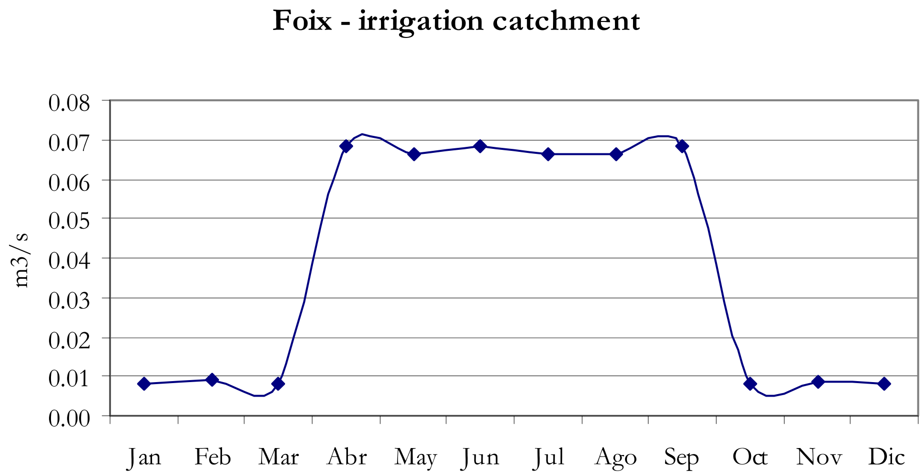


Figure 6.76. Foix-irrigation catchemt

Urban uses

Two different uses are distinguished within the *urban uses* classification: connected and non-connected to the sewage network. In this watershed, there was none reported input because most catchments are from aquifers or from external basins.

Total inflows are shown in Figure 6.77. As already mentioned, the EDAR located in Villafranca del Penedés is the most important contribution to the river flow. Because of its different magnitude, the rest of inputs can not be seen in this graph.

For the sake of clarity, the flows provided by the small WWTP along the year have been represented in Figure 6.78, and the non-connected urban uses can be seen in Figure 6.79. In the latter, the constant inflow corresponds to the *Pac del Penedes Industry*. The provided data for this industrial use connected to the urban network was a yearly periodicity; the average for the twelve month was linearly made.

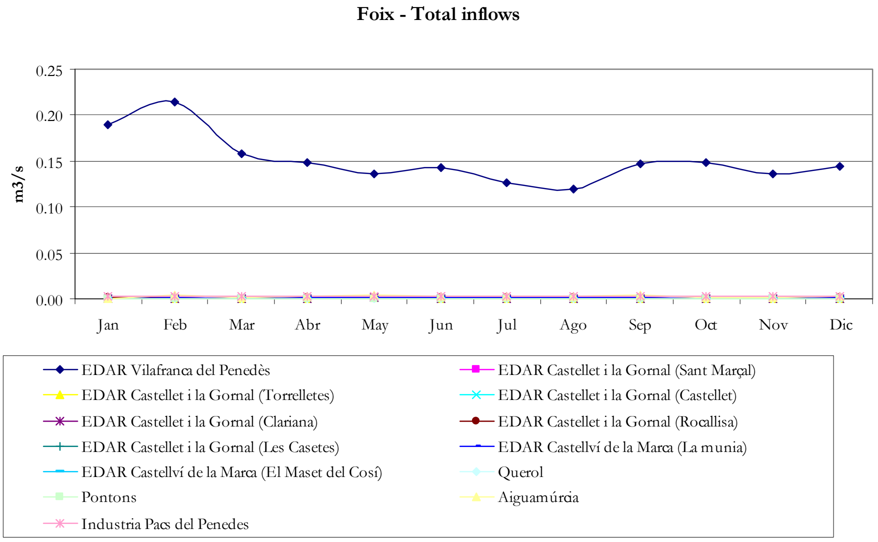


Figure 6.77. Foix. Total inflows

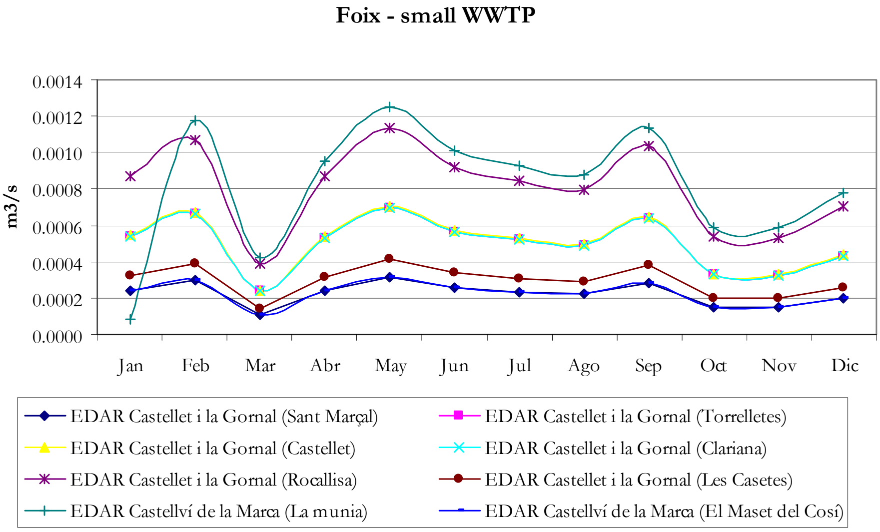


Figure 6.78. Foix- small WWTP

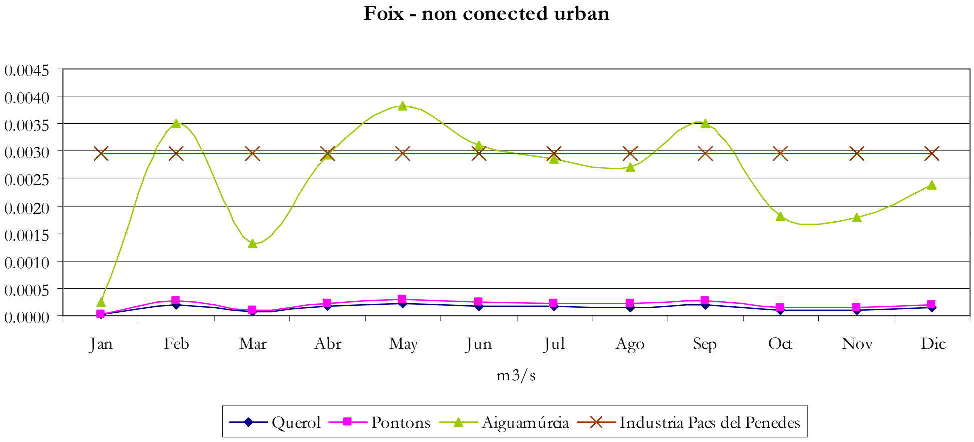


Figure 6.79. Foix- non conected urban

Foix Dam

General characteristics for the Foix Dam were already described in the introduction to this case study. Here, the variations in the input-output flows are given.

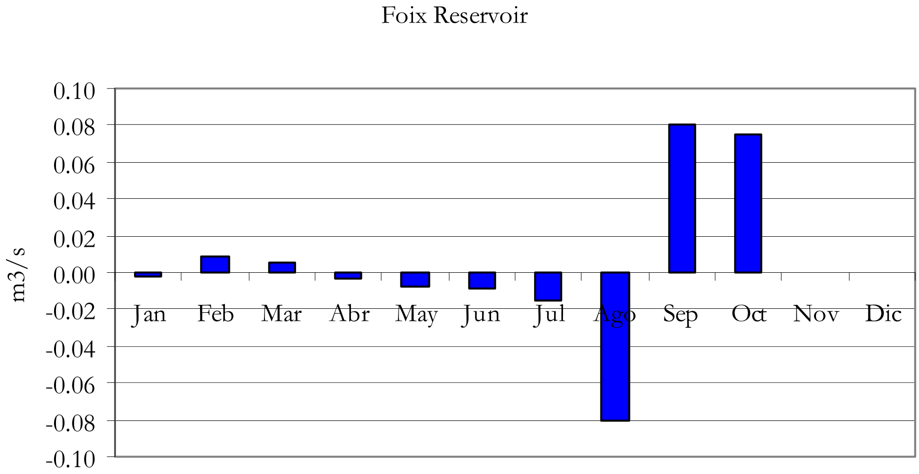


Figure 6.80. Foix Reservoir

As already explained in the Muga's Dam, it is represented in the simulator as an additional flow. The negative sign represents water releasing the dam. Summer months are the ones where water for irrigation is demanded. Rainfall means higher input flows in the fall.

Water residence time has average values higher than one year but shows strong fluctuations matching the large inflow variability. Nutrient concentrations are very high, especially ammonia and soluble reactive phosphorus (SRP). These lead to high chlorophyll concentrations, causing a permanent oxicline with anoxic periods during stratification (Marcé et al., 2000).

6.5.2.4 Diffuses sources

Rainfall in each contributor and irrigation returns along the main course constitute the diffuse sources included in the simulation. They are summarized in Table 6.38 and its behaviour along the year is drawn in Figure 6.81. They clearly respond to the expected behaviour in Mediterranean rivers.

			Location	
	Headwater	**Headwater**	**Up stream**	**Down stream**
Name	**ID**	**Name**	**km**	**km**
Retorn Regadiu	1	Foix	10.476	0.000
Pontons	2	Pontons	18.08	0.00
Llitrà	3	Llitrà	18.68	0.00
Torrent de la Bruixa	1	Foix	18.98	18.88
Marmellar	4	Marmellar	35.49	0.00
Foix aigua amunt Llitrà	1	Foix	35.49	0.00

Table 6.38. Diffuses sources

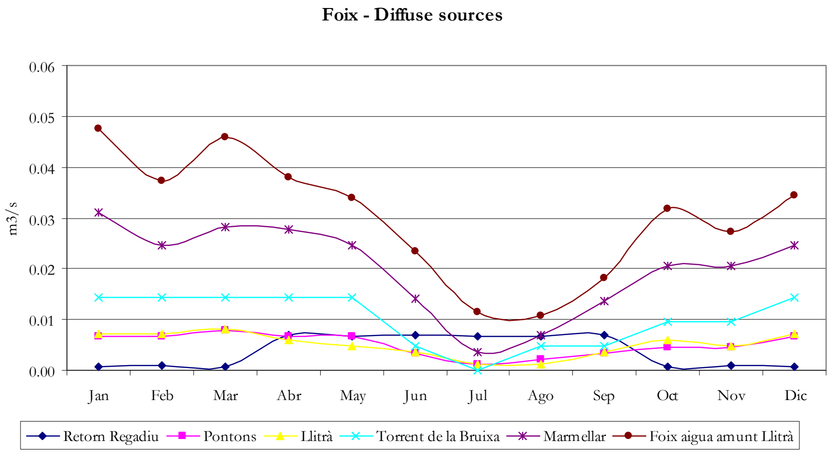


Figure 6.81. Foix- Diffuse sources

6.5.2.5 Quality data

Available sampling stations (FO000J125, FO005, FO010C091 and FO015J008) were enough to cover the requirements of quality inputs.

6.5.2.6 Calibration

The calibration was performed in the way described in the Calibration section of the Muga case study. The schema of the Foix river is presented in Figure 6.82.

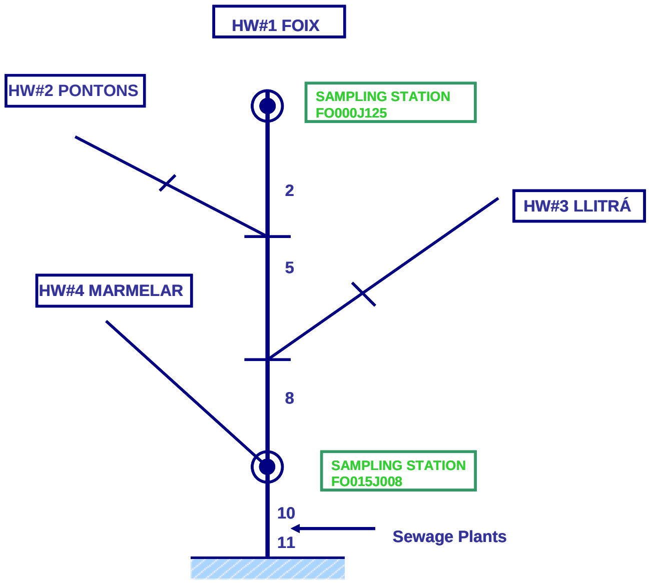


Figure 6.82. Foix schema for calibration

6.5.3. Results of Physical Hydronomics in the Foix Watershed

The exergy gap among the different river states defining the minimum exergy cost, the real exergy cost, and the WFD costs for the Foix Watershed, are explained in this section. As in the Muga case, a summary of results is presented here. The detailed calculations can be found in the Annex A.

Following the same exposition sequence as in the previous case study, flows along the Foix course can be seen in Figure 6.83. The represented main course is composed here by reaches 1, 2 5, 8, 10 and 11 (see Figure 6.82).

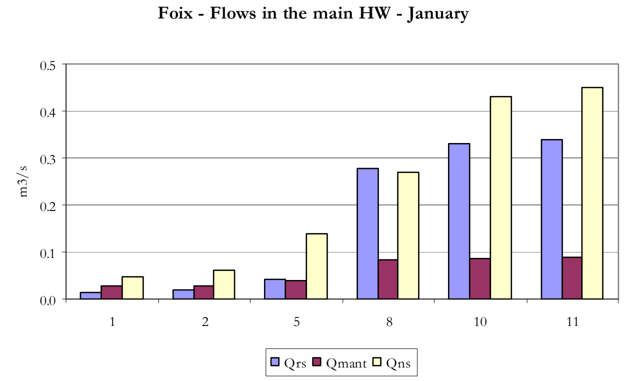


Figure 6.83. Flows (real, maintenance and natural) in the main course of the Foix river

In correspondence with its definition, the maintenance flow regime (Q_{man}) presents the lowest values for all the river reaches. The natural flow (Q_{ns}) should theoretically be the highest and, effectively, this fact can be observed in all the reaches, except in the eighth one. The Foix Dam is just located in reach 8, what is translated into an anomalous behaviour of the flows: the real flow (Q_{rs}) is there higher than the natural state. Obviously, it makes sense because the river course has been altered as water is stored and because water is abstracted to be used and returned into the river afterwards. This characteristic is maintained all over the year (see section A.5 in Annex A).

That described circumstance leads to some calculation difficulties in those river reaches where the real existing flow is higher than the flow in the natural state. As mentioned, it usually happens in those areas affected by reservoirs, presenting a lag in the flow regime pattern. That is, Q_{PS} is affected by such variation, while Q_{NS} does not.

In addition to that, it is important to point out that the Foix river is an specially dry Mediterranean river, with about 130 days of drought bed. The flow averages presented in the historical studies make up that circumstance, but such drought periods can be appreciated in individual yearly records.

6.5.3.1 Global exergy value of the Foix watershed

The global exergy values for the Foix watershed are summarized in Table 6.39, where the potential and the chemical components for the PS, OS and NS are given. The potential and the IM power present, as expected, the same order of magnitude. The minimum values are close to cero. It is due to the very small flow values in the Foix river during some dry periods happened in September and November. The maximums correspond to February and March.

The study was carried out for each month. Here, for the sake of clarity, only the values range (minimum and maximum), have been reproduced. The complete results, as well as the values for all the considered river states (PS, FS, ES, OS and NS) can be found in Annex A.

The average of the exergy global values in the Foix river can be seen in Table 6.40. In the PS, the average potential exergy value is 0.75 MW and the chemical exergy is 0.53 MW. The OS and NS present, as logic, higher values.

B_{pot} (MW)

	Min	Max
PS	0.03	1.11
OS	0.05	1.48
NS	0.04	2.11

B_{chem} (MW)

	Min	Max
PS	0.18	0.82
OS	0.25	0.93
NS	0.34	1.12

Table 6.39. Minimum and maximum exergy values of the Foix river

	$B_{av,pot}$ (MW)	$B_{av,chem}$ (MW)
PS	0.75	0.53
OS	1.00	0.63
NS	1.34	0.78

Table 6.40. Average exergy values of the Foix river

As it was done in the Muga case study, these global exergy chemical values were compared with the power currently used to clean the Foix river waters. That power is about 1 MW, which is almost double the chemical exergy of the PS. It gives idea of the huge amount of energy required to keep clean the water.

Finally, the indices related to the potential and chemical use of the river can be calculated:

P_{pot}	P_{chem}	F_{pot}	F_{chem}	R	F_R	PURI	CURI	RRI	F_RRI
0.00	0.00	0.75	0.53	0.21	0.96	0.00	0.00	0.22	1.83

Table 6.41. Index Refining the exergy value of the Foix river in its PS.

In this watershed, there is not any hydroelectricity utility, so both index PURI and CURI are zero. The Foix river is, as it has been seen, more polluted than the Muga river. It can be also concluded from the value of the RRI and F_RRI, which present higher values than in the previous case study.

6.5.3.2 Exergy profiles in the Foix watershed

Real data, output simulation figures and legally defined parameters provided information to proceed with the exergy profiles drawing. Foix river profiles are shown in the next figures (Figure 6.84 to Figure 6.89) for January (hydrologic year 2003-04).

Again, only the potential component follows the theoretical tendency. Obviously, the ideal curve presented in Chapter 3 for the river profiles is only an idealized river. Water uses along the river imply flow variance and, in general, quality degradation. Those features can be seen with the exergy profiles.

The overlapped exergy profiles of the Foix river, corresponding to the PS, FS and OS can be seen in the next figures. The corresponding flows are given in Figure 6.90, while the specific and total exergies are shown in Figure 6.91 to Figure 6.96.

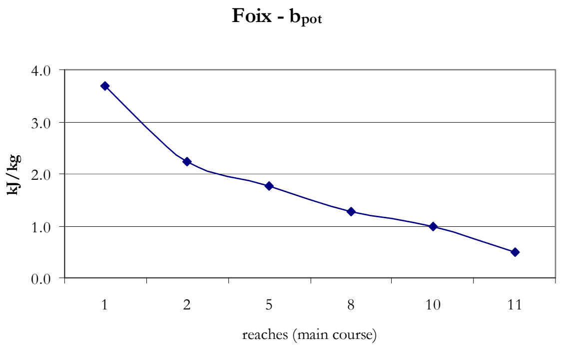


Figure 6.84. Specific exergy profile of the potential component in the Foix river in January (PS)

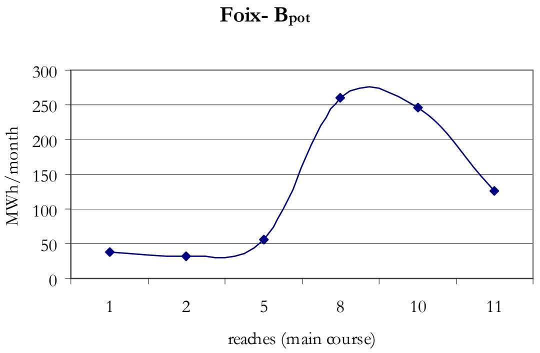


Figure 6.85. Exergy profile of the potential component in the Foix river in January (PS)

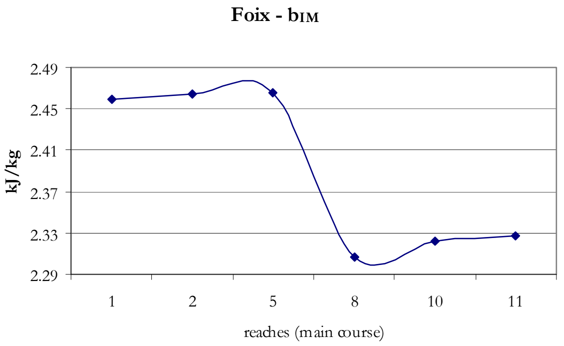


Figure 6.86. Specific exergy profile of the IM chemical component in the Foix river in January (PS)

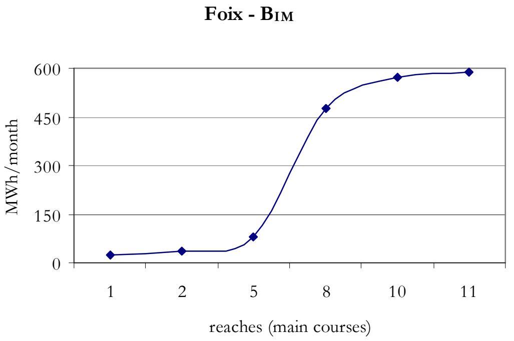


Figure 6.87. Exergy profile of the IM chemical component in the Foix river in January (PS)

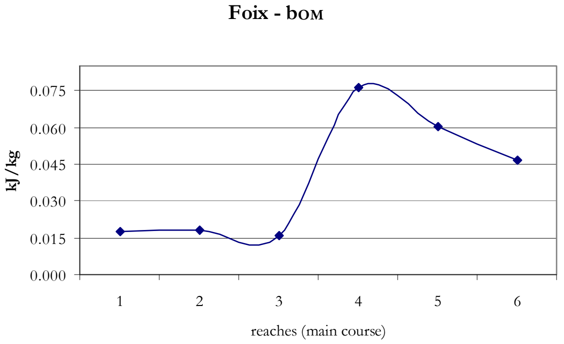


Figure 6.88. Specific exergy profile of the OM chemical component in the Foix river in January (PS)

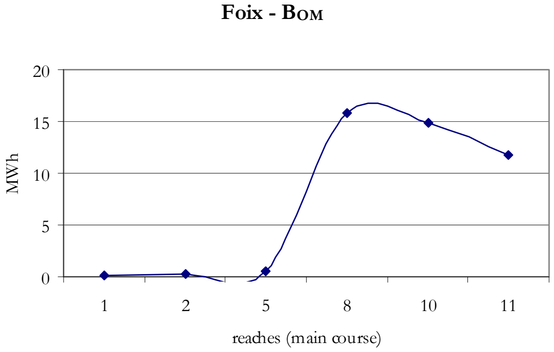


Figure 6.89. Exergy profile of the OM chemical component in the Foix river in January (PS)

As it was already seen in the previous case study, the Muga basin, these curves are far from ideality. The flow is highly affected by the reservoir presence in reach 8. The potential component follows the expected decreasing behaviour, but it does not happen for the IM and the OM component. The IM component was expected to present the theoretical parabola behaviour described in Chapter 5, but the effect of water uses make the difference. The specific OM component, as well as the flow, is expected to grow along the river course, as the OM pollution and the flow grow. In this example, the tendency is maintained, but there is a small decrease after reach 8, which is due to the presence of WWTPs and the dam.

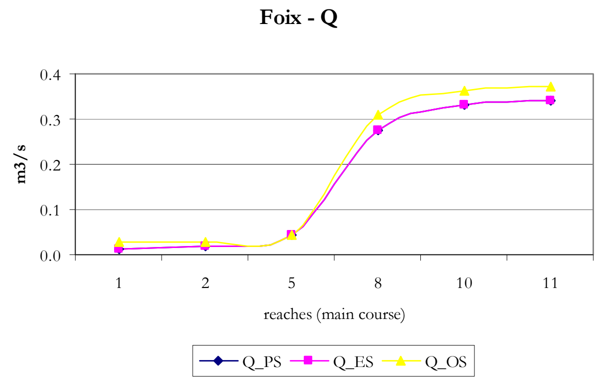


Figure 6.90. Flows in the PS, ES and OS in the Foix river in January

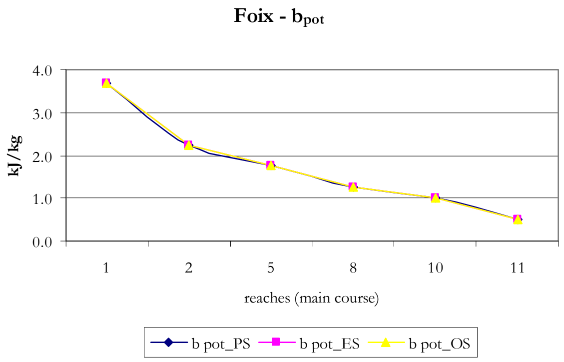


Figure 6.91. Specific exergy profiles of the potential component in the Foix river in January

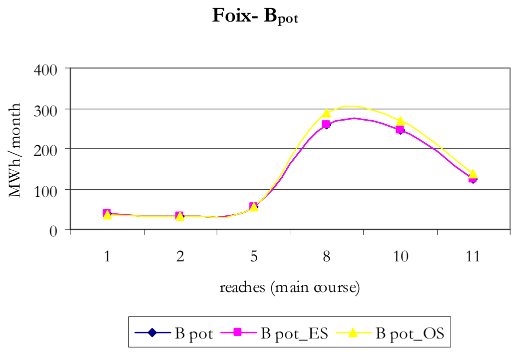


Figure 6.92. Exergy profiles of the potential component in the Foix river in January

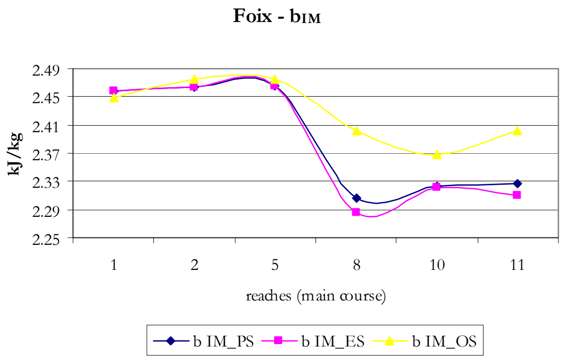


Figure 6.93. Specific exergy profiles of the IM chemical component in the Foix river in January

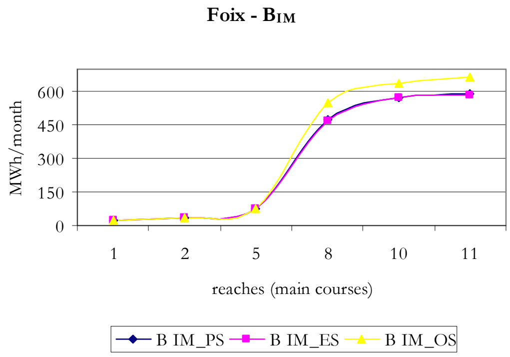


Figure 6.94. Exergy profiles of the IM chemical component in the Foix river in January

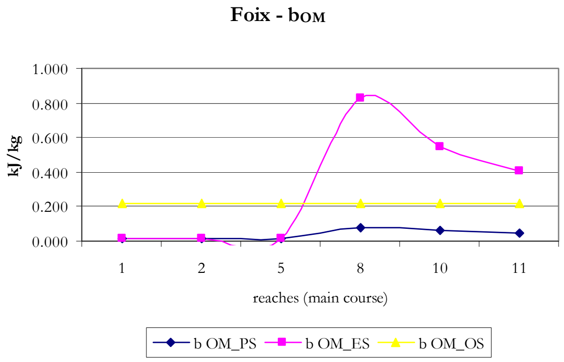


Figure 6.95. Specific exergy profiles of the OM chemical component in the Foix river in January

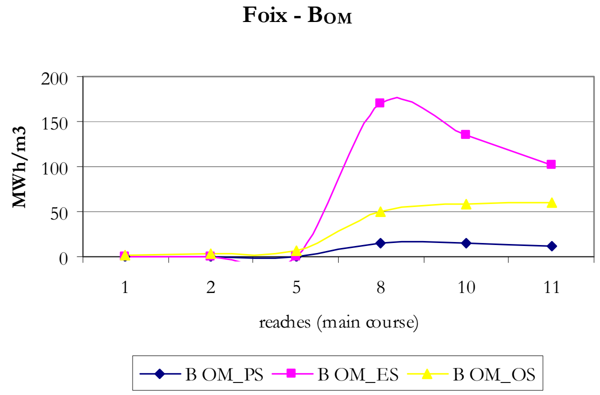


Figure 6.96. Exergy profiles of the OM chemical component in the Foix river in January

Then, exergy profiles are substracted according to the exergy gaps associated t the defined water costs, giving the figures reproduced in Table 6.42.

MWh/month		**Quantity**			**Quality**		
		$\Delta B_{t,pot}$	**$\Delta B_{t,IM}$**	**$\Delta B_{t,OM}$**	**$\Delta B_{l,pot}$**	**$\Delta B_{l,IM}$**	**$\Delta B_{l,OM}$**
PS-ES	**Jan**	0.00	0.00	0.00	0.00	1.03	-236.04
	Feb	0.00	0.00	0.00	0.00	0.75	-233.14
	Mar	0.00	0.00	0.00	0.00	2.58	-159.73
	Apr	0.00	0.00	0.00	0.00	2.34	-137.42
	May	0.00	0.00	0.00	0.00	1.90	-141.31
	Jun	0.00	0.00	0.00	0.00	0.79	-137.89
	Jul	0.00	0.00	0.00	0.00	2.22	-107.38
	Ago	0.00	0.00	0.00	0.00	2.30	-118.31
	Sep	0.00	0.00	0.00	0.00	2.06	-132.36
	Oct	0.00	0.00	0.00	0.00	1.33	-140.71
	Nov	0.00	0.00	0.00	0.00	1.64	-134.95
	Dec	0.00	0.00	0.00	0.00	2.05	-164.15
	TOT	**0.00**	**0.00**	**0.00**	**0.00**	**20.97**	**-1,843.37**
OS(GEE)-FS	**Jan**	47.77	-0.58	0.00	0.00	7.94	-26.74
	Feb	43.30	-0.55	0.00	0.00	8.53	-102.22
	Mar	74.11	-1.77	0.00	0.00	14.17	0.33
	Apr	81.66	-1.96	0.00	0.00	18.93	-3.58
	May	85.04	-2.11	0.00	0.00	11.42	7.38
	Jun	129.99	-3.25	0.00	0.00	12.41	7.34
	Jul	218.06	-4.41	0.00	0.00	14.31	-11.24
	Ago	201.33	-3.67	0.00	0.00	11.94	4.99
	Sep	139.68	-3.06	0.00	0.00	5.67	-5.54
	Oct	109.66	-2.28	0.00	0.00	9.00	6.03
	Nov	106.79	-2.40	0.00	0.00	12.59	13.68
	Dec	85.36	-1.97	0.00	0.00	14.19	23.85
	TOT	**1,322.73**	**-28.02**	**0.00**	**0.00**	**141.12**	**-85.70**
NS-OS(GEE)	**Jan**	331.13	141.64	7.44	0.00	4.64	-23.96
	Feb	294.55	119.05	6.20	0.00	4.04	-21.99
	Mar	602.00	230.11	12.39	0.00	6.56	-21.30
	Apr	439.77	33.87	1.99	0.00	6.96	-23.56
	May	490.57	224.75	12.00	0.00	4.88	-15.78
	Jun	156.62	22.66	1.19	0.00	3.86	-12.27
	Jul	0.00	0.00	0.00	0.00	2.93	-9.00
	Ago	0.00	0.00	0.00	0.00	4.06	-13.27
	Sep	169.26	148.77	7.78	0.00	2.31	-6.63
	Oct	95.18	180.92	9.65	0.00	3.61	-12.84
	Nov	253.96	47.17	2.49	0.00	4.60	-15.76
	Dec	465.31	144.27	7.77	0.00	5.59	-19.25
	TOT	**3,298.33**	**1,293.22**	**68.89**	**0.00**	**54.04**	**-195.61**

Table 6.42. Exergy gaps among the different river statuses in the Foix Watershed

Analyzing the quantity contributions, as expected, the gap PS-ES is null because of the flows equality. In the OS-FS difference, there are positive contribution for the potential component and negative for the IM component. In consequence, restoration measurements will be only needed for the potential component. Because of those values, it is clear that there exists a flow difference between the FS and the OS and, consequently, the null value of the inorganic component comes from the OM quality objectives.

The quality contribution comes from the IM and OM components. In the PS-ES difference, the regular behavior is observed: the highest OM values respond to the ES characteristics. The positive and negative signs of the IM and the OM, respectively, indicate the need of restoration measurements for both cases. The salts contribution is higher in the OS-FS gap, but quite lower in the OM. In fact, there are some month were OM cleaning would be not needed (positive signs). Finally, the difference NS-OS present values which derive in restoration measurements (brackish desalination and WWTPs)..

These values, which are also separated between quantity and quality, can be understood as a minimum cost. However, the meaning of the obtained signs for the components needs also to be analyzed: negative results for the IM component are neglected because existing flow is less salty than the OS; moreover, the positive results in the organic matter imply that none restoration is required. By implementing these considerations, Table 6.42 becomes Table 6.43.

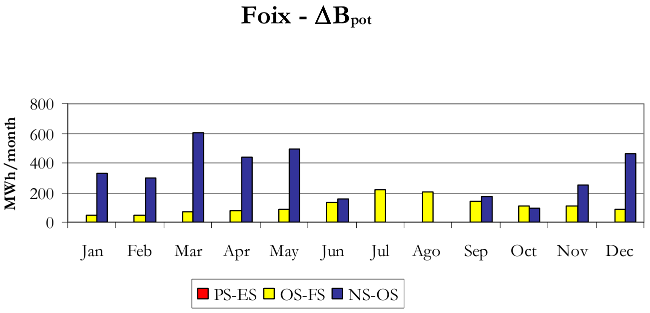

Foix - ΔB_{pot}

Figure 6.97. Potential exergy profile (here, $B_{pot}=B_{pot,t}$ because $B_{pot,l}=0$)

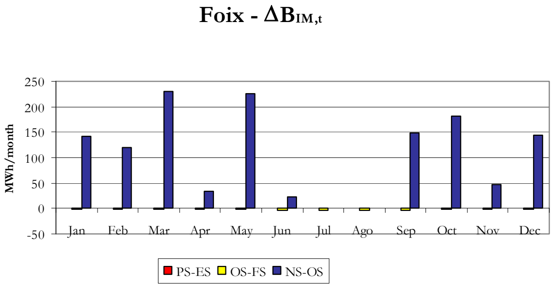

Foix - $\Delta B_{IM,t}$

Figure 6.98. IM-chem exergy profile (quantity)

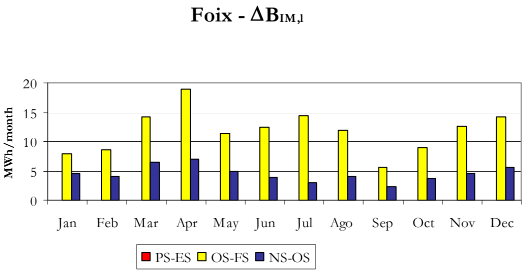

Foix - $\Delta B_{IM,l}$

Figure 6.99. IM-chem exergy profile (quality)

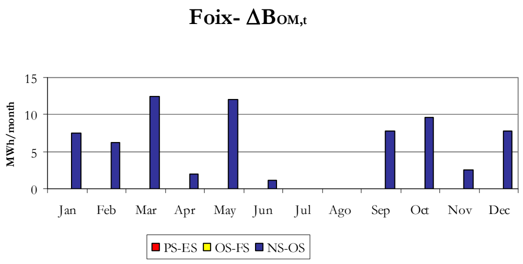


Figure 6.100. OM-chem exergy profile (quantity)

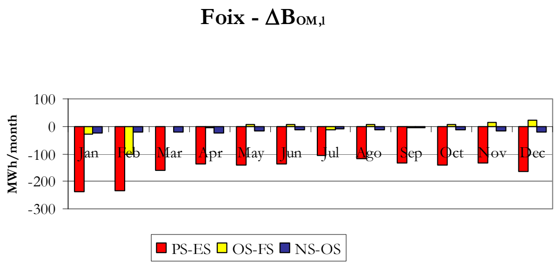


Figure 6.101. OM-chem exergy profile (quality)

The potential component responds to the expected behaviour, similar to the one described in the Muga watershed. The OM and IM are proportional, as it was already justified in that previous example.

6.5.3.3 Exergy cost assesment in the Foix watershed

The main contribution to the quantity IM exergy component comes from the difference between the NS and the OS because of the flow in the former, which is considerably higher. The OS-FS gap has also a small contribution, hardly distinguished in the graph Figure 6.98

MWh/month		**Quantity**			**Quality**		
		$\Delta B_{t,pot}$	**$\Delta B_{t,IM}$**	**$\Delta B_{t,OM}$**	**$\Delta B_{l,pot}$**	**$\Delta B_{l,IM}$**	**$\Delta B_{l,OM}$**
SC	**Jan**	0.00	0.00	0.00	0.00	1.03	-236.04
PS-ES	**Feb**	0.00	0.00	0.00	0.00	0.75	-233.14
	Mar	0.00	0.00	0.00	0.00	2.58	-159.73
	Apr	0.00	0.00	0.00	0.00	2.34	-137.42
	May	0.00	0.00	0.00	0.00	1.90	-141.31
	Jun	0.00	0.00	0.00	0.00	0.79	-137.89
	Jul	0.00	0.00	0.00	0.00	2.22	-107.38
	Ago	0.00	0.00	0.00	0.00	2.30	-118.31
	Sep	0.00	0.00	0.00	0.00	2.06	-132.36
	Oct	0.00	0.00	0.00	0.00	1.33	-140.71
	Nov	0.00	0.00	0.00	0.00	1.64	-134.95
	Dec	0.00	0.00	0.00	0.00	2.05	-164.15
	TOT	**0.00**	**0.00**	**0.00**	**0.00**	**20.97**	**-1,843.37**
EC	**Jan**	47.77	-0.58	0.00	0.00	7.94	-26.74
OS(GEE)-FS	**Feb**	43.30	-0.55	0.00	0.00	8.53	-102.22
	Mar	74.11	-1.77	0.00	0.00	14.17	0.33
	Apr	81.66	-1.96	0.00	0.00	18.93	-3.58
	May	85.04	-2.11	0.00	0.00	11.42	7.38
	Jun	129.99	-3.25	0.00	0.00	12.41	7.34
	Jul	218.06	-4.41	0.00	0.00	14.31	-11.24
	Ago	201.33	-3.67	0.00	0.00	11.94	4.99
	Sep	139.68	-3.06	0.00	0.00	5.67	-5.54
	Oct	109.66	-2.28	0.00	0.00	9.00	6.03
	Nov	106.79	-2.40	0.00	0.00	12.59	13.68
	Dec	85.36	-1.97	0.00	0.00	14.19	23.85
	TOT	**1,322.73**	**0.00**	**0.00**	**0.00**	**141.12**	**-149.32**

RRC	**Jan**	331.13	141.64	7.44	0.00	4.64	-23.96
NS-OS(GEE)	**Feb**	294.55	119.05	6.20	0.00	4.04	-21.99
	Mar	602.00	230.11	12.39	0.00	6.56	-21.30
	Apr	439.77	33.87	1.99	0.00	6.96	-23.56
	May	490.57	224.75	12.00	0.00	4.88	-15.78
	Jun	156.62	22.66	1.19	0.00	3.86	-12.27
	Jul	0.00	0.00	0.00	0.00	2.93	-9.00
	Ago	0.00	0.00	0.00	0.00	4.06	-13.27
	Sep	169.26	148.77	7.78	0.00	2.31	-6.63
	Oct	95.18	180.92	9.65	0.00	3.61	-12.84
	Nov	253.96	47.17	2.49	0.00	4.60	-15.76
	Dec	465.31	144.27	7.77	0.00	5.59	-19.25
	TOT	**3,298.33**	**1,293.22**	**68.89**	**0.00**	**54.04**	**-195.61**
IRC		**4,621**	**1,293**	**69**	**0**	**216**	**-2,188**

Table 6.43. Minimum exergy costs for the Foix watershed

At this point, it is finally possible to correctly apply the unit exergy cost of the different restoration measurements in order to get the real exergy cost (SC^*, EC^*, RRC^*); then, the energy price to get the economic cost. It has been done in the same way as in the Muga case study.

A summary of results, following the steps in the procedure, can be seen in Table 6.44.

(a) **Exergy gap**

MWh/yr		$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,pot}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
	SC	0	0	0	0	21	1,843
	EC	1,323	0	0	0	141	149
	RRC	3,298	1,293	69	0	54	196
	IRC	**4,621**	**1,293**	**69**	**0**	**216**	**2,188**

(b) **Exergy cost ***

MWh/yr		$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,pot}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
	SC*	0	0	0	0	168	8,203
	EC*	9,167	0	0	0	1,129	664
	RRC*	22,857	7,113	379	0	432	870
	IRC*	**32,024**	**7,113**	**379**	**0**	**1,729**	**9,738**

(c) **Economic cost**

€/yr		$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,pot}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
	***ec*SC**	0	0	0	0	13,424	656,240
	***ec*EC**	733,322	0	0	0	90,315	53,158
	***ec*RRC**	1,828,593	569,016	30,313	0	34,582	69,636
	***ec*IRC**	**2,561,915**	**569,016**	**30,313**	**0**	**138,321**	**709,398**

Table 6.44. IRC, IRC* and ecIRC for the Foix watershed, disaggregated by components

As it was already done in the first case study, some additional graphs are included at this point of the analysis, in order to clarify the obtained results.

Figure 6.102 shows the IRC (SC+EC+RRC) for each exergy component in economic units, keeping the separation between the quantity and quality terms of each component (pot, IM and OM). That difference disappears in the following figures, where the quality and quantity have been added in order to see the specific contribution of the pot, IM and OM exergy components.

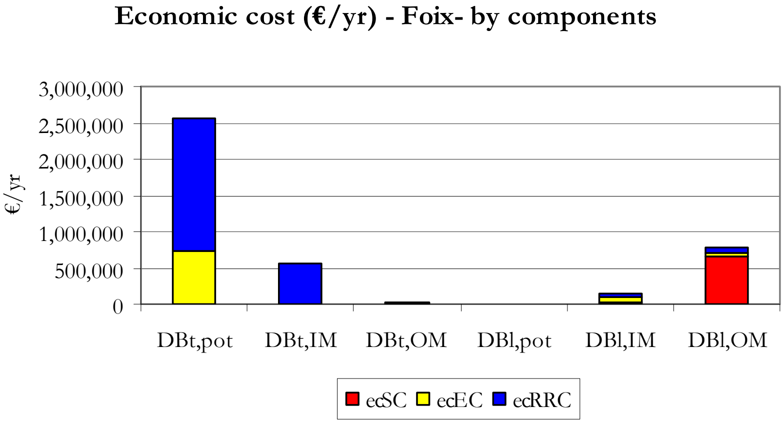


Figure 6.102. Components of the IRC (SC+EC+RRC) for each exergy component in economic terms (€/yr), in the Foix Watershed

The detailed percentages of the exergy components represented in Figure 6.102 are given in Table 6.45. The RRC is, as expected, the highest contributor, but the EC is here more relevant than in the previous Muga example: the EC potential quantity component rises up until 28.6% and the quality organic matter component is 7.5%. It means that restoration measures will be needed (in the Muga example this component did not exist). The main part of the OM quality component, again, is due to the existing WWTPs (92.5%).

	$\Delta B_{t,pot}$	$\Delta B_{t,IM}$	$\Delta B_{t,OM}$	$\Delta B_{l,IM}$	$\Delta B_{l,OM}$
SC	0.0%	0.0%	0.0%	9.7%	92.5%
EC	28.6%	0.0%	0.0%	65.3%	7.5%
RRC	71.4%	100.0%	100.0%	25.0%	9.8%

Table 6.45. Percentages of the ecIRC components (ecSC, ecEC and ecRRC) in the Foix watershed, by exergy components

Because of its relevance, the exergy costs are separately presented in Figure 6.103 (minimum costs) and Figure 6.104 (real exergy cost). The same scale has been maintained in both graphs to facilitate the comparison. The difference between the bars for each component (pot, IM and OM) is due to the irreversibility of the water restoration techniques.

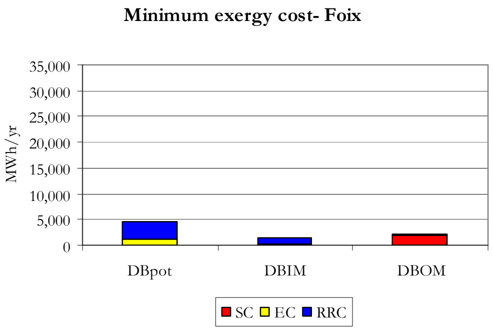


Figure 6.103. IRC$_{pot}$, IRC$_{IM}$ and IRC$_{OM}$ in the Muga watershed

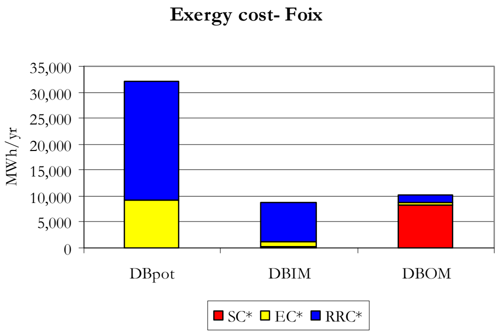


Figure 6.104. IRC$^*_{pot}$, IRC$^*_{IM}$ and IRC$^*_{OM}$ in the Muga watershed

The OM component comprises mainly the SC that accounts for the WWTPs (red bar). The IM component is only related to the different salts content between the FS and the OS. Attending to the EC, no additional cost comes then from this IM contribution. The potential component has a non negligible contribution due to the flow of the OS, which would need to be higher than the current flow (yellow bar).

As it has been seen, including at any time the quality aspects in the analysis, provide additional and fruitful information. The values given in Table 6.44 are aggregated in quantity and quality and presented in next figures: Figure 6.105 summarizes the minimum IRC as addition of the SC, EC and RRC, and disaggregated in quantity and quality; Figure 6.106 represents the exergy cost maintaining the same disaggregation; and finally the economic cost is given in Figure 6.107.

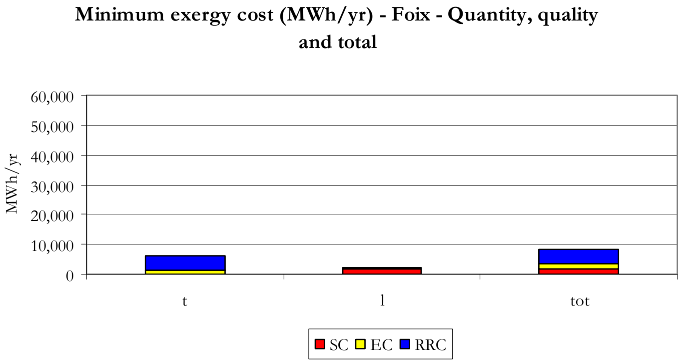


Figure 6.105. Components of the minimum IRC (SC+EC+RRC), disaggregated in quantity and quality

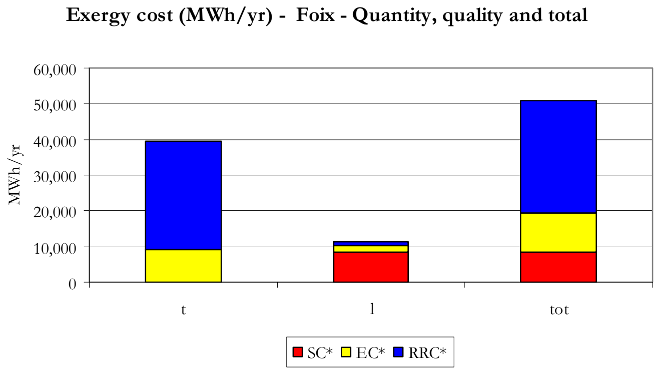


Figure 6.106. Components of the IRC* (SC*+EC*+RRC*), disaggregated in quantity and quality

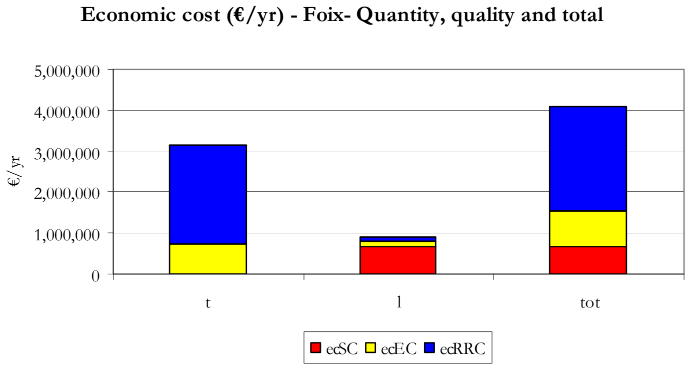


Figure 6.107. Components of the ecIRC (ecSC+ecEC+ecRRC), disaggregated in quantity and quality

The minimum cost drawn in Figure 6.105 are detailed in Table 6.46: the quantity degradation component in the IRC is mainly due to the RRC contribution (77.9%), while the quality part has 77.5% from the SC, 12.1% from the EC and 10.4% coming from the RRC. The EC contribution for each of the parameters is quite low (22.1% in quantity and 12.1% in quality).

	t	l	tot
SC	0.0%	77.5%	22.2%
EC	22.1%	12.1%	19.2%
RRC	77.9%	10.4%	58.5%

Table 6.46. IRC distribution in quantity, quality, and total in the Foix watershed

Those percentages are slightly varied in Figure 6.106 because the unit exergy costs of the different technologies are included in the analysis. Figure 6.107 presents the same allocation as Figure 6.106 because the relation factor between the exergy cost and the economic costs is just the energy price. No important differences with the reversible values can be observed.

	t	l	tot
SC	0.0%	73.0%	16.4%
EC	23.2%	15.6%	21.5%
RRC	76.8%	11.4%	62.1%

Table 6.47. IRC distribution in quantity, quality, and total in the Foix watershed

6.5.3.4 Service Cost in the Foix watershed

The only components of the SC are the IM and OM quality components. The value of the $\Delta B_{l,OM}$ is specially high, 8,203 MWh/yr (84% or the $IRC^{*}_{l,OM}$), but it corresponds to the SC definition, that is, such a value comes from the non-treated wastewater in the ES.

By adding each component, it results that the SC is composed by 0 (SC_{pot}) plus 21 MWh/yr (SC_{IM}) plus 1,843 MWh/yr (SC_{OM}). When those minimum energy figures are translated into economic values, they lead to 0 ($ecSC_{pot}$) plus 13,424 MWh/yr ($ecSC_{IM}$) plus 656,240 MWh/yr ($ecSC_{OM}$).

6.5.3.5 Environmental Cost in the Foix watershed

Quantity and quality contributions appear in the EC definition. The quantity component is only comprises by the potential component, since the IM and the OM are zero. In the quality, IM and OM account for 1,129 (65% of the $IRC^{*}_{l,IM}$) and 664 MWh/yr (only 7% of the $IRC^{*}_{l,OM}$), respectively.

When the values were grouped by components, without the quantity-quality separation, it was obtained that EC_{pot}, EC_{IM} and EC_{OM} are 1, 323 MWh/yr, 141 MWh/yr and 149 MWh/yr, respectively.

6.5.3.6 Remaining Resource Cost in the Foix watershed

The RRC represents, as always, the highest contribution to the IRC. Its quantity component is much higher than the other cost for any of the contributions ($\Delta B_{t,pot}$, $\Delta B_{t,IM}$ and $\Delta B_{t,OM}$). Regarding the quality component, the IM contribution is 432 MWh/yr, which is even lower than the corresponding component in the EC; and the OM is 870 MWh/yr, a similar value to the one in the EC. From these considerations, it is clear than the RRC is mainly determined by the flows difference between the OS and the NS.

Attending to the three calculated exergy components, the RRC values are 3,298 for the RRC_{pot}, 1,347 for the RRC_{IM} and 265 for the RRC_{OM}.

6.5.3.7 Economic cost of water in the Foix watershed

Going forward, the economic costs for the Foix watershed have been obtained using the same k^{*}s and installation cost for the technologies as in the Muga case study. Then, the parameters given in Table 6.20 and Table 6.25. Thus, the economic EC of the Foix watershed, as well as the other contributions to the IRC, are summarized in Table 6.48. The EC of the Foix watershed is, according to the PH methodology 1,831,890€/yr.

Operation Cost (€/yr)		
Op (t)	**Op (l)**	**Op**
0	669,664	669,664
733,322	143,473	876,795
2,427,922	104,218	2,532,140
3,161,244	847,719	4,008,963

Economic Cost	**€/yr**
***ec*SC**	1,624,759
***ec*EC**	**1,831,890**
***ec*RRC**	3,487,235
***ec*IRC**	4,964,058

Investment Cost (€/yr)		
Pumping	**Desalination**	**WTP**
4,463	535,509	415,123

Table 6.48. Economic EC in the Foix watershed

As it was explained in the Muga analysis, the investment cost was calculated from the specific costs indicated in Table 6.25, taking into account the treated water by each of the restoration technologies. The natural contribution of the river is 25,945 m^3/d and the missed water to reach the OS was assessed as 86% of it.

Although the EC has been already calculated, the fundamental part about cost allocation can not be forgotten, since it is one of the main PH's strengths.

6.5.3.8 Cost distribution among the water users

The exergy study of the water uses within the Foix basin led to the following results (Table 6.49), organized in the same way as in the previous case. The information about exergy degradation is given in percentages in Table 6.50 to facilitate the cost allocation.

IM	**Quantity**			**Quality**		
type of water use	**ΔQ_{c-r}**	**b_c**	**ΔB_t**	**Q_r**	**Δb_{c-r}**	**ΔB_l**
domestic	0.21	2.6690	4,912.12	1.89	0.17	2,822.49
industrial	0.01	2.6695	146.19	0.04	0.53	164.31
irrigation	0.41	2.3600	8,567.49	0.05	0.36	143.75

OM	**Quantity**			**Quality**		
type of water use	**ΔQ_{c-r}**	**b_c**	**ΔB_t**	**Q_r**	**Δb_{c-r}**	**ΔB_l**
domestic	0.21	0.6902	1,270.27	1.89	-6.7198	-111,306.12
industrial	0.01	1.9040	104.27	0.04	-1.2610	-391.31
irrigation	0.41	0.4641	1,684.82	0.05	-0.3667	-146.43

Table 6.49. Quantity and quality contribution to water degradation (IM and OM) by each water use

The highest water mass loss corresponds to irrigation, around 60%. But water pollution is mainly due to the urban water use.

IM

	t	l
domestic	36.1%	90.2%
industrial	1.1%	5.2%
irrigation	62.9%	4.6%

OM

	t	l
domestic	41.5%	99.5%
industrial	3.4%	0.3%
irrigation	55.1%	0.1%

Table 6.50. Contribution to water degradation (IM and OM) by each water use, in percentage, for quantity and quality.

On average, the degradation provoked by each water use present a quantity and a quality contribution, as it is shown in Figure 6.108. The main conclusion could be easity expected: main damage of the agricultural sector comes from the amount of used water, while in the case of the domestic and the industry, the problem is the water pollution that they produce.

The quantity degradation distribution is quite different from the Muga example. Here, the domestic use accounts for 38.8% of the quantity degradation, while it was only 3.6% in the Muga case study. Regarding the quality component, the domestic (urban) water use is responsible for the 94.8% of the degradation in the Foix river, while this concept was 87.9% in the Foix river. These results confirm that the Foix river present higher water scarcity and that the demands for urban use are relevant.

In detail, the general user's contribution to the water degradation appears in Figure 6.109 (quantity degradation) and Figure 6.110 (quality degradation, commonly designed as *pollution*). If the cost allocation were carried out only attending to the information given in Figure 6.110, only the quality aspects would be included. That is commonly identified with pollution.

Figure 6.111 accounts for the total degradation attending to the EC. It can be seen that the domestic sector is responsible for 60% of that total damage on waters. In fact, because of the already explained aggregation of industrial uses to the urban sewage system, it can be understood as domestic plus industry responsibility. Figure 6.112 accounts for the total degradation when the IRC, and not only the EC is considered. In that case, the energy cost is considerably higher. The consequence is that in this situation the major contributor to the water degradation is the agricultural sector, where important amounts of water are demanded.

It is possible to observe, again, that the cost allocation would always depends on the interpretation given to the obtained results. Even having use an objective methodology to determine the final cost allocation numbers, partial use of them can be done. This idea is further developed in the following and it becomes especially clear in figures from Figure 6.113 to Figure 6.118.

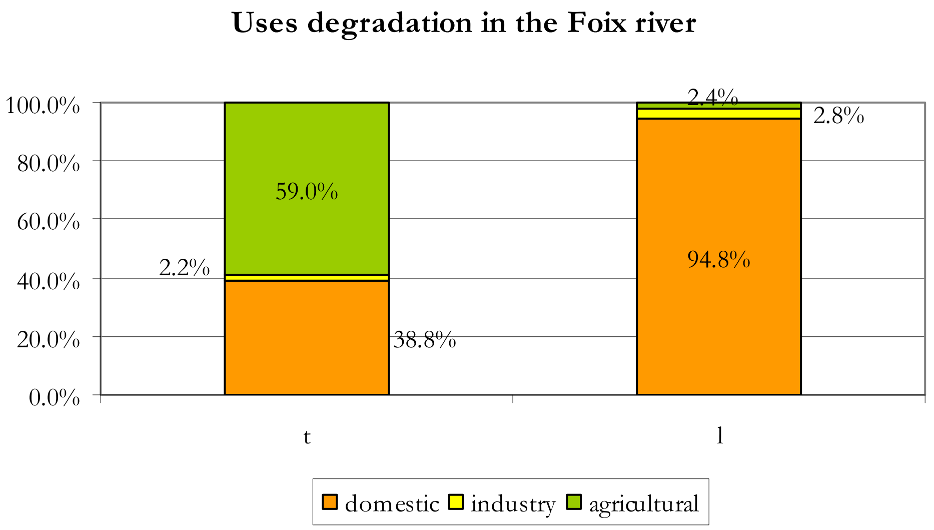


Figure 6.108. Quantity and quality allocation for the total degradation provoked by each water use.

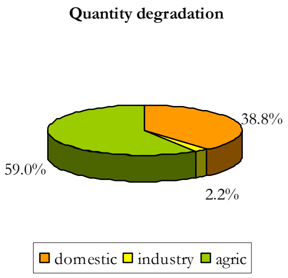


Figure 6.109. User's contribution to the general quantity degradation in the Foix watershed

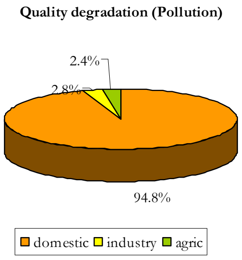


Figure 6.110. User's contribution to the general quality degradation in the Foix watershed

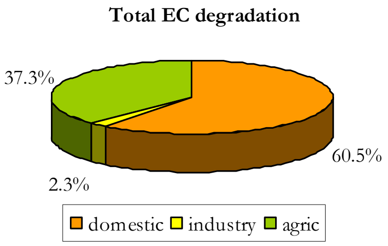


Figure 6.111. User's contribution to the EC in the Foix watershed

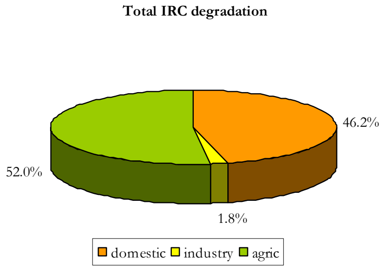


Figure 6.112. User's contribution to the IRC in the Foix watershed

The cost allocation of the EC, according to the produced exergy variation by each water user, results in the distribution shown in Table 6.51.

Op. Cost (€/yr)

	EC_t	EC_l
domestic	284,422	136,068
industrial	16,430	4,016
irrigation	432,469	3,388

Ins.t Cost (€/yr)

	EC_t	EC_l
domestic	209,430	393,700
industrial	12,098	11,621
irrigation	318,443	9,803

Total cost €/yr

	EC_t	EC_l	EC
domestic	493,853	529,769	1,023,621
industrial	28,528	15,637	44,165
irrigation	750,912	13,191	764,103
			1,831,890

Table 6.51. EC in economic terms, distributed by sectors and disaggregated in quantity and quality, and total.

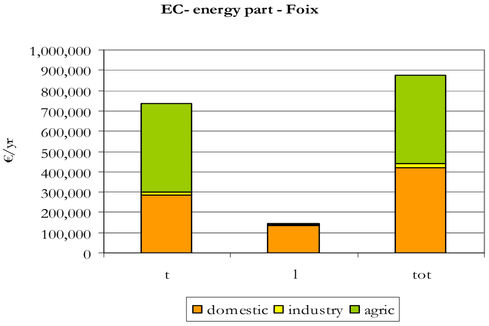


Figure 6.113. Quantity and quantity components of EC (operating cost)

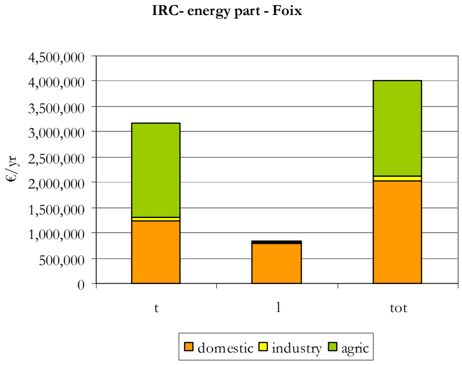


Figure 6.114. Quantity and quantity components of IRC (operating cost)

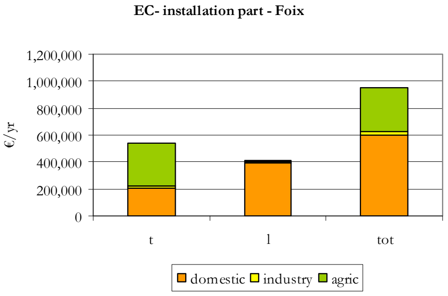


Figure 6.115. Quantity and quantity components of EC (installation cost)

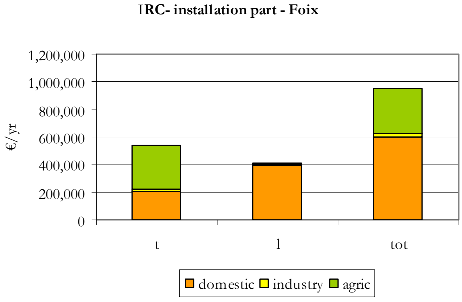


Figure 6.116. Quantity and quantity components of IRC (installation cost)

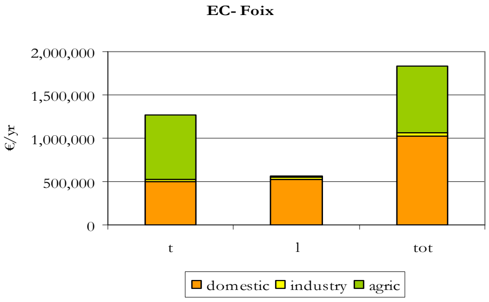


Figure 6.117. Quantity and quantity components of EC (total cost)

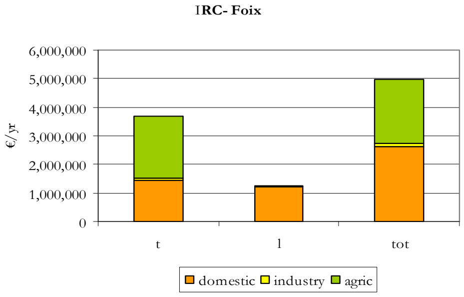


Figure 6.118. Quantity and quantity components of IRC (total cost)

The total EC in the Foix basin rises up until 1.8 M€, distributed as 1,023,621 €/yr to the domestic sector, 44,165 €/yr to the industrial sector, and 764,103 €/yr to the irrigation. As it can be seen, the poor quality of the river is translated in higher economic cost to be charged to the most polluted sectors in the area: the urban one in this case study.

Again, it can be seen that it is not he same considering only the energy cost than attending to the whole costs, including the installation. The most relevant costs within the WFD for the Foix basin are graphed in next figures. Domestic and agricultural sectors are important in this basin.

The EC is in this river more relevant than in the Muga previous example. It makes that the cost allocation attending to the EC or to the IRC were not so different, as it can be appreciated by comparing Table 6.52 and Table 6.53. The urban sector, understood as domestic plus industry, is responsible for about 58% of the EC, and the remaining is due to the agricultural sector. For the Muga example, the domestic was 60.5% when the EC is considered, and that sector was responsible for 46.2% in the case of considering the IRC.

	energy cost	**installation cost**	**total EC**
domestic	48.0%	63.1%	55.9%
industry	2.3%	2.5%	2.4%
agric	49.7%	34.4%	41.7%

Table 6.52. EC* allocation according to the DPP in the Foix watershed

	energy cost	**installation cost**	**total IRC**
domestic	50.6%	63.1%	53.0%
industry	2.4%	2.5%	2.4%
agric	47.0%	34.4%	44.6%

Table 6.53. IRC* allocation according to the DPP in the Foix watershed

6.5.3.9 Sensitivity analysis of the results

The same parameters as in the first case study have been varied for the Foix watershed. Since the investment unit values are the same, similar results of the tendencies are obtained. The utilities life time is the parameter that more directly affects the EC, much more than the energy price. In general, it can be said that the investment cost and the life time of those investments are the key factors for the EC determination.

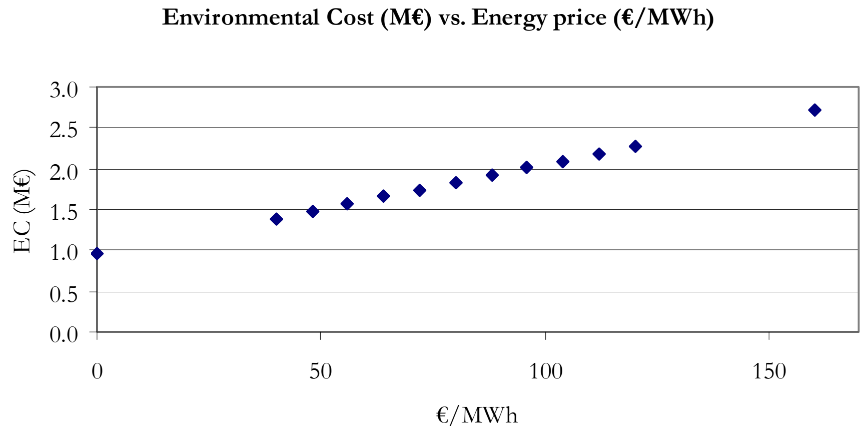


Figure 6.119. Sensitivity analysis: EC vs Energy price

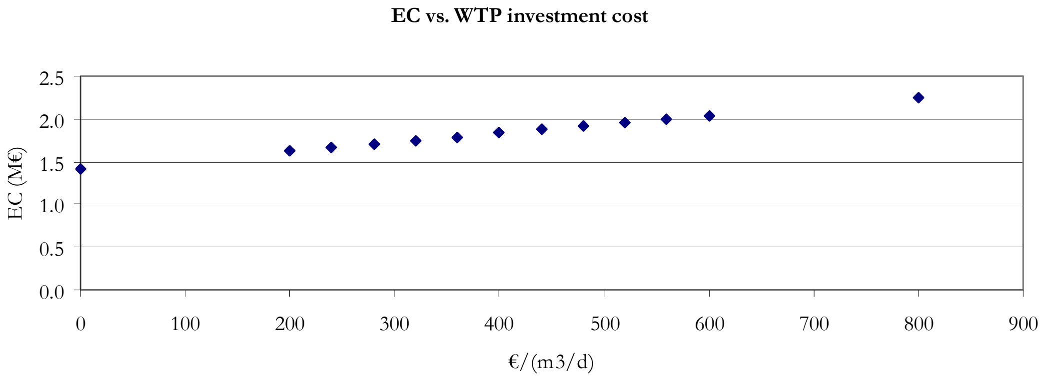


Figure 6.120. Sensitivity analysis: EC vs WTP investment cost

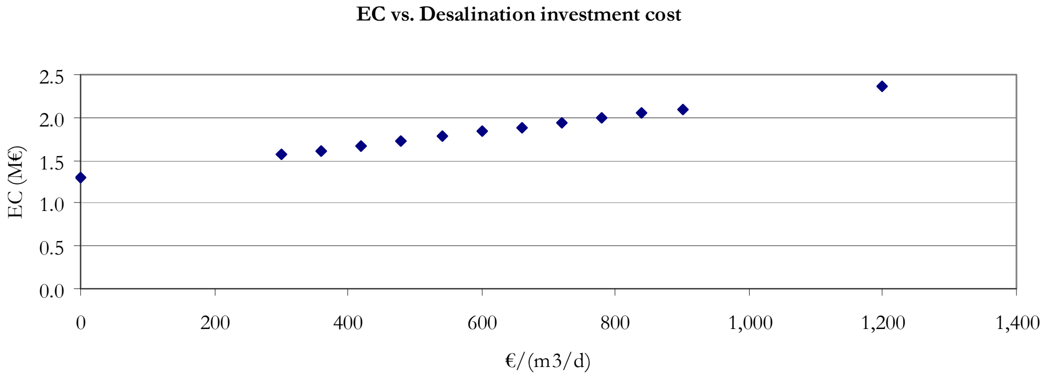


Figure 6.121. Sensitivity analysis: EC vs desalination plant investment cost

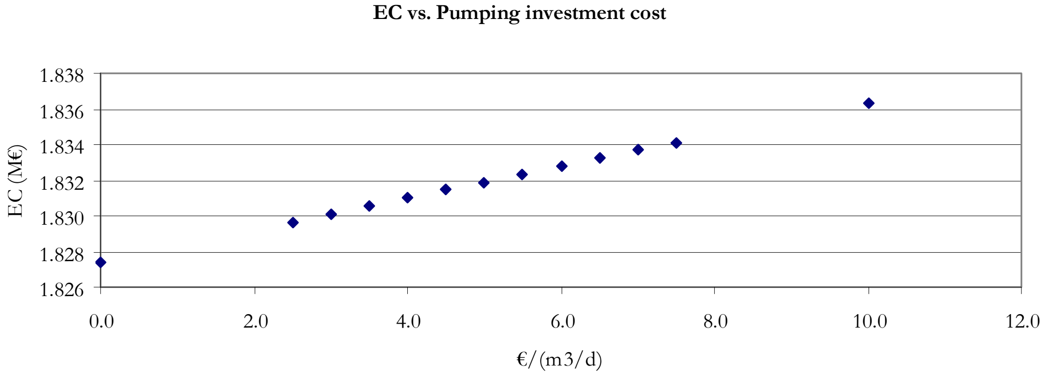


Figure 6.122. Sensitivity analysis: EC vs pumpling investment cost

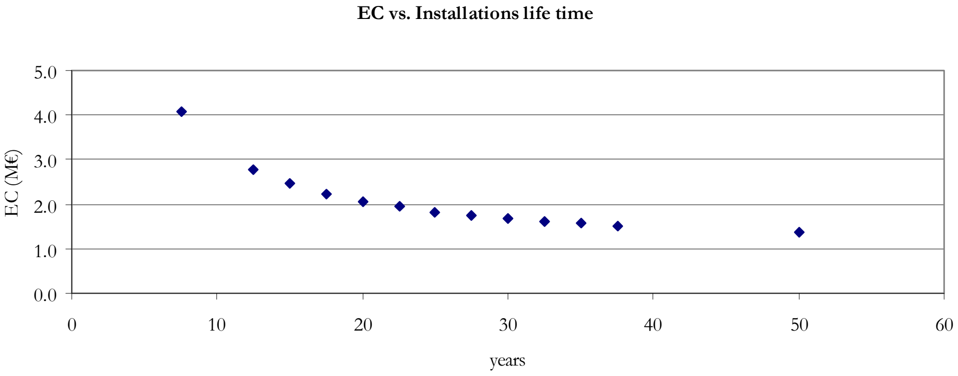


Figure 6.123. Sensitivity analysis: EC vs installations life time

6.5.4. Results comparison with previous studies

The Foix is a particular watershed because its special features: water scarcity, high aquifers exploitation and water coming from external sources. In consequence, the obtained results make sense. They are coherent and the cost allocation, attending to the quantity and quality gaps, seems to be fair enough.

Unfortunately, none comparable study about the Foix watershed has been found and, therefore, no contrasting results were possible. In spite of this, the possibility of comparison does exist with the previous case study. Total EC in the Muga basin was about 9.6 million euros and it resulted 1.7 million euros for the Foix Basin. Attending to their main features (rainfall, characteristics as surface and population, economic activities and their corresponding water uses…), it can be concluded that the order of magnitude is correct. Average annual rainfall, average annual contribution and area have been weighted between both basins and results indicate that the obtained values for the Foix Watershed are accurate enough.

Looking at the EC^* values (Table 6.51), it can be deduced that the Foix watershed has much more deficit to reach the WFD objectives than the previously studied Muga watershed. In particular, the quantity potential component is higher although the basin area is lower. On the quality side, IM restoration measures, as well as OM, are required, while in the Muga basin only smaller water salinity needs to be eliminated. To sum up, the Foix area presents a high water stress because of the intensive appropriation of the water resources and the effect of those uses.

	S	**Av contrib**	**Rainfall**	**$EC^*_{t,pot}$**	**$EC^*_{t,IM}$**	**$EC^*_{t,OM}$**	**$EC^*_{l,pot}$**	**$EC^*_{l,IM}$**	**$EC^*_{l,OM}$**
Muga	758	147.76	612	5,494	72	0	0	248	0
Foix	301	9.47	586	**9,167**	0	0	0	**1,129**	**664**

Table 6.54. Comparison of the surface, average annual contribution, rainfall and EC^* components between the Muga and the Foix watersheds. Units: S (km^2), average contribution (hm^3/yr), rainfall (mm) and EC^* (kWh/yr)

As summary of results for the Foix river, the quantity and quality contributions are synthesized in Table 6.55.

	Total	**Energy cost**	**Installation cost**
Quantity	69.51%	83.6%	56.5%
Quality	30.49%	16.4%	43.5%

Table 6.55. Summary of results: quantity-quality distribution attending to different costs.

Moreover, the differences in the cost allocation depending on the exergy results taken for the analysis are shown in Table 6.56: if the conventional PPP is applied, the domestic sector is responsible for about 95% of the damage on the river. However, when the quantity aspects are introduced in the analysis and the DPP is considered, that sector contribution is between 53% and 56%, depending on the criteria (EC or IRC).

	PPP	DPP (EC)	DPP (IRC)
domestic	94.8%	55.9%	53%
industry	2.8%	2.4%	2%
agric	2.4%	41.7%	45%

Table 6.56. Summary and comparison of results for the cost allocation in the Foix watershed

In addition to these considerations, there exists a comparison alternative for the results in the Foix watershed. An alternative study of the water cost in that area has been carried out in Chapter 7, by applying the Emergy approach. Water costs definitions are different from one methodology to the other.

6.6. Summary of the chapter.

The PH methodology has been applied to two specific watersheds within the IBC, the Muga Basin and the Foix Basin. To carry out this task, it was needed to describe the geographical and hydro morphological features of those areas, in addition to exhaustively characterize the water uses taking place along the watersheds.

The EC of the Muga watershed is about 9.6 M€ and, according to this study, it should be paid by users with the following distribution: urban (60%), industry (3%) and agricultural uses (37%). In the Foix watershed, the resulted EC is 1.8 M€, allocated as follows: urban (56%), industry (2%) and agricultural uses (42%). The cost allocation has been done attending to the total degradation produced, i.e., the Polluter Pays Principle y extended to the Degrader Pays Principle, since both quantity and quality are introduced in the analysis.

In spite of that, it has been shown along the results analysis that the cost allocation can be varied depending on the exergy values considered. Then, considerable variations can be found when the IRC is taken, instead of the EC; or, for instance, it is not the same accounting only for the energy costs than including the water utilities investment cost in the cost allocation.

Although most of the used data have been collected from the CWA, they have needed an important previous treatment, since the input data required to apply PH are very specific. The lack of data meant that some literature sources were required in order to complete the methodology requirements.

Some of the found difficulties in the procedure are synthesized here:

- The presence of a dam is translated in an anomalous behaviour of the real flows, which does not respond their natural pattern anymore. In general, in the IBC, presents a high density of dams and weirs, diversions for mini-hydroelectric power stations and altered flow systems.

- The objective flow is not defined in the Directive, so it was to be studied and defined in this work. In this sense, the minimum flow regime defined by the CWA was crucial, as well as the natural flow regime.

- Since the exergy calculation needs an important amount of information to construct the river exergy profiles, the simulation software for surface waters was fundamental in the data obtaining procedure.

- The amount and quality of the data regarding the water uses in the area are very important and, as far as the experience is concerned, they are not complete (specially in the industrial sector) in the general CWA's studies. It is translated in a certain inaccuracy.

- When individual basins are studied, there is some kind of information missing. Once the PH methodology is defined, studying the whole IBC or, for example, the Ebro river (what mean the study of all its tributaries) could give a more complete vision.

Chapter 7

Alternative assessment of the water Environmental Cost through the Emergy approach

In this chapter, an aditional water costs calculation is developed. With the basic Emergy Theory background, an alternative interpretation of the WFD was elaborated by defining the different water costs.

Emergy is used as an environmental accounting tool able to compare the work of the environment with the work of the human economy on a common basis; i.e., it can be understood as a biophysical approach to estimate the contribution of nature to economic activity as opposed to other methods that rely on a populations' perceived value of nature's contribution. Odum identified the free environmental work as the donor of resources supporting human activities, connecting the interfaces between human societies and fossil sources to that between human societies and the environment.

Emergy measures the solar work of nature and that of humans in generating products and services: it is available to represent both the environmental values and the economic values with a common measure.

A systems diagram is presented, previously to the cost calculation, in order to identify the whole watershed behaviour. It is used as a way to clearly understand the system dynamics of the watershed (global water storages and flows) in this study. However, the WFD application from the emergy approach is based on the emergy value of the water cycle and on the value that is added by water in the economic system.

7.1. Introduction to Emergy Accounting

Most of the commonly used evaluation procedures are based on *utility*, that is, the attention is focussed on the final product of any energy transformation process. That is the subjacent perspective under, for example, the fossil fuels transformation or crops production. In the same line, any economic assessment is based on the willingness to pay for any perceived utility.

An opposite view of value in the Biosphere could be based on what is put into something rather than what is received. That is, the more energy, time, and materials that are invested in something, the greater its value (Brown and Ulgiati, 1999). This approach could be design as a *donor system of value*, while the mentioned heat-energy assessment and economic valuations are considered as *receiver systems of value*. This perception is, although with special particularities, shared by different exergy researchers: Valero, Szargut and others in their search of exergy costs of industrial processes, and Jorgensen and Svirezhev using exergy accounting of ecosystems.

Emergy Accounting uses the thermodynamic basis of all forms of energy and materials, but converts them into equivalents of one form of energy, usually sunlight. Emergy is defined as the *available energy of one kind (commonly solar radiant power) required directly and indirectly to make a product, to provide a service or to support a given flow* (Odum, 1988); it is the *memory of energy* that was degraded in a transformation process.

It is possible therefore, to define an oil emergy, a coal emergy, etc. according to the specific goal and scale of the process. The units of emergy are emjoules (emJ), to distinguish them from Joules (J). This distinction is a matter of principle, and it is a reminder of the different 'quality' of different forms of energy, which cannot be properly expressed solely by their energy. The most commonly reference is the solar energy, and the corresponding units are the solar emjoules (seJ).

The main idea is that different forms of energy have different abilities to do work, and it is necessary to account for these different abilities if energies have to be evaluated correctly. Those different types of energy are compared using the transformity, which is emergy per unit of available energy of one form (e.g., chemical potential of freshwater). For example, electricity has a solar transformity of about 160,000 seJ/J, while coal has a solar transformity of approximately 40,000 seJ/J (Odum, 1996). Emergy evaluations use solar transformities of input energies to determine their solar emergy.

Emergy evaluation has been evolving over the past three decades as an environmental accounting tool to measure contribution of nature's services to economic activities. The General System Theory (von Bertalanffy, 1968) is considered as the theoretical and conceptual basis for the emergy methodology. The first developments can be found in Odum's book 'Environment, Power and Society' (Odum, 1971), while its evolution is summarized in Hall (1995) and in Odum (1996), with the books *Maximum Power* and *Environmental Accounting*, respectively. From then on, the publication of emergy evaluations of environmental, energy and ecological-economic systems has been accelerated (Brown and Ulgiati, 2004).

An amount of new contributions have been published regarding specific points of Emergy accounting. As example, the contributions cited by Tilley and Brown (2006), and Beck et al. (2001) compared the emergy inputs required to develop and operate four types of urban food production systems, and identified the systems were unsustainable and dominated by the massive economic inputs (e.g., labor and plant materials). Brown and Vivas (2005) proposed a Landscape Development Intensity (LDI) index based on non-renewable emergy consumed on land. Brown and Ulgiati (2001) found that coastal eco-tourism projects in Papua New Guinea and Mexico had environmental loads, based on emergy flows, 150 and 24 times as intense as the local economy, respectively, which lead them to conclude the projects were unsustainable. In that same line, Campbell (1998) applied emergy evaluation to assess the human carrying capacity of the U.S. state of Maine, concluding that human populations must adjust their environmental load in the context of global-scale pattern of economic pulsing cycles. Higgins (2003) and Tilley and Swank (2003) explored the nuances of conducting emergy evaluations of ecological systems that supported unique human cultural and scientific endeavours with multiple public benefits.Considerations about properly modelling information flow in service industries to be able to conduct emergy evaluations were discussed by Tilley (2003).

The comparison of emergy evaluation with other energy and environmental accounting methodologies, such as ecological cumulative exergy accounting, embodied energy analysis and extended exergy accounting can be found in Hau and Bakshi (2004), Herendeen (2004) or Sciubba and Ulgiati (2005).

7.1.1. Hierarchy

The energy quality is the central concept addressed by emergy analysts. As already indicated, the emergy concept supports the idea that something has a value according to what was invested into making it along with a generative 'trial and error' process (Maximum Power Principle, Lotka 1922). The higher the required investment under maximum power-output selection, the higher the quality assigned to the item.

In consequence, to derive solar emergy of a resource or commodity, it is necessary to trace back through all the resources and energy that are used to produce it, and express each of them in the amount of solar energy that went into their production. According to Odum (1996), by selecting choices that maximize emergy production and use, policies and judgments can favour those environmental alternatives that maximize real wealth, the whole economy and the public benefit.

This idea is summarized in the *Maximum Empower Principle*, which states that self-organized systems develop the most useful work with inflowing emergy sources, by reinforcing productive processes and overcoming limitations through system organization, and will prevail in competition with others.

Fath et al. (2001) showed that ten extremal principles involving orientors (power, storage, empower, emergy, ascendency, dissipation, cycling, residence time, specific dissipation and empower/exergy ratio) can be unified by an ecological network notation. They also try to give a general principle encompassing all the aspects of the orientors: *Get as much as you can (maximize input and first-passage flow), hold on to it for as long as you can (maximize retention time) and, if you must let it go, then try to get it back (maximize cycling)*. They conclude that the these three aspects can be summarized in the specific dissipation minimization.

Afterwards, Bastianioni et al. (2006) showed how three of the above mentioned principles, maximum empower, maximum exergy and minimum empower to emergy ratio (or maximum exergy/empower ratio), can be practically consistent, using the time order in maximizations.

7.1.2. Basic definitions

Unit emergy values are calculated based on the emergy required to produce them. There are three main types of unit emergy values. Using the works by Odum (1996) and by Brown and Ulgiati (1999), a synthesis was done and it is reproduced here.

Transformity is one example of a unit emergy value and is defined as the emergy per unit of available energy. For example, if 4,000 solar emjoules are required to generate a joule of wood, then the solar transformity of that wood is 4000 solar emjoules per joule (abbreviated sej/J). Solar energy is the largest but most dispersed energy input to the Earth. The solar transformity of the sunlight absorbed by the Earth is 1 by definition.

Specific Emergy is the unit emergy value of matter defined as the emergy per mass, usually expressed as solar emergy per gram (sej/g). Solids may better be evaluated with data on emergy per unit mass due to its concentration. Because energy is required to concentrate materials, the unit emergy value of any substance increases with concentration. Elements and compounds not abundant in nature therefore have higher emergy/mass ratios when found concentrated form since more work was required to concentrate them (both spatially and chemically).

Emergy per unit money is a unit emergy value used to convert money payments in emergy units. Since money is paid to people for their services and not to the environment, the contribution to a process represented by monetary payments is the emergy that people purchase with the money. The amount of resources that money buys depends on the amount of emergy supporting the Economy and the amount of money circulating. An average emergy/money ratio in solar emjoules/$ can be calculated by dividing the total emergy use of a state or nation by its gross economic product. It varies by country and has been shown to decrease each year. This emergy/money ratio is useful for evaluating service inputs given in money units where an average wage rate is appropriate.

Em-power: emergy per time

Em-Money (Em$ or Em€, *Em-dollars* or *Em-euros)*: they represent the equivalent amount of money that circulates in an Economy due to the use of emergy (Odum, 1996).

Conversion of emergy flows to emdollars redistributes total money flow in proportion to system emergy flow (Campbell et al., 2004). Em-Money value is calculated by dividing an emergy flow by the mean emergy-to-money ratio of the Economy that encompasses the system investigated for a particular time period (i.e., typically a year). Quantitatively, Em$ (or Em€) indicate how much an ecosystem service or product contributes to the Economy. This allows environmental contributions, which are free to an Economy, to be compared to more traditional macroeconomic measures. Because Em$ include measures of both environmental work and economic activity, a direct comparison of emdollars to dollars indicates the additional value contributed by nature.

There are many other relevant aspects regarding Emergy background. For the sake of completeness, they have been collected in Annex E of this dissertation.

7.2. Emergy values of natural capital

The Biosphere is driven by the flux of renewable energies in sunlight, tidal momentum, and deep Earth heat. Human society draws energy directly from the Environment, from short term storages (from 10-1,000 years turnover times) like wood, soils, and ground water, and from long term storages of fossil fuels and minerals.

The storages of environmental resources (fresh water, soil organic matter, plant biomass, animal biomass) are considered natural capital; these storages are considered slowly-renewable. Non-renewable resources such as fossil fuel, metals and phosphorus are also consider as natural capital (see Annex E).

Flows of energy that cycle materials and information are the fuels that maintain the biosphere. Otherwise, they will be degraded away. It is through cycling that those systems remain adaptive and vital. Materials or information sequestered in unreachable or unusable storages are of no value and often soon lose their importance or relevance. Cycling allows for the continuous convergence and divergence of energy, materials and information Processes of convergence build order, adding structure, reassembling materials, upgrading energy and creating new information. Divergence processes disorder structure and disperse materials and information, allowing concentrated energy to interact in amplifier actions with lower quality energies that maximize power flows (Brown and Ulgiati, 1999)..

A detailed synthesis of the average emergy unit values for main global processes can be found in Annex E.

7.3. Emergy Algebra

The way in which networks are defined for different purposes affects emergy flow on pathways. Models may be aggregated differently, according to different concepts and scales. A typical basic configuration commonly observed contains at least one source, a producer, a consumer, a heat sink and the connecting pathways including feedback reinforcement.

The emergy algebra helps in the task for translating input values through the complete system of analysis. In general, in systems networks there are several kinds of branches and intersections. Accounting of emergy flows depends on the type. Much of the confusion in network accounting comes when the kinds of branches and connections are not identified for the appropriate evaluation procedure.

Some basic ideas indicate that in a *split branching*, a pathway divides into two branches of the same kind, each with the same transformity. However, in a *coproduct branching*, the flow in each branch is a different kind a has a different transformity.

The basic rules of Emergy Algebra can be synthesized as follows (Brown and Herendeen, 1996):

> 1st rule: "All Source Emergy to a process is assigned to the Process's output"
> 2nd rule: "By-products from a process have the total Emergy assigned to each pathway"
> 3rd rule: "When a pathway splits, the Emergy is assigned to each "leg" of the split based on their percent of the total Exergy flow on the pathway"
> 4th rule: "Emergy cannot be counted twice within a system. In particular:
> a) by-products, when reunited cannot be summed;
> b) Emergy in feedbacks should not be double counted".

However, for the sake of completeness, it is worth adding a fifth rule concerning a more sophisticated process termed as Interaction: "Output Emergy of an interaction Process is proportional to the product of the Emergy inputs" (Odum, 1994).

A rapid glance to the above-mentioned rules allows to immediately point out that:

- The first rule represents a sort of "closure" rule in the case of one sole output;
- The second rule is extremely important because it shows how co-generative Processes represent the basic processes mostly responsible for the increase in Emergy in self-organizing Systems;
- The third rule points out the basic distinction between a co-production process and a simple split process (a mere subdivision of a flow into two equivalent sub-flows);
- Rule 4a) prevents from erroneous accounting which would lead to an "artificial" amplification of Emergy, not be related to a generative process (such as, for instance, a co-production), but to a simple "double counting" of an identical contribution, already accounted for in its primary generative phase;
- Rule 4b) can be simply seen as a particular case explicitly pointed out for the sake of clarity.

In such a context, the consideration of a fifth rule pertaining to interaction not only completes the list of basic processes capable of generating an exceeding Emergy but, at the same time, also enables us to consider the feedback process as a particular form of self-interaction. In such that perspective the basic generative processes are: co-production, interaction and feed-back.

It is also known that such rules are assumed as being valid under steady state conditions and are also used, without any modification (but also without any basic justification), under stationary or slow transient conditions.

7.3.1. Differential bases of emergy algebra

One fundamental problem is thus represented by the extension of the validity of the emergy algebra rules to whatever variable conditions. In this case it is of primary importance to recognize whether they are well-founded in differential terms (which is equivalent to research for their basic dynamic foundations). This aspect shows all its relevance if we take into account that the rules of Emergy Algebra represent an integrating part of the definition of Emergy. In fact Emergy is rigorously defined on the basis of two distinct elements: a correct dynamic Balance Equation (i.e. accounting rules) and an additional assumption concerning its reference level (i.e., solar Emergy with an associated conventional value of transformity, for instance 1 seJ/J) (Giannantoni, 2000).

The reference author regarding the differential bases of emergy algebra is Corrado Giannantoni. He owns an extensive work regarding the convergence of Emergy with the basic Thermodynamics. The fundamental background for the understanding of Emergy from this perspective can be found in his book *The Maximum Em-Power Principle as the basis for Thermodynamics of quality* (Giannantoni, 2002). It starts synthesizing the Thermodynamic cultural context in the last two centuries and formulates the Maximum Em-Power Principle as a possible 4th Principle of Thermodynamics. Giannantoni points out that the prevailing research perspective in Thermodynamics field has been usually dominated by quantity instead of quality, which passes unobserved, although Quality had appeared before Quantity (Carnot's discovery).

He follows summarizing that it gradually became more evident that two distinct forms of Energy, although characterized by the same amount of Exergy, were able to induce different effects, especially in Living Systems, because they are able to vehicle another intrinsic form of Quality, which is associated to their particular processes of genesis. Such a new kind of Quality was termed Transformity, consisting basically in the fact that it is the result of something else which has been radically transformed. This fundamental concept of Transformity allowed the introduction of the Emergy concept according to Giannantoni's ideas.

Tr_i is thus that quality factor which take into account the emerging quality associated to other forms of energy (not necessarily of mechanical nature), which is transported by the associated exergy, Ex_i. It can be written as

Eq. 7.1.
$$Tr_i = \frac{Em_i}{Ex_i}$$

It refers to a new kind of quality, completely different from the one associated to the Second Thermodynamics Law. In fact, Eq. 7.1 does not represent an amplification of mechanical effects, but it accounts for other effects which are not, strictly speaking, of mechanical nature (A, B, C…), symbolically represented by the pedex i.

The progressive development of Thermodynamics can be thus synthesized in the following three factors formula, which can be easily derived from Eq. 7.1 and the Carnot's factor Θ_i (Ex_i/En_i):

Eq. 7.2.
$$Em_i = Tr_i \cdot En_i \cdot \Theta_i$$

Various possible approaches to the analysis of Thermodynamic Systems can be deduced from Eq. 7.2:

- If Tr_i is neglected, the exergy analysis is left
- If Tr_i and Θ_i are neglected, the traditional energy analysis is left

- If Θ_i is neglected, the emergy analysis of those special systems termed as *conservative* is being done.

Much more detail about the mathematical definition of Emergy and its framework on the traditional thermodynamic context can be found in Gianantoni's works (Giannantoni, 2006). Important advances have been done and specific examples for the different emergy algebra rules are being elaborated. The meeting of this complex Theory with a real example is currently being developed with the *International Society for the Advancement of Emergy Research* (ISAER).

At this point, it is worth to remember the fuel-product propositions of the exergy accounting described in Chapter 4 (see section 4.3.2) and make a quick comparison. First of all, it can be clearly stated that the exergy cost concept is related to the emergy concept, while the unit exergy cost information is provided by the transformity in the emergy approach. Then, it can be concluded that:

- the first emergy algebra rule is equivalent to the Cost proposition in Thermoeconomis
- the following emergy algebra rules are related to the F, P and R propositions in Thermoeconomics. They present different nuances because of the nature of the involved concepts.

Table 7.1 summarizes the mentioned characteristics.

Emergy approach	*Exergy approach*
- All Source Emergy to a process is assigned to the Process's output	- *Cost balance*: The average cost of inputs is equal to the average cost of outputs
- By-products from a process have the total Emergy assigned to each pathway - When a pathway splits, the Emergy is assigned to each "leg" of the split based on their percent of the total Exergy flow on the pathway.	- *F proposition*: The output flow of a subsystem, identified as a non-spent resource, maintains the same cost per unit of exergy as at the input. - *P proposition*: The cost of products, obtained simultaneously in a single subsystem, are allocated in proportion to their exergy. - *R proposition*: The cost of wastes is as much negative as the additional resources needed to dispose of them.

Table 7.1. Rules comparison

7.4. Emergy and water

Under the Geobiosphere organization, the hydrologic cycle has undoubtedly a special role as one of the main ways that the solar energy is coupled to earth energies. By applying the emergy accounting, the average emergy for the rain, for the oceans or for a watershed can be calculated. When rain falls on land, it splits into two flows: one component is transpired by the plants and a remainder flow runs off downhill or into groundwater storages. To evaluate their emergy, an appropriate transformity is multiplied by the available energy used up in each of the two flow divisions (split).

In evaluating ecosystems, the water flows that contribute to transpiration and photosysthesis are a principal emergy source. In fact, the studied transformities shown that like other environmental products, water contributes more emergy than is usually paid for it. Figure 7.1 summarizes the principal storages and flows of the global hydrologic cycle.

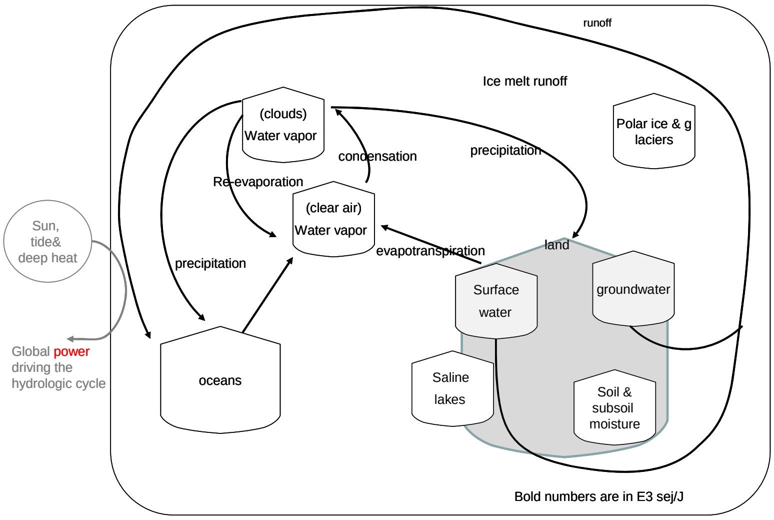


Figure 7.1. Storages and flows of the hydrologic cycle (Source: adapted from Buenfill, 2001)

Emergy would, for example, estimate the natural value of the water of the Mediterranean aquifers based on the work of the environment to create and maintain the storage, whereas an approach based on a human's perspective might value it according to the market price of the water withdrawn. After estimating its natural value, emergy accounting would estimate the water's value to the public by considering the human-controlled energies used for its extraction and the potential economic amplification that water could produce in the economy (Buenfil, 2001a). Inexpensive, clean, plentiful water from the aquifers (if they have not been polluted) provides a significant amount of the free-energy base to the Economy and its use has a multiplier effect on economic activity.

Emergy water issues, as it already happened with the PH approach, can be faced from a static or a dynamic perspective: world water storages can be analyzed from their basic characterization parameters such as storage and residence time; the water flows associated to the water cycle can be also characterized and average transformities values can be obtained. On the other hand, when the boundaries of the system are reduced, it is possible to perform a quite specific dynamic watershed analysis.

Historically, nearly all emergy evaluations assumed an steady state system and constant solar transformities (solar emergy per available energy), which transform available energy (exergy) to solar emergy. They integrate multiple system forcing factors such as rain, soil genesis and fuel use, into one metric (i.e., solar emergy). Nevertheless, Odum lead the way in developing the task of accounting for how system stocks accumulate solar emergy across the time, that is, temporally dynamic emergy accounting as a modelling framework for defining mathematical equations and simulation models that incorporate temporal dynamics for emergy and transformities (Odum and Peterson, 1996; Odum, 1996; Odum and Odum, 2000).

7.5. Steady State Emergy Accounting

As mentioned, the traditional emergy assessment of global water resources has been carried out assuming an steady state. In this section, global water storages and flows are characterized from an Emergy perspective. Emergy evaluations of both the main storages and flows of water in the Biosphere are summarized in Table 7.2 and Table 7.3, respectively.

The water in the cycle from sea to land is carrying two kinds of potential energy: water carries chemical potential energy of its purity relative to the seawater from which sun and wind distilled it into vapour. Depending on the altitude, rain carries the geopotential energy of its elevation above the sea. Thus, there are two average solar transformities for rain, one for chemical potential and a second one for geopotential. In the self organization of watersheds the geopotential energy carves the landscape, distributes sediments, and spreads the water out through vegetation in floodplains and coastal wetlands so that the chemical potential is better used by vegetation for organic productivity.

- For the transpiration flow, the energy used is the Gibbs free energy for the concentration difference between the rainwater and the high-salinity water maintained within the leaves by sun and wind (for typical vegetation, it is about 5J/g of water transpired).

- For the runoff water, the energy being used up is the geopotential energy converted into frictional work by the flowing water. This physical energy use is calculated as the product of the water-level change, the water density and the gravity. Water that leaves the boundary defined for evaluation carries its emergy to the next system in some kinds of watersheds with converging streams, and the transformities increase as the water collects and converges.

7.5.1. Distribution and emergy values of global water storages

In this section, global water storages are studied. The followed schema for the different types of water forming the hydrological cycle is the same as the one used in Chapter 2 (general description) and Chapter 4 (exergy assessment of world water resources).

Water storages in Table 7.2 are arranged by increasing transformity, which is the result of increasing turnover times. Atmospheric water vapour has the lowest transformity, while polar ice and glaciers, because of their long turnover times, have the highest transformity. Since seawater is considered the *ground state,* it has no chemical potential energy and therefore its transformity is zero.

The energy for fresh water is calculated as the chemical potential relative to seawater. An average transformity for all fresh water in the Biosphere is given in the last row of Table 7.2, as the weighted average of all transformities. The weighted average is relatively high as a result of the large portion of Biosphere water that is content in polar ice and glaciers.

Emergy per volume values were used to calculate emergy-per-mass (seJ/g), transformities (sej/J), and Em-dollar (Em$/m^3) values. Transformities for those water storages varied between $5.95 \cdot 10^3$ sej/J for water vapour in clouds and $1.7 \cdot 10^6$ sej/J for polar ice and glaciers.

water stock	**average replacement time (yr)**	**volume (*10^3 km^3)**	**emergy per mass (seJ/g)**	**emergy per volume (seJ/m^3)**	**Tr (seJ/J)**	**Em-euro per volume (Em€/m^3)**	**Total Em€ of water storage**
World Ocean	2889	1,338,000					
Ground water (gravity and capillary)	1400	23,400	9.47E+05	9.47E+11	1.92E+05	0.37	8.73E+15
Predominantly fresh ground water	994	10,530	1.49E+06	1.49E+12	3.02E+05	0.59	6.20E+15
Soil moisture	0.885	17	8.49E+05	8.49E+11	1.72E+05	0.33	5.52E+12
Glaciers and permanent snow cover:	12850	24,064	8.45E+06	8.45E+12	1.71E+06	3.33	8.01E+16
Antarctica	12850	21,600	9.42E+06	9.42E+12	1.91E+06	3.71	8.01E+16
Greenland	12850	2,340	8.69E+07	8.69E+13	1.76E+07	34.24	8.01E+16
Arctic Islands	12850	84	2.44E+09	2.44E+15	4.93E+08	959.55	8.01E+16
Mountainous regions	1600	41	6.24E+08	6.24E+14	1.26E+08	245.72	9.98E+15
Ground ice of permafrost zone	10000	300	5.28E+08	5.28E+14	1.07E+08	207.84	6.24E+16
Water in lakes:	10	176	8.97E+05	8.97E+11	1.82E+05	0.35	6.24E+13
Fresh	10	91	1.74E+06	1.74E+12	3.52E+05	0.69	6.24E+13
Salt	10	85					
Swamp water	3	11.5	4.13E+06	4.13E+12	8.36E+05	1.63	1.87E+13
River stream water	0.044	2.1	3.27E+05	3.27E+11	6.63E+04	0.13	2.73E+11
Biological water	0.026	1.1	3.73E+05	3.73E+11	7.54E+04	0.15	1.64E+11
Water in air	0.024	12.9	2.94E+04	2.94E+10	5.95E+03	0.01	1.49E+11
Total volume of the hydrosphere	3023	1,396,515	3.43E+04	3.43E+10	6.94E+03	0.01	1.88E+16
Fresh water							**1.49E+17**

NOTES

total emergy flow	1.58E+25	seJ/yr
km3 to m3	1.00E+09	m3/km3
water density	1.00E+06	g/m3
Gibbs free energy	4.94	J/g

calculated using the chemical potential energy of fresh water (10 ppm) relative to seawater (35000 ppm)

world emergy per dollar ratio 2.54E+12 seJ/€ 2.00E+12 seJ/$

It was assumed that all global water storages are co-products of the global empower base (15,83E24 seJ/yr)

(a) Ocean and saline lakes: emergy and transformity are 0,0 since salt water is considered the ground state

(b) Emergy per mass

sej/g=15,83E24 seJ/yr)(turn over time)/((km3)(1E9m3/km3)(1E6g/m3))

(c) Emergy per volume (sej/m3)
sej/m3=(sej/g)(1E6 g/m3)

(d) Water carries different available energies (e.g. Gibbs free energy of its chemical potential, geopotential, thermal gradient potential) from which transformities can be calculated (Odum, 1994). Sej/J=(sej/g)/(4,94J/g). Since transformities were calculated using the chemical potential energy of freshwater relative to ocean water, the transformities of saline waters (e.g. ocean water) do not have chemical potential energy and, thus, their chemical potential energy-transformity is zero.

(e) Em$/m3=(sej/m3) divided by 2,0E12 sej/$, which is the world emergy per dollar ratio; sej/$ from Odum, 1996

(f) Em$=(15,83E24 sej/yr)(replacement time in years)/(2,54E12 sej/€)

Table 7.2. Emergy Evaluation of Global Water Storages (adapted from Buenfill, 2001a)

The emergy values of global water storages was calculated by assuming that those storages are co-products of the global empower base ($15.83 \cdot 10^{24}$ seJ/yr). The global empower represents the annual emergy flowing to Earth and was calculated by Odum (1996) by summing the annual emergy of the sun ($3.93 \cdot 10^{24}$ seJ/yr), tide ($3.85 \cdot 10^{24}$ seJ/yr), and deep heat ($8.06 \cdot 10^{24}$ seJ/yr) –see Annex E for further details-.

Emergy per volume (seJ/m^3) values of global water storages were calculated by dividing the empower base by the annual average volumetric flow of each water storage. Volumetric flow rates were calculated by dividing the volume of each water storage by its replacement time.

In Odum (2000), a study about the emergy of some products of the global energy system can be found. The calculation is doing in the same way, assuming the different flows (global latent heat, global wind circulation, global precipitation on land, etc.) are co-products, that is, taking as primary emergy the total baseline $15.83 \cdot 10^{24}$ seJ/yr.

7.5.2. Distribution and emergy values of global water flows

The main global water flows were also analyzed to obtain their emergy values. Similarly to the previous calculations, those flows were assumed to be co-products of the global empower base. Emergy per volume of global water flows were calculated also by dividing the empower base by the annual volumetric flow of each global water flow.

Transformities for evaporation and for several types of global precipitation were calculated by dividing the global empower base by the volumetric flow rate of each type of flow by means of evaporation or precipitation.

In Table 7.3, the flows of water in the Biosphere are listed in ascending order of transformity. Several rainfall types were calculated. These data represent global averages. Rainfall in any particular location could have higher or lower transformities depending on local atmospheric conditions.

Tropical and temperate precipitation on land were estimated by using the corresponding land surface areas. For example, the volumetric flow of tropical rainfall was estimated by multiplying the average rainfall between the tropics by the total surface area between the same latitudes (23.5N and 23.5S). The volumetric flow rate of temperate rain was assumed to be the difference between the global precipitation and the estimated tropical precipitation (Buenfil, 2001a).

The transformity of global surface runoff to oceans ($7.52 \cdot 10^4$ seJ/J) is about 2.6 times the transformity of average rainfall on land ($2.91 \cdot 10^4$ seJ/J), while global groundwater recharge ($1.46\cdot10^6$ seJ/J) is more than 50 times that of rainfall on land. As the flow rates decrease, as expected, transformities increase.

The emergy value of the world water flows leads to a value of $6.24\cdot10^{12}$ €/yr (about 43% of the emdollars of global renewable energies, $1.44\cdot10^{13}$ Em$ –see Table E.1-). It is understood as the em-money that Nature (in particular, the hydrological cycle) gives us for free.

water flow	**anual flow rate (km3/yr)**	**emergy per mass (sej/g)**	**emergy per volume (sej/m3)**	**Tr (chem. Potential) sej/J**	**Em-euro per volume (Em€/m3)**	**Total Em€ of water flows**
Evaporation	**568,000**	2.79E+04	2.79E+10	5.64E+03	0.01	6.24E+12
from oceans	502,800	3.15E+04	3.15E+10	6.37E+03	0.01	6.24E+12
*from land areas**	65,200	2.43E+05	2.43E+11	4.91E+04	0.10	6.24E+12
Precipitation	**568,000**	2.79E+04	2.79E+10	5.64E+03	0.01	6.24E+12
temperate rain	301,000	5.26E+04	5.26E+10	1.06E+04	0.02	6.24E+12
tropical rain	267,000	5.93E+04	5.93E+10	1.20E+04	0.02	6.24E+12
to ocean	458,000	3.46E+04	3.46E+10	7.00E+03	0.01	6.24E+12
to land	110,000	1.44E+05	1.44E+11	2.91E+04	0.06	6.24E+12
Surface runoff to oceans	42,600	3.72E+05	3.72E+11	7.52E+04	0.15	6.24E+12
Global grounwater recharge	2,200	7.20E+06	7.20E+12	1.46E+06	2.83	6.24E+12
Ice melt	2,000	7.92E+06	7.92E+12	1.60E+06	3.12	6.24E+12

Table 7.3.Distribution and Emergy values of mean Earth water flows (adapted from Buenfill, 2001)

7.6. Dynamic Emergy Accounting.

Historically, nearly all emergy evaluations assumed system steady state and constant solar transformities (solar emergy per available energy), which transform available energy (exergy) to solar emergy. However, H.T. Odum lead the way in developing temporally dynamic emergy accounting as a modeling framework for defining mathematical equations and simulation models that incorporate temporal dynamics for emergy and transformities (Odum and Peterson, 1996; Odum, 1996; Odum and Odum, 2000).

The emergy of water can be also faced from a dynamic perspective. As mentioned, it is the current tendency to study river basins and watersheds from this dynamic-emergy perspective. Depending on the regional hydrogeology and geomorphology, flows in a watershed can imply important differences. The account of the daily changes in the solar emergy of these flows and stock changes can be accomplished by employing temporally dynamic emergy accounting.

Traditionally, Odum's energy systems language has been used to develop a spatially aggregated, eco-hydrologic watershed simulation model. The models combine hydrological and ecological processes to track surface discharge, groundwater exchange, evaporation, transpiration and changes in surface water storage to estimate the solar emergy and solar transformities of the hydrologic into a watershed.

In addition to the works cited in section 7.4, an interesting study regarding watersheds simulation was published by Tilley and Brown in 2006. These authors showed some tools to measure the ecological and hydrological benefits that urban storm water wetland provide. They developed an eco-hydrological model of a subtropical urbanizing watershed in south Florida to provide dynamic valuation of a wetland storm water management system, and demonstrated how solar emergy may be continuously tracked through an ecosystem in order to estimate the value of nature's life-support services (temporal variability of solar transformities of water in various ecological processes and storages). In consequence, society can more fully assess their multiple benefits and economic costs.

The energy systems language was also used by Cohen and Brown (2007) in their dynamic system model, developed to compare stormwater management using a hierarchical network of treatment wetlands. In the same direction worked Tilley and Brown (1998), when they assessed the environmental benefits of subtropical wetland storm water management systems by using the dynamic-emergy accounting.

Furthermore, emergy was proposed as a tool for studying the River Basin Management Plans in Taiwan (Chou and Lee, 2007). The Lan-Yang watershed was analyzed and few indices were calculated to explain and verify their management conditions

7.6.1. Some basic ideas for watersheds simulation

Rainfall accumulates on the surface and seeps into the soil. Groundwater in the aquifer is replenished by surface water that leaches into the water-bearing limestone bedrock. Beneath the surface, groundwater moves from areas of recharge and replenishment, such as sinkholes, to areas of discharge, such as springs. Water that is not absorbed by plants percolates deep underground into the porous limestone bedrock until it reaches the water-table, the level where the limestone is saturated with water.

The quantity of water stored in the bedrock depends on the porosity of the limestone. When the aquifer is full and unable to accept additional water, surface water drains into nearby lakes, rivers, and oceans where it evaporates back into the atmosphere and eventually precipitates to the surface again. However, this is not the case in Spain, since most of the aquifers are over-exploited.

Groundwater travels along a hydraulic gradient, the downward horizontal slope of the subsurface bedding plane. As water accumulates underground, water pressure, or the hydrostatic head, increases. Groundwater movement is directed by a combination of the hydraulic gradient, the hydrostatic head, and confining beds of impermeable materials such as clay.

Moving groundwater chemically erodes joints and fractures in the limestone bedding plane creating subsurface cavities, caves, drainage basins, sinkholes and other geologic features that characterize the area's topography.

Water is taken from aquifers by means of wells, which penetrate the water-table. The amount of water released from a well depends on the permeability of the bedrock. Wells drilled into confined aquifers must pierce the confining bed. When the well penetrates the aquifer, the hydrostatic pressure pushes the water above the confining bed where it can be pumped to the surface.

The demand for well-pumping increases as population continues to rise. Over-pumping can lower the water-table, and as a result, accelerate sinkhole formation and decrease spring flow.

Beneath the surface, organic matter and impurities are removed from groundwater as it filters through the porous limestone bedrock. Water that has not spent enough time filtering through the aquifer can emerge turbid or smelly when it is extracted. Clean groundwater can become polluted by certain contaminants coming from the surface water that replenishes the aquifer, or by subsurface septic tanks and fuel receptacles.

7.7. WFD from an emergy perspective

The wide approach to ecosystems studies provided by Emergy, led to consider the possibility of applying it to determine the water costs required by the WFD. This complementary contribution is presented here.

7.7.1. Water costs definitions from the emergy approach

When the emergy approach is used to determine the cost of water following the WFD guidelines, the three classes of costs are defined in emergy terms, evaluated and converted to monetary equivalents. The difference between emergy accounting and financial cost accounting is that the emergy approach does not rely on markets to impute prices, yet once the emergy values are calculated it is common practice to convert them to monetary units for ease of communication and to incorporate costs within the economic system to support full cost recovery. Conversion of emegy to currency is accomplished by dividing emergy values by a conversion factor computed from the economy within which the evaluation is being conducted. For the purposes of this paper, emergy was converted to Euros using a conversion factor derived from the economy of Spain (the country of focus in the case study that follows).

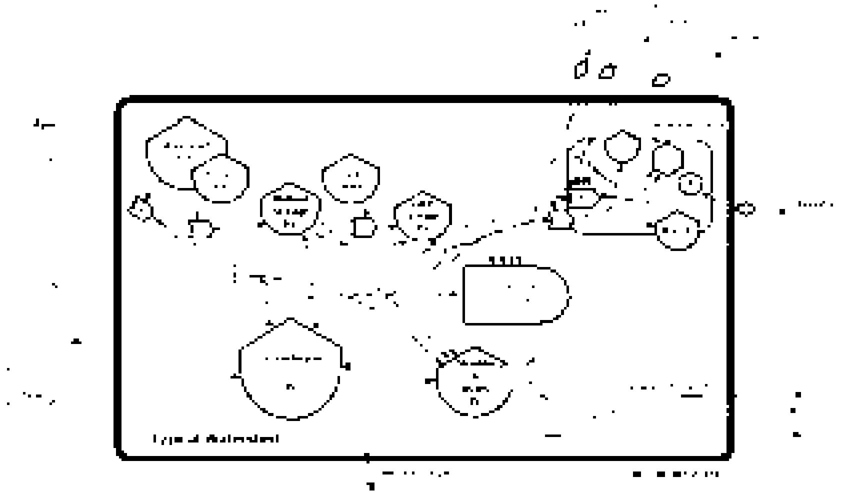


Figure 7.2. Systems diagram of a typical watershed showing the various water values. RV = Resource value, FV = Financial value, EC = Environmental Costs. (Source: Brown, 2009)

Emergy evaluation of the three classes of water costs requires a systems perspective. Shown in Figure 7.2 is a systems diagram of a typical watershed emphasizing the flows and storages of water. The diagram is annotated with Financial Value (FV: the monetary equivalent emergy costs of water and water infrastructure) Resource Value (RV: from which Resource Cost can be computed) Environmental Value (EV: from which the Environmental Costs can be computed) to indicate at what point in the system the emergy value of the water resources are calculated. Since there are numerous different water storages within a typical watershed, each one can be evaluated separately and each has different emergy values.

7.7.1.1. Financial Cost

The *Financial Value* is clearly understood as the costs associated with the provision of water that include costs of water and the water infrastructure. Table 7.4 lists several sources of water and the emergy and Euro costs of making the water available; the costs do not include delivering the water to the end user. These data were derived from water costs in the USA (Buenfil, 2001a). Our assumption is that European systems of water treatment are similar to those in the USA; obviously detailed analysis of treatment costs in Europe should be conducted to better refine these data.

Type of water	**Human Service (E12 sej/m³)**	**Fuels & Electricity (E12 sej/m³)**	**Chemicals & Supplies (E12 sej/m³)**	**Plant Assets (E12 sej/m³)**	**Total (E12 sej/m³)**	**ᵉᵐ€. Spain # (2008 em€/m³)**
Irrigation / Groundwater	0.41	0.25	0.00	0.16	0.82	0.17
Hard Surface Water	1.63	0.25	1.91	0.41	4.20	0.87
Soft SurfaceWater	2.59	0.30	4.90	0.41	8.20	1.71
Aquifer Water	1.91	0.54	2.86	0.41	5.71	1.19
Reverse Osmosis (brackish gdw)	5.72	1.01	0.54	0.54	7.81	1.63
Reverse Osmosis (saltwater)	5.44	3.26	0.27	0.54	9.52	1.98

1. After Buenfil, 2000

 # Emergy is converted to Euros using the emergy Euro ratio for Spain (2008) = 4.8 E12 sej/€

Table 7.4. Emergy costs of irrigation and potable water including production costs and assets and infrastructure to produce1.

7.7.1.2. Resource Cost

The *Resource Value* (RV) is computed from the emergy in the water itself, and is determined for each type of water: rain, water stored in wetlands, water stored in lakes, river water, and ground water separately by computing the resource value that is used by a consumer. Thus the Resources Cost (RC) is computed from the RV and depends on the quantity of water that is used and the water source.

Water has two important resource values. The first is the chemical potential energy in water and is expressed as its purity relative to seawater (at 35 ppt). The chemical potential energy in water within a watershed is computed from the Gibbs free energy of each type of water relative to salt water within evapotranspiring plants or relative to oceans receiving the rain (generally both are assumed to be 35 ppt). The Gibbs free energy of rainfall is equal to 4.94 J/g assuming rain with dissolved solids concentrations of 10 ppb (Odum, 1996) and is calculated as follows:

Eq. 7.3.
$$G = \frac{RT}{M_w} \ln(\frac{C_2}{C_1}) = 4.94 J/g$$

where G stands for the Gibbs free energy, R is the universal gas constant (8.314J/mole/degree), T the emperature (300 K), M_w molecular weight of water (18 g/mole), C_1 the concentration of water in sea water (965,000ppm), and C_2 the concentration of water in rain (999,990ppm).

Each type of water (lakes, wetland water, groundwater etc) has differing dissolved solids concentrations and thus will have slightly different chemical potential energy. The emergy of each type of water is computed by multiplying its energy by an appropriate transformity (calculated separately) as follows:

Eq. 7.4.
$$Em_{w, ChemPot} = En_w \cdot Tr_w$$

The emergy is equated to the resource value. Table 7.5 lists average chemical potential emergy and the resource value in Euros per cubic meter for the different types of water shown in Figure 7.2. The footnotes to the table explain the assumptions and provide the computations for energy and emergy.

Note	Item	Data	Units	Transformity (sej/unit)	Solar Emergy (E+12 sej/m^3)	Monetary value (2008 em€/m^3)
1	Rain	4.9E+06	J/m^3	31000	0.15	0.03
3	Wetland water	4.7E+06	J/m^3	43100	0.20	0.04
4	Lake water	4.9E+06	J/m^4	50400	0.25	0.05
2	River	4.8E+06	J/m^3	81000	0.39	0.08
5	Ground Water	4.4E+06	J/m^5	191400	0.85	0.18

based on 4.8 E12 sej/€ in Spain

Notes to Table 1

1 Rain

Volume = 1.0E+00 m^3
Density = 1.0E+06 g/m^3
Concentration Rain 10 ppb = 999,990 ppb water
Concentraion sea water 35ppt = 965000 ppb water
R = 8.33 J/mole/degree
T = 300^o K
Mw = 18 g/mole

Energy in rain = 1.0 m^3* 1.0E6 g/m^3*4.94J/g

= 4.94 E6 J/m^3
Transformity = 31000 (Odum, 2000)

2 Wetland Water

Volume of water taken as 89.6% moisture content of volume of peat plus avg. standing water

Peat water = 8.96E-01 m3
Avg. water depth= 2.00E-01 m
Gibbs Free Energy = 4.94 J/g
Volume = 1.0E+00 m^3
Density = 1.0E+06 g/m3
Concentration Water 2ppm 998,000 ppb water
Concentraion sea water 35ppt = 965000 ppb water
R = 8.33 J/mole/degree
T = 300^o K
Mw= 18 g/mole
Energy in water = 1.0 m^3* 1.0E6 g/m^3*4.67J/g
= 4.67E+06 J/m^3
Transformity: 43,100 (Baedi & Brown, 2004)

3 Lake Water

Volume = 1.0E+00 m^3
Density = 1.0E+06 g/m^3
Concentration Lake 500 ppb = 999,500 ppb water
Concentraion sea water 35ppt = 965,000 ppb water
R = 8.33 J/mole/degree
T = 300^o K
Mw = 18 g/mole
Energy in lake water= 1.0 m^3· 1.0E6 g/m^3*4.38J/g
= 4.87E+06 J/m^3
Transformity = 50400 (Brand-Williams, 2000)

4 River Chemical Potential

Volume = 1.0E+00 m^3
Density = 1.0E+06 g/m3
Concentration River 1ppm = 999,000 ppb water
Concentraion sea water 35ppt = 965000 ppb water
R = 8.33 J/mole/degree
T = 300^o K
Mw = 18 g/mole
Energy in river = 1.0 m^3* 1.0E6 g/m^3*4.81J/g
= 4.81E+06 J/m^3
Transformity = 81000 (Odum, 2000b)

5 Ground Water

Based on Floridan Aquifer in Florida, USA

Volume = 1.0E+00 m^3
Density = 1.0E+06 g/m3
Concentration gd. water 10 ppb = 999,900 ppb water
Concentraion sea water 35ppt = 965000 ppb water
R = 8.33 J/mole/degree
T = 300^o K

Mw = 18 g/mole

Energy in water = 1.0 m^3* 1.0E6 g/m^3*4.38J/g

= 4.87E+06 J/m^3

Transformity = 191400 Brown, 2009

Table 7.5. Global average chemical potential energy , transformities, emergy and Euro values of several terrestrial water storages

The second value of water is in its geopotential energy; the work that water running off the landscape can do as it falls from higher elevations to lower elevations. The energy of geopotential is calculated from the product of flow (Q), density of water (ρ), average altitude (h), and gravity (g) as follows:

Eq. 7.5. $$En_{geop} = Q(m^3)\cdot\rho(kg/m^3)\cdot h(m)\cdot g(m/s^2)$$

The emergy of geopotential energy of water is computed by multiplying the geopotetial energy by an average transformity for each elevation (after Odum, 2000) as follows:

Eq. 7.6. $$Em_{geop} = En_{geop}\cdot Tr_{geop}$$

Table 7.6 lists examples of the geopotential energy of water at different elevations and the emergy and Euro value per cubic meter. The footnotes to the table explain the assumptions and provide the computations for energy and emergy.

Elevation (meters)	**Energy *** (J/m3)	**Transformity**** (sej/J)	**Emergy** (E12 seJ/m3)	**Monetary value** (2008 em€/m3)
Surface	4.31E+06	34381	0.15	0.03
990	9.70E+06	37178	0.36	0.08
1950	1.91E+07	35354	0.68	0.14
3010	2.95E+07	50370	1.49	0.31
4200	4.12E+07	59484	2.45	0.51
5570	5.46E+07	130122	7.10	1.48
7180	7.04E+07	187376	13.18	2.75

** *after Odum, 2000*

\# *based on 4.8 E12 sej/€ in Spain*

Table 7.6. Global average geopotential energy, transformities, emergy and Euro value of water at different elevations

With two separate values of water, chemical potential and geopotential, it is possible to compute the resource values that are used when water is consumed or otherwise depleted in quantity or quality. For instance, if a user takes water at a given elevation in a watershed and only half is returned at the same elevation then the user should pay the value of the lost geopotential work (ie, the work the water would have done if it had not been removed from the stream or river) as well as the chemical potential va;ue that is no longer avalaible. In like manner, if a user removes some water and returns all of it, but it has lost some of its chemical potential, because it now carries a higher dissolved solids load, then the user should pay the difference in the resource quality calculated as the difference in the chemical potential.; yet since all the water is returned, it still has its geopotential.

7.7.1.3. Environmental Cost

Evaluating the *Environmental Costs* (ECs) as defined by the Directive presents a relatively complex undertaking. First ECs are defined as damages that water-uses impose on the environment, ecosystems and those who use the environment. Second they may also include potential risks, for instance, a water use that may increase the likelihood of a flood. Under this second category it is suggested that a risk premium reflecting insurance costs be included. In our analysis of environmental costs we have chosen to ignore potential risks, recognizing the inherent difficulties of providing a generalized risk factor for water uses. Instead we focus on the actual potential damages.

Two EC alternatives for the assessment of the water EC are presented here. They both share the background conception of water being a very key underlying factor in the economic development of any region.

EC assessment through the land uses

The condition of landscapes and the ecological communities within them are strongly related to levels of human activity. Since the EC regards the alteration of the physical and biological aspects of water bodies due to human activities, land uses can be a good indicator for its calculation. Human-dominated land use and, in particular, the intensity of the uses, can affect adjacent natural resources and ecological communities through direct, secondary, and cumulative impacts.

From the emergy perspective, such impact is content in the land uses index, defined by Brown and Vivas (2005). They developed a GIS-based method to quantify land use development intensity affecting aquatic organisms within a given basin, by means of the Landscape Development Intensity index, or LDI, a measure of annual non-renewable energy use within land uses directly adjacent to affected ecosystems. It can be calculated from aerial photos or land use maps, basic GIS software, and landscape development intensity coefficients obtained through published literature.

Eq. 7.7. $$LDI_{tot} = \sum_i LU_i \cdot LDI_i$$

Where LDI_{tot} is the LDI ranking for the landscape/watershed unit; LU_i is the percent of the total area of influence in land use *i* (%), and LDI_i is the landscape development intensity coefficient for land use *i* (Brown and Vivas, 2005)

In order to define the LDI for each land use i, a complete study about the renewable and non-renewable inputs is imperative, i.e., the total areal empower intensity ($sej \cdot ha \cdot yr^{-1}$) has to be obtained. The use of non-renewable energy to differentiate anthropogenic inputs from natural renewable inputs joins disparate land uses into a disturbance gradient using a single quantitative measurement of human disturbance intensity (Lane and Brown, 2006).

In consequence, the LDI studies associate always their corresponding non-renewable Areal Empower Intensity ($\mathrm{aEmI_{NR}}$), in sej·ha^{-1}.yr^{-1}, for each of the land uses. Those are required parameters to be included in the EC definition.

Therefore, the EC of water could be defined as the ratio between the $\mathrm{aEmI_{NR}}$ (which accounts for the non renewable resources flowing into the watershed every year), and the annual water use, as expressed in Eq. 7.8.

Eq. 7.8.
$$EC = \frac{\sum_{\mathrm{i}} (\mathrm{aEmI_{NR,i}} \cdot LU_i)}{Water_{total use}}$$

The main difficulty by applying the LDI and, in particular the $\mathrm{aEmI_{NR}}$ to asses the EC of water, is the constraint derived from the lack of coefficients for Europe and, consequently, for Spain. The currently published literature on them is focused in USA (Brown and Vivas, 2005).

EC assessment through the GEmP

Using Figure 7.2 as a guide, the assumption of EC is that water is a necessary input to the productive processes of any region. Shown in the diagram, total productivity (regional Gross Emergy Product, GEmP) measured in emergy, is the sum of inputs from water, environmental systems, and imported energy, goods and services. If a linear relationship between total production and water availability and use is assumed, then the marginal emergy value of water is the GEmP divided by quantity of water. While it may be that a linear relationship is not accurate, especially at the extremes, we assume linearity in this analysis. The equation to determine the marginal emergy value of water is given in Eq. 7.9:

Eq. 7.9.
$$MEmV_{water} = \frac{GEmP}{Water_{total use}}$$

Where $\mathrm{MEmV_{water}}$ represents the marginal emergy value of water in sej/m^3; GEmP stands for the Emergy value of regional Gross Domestic Product (sej/yr).

7.7.2. Converting Emergy to Monetary Equivalents

Conversions of emergy to Euro value are based on the conversion factor of 4.8 E12 sej/€ for Spain (2008). The conversion factor was calculated as indicated in Eq. 7.10.

Eq. 7.10.
$$EIMV(sej/euro) = \frac{GEmP(sej)}{GDP(euros)} = \frac{5.76E24 sej/yr}{1.18E12 euros/yr} = 4.8E12 sej/euro$$

Where EIMV is the Emergy Intensity of Monetary Value; GEmP is the Gross Emergy Product (total emergy use in economy, 2008), and GDP is the Spanish Gross Domestic Product (2008).

7.8. Case study: Foix watershed

The described Emergy-base methodology to asses the water costs according to the WFD has been applied to the Foix watershed, one of the areas already studied in Chapter 6. In consequence, none additional description of that basin is repeated here. Its main features and hydro-geographical data can be consulted in section 6.5. Figure 7.3 shows the scheme for the Foix River Basin, including its partition into eleven sub-basins.

As mentioned in Chapter 6, the scarce real data collected from sampling stations led to the use of a surface water simulation software, Qual2kW, to complete the required input data for the study. In addition to that, the natural flow regime given by the CWA (CWA, 2004) provides an average restored flow value for each sub-basin.

Figure 7.3. The Foix watershed, showing eleven sub-basins used in the spatial and temporal emergy evaluation of resource values of water. Grey shadow indicates the main urban areas, while pink colour represents the industrial ones.

Regarding the land uses, detailed information was taken from the CORINE[1] application, in order to use uniform European data sets for the analysis. Finally, figures about the Spanish global emergy evaluation carried out by Sweeney et al. (2006) were used.

7.8.1. Evaluation of Financial Value of Foix Water Resources.

The financial value from which Financial Cost was calculated for the Foix Basin was based on averages of current cost of water using a weighted average of current costs to provide water for urban and industry (46%), livestock (2%), and irrigation (52%), extracted from the IMPRESS report (CWA, 2005a).

The estimation of the annual financial costs to provide water for all sectors of the economy in the Foix basin was 5.2 million €/yr^3. Thus the average cost was 0.54 €/m^3 which compares well with the average global values for surface and aquifer water in Table 7.4.

7.8.2. Emergy Evaluation of the Resource Value of Foix Water Resources

Evaluation of the resource value of surface water was undertaken in two parts: the chemical potential and the geopotential energy were evaluated. Together, these comprise the resource value from which Resource Costs were computed. Since there is significant spatial and temporal variability to the water resources, a GIS-based method to evaluate water resources by basin and for each month of the year was used.

The time series of Geopotential and Chemical potential components in each hydrologic unit within the Foix Watershed are presented in Figure 7.4. It is observed that the shape of the curves is similar for all the hydrologic units. The geopotential component is linearly dependent on the flow and the altitude and the chemical potential on the area of the hydrological unit and on the rainfall.

The resource values were computed on a monthly basis for each of the sub-basins of the Foix watershed. Table 7.7 and Table 7.8 list the chemical potential and geopotential resource values for each of the basins in the Foix watershed emergy, using January as an example. The tables show both the emergy values and the monetary value per cubic meter of water. For the month of January, the monetary value of chemical potential emergy in water varied between 0.62 and 0.75 €/m^3, while the monetary value of geopotential emergy was between 0.01 and 0.04 €/m^3. Obviously in the Foix basin, the chemical potential of water is the most important. Sub-basins with the highest relief (8001, 8002, 8008 and 8009) had the highest monetary value of geopotential.

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[1] CORINE (Coordination of information on the environment) is a European programme initiated in 1985 by the European Commission, aimed at gathering information relating to the environment on certain priority topics for the European Union (air, water, soil, land cover, coastal erosion, biotopes, etc.). Since 1994, the European Environment Agency (EEA) integrated CORINE in its work programme. EEA is responsible for providing objective, timely and targeted information on Europe's environment

Sub-basin	Rainfall[1] (mm/month)	Energy Rain[2] (J/month)	Tr[3] (sej/J)	Emergy Rain[4] (sej/month)	Discharge[5] (m^3/month)	Discharge Emergy[6] (sej/m^3)	Monetary Value[7] (2008 em€/m^3)
8001	72.65	1.53E+13	31000	4.75E+17	1.61E+05	2.95E+12	0.62
8002	72.81	1.55E+13	31000	4.79E+17	1.61E+05	2.98E+12	0.62
8003	79.20	3.62E+13	31000	1.12E+18	3.75E+05	2.99E+12	0.62
8004	76.13	1.86E+13	31000	5.76E+17	1.61E+05	3.58E+12	0.75
8005	81.25	6.06E+13	31000	1.88E+18	5.62E+05	3.34E+12	0.70
8006	80.43	7.84E+12	31000	2.43E+17	8.04E+04	3.03E+12	0.63
8007	81.18	1.12E+14	31000	3.47E+18	1.10E+06	3.16E+12	0.66
8008	70.53	1.23E+13	31000	3.82E+17	1.34E+05	2.85E+12	0.59
8009	75.57	3.58E+13	31000	1.11E+18	3.75E+05	2.96E+12	0.62
8010	81.07	1.17E+14	31000	3.64E+18	1.15E+06	3.16E+12	0.66
8011	80.94	1.24E+14	31000	3.85E+18	1.21E+06	3.19E+12	0.66

Notes to Table 4

1 Data from CWA
2 Rain chemical potential energy
3 Transformity = 31000 (Odum, 2000)
4 Emergy in rain
Emergy (sej) = Energy * transformity
5 Data from CWA
6 Discharge Emergy
Emergy (sej/m^3) = emergy in rain (sej) / discharge (m^3)
7 Monetary Value
em€/m^3 = Discharge Emergy/ 4.8 E12 sej/€

Table 7.7. Resource value of chemical potential of water discharge in the Foix basin by sub-basin (January)

Hidrologic unit	**Height[1] (m)**	**Discharge[2] (m3/month)**	**Geopotential Energy[3] (J/month)**	**Tr[4] (sej/J)**	**Geopotential Emergy[5] (seJ/month)**	**Monetary Value[6] (2008 em€)**	**Monetary Value[7] (2008 em€/m3)**
8001	500.9	1.61E+05	7.89E+11	34300	2.71E+16	5.65E+03	0.04
8002	586.4	1.61E+05	9.24E+11	34300	3.17E+16	6.61E+03	0.04
8003	168.9	3.75E+05	6.21E+11	34300	2.13E+16	4.45E+03	0.01
8004	347.3	1.61E+05	5.47E+11	34300	1.88E+16	3.92E+03	0.02
8005	155.1	5.62E+05	8.55E+11	34300	2.94E+16	6.12E+03	0.01
8006	202.9	8.04E+04	1.60E+11	34300	5.49E+15	1.14E+03	0.01
8007	155.1	1.10E+06	1.67E+12	34300	5.74E+16	1.20E+04	0.01
8008	588.8	1.34E+05	7.73E+11	34300	2.65E+16	5.53E+03	0.04
8009	588.8	3.75E+05	2.16E+12	34300	7.43E+16	1.55E+04	0.04
8010	102.1	1.15E+06	1.15E+12	34300	3.96E+16	8.25E+03	0.01
8011	101.1	1.21E+06	1.19E+12	34300	4.10E+16	8.55E+03	0.01

Notes to Table 5.

1 Average height of Sub-basin. Data from CWA.
2 Data from CWA
3 Geopotential energy
6 Monetaray value = geopotential emergy / 4.8 E12 sej/€
7 Monetary value per m3= monetary value / discharge
5 Geopotential emergy = Energy * transformity
4 From Odum, 2000

Table 7.8. Resource value of geopotential potential of water discharge in the Foix Basin by sub-basin (January)

Graphed in Figure 7.4 are the monthly emergy values of geopotential and chemical potential for the sub-basins of the Foix watershed. The highest chemical potential and geopotential emergy was during the winter months (highest rainfall months, as to be expected), yet there is an increase in chemical potential emergy in late summer that is not reflected in the geopotential. Presumably because the evapotranspiration is highest during that period of the year and therefore there is less total runoff.

Geopotential is the lowest during the dry season, while the chemical potential exhibits an increase during that dry season.

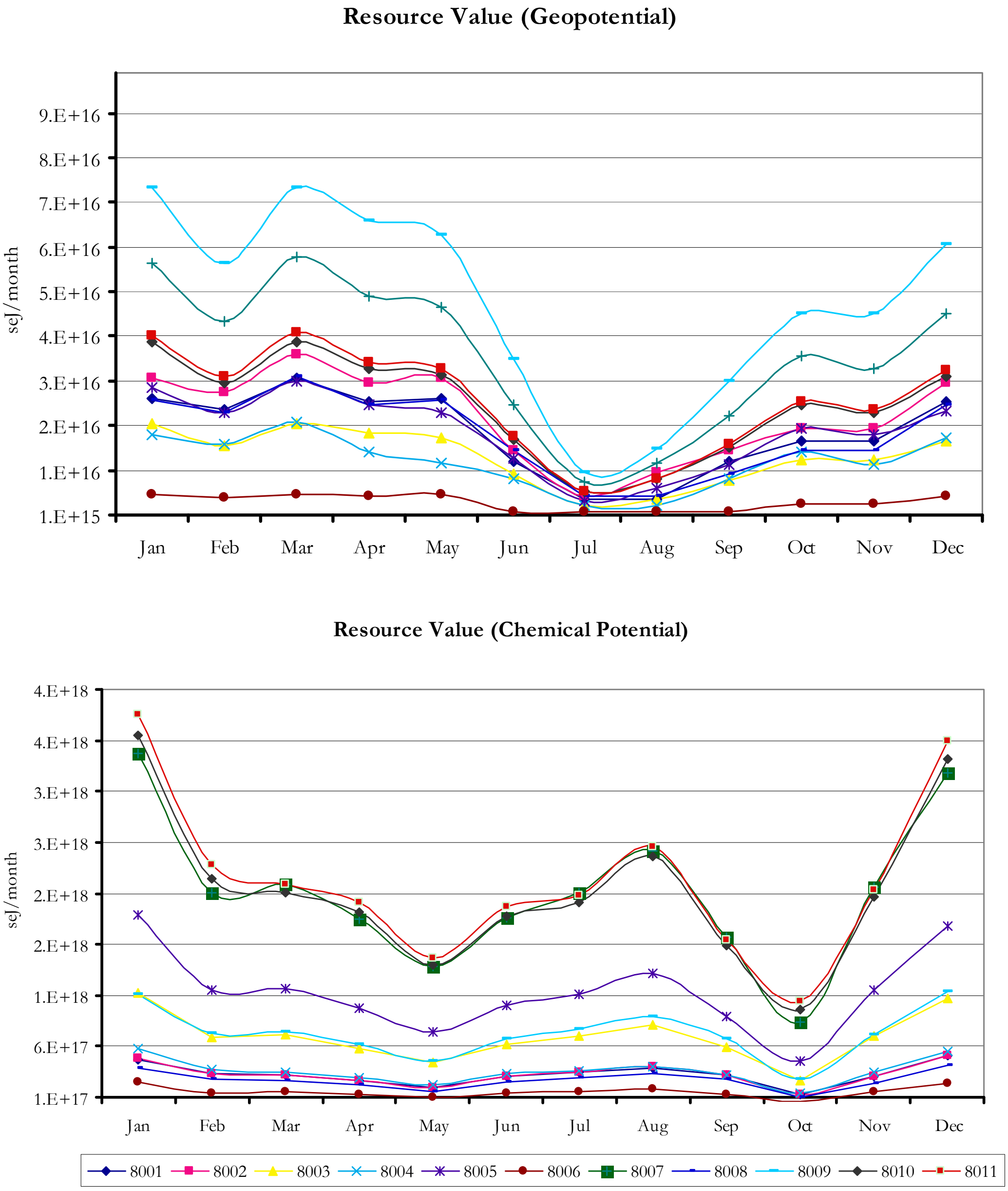


Figure 7.4. Time series of Geopotential and Chemical potential components in each hydrologic unit within the Foix Watershed.

Monetary value of total resource emergy (sum of chemical potential and geopotential) per cubic meter of discharge is graphed in Figure 7.5 for all sub-basins in the Foix watershed. It is most interesting to note that the highest monetary values per cubic meter of discharge occur in the driest months when discharges are lowest. Rain input per stream discharge is highest during these low flow months, which generates the highest emergy and monetary values. On the average, during the majority of the year (January to April and October to December) monetary resource value is about 0.50 €/m^3, while it averages 1.62 €/m^3 the four rainy months (May to September).

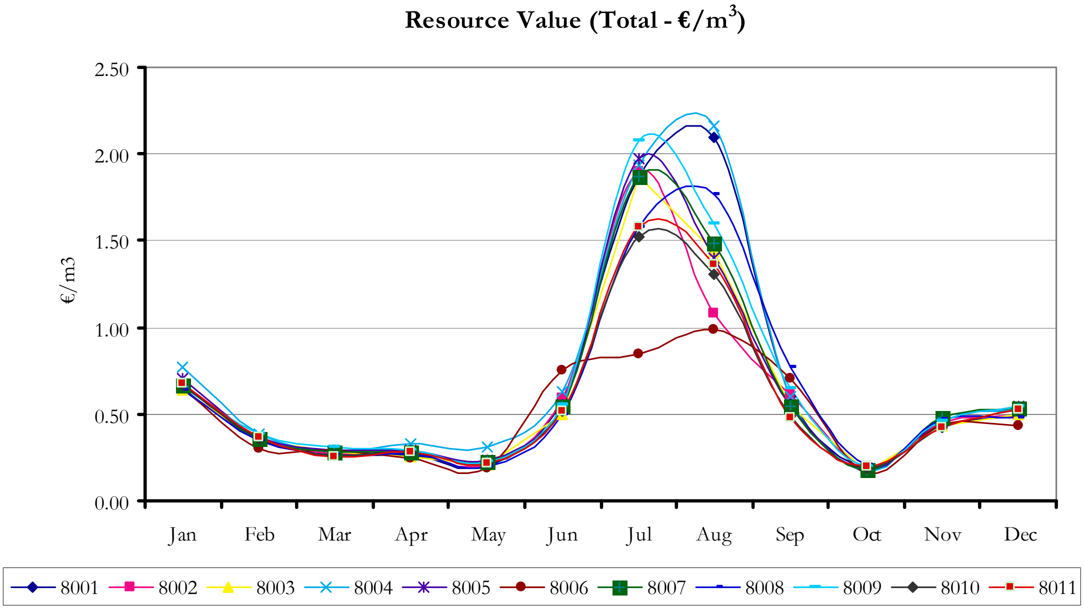


Figure 7.5. Total resource value expressed in €/m^3

The highest values per m^3 occur during the dry season. For the majority of the year resource values are relatively consistent between basins, varying somewhat during the dry season.

7.8.3. Environmental Value of Foix Water Resources

According to the two methodological options for assessing the EC of water within the Emergy approach, the corresponding calculations have been carried out for this example.

First, GIS layers (urban, industrial, railways, agricultural and natural lands) were used to exactly determinate the land use within the Foix Watershed, and the Non-Renewable Areal Empower Intensity was taken from previous emergy studies (Brown and Vivas, 2005), as it can be seen in Table 7.9.

Although urban and industrial land represent only 6% of the area in the watershed, these uses are the more emergy intensive and, therefore they are the responsible of the higher non-renewable emergy input in the region. By applying Eq. 7.8, the environmental cost rose up until 1.95 €/m^3.

Secondly, that environmental value resources was evaluated at the scale of the country, since data on the Gross Regional Product for the Foix Basin were not available and assuming that the development capacity of the watershed is similar to that of Spain as a whole. In Eq. 7.9 and Eq. 7.10, the total available water that includes both rainfall and groundwater use in Spain for the year 2008 and the GDP of Spain for the same year, were included. The rationale is that all the rainfall is utilized in regional production either directly as irrigation or urban supply, or indirectly through production of resources like soils, forests, or fisheries that humans may benefit from through their harvest. The environmental value calculated in this manner corresponds to the concept of Environment Cost as enunciated in the Water Directive.

LAND USES	**Non-Renewable Areal Empower Intensity $\cdot 10^{15}$ seJ·(ha·yr)$^{-1}$**	**land used (ha)**	**Non-Renew inputs (seJ/yr)**
Industrial and commercial zones	5210.6	38.98	2.03E+20
Single family residential (low density)	197.5	232.54	4.59E+19
Single family residential (Med-density)	658.3	418.17	2.75E+20
Single family residential (high-density)	921.7	110.82	1.02E+20
Multi-family residential (high rise)	4213.3	1166.10	4.91E+21
Road Network	2533.7	175.38	4.44E+20
Agriculture			
Vineyard (General agriculture)	15.1	12706.39	1.92E+20
Irrigated crops (Row crops)	20.3	1704.00	3.46E+19
Unirrigated crops (Citrus)	7.8	1205.99	9.41E+18
Forest	0.5	7183.56	3.59E+18
Bushs and meadows	0.5	4672.84	2.34E+18
Pasture	2	2285.78	4.57E+18
Open spaces with low or no vegetation			
Natural Land/open water	0	38.19	0.00E+00
Sand and beaches	0	0.01	0.00E+00
Snow acummulation	0	0	0.00E+00
Water	0	87.23	0.00E+00
		TOT	6.23E+21

Table 7.9.Land uses in the Foix Watershed

Total water resource use in Spain was $8.4 \cdot 10^{11}$ m^3 from rainfall (Sweeney et al. 2006) and $7.8 \cdot 10^{9}$ m^3 from groundwater (FAO, 2009) for a total of $8.5 \cdot 10^{11}$ m^3/yr. Spain's GEmP in 2008 was $4.55 \cdot 10^{24}$ sej. Using Eq. 7.9, the marginal emergy value of water resources in Spain was $6.8 \cdot 10^{12}$ sej/m^3.

Euro equivalent of the emergy value of Foix water, which we define as the average environmental value from which environmental cost (EC) of water may be computed, was obtained by dividing the marginal emergy value of water ($6.8 \cdot 10^{12}$ sej/m^3) by the EIMV ($4.8 \cdot 10^{12}$ sej/€) for the economy of Spain, and the result is 1.42 €/m^3.

Because of the already explained limitation of using LDI parameters in studies out of the area where they have been calculated for, the second calculation alternative is taken in this case study.

7.8.4. Summary: Full Cost Recovery of Foix Water Resources.

Full cost recovery on a volume basis was computed as the sum the three monetary values (financial, resource and environmental) and average values are shown in Figure 5. The financial costs of water resources were estimated to be 0.54 €/m^3. The resource values, from which costs can be inferred were between 0.21€/m^3 and 3.17 €/m^3 depending on time of year and sub-basin. Overall, average resource value of Foix water, across all sub-basins and all periods of the year, was 0.87 €/m^3. The environmental costs (based on the marginal emergy value) was 1.42 €/m^3. Overall, the total average costs were 2.83 €/m^3.

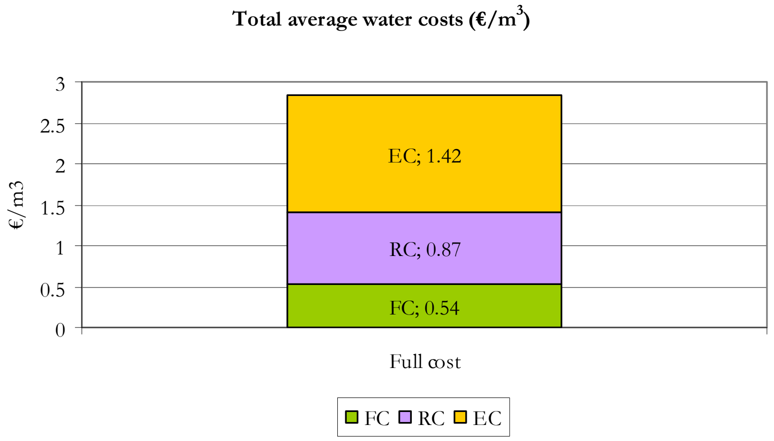


Figure 7.6. Contributions to total average water costs in the Foix watershed (Full cost as addition of the financial cost (FC), resource cost (RC) and environmental cost (EC)

While each of these costs varies depending on source, geography, climate, and to some extent economic system, the method of determining values from which costs are computed can be applied to any river system with similar results.

Finally, if a global number for the EC of the Foix watersheds want to be obtained, the 1.42 €/m^3 factor has to be multiplied by a defined flow. Different interpretation can be carried out. Attending to the yearly natural contribution (9.47 hm^3/yr), the final value would rise up until 13.5 M€.

7.8.5. Concluding remarks

Several things must be taken into consideration before applying a fixed number based on an average value of water resources. First, to recover full costs for a cubic meter of water assumes that all of the water was taken out of the system and not returned, for instance water that is used for irrigation and is evapotranspired or cooling water that is evaporated. If some water is returned, then only that portion that was used would be charged.

Obviously if the portion returned was polluted beyond use, then full cost recovery would be in order. Second, using the same reasoning if water is 'borrowed" for some time, used in some process and returned unaltered (highly unlikely) then there would be no charge. If all the water is returned however in a more polluted state, using the chemical potential equations give above, it is possible to determine the quantity of chemical potential that has been used up. Third, using averages while easy to apply misses the fact that not all water is created equal, both in time and in space. For instance, in the Foix watershed, the resource value of water varies over one order of magnitude (0.21 to 3.17 €/m^3) throughout the year and from one watershed to the next.

The case study of the Foix watershed evaluates only the surface water supplies. Similar methods can apply to groundwaters. Note in Table 2 that the chemical potential emergy of aquifer water, on average, is about 6 times the chemical potential in rain water. Thus, it might be assumed that the resource values for aquifer water within the Foix watershed would be significantly higher than these surface water values. To determine the actual value of groundwater in the Foix watershed would require a more detailed study of groundwater dynamics within the basin.

Correct implementation of the concepts and regulations established by the WFD involves a complex structure of initiatives that will provide the necessary tools and proper criteria for new water management policies. These policies are to be based on sustainability criteria from a perspective of the environment, economy, maintenance of water resources, and complete transparency. In addition, without a doubt, the demand for tax collections that will ensure total cost recovery will require the WFD to set out, in a clear way, a method to calculate the environmental costs and those of the resource....no easy task using traditional economic analysis. The approach outlined and demonstrated in this paper may be of value in setting up a program of full cost accounting that could then lead to recovering the truer costs of water, but more importantly a program of incentives to maintain and protect water resources.

7.9. Summary of the chapter

Like other environmental products, water contributes to more emergy than is usually paid for. Water is worth more to the public interest than people pay for it. In ecosystems, the water flows that contribute to transpiration and thus photosynthesis are principal emergy source. Much of the emergy in agricultural and forestry products comes from the emergy of the transpired water. As water is processed through purification processes for city use, there are additional emergy and money values added. Integrating the ecological and hydrologic systems of urban centers into the developed landscape to serve as water quality filters, wildlife habitat and water reservoirs are important goals for achieving economic and environmental sustainability.

Implementation of the concepts and regulations established by the WFD involves a complex structure of initiatives that will provide the necessary tools and proper criteria for a new water management regime. This regime is to be based on sustainability criteria considering the environment, the economy, the maintenance of water resources, and complete transparency in enforcement. In addition, without a doubt, the demand for tax collections that ensure cost recovery will require a matter as complex as that of how to calculate the environmental and resource costs of water use, to be set out in a clear way.

As it has been shown in this chapter, Emergy can help quantify the environmental and resource costs of water use. It is apparent that a fairer price for water can be calculated by applying the emergy approach, which allows including the resource and the environmental cost in the water economy. The main advantage of the procedure is that it is a comprehensive approach than can be easily applied by technicians, using input data that are quite common in the hydrological records systems. The resource and the environmental cost of water calculated using the Emergy approach showed that to meet the WFD requirements for full cost recovery, the price for water would have to increases two and a half fold.

Some drawbacks of the methodology are that all the important aspects of the cost accounting are not fully taken into account: for instance, the non inclusion of specific parameters measuring the chemical quality of water, apart from the conductivity and parameters for measuring the biological quality of waters are lacking.

Comparison between PH and Emergy approach is quite complicated, since many of the background hypothesis are different. In addition to that, the parameters included in the analysis are not exactly the same. While the natural flow is only one additional parameter for obtaining the RRC in the PH, it is a key factor in the RC and EC calculation in the Emergy approach.

However, there exist some coincidences in both methodologies background. As it happened with the exergy of ocean, the ocean transformity is zero, since no chemical potential is assigned to it. The chemical potential is calculated relative to seawater.

Chapter 8

Synthesis, Contributions and Perspectives

This last Chapter is devoted to summarize the work described along this dissertation and to state the possible working lines opened by this PhD thesis.

8.1. Synthesis

The connexion between the exergy analysis and the economic analysis of a river has been developed in this work. The exergy analysis of water comprises the quantity and the quality of the water flow and, in addition to that, it evolves in the space, as well as in the time: spring water gets degraded as it flows along the river course until the sea. That degradation means a loss in its quantity because of the water uses, as well as a decrease in its quality due to the natural and the anthropic pollution, being this last one the most important contribution. The natural degradation of the river occurs when the river swept away different materials in its path; the human one comes from the specific water uses.

Those physical interactions are translated into numerical values through the methodology presented in this dissertation, the Physical Hydronomics: it allows expressing the flows involved in the hydrologic cycle in exergy values, that is, into MWh. The exergy of any water flow represents the maximum work that can be obtained from it until reaching the equilibrium with the reference environment (the ocean) or, it can be also understood as the minimum energy that needs to be invested in order to restore such a resource. This idea is, nevertheless, still insufficient because of the inherent irreversibility to any real process. Then, the next step was to introduce the exergy cost, which informs about the real amount of exergy required to produce any physical flow in a system whose limits, aggregation level and subsystem efficiencies have been defined. Finally, once the real physical cost of the water flow is established, it can be given in economic cost by introducing the energy price in the region when the study is carried out. In this part, both physical direct costs measured in energy units (energy operation cost), as well as physical indirect cost given in monetary units (global investment and maintenance costs), are aggregated.

The described methodology perfectly connects with the international concern about fresh water resources in general, and about the preservation of aquatic ecosystems in particular. In Europe, the WFD highly contributes to conceptualize those worries, establishing a new, integrated approach to the protection, improvement and sustainable use of Europe's rivers, lakes, estuaries, coastal waters and groundwater. Its final target is achieving the good ecological states for those water bodies by 2015. Such objective states are defined within the Directive and, by applying the PH, they are expressed in exergy terms. It allows to use the objective energy units to asses the water cost and to allocate the corresponding restoration costs among the water users.

8.2. Summary

To a large extent, water shapes the Earth through erosion and deposition of sediments and minerals. It is also fundamental to life on Earth, where water makes up a substantial part of living organisms, and those organisms need water for life. Therefore, managing water resources by thoroughly understanding the hydrologic cycle at scales ranging from the entire Earth to the smallest of watersheds is one of the greatest responsibilities of humans. This background idea, together with the new European legal requirements regarding aquatic ecosystems preservation, originated the present work.

The foundations of Physical Hydronomics have been laid in this dissertation. After analyzing the basic exergy theory related to water, the methodological background has been stated and applied to two specific watersheds. In this way, important obstacles have been overcomed, many of them related to the imprecise definitions of the WFD. Contrary to the quality parameters, the flow of the objective states is not given and, therefore, it was required to select them. The cost definitions was neither clearly defined, although some further detail was provided by the WATECO guide. Those ideas, tightly developed with a bibliography revision about the economics of natural resources, was used to give the service, environmental and remaining cost definitions that comprise the integral replacement cost of water considered in this PhD.

In the bibliography revision summarized in Chapter 3, it became evident, firstly, the commonly indistinct use of *value, price* and *cost* concepts and, secondly, the shortages of the current economic assessment of natural resources, in particular of water. Cost is determined as the objective parameter to be assessed because it accounts for the physical inputs in any product or service. Thus, the information coming from a physical valuation of resources has to be included in any methodology aimed to obtain the environmental cost of water.

Exergy was proposed as the thermodynamic variable to be implemented in the study and, more specifically, the exergy cost, understood as the real amount of exergy required to produce any physical flow in a system whose limits, aggregation level and subsystem efficiencies have been defined.

The reference environment (RE) is one of the key points for the exergy analysis. A complete study about the RE features for the PH application was developed in Chapter 4, paying special attention to the presence of organic matter (OM), nitrogen and phosphor (NP). Finally, seawater without those components was selected as the most adequate reference. In consequence, OM and NP contribute to the analysis with their formation exergies.

In addition to that, the parameters defining each of the exergy components in a water body (thermal, mechanical, chemical, kinetic and potential) must be clearly stated as well. The study of the best exergy evaluation of organic matter in water bodies was also developed. After reviewing and trying the existing methodologies in the literature, a proposal was done to give exergy value to the OM parameter measured in the river. The molecule CH_2O was proposed as the most representative one; its presence in the river is measured by the TOC, although it would always depend on the type of considered water. TOC is the most suitable parameter in surface waters but, if water goes into a WWTP, the BOD and COD will be very probably the best option.

For the sake of completeness, the possibility of including the biological information of organism in exergy terms in the analysis (Jorgensen's eco-exergy approach) was considered. However, the important conceptual differences, together with the lack of detailed information about fishes and plants living in each stretch of the studied river that is being analyzed, inclined us to neglect that contribution at this stage of the study.

The exergy assessment of water resources can be tacked from a global or a local scale. In this work, global fresh water resources and icecaps were firstly considered attending to their chemical, potential and thermal components. Afterwards, a local analysis was developed for specific watersheds, where any of the exergy components is included in the analysis.

The exergy assessment of the fresh world water resource presented in Chapter 4 gives improved methodological tools for the exergy analysis of water resources. The exergy replacement cost (ERC) of the yearly available fresh water gives idea of the huge energy amount that the hydrological cycle provides for free. Besides, the study of the exergy requirements to replace the water yearly withdrawal in solar energy terms help to quantify and valuate that huge amount of exergy, that greatly exceeds the electricity yearly produced all over the world.

The ERC of the world fresh water resources resulted about 380,000 TWh/yr, where about 63% of its contribution comes from the chemical component. When only the real yearly demanded water is analyzed, more realistic results and conclusions are obtained for the energy assessment of water resources. This ERC value can be understood as the energy that would be needed to invest in pumping and desalination utilities in order to replace the fresh water taken by humans from the hydrologic cycle every year. The total ERC of the global water withdrawal is about 33,000 TWh/yr (almost twice the world electricity production).

Once the ERCs to restore the fresh water withdrawal was calculated, land requirement to obtain it if solar energy was the only source, was considered. Firstly, the photovoltaic (PV) technology is studied, analyzing different alternatives (fixed or tracking systems, more and less efficient modules). Secondly, the solar energy generation systems using parabolic through collectors (PTC) were considered. In both cases land requirements are lower than 2% of the territory in each continent. That is, to replace the hydrological cycle, the world electricity production would need to be more than doubled and, of course, that would never could replace all the natural ecosystem functions.

On the other hand, the total exergy contained in the world ice sheets is $1.2 \cdot 10^{21}$ J (1,200,000 EJ or 28,000 Gtoe), what is more than 2,300 times higher than the world annual primary energy demand (500 EJ), or 175 times higher than the proved world oil reserves (about $162 \cdot 10^{9}$ toe or $1.2 \cdot 10^{12}$ barrels).

Main basis of the PH methodology were stated in Chapter 5. PH was defined as the specific application of Thermodynamics to physically characterize the degradation and correction of water bodies. i.e., the physical application to economic aspects of the European Water Framework Directive. It constitutes the mentioned local application of Exergoecology to water resources. The construction of the river exergy profiles is the first and fundamental step of the methodology. This task demands an important amount of available information: the pair quantity-quality in different reaches along the river. Therefore, a surface water simulation program is needed; Qual2kW is the software used in this work.

As first result of the PH application, the global potential and chemical value of a water body can be given after studying its evolution along the time and space. The obtained figure gives idea about the exergy value of the considered river and allows its comparison with other parameters such as the power consumed by the current WWTPs installed along its course.

The exergy river profiles, together with the costs definitions leads to obtain the minimum exergy costs, where reversibility of processes is assumed. Once the real performance of the quantity and quality water restoration technologies is included, the real exergy restoration costs are defined. The irreversibility of such processes is calculated through their unit exergy costs, which were calculated for different water-related technologies. In particular, pumping and desalination unit cost can be found in Chapter 4, and the unit cost for the water treatment plants devoted to restore the water quality is developed in Chapter 5. The most relevant water desalination techniques were studied, as well as the conventional pumping. But due to the important heterogeneity of the waste water treatment plants, none standard utility has been analyzed. Instead, twelve real WWTP with different internal processes were considered and their unit exergy costs obtained. In both cases, desalination and depuration, the flows diagram and also the exergy content of each flow were provided.

From the previous explanations, it is clear that the pair quantity-quality along the river is the basis for the exergy profiles construction, which are finally the starting point for the exergy cost calculation and, finally, to get the economic EC of water. The degradation provoked by water users was also analyzed in exergy terms, which facilitates the cost allocation among the different water users. That further possibility of cost allocation is one of the main strengths of PH.

These steps were all designed to obtain the economic water cost. Then, the exergy costs can be translated into economic cost by introducing the energy price in the analysis. The cost obtained from the river exergy profiles can be understood just as the operation cost and, in order to complete the analysis, the installation costs corresponding to the program of measures have to be added to reach the total economic cost.

The water costs are therefore calculated but a further step needs still to be carried out: the cost allocation among the water users. The polluter (or degrader) pays principle founds its best allied in the PH application because the methodology allows that cost distribution. This is a strong support for the exergy as the working tool, since there is no other comprehensive methodology able to directly give such results.

The proceeding to reach an allocation cost was also deeply analyzed in Chapter 5; in short, the total degradation of water due to its uses can be calculated and it is possible to distinguish the percentage of degradation (in quantity and quality) corresponding to each sector. Then, this distribution can be used to allocate the obtained total cost of the watershed.

Although each defined cost (SC, EC and RRC) was calculated, the last part of the analysis is mainly focussed on the EC, since it constitutes the main unknown of the WFD in its 9th Article.

Afterwards, in Chapter 6, the PH methodology was applied to two specific and quite different river basins located in the Catalonian Internal Basins. The first presented results were the global exergy values of the river. It was seen that the potential and chemical potentials are similar. Then, the exergy profiles of the rivers were built.

In particular, the exergy potential value of the Muga watershed is about 5 MW, as much as its chemical potential. That value fits quite well with the figure of the hydroelectricity plant installed in the Boadella dam (3.6 MW), close to the river headwater. Attending to the power required in the WWTPs along the river, it was obtained that about 4 MW are required. It leads to think about the huge amount of energy required to clean the human-polluted waters,e specially when that required power is compared with the river energy availability.

The potential value of the Foix river resulted about 0.75 MW in the PS, and the chemical potential, about 0.5 MW. The power currently required to keep clean the Foix waters is about 1MW, double its chemical exergy value. It is a relevant relation, which confirms that this river has an important human pressure.

In addition to obtain the economic environmental cost of water (the basic new requirement of the WFD), the integral replacement cost was also given. Besides, the PH allows a comprehensive analysis of the introduced parameters: the Muga basin seems to be accurately evaluated and the ecological flows given by the authorities lead to expected results. However, the origin of the close values for the EC and the RRC in the Foix case indicate that the objective flows could be reviewed.

The last part of this dissertation, the Chapter 7, is devoted to a different methodology that the PH: the emergy approach. The WFD costs are defined according to the emergy basis and a emergy-based price of water was obtained. In this case, there is not any projection to 2015, just an evaluation of the current situation of the Foix watershed, which was the river basin selected to show the methodology.

8.2.1. Considerations about the results

Any person trained in water management will agree on the huge amount of information associated to the water world. A comprehensive work can not be executed solely by technicians, hydrologists, economists, or any other monothematic specialists. On the contrary, it is possible through the joint efforts of a transdisciplinary team of experts whose approaches managed to overcome, from scientific bases, the difference of specialities involved, and who managed to agree on horizontal problems. Keeping in mind that limitation, the PH methodology has been presented here. Many different information sources have been reviewed and numerous experts have been at some point consulted.

An important handicap of the WFD is that the objective river flows are not given. Nor specific number for each basin, neither a standard methodology to define them is provided. Then, the flows for each objective (GEE, HS) state has been defined in this work using the data of real and expected flows, together with the maintenance flow provided by the competent organism, the CWA.

The information quantity-quality is crucial in each point of the analysis, but it has been demonstrated that the quantity (Q) component is always the most weighting factor because the change in exergy terms (Δb) are lower than those of the flow. Furthermore, the IM component, for example, is a clear example due to its non-linearity.

Definitions of the quality objectives in the OS, which seem to be greatly determined by the biological components, present an important limitation because they are usually kept constant in several consecutive reaches. It provokes null values in the db calculations, what is not the best circumstance when the comparative profiles are drawn: the real curve consist on a set of pulses and, because of that constant objective value, a higher discretization does not provide better information.

In the same way, important difficulties have been identified dealing with the mathematical treatment of the river exergy profiles due to its high monthly variability coming from the intrinsic features of the Mediterranean rivers. For instance, real values could be zero (as it happened in the Foix basin), but nature ones are always positive. They are calculated from different perspectives: one comes from individual series, while the other is the average value of a temporal series.

The presence of the reservoirs means a clear shift (time delay) in the flow regime and, therefore, in the exergy profiles. It can be clearly demonstrated in the Muga B curves, since the dam is located very close to the river source.

Regarding the Program of Measures to reach the OS, the proposed quantity restoration measurements that were considered were desalination and pumping. This assumption requires some additional comments because, as it is clearly understood, planning to restore the quantity term of exergy degradation through desalination would lead to a huge energy demand (as it was shown in Chapter 4), and therefore its environmental impact. In consequence, this part of the PH methodology has to be understood as a tool to quantify the degradation and to give a value for the EC. In practice, additional quantity restoration measurements would unavoidable need to be implemented: demand management planning, sustainable aquifers exploitation, water markets, downstream water pumping or desalination of brackish water, as the most evident and alternatives examples.

Anyway, a Program of Measures based on coastal desalination is actually restoring the quantity component of exergy degradation. For instance, in areas with high scarcity as the Foix basin, does exist a very big coastal desalination plant (Cunit) providing fresh water upstream. It can somehow be considered equivalent to the proposed restoration measurements.

Together with the previous idea, it is worth to bring here the reality about the man-water relationship. Humankind is not thinking in restoring all the demanded water through desalination and pumping. The solution to flooding episodes and growing demands has traditionally consisted of the construction of regulation dams. On the other hand, drought periods are reflected in the river exergy profiles, but they are difficulty treated by PH.

In addition to that, the idea of restoring water quality by means of a simple dilution, by adding *clean* water to the polluted stream, contradicts the WFD (a higher flow than natural one is not really restored water body). WTPs are required at some strategic points to improve the quality of water along the river. This fact should also be enhanced when selected measures have to be applied to restore the objective status of water bodies, what is the final target in the WFD, according to the Plan of Measurements to be implemented in each watershed. Furthermore, the downstream effect that any corrective measure has in the river, and its adequate mathematical treatment, have to be carefully observed in the analysis. The complete exergy profiles of a river status will include the effects of measures applied upstream (see Figure 8.1).

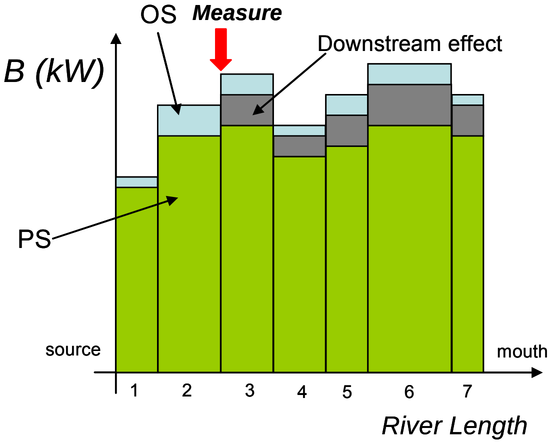


Figure 8.1. Discrete profile of a river when simulation models are used, and downstream effect of an applied technique.

Two well-differenced watersheds have been analyzed. Muga area far exceeds double the Foix one and the annual contribution in the Foix is considerable lower (see the summary of features in section 6.5.4). The Muga basin is an average populated area, with not severe water restrictions, and with a reservoir close to its source. Therefore its flows regime severely separated from the natural one. On the contrary, the reservoir of the Foix basin is located close to its mouth, what significantly differs from the Muga case.

The Foix area is a highly populated region, with an important pressure in the summer season due to tourism. Groundwater also plays an important role in water supply, and shortage episodes may occur. Despite those differences, comparison between figures is understandable: EC rises to 9.6 M€ for the Muga watershed and it is about 1.7 M€ in the Foix watershed.

The obtained EC can be apparently high. Nevertheless, it has to be observed that it means only a small part of the IRC. The highest contribution comes from the RRC (defined by the PH but not mentioned in the Directive), which mainly accounts for the physical water consumption associated to the uses, and the one which is really high (17.7 M€ versus 9.6 M€ of the EC in the Muga basin; and 3.5 M€ versus 1.8 M€ of the EC in the Foix basin). The direct conclusion is that EC (the compulsory one of the WFD) is not an expensive demand, since the complete restoration of the hydrological cycle would be much higher.

The different objectives defining the water costs may change along the time, especially in these implementation periods when the WFD is still being interpreted by the diverse agents acting in the process. The flexibility of the PH for assuming those changes is worth to be highlighted.

8.3. Contributions

1. An important effort was done in Chapter 2 in order to summarize the background information needed for the elaboration of this work. Special attention was devoted to quantitatively and qualitatively characterize the water uses because that information was highly relevant for one of the final targets of the PH, the cost allocation.

2. The statement of the problem aimed in this phD was explained in Chapter 3. The relationship between Economics and Environment can be faced from two different perspectives, Environmental Economics and Ecological Economics. They were briefly explained and the Ecointegrator approach, coming from the second one, was presented as the background for the PH definition.

3. The main contribution of this PhD Thesis is the presentation of the foundations of the Physical Hydronomics methodology, that is, the Exergo-Ecology approach applied to river waters and its further application to fulfil the cost included in the WFD. This methodology consists of constructing of the exergy profiles of the river for the different defined water states (ES, PS, FS, OS and NS). The existing exergy gap among those river states allows the definition of the minimum exergy cost, which stand the basis for the end resolution of the economic cost of achieving the ecological objectives stated by the legislation. In particular, the PS-ES definition leads to the SC; the FS-OS gap leads to the EC; and the NS-OS difference allows the calculation of the RRC.

   The existing irreversibility of any real process is included by means of the exergy cost concept, which accounts for all the real physical flows that need to be invested in order to provide the exergy demanded for achieving the final desired state. To accurately define them, the energy study of different water-related technologies was required.

Once the water costs were calculated, the exergy characterization of the water uses was developed. Then, that calculated costs can be allocated among the water users according to the degradation that each of them produce, which has been assessed in exergy units. The explained steps are summarized in Figure 8.2.

It has been shown that the exergy procedure, although thermodynamics-based, allows several water cost allocation alternatives. The allocation would always depend on the exergy component that is considered in the analysis. As an example, the Polluter Pays Principle has just traditionally included the quality component. However, the Degrader Pays Principle proposed in this dissertation jointly accounts for the quantity and quality losses.

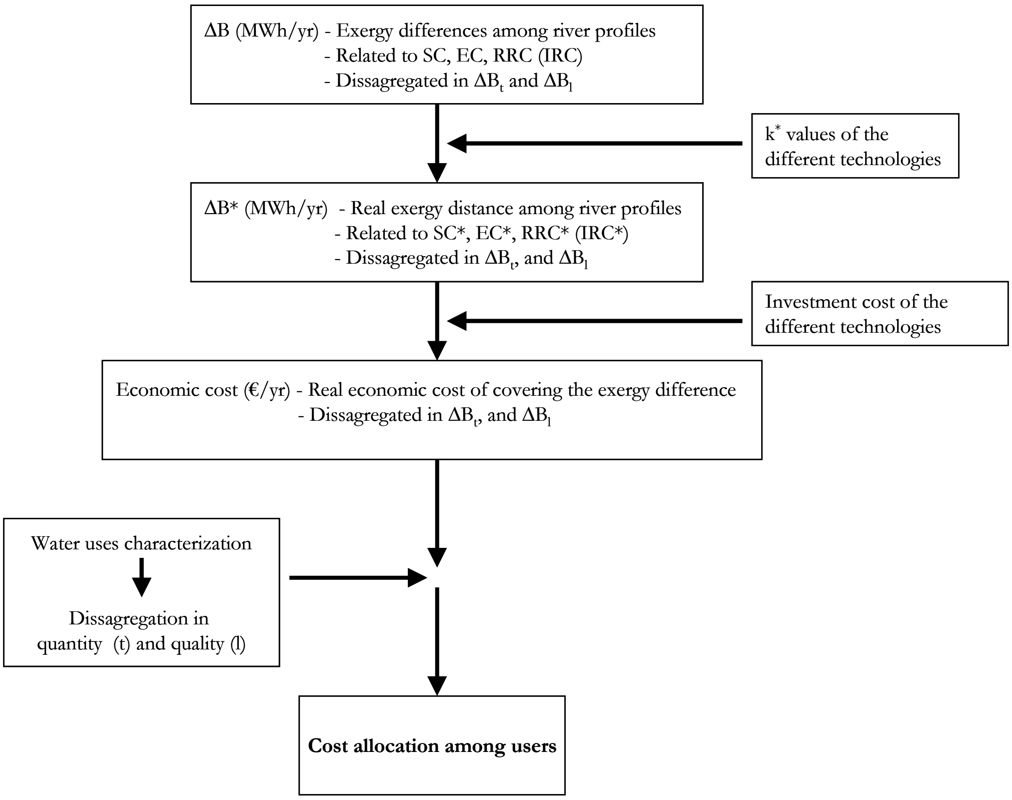


Figure 8.2. Basic steps in the PH's methodology

4. In particular, to the PH's complete development, several aspects have been developed in the course of this dissertation:

    - Selection of the RE was deeply analyzed in order to find out the most adequate reference environment for the water cycle evaluation. It was finally defined as seawater without any organic matter presence.

- Any of the exergy components defining the water flow was considered. Because of its complexity, the chemical exergy assessment of organic matter in fresh water was studied and the TOC value was defined as the preferable parameter to be used in river waters.

- Biological exergy was also studied. The eco-exergy value proposed by Jorgensen to introduce the biological information content in the organism was analyzed and reasonably ruled out from the methodology at this stage.

- The exergy value of the hydrological cycle, attending to its potential and chemical features, was obtained in energy units and, for the sake for clarity, it was expressed in times the electricity demand on Earth. The surface requirements to obtain such energy through solar technologies were calculated as well.

- To complete the hydrological cycle study, the exergy of the world ice caps and glaciers was assessed. Thermal, potential and chemical exergy components were included in the calculation.

- Taking the initial works from Valero and Uche as basis for characterize the exergy profile of a river, the special features affecting that ideal behaviour of a river along its course were identified and studied.

- The different river states (ES, PS, FS, OS and NS), as well as the costs associated to their differences (SC, EC and RRC), in compliance with the WFD requirements, were defined both in quantity and quality.

- The WFD is structured in biological, hydro-morphological and physico-chemical objectives to be reached. Within the PH definition, its limitations were identified. PH only deals with physico-chemical aspects. As far biological, they can only be partially introduced through the environmental flows.

- Quality objectives can be collected from official organism, but quantity objectives values needed to be defined in order to apply the methodology. As mentioned, it is a part missing in the Directive that needs to be completed and suggested in this PhD thesis.

- The global exergy values for the potential and chemical components of the studied rivers were given. Those average power figures provided a general idea of the river power and allowed its comparison with, for example, the power demanded by the currently exisiting WWTPs in the watersheds.

  - Particular calculation procedures integration for the different quantity and quality exergy components have been provided along the Chapter 5. Different situations have been analyzed, pointing out the existing difficulties.

  - The way of including the values of the different exergy parameters within the mathematical procedure in order to get the total account along the watershed has been considered. The observed limitations have been explained.

  - As a particular feature of the PH, the RRC has been defined as the existing difference between the NS and the OS of the river. It is a non-mentioned cost in the Directive, but that was considered interesting to be included for the sake of completeness. In this way, the complete restoration of the water cycle can be better accounted for.

  - As a fundamental part before the economic evaluation, the exergy analysis of restoration technologies is required. So, the unit exergy cost for desalination, pumping and water treatment technologies was obtained. Four desalination technologies were studied with their average figures. In the case of the WTPs, the parameter of twelve real plants were used in the analysis. The exergy flow of each input and output stream was calculated. Exergy flow corresponding to chemicals going into the WWTPs needed a careful analysis.

  - The exergy characterization of the different (domestic, industrial and agricultural) water uses was carried out. The total exergy degradation in quantity and quality due to those uses was obtained and the proportion corresponding to each of them was identified. Then, those values were used to allocate the environmental water cost among the water users along the river.

5. After the complete development of the PH fundamentals, it was time to put it in practise. The whole PH methodology was applied to two different river watersheds to finally obtain their EC and its allocation among the different water users. Results were compared with existing studies, so validating the calculations that were carried out.

    - The two well-differentiated watersheds allowed to observe the PH results in diverse local conditions: reservoir close to the source or about the mouth; regular water availability versus an area with scarcity; stable population along the year and important variablility; surface water versus groundwater as main water supply.

    - The rivers exergy profiles (B) were constructed, starting from the two basic factors: flow (Q) and quality (b). Those curves were compared with the theoretical ones, observing important divergences both in time, because of the dams presence, as in shape, because of the water uses.

6. The Emergy approach provides an alternative cost estimation methodology. It has been used to interpret the WFD and to give emergy definitions for the cost of the resource and for the environmental cost from a quite different from PH perspective.

    - The EC calculation by applying Emergy was developed in two different ways. First, it was based on the lands use, but the limitation of the available LDI –restricted to USA- make us look for further alternatives. Second, the marginal price of water within the area of study, the Spanish economy, was the basis of the EC emergy assesssment.

    - Water prices from the emergy procedure for the Foix watershed have been given and compared with the PH methodology, highlighting the important background differences among both approaches.

7. Different issues content in this dissertation have been published in international journals and books:

    - Valero, A; Uche, J; Valero, Al. and Martínez, A. *Physical Hydronomics: application of the exergy analysis to the assessment of environmental costs of water bodies. The case of the inland basins of Catalonia.* Energy. doi:10.1016/j.energy.2008.08.020

    - Martínez, A; Uche, J; Valero, A. and Valero, Al. *Environmental costs of a river watershed within the European water framework directive: Results from Physical Hydronomics.* Energy. doi:10.1016/j.energy.2009.06.026

    - Valero, A; Uche, J; Valero, Al; Martínez, A; Naredo, J. and Escriu, J. *The Fundamentals of Physical Hydronomics: a novel approach for physico-chemical water valuation.* In "Water, Agriculture, and Sustainable Well-Being" Chapter 5, pp. 97-118. Oxford University Press. 2009.

    - Martínez, A. and Uche, J. *Exergy of organic matter in a water flow.* Energy. doi:10.1016/j.energy.2009.08.032

    - Martínez, A.; Uche, J.; Bayod, A. and Rubio, C. *Assessment of the world fresh water resources through energy requirements in desalination technologies.* Desalination and Water Treatment. Volume 10 (in press).

    - Brown, M. T.; Martínez, A. and Uche, J. *Emergy analysis applied to the estimation of the recovery of costs for water services under the European Water Directive Framework.* Ecological Modelling. Under review.

In addition to these articles, some contributions have been presented in international conferences and workshops and published in the corresponding books of proceedings. They can be consulted in the references section.

8.4. Perspectives and future developments

At the time of concluding this dissertation, the overall feeling is that, far from having close the problem stated in Chapter 3, a huge amount of working lines have been opened. Then, this dissertation should just be understood as the first stretch of a new, fruitful, interesting, sometimes narrow, way to be walked.

This dissertation, as first milestone of PH, has meant many comings and goings, some ways that have been closed after a quite long working time of analysis, and the repetition of calculations with adjustment of parameters, looking for more accurate results. In this sense, there exist numerous possibilities of improvement and further development: the inclusion of groundwaters in the simulation interface, the refinement of the dams simulation, the improvement in the information regarding water uses, among others. As a summary, different interesting aspects need still to be studied in order to complete PH discipline. The most immediate ones are reported next.

The sliceage of the river means an important limitation in the PH application. The river reaches used in the presented case studies, Muga and Foix basins, were provided by the IMPRESS document of the CWA. The type of river defines the objectives for each stretch. However, they do not coincide with the reaches that need to be defined in order to properly account for all the water uses, inputs and outputs along the river. In the basic application example presented in Chapter 5, the reaches have been correctly laid down. It was possible in that theoretical illustration, but it is not the real usual case.

In the same way, the quality objective definition for each river reach in each river type is a key starting point for the PH methodology. Those values are directly taken from the competent legal organism in each hydrologic unit. From the experience with the considered values in this PhD thesis, it can be concluded that some additional detail in those parameters definition would considerably help for the completeness of the PH results.

Both of the rivers studied in this dissertation presented a dam within the watershed and they have been indirectly included in the analyses as input-output flow. However, a more detailed investigation would be needed to completely asses the exergy description of reservoirs. Some simulation softwares, as for example the Aquatool, allow the definition of different reservoir types, even adding the analysis of a feasible stratification process. A similar situation happens with the aquifers, which can also typify in simulators such as the mentioned Aquatool. The infiltration along the river is included in the simulation, but the interface with those deep waters is not described by the simulator. The exchange with the atmosphere is also included in the software.

Simulation software management is obviously a very important tool for the PH application. In addition to the Qual2k software, some other available programs could help to introduce the whole water system in the study, including the aquifers. In this sense, a new project regarding the Ebro river is being develop in our research group, where the simulation software used by the Spanish Environment Ministry, Aquatool (SIMGES+GESCAL), is going to be applied. In spite of the mentioned weakness of the software in relation to the provided quality parameters, it was decided to use it to facilitate the data exchange with the involved public organisms. Moreover, groundwaters will be included in the simulation by means of an additional module.

The amount of water uses included in the analysis, as well as their quantity and quality characterization, could be extended if more detailed information were available: the more detailed information, the more accurate results. Of special importance is getting accurate values of the quality in the return coefficients flows. The lack of this information means always an additional uncertainty in the results, since the additional load coming from the different water uses have to be estimated from literature or extrapolated from similar, close, known sources. In fact, there are several uncertainty factors: along the PH process, it was dealt with those return factors, but also with the exergy degradation produced by each use (salinity change depending on the industry, losses in the pipes networks…). It is usually not well defined and external values have to be introduced in the analysis.

Moreover, the dangerous substances described in the legislation are hardly includable in the PH at its current state. Because of its high relevance in the achievement of the objective state of waters, this aspect needs to be present. However, the convenience or not of including those substances in exergy terms has to be valuated. In any case, its abatement exergy cost, not only its exergy, should be included.

A deeper exergy analysis of the water treatment plants can lead to an adjustment of the presented unit exergy cost. The unit exergy cost for desalination could be improved if an exergy analysis is carried out for the desalination plants located in the area, instead as average plants by technology. For the depuration utilities, the unit exergy cost could be improved if more real data were available. In addition, the operation and maintenance cost should be better included if complete information about labor, reactives and other chemical compounds, taxes and fuels, among others, were reported. That is, carrying out the life cycle costing of each treatment plant.

The connexion between the physical and the economic aspects of the river waters need to be wider developed in order to include as much information as possible. In this dissertation, two different aspects were covered in the wayfrom the physical cost to the economic cost. Firstly, the exergy cost was multiplied by the energy price and, in this way, the operation cost were obtained. Secondly, the investment costs of those plants needed to restore the water degradation were added by introducing the average cost per capacity unit. This analysis could be improved if maintenance costs were added and also if the specific size of each plant were detailed, since they can vary in a wide range. In addition to that, its is clear that a more disaggregated and complete information about the different costs would lead to more accurate results.

Water management, what is called non-technical measurements, is called to play a relevant role in the future. If less water is spent, the replacement cost will be lower. The cost of such measurements could also be calculated by PH. The river profiles would be defined by the variation in the consumed water resource. The underlying idea is that the environmental costs must be minimized in any considered point, always looking for the costs equilibrium. For instance, it would have no sense to propose a highly energy demanded desalination in an area where the water extraction from an aquifer is feasible.

The definition of a Measurements Planning (MP) is a requirement of the WFD. Once the PH methodological background has been established, the definition of a MP can be proposed. In this dissertation, only global restoration measures were included with an average medium hypothetical WWTPs to restore and SWPPs to produce the water. In order to really restore the watersheds degradation, a detailed Plan would be needed, detailing location, size and other main features of the plants. But the optimization of such MP would be really complicated. Plans such as the PSARU in Catalonia should be taken as starting reference. Then, the real picture of the MP applied in each watershed can be realistically made. Some studies in this direction are being carried out by the CWA in collaboration with the Polythecnical University of Madrid by applying a specific multicriteria analysis.

The rivers considered in this work can be framed as one of the most difficult rivers to work with because they are characterized as Mediterranean rivers, with important variations along the year and a strong human pressure. Since the PH has been proved to be able to deal with them, it should not be complicated to extend the methodology to any European river. It could constitute a comprehensive European project, where experts of many different fields should collaborate: from the biologists and ecologists defining the objective states, to the economists detailing the financial issues to be included, going through the hydrologists, physicists and engineers for the PH application and the measures plan definition.

The Emergy approach, although briefly brought to this dissertation, presents an interesting added value because of the possibility of including biological aspects in the analysis (if the amount and transformities of plants and fishes were introduced), as well as the chance of accounting for the aquifers if the whole watershed were represented as an only system. Additional studies are currently being developed in that way, in collaboration with the Center for Environmental Policy of the University of Florida.

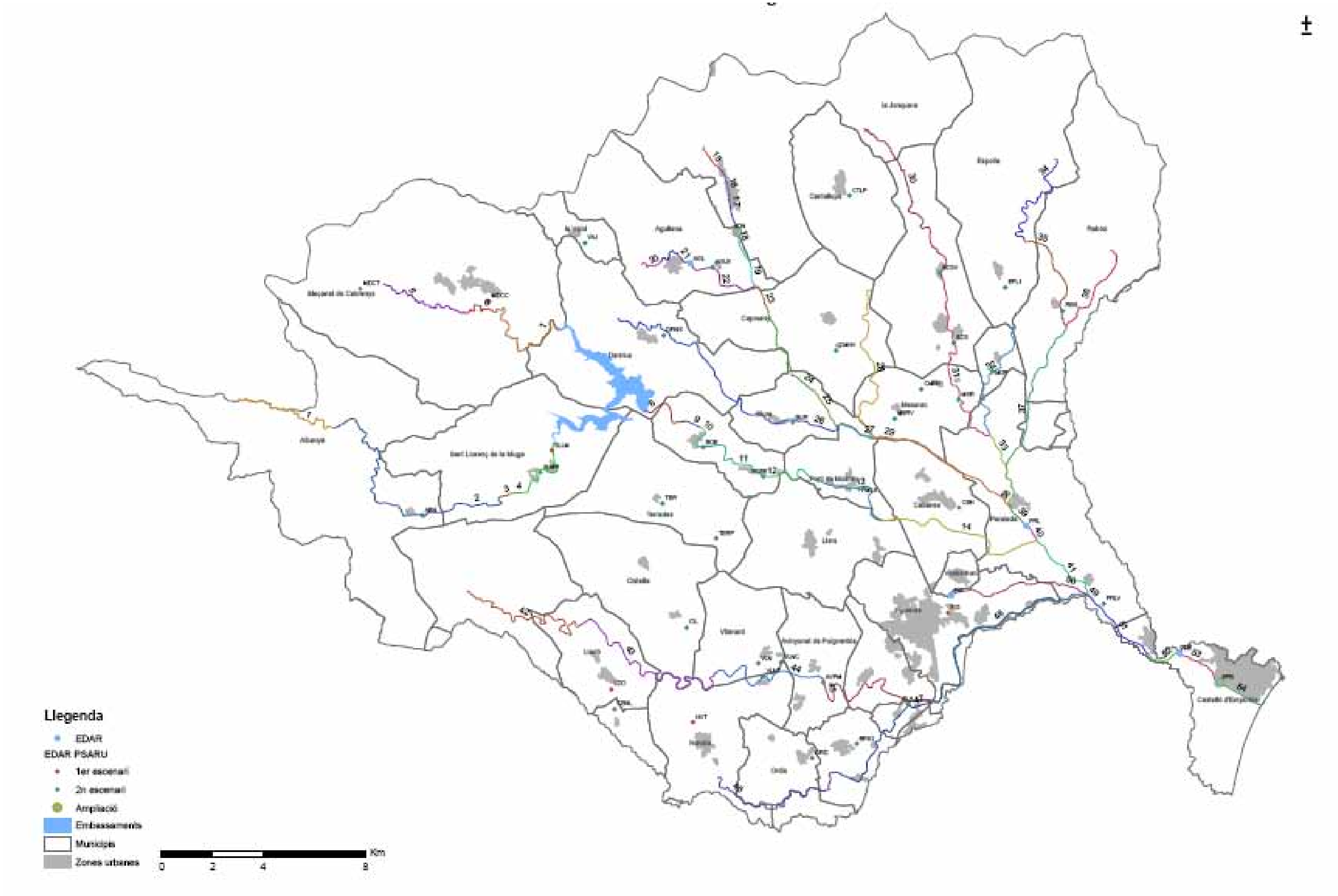
The final reflexion would be that for every country, no matter its economic position, the environmentally sustainable development and management of water resources has become a critical and complex issue. It is technically challenging and often entails difficult trade-offs among social, economic, and political considerations. Typically, the environment is treated as a marginal issue when it is actually crucial for a sustainable water management. PH fulfils the opportunity provided by the WFD in relation to water values and resources assessment.

Annex A

Results

Many calculations have been explained in the text, but only some graphs has been included. This annex presents the value for additional months.

A.1. Muga map


Llegenda
EDAR
EDAR PSARU
1er escenari
2n escenari
Ampliació
Embassaments
Municipis
Zones urbanes
Km
0
2
4
8

A.2. Flows in the Muga river

The different flow regimes (real state, maintenance and natural state) in the main headwater of the Muga river are presented (for any month) in this Annex D. This section increase the information given in Chapter 6, where only one of the graphs (January), was included.

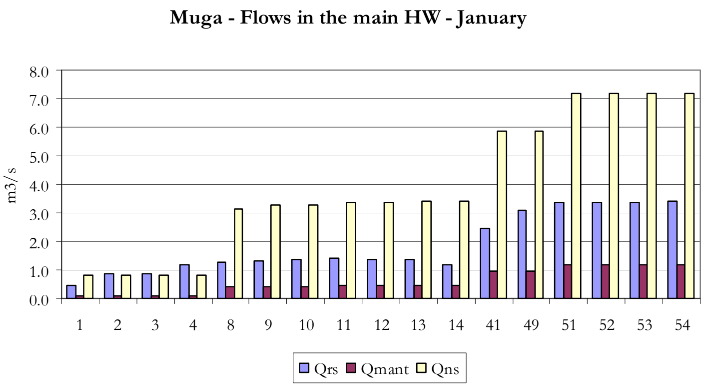

Muga - Flows in the main HW - January

Figure A.1. Flows (real, maintenance and natural) in the main course of the Muga river (January)

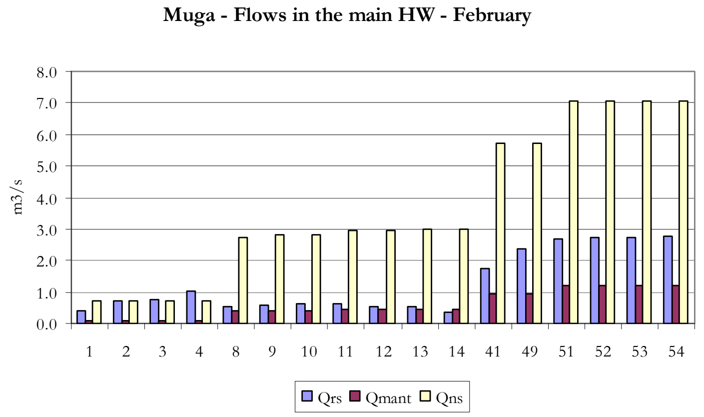

Muga - Flows in the main HW - February

Figure A.2. Flows (real, maintenance and natural) in the main course of the Muga river (February)

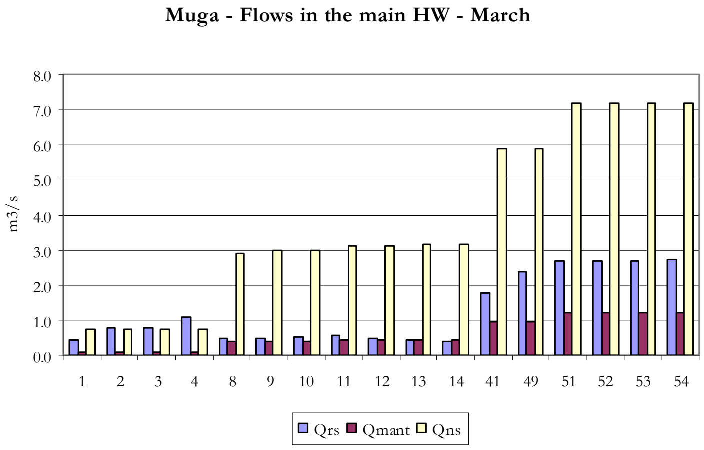

Muga - Flows in the main HW - March

Figure A.3. Flows (real, maintenance and natural) in the main course of the Muga river (March)

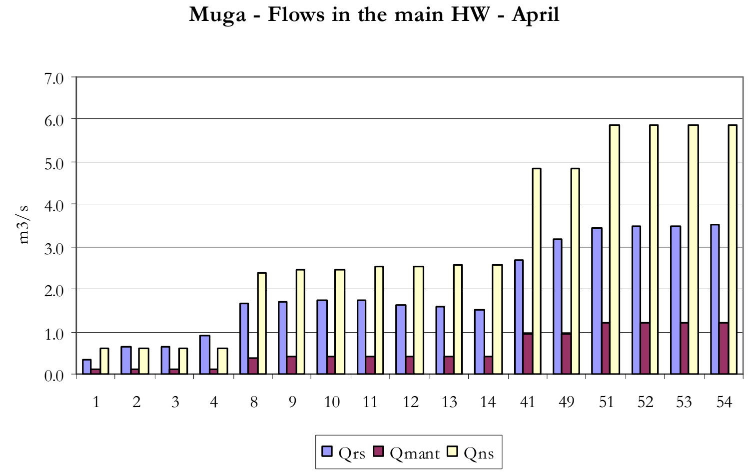


Figure A.4. Flows (real, maintenance and natural) in the main course of the Muga river (April)

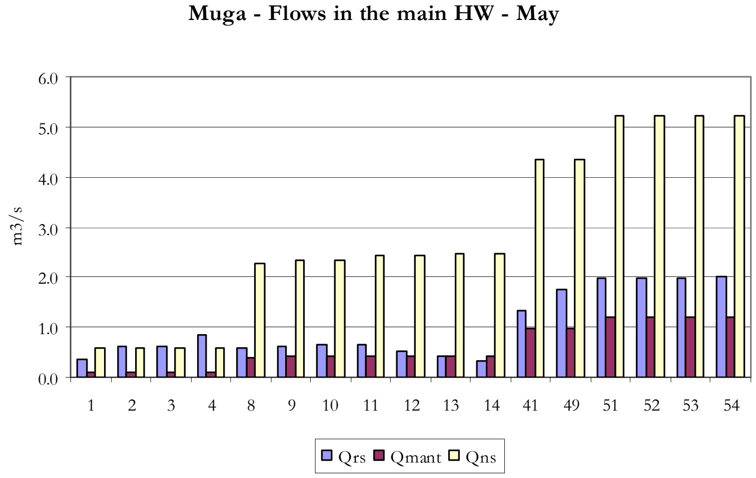


Figure A.5. Flows (real, maintenance and natural) in the main course of the Muga river (May)

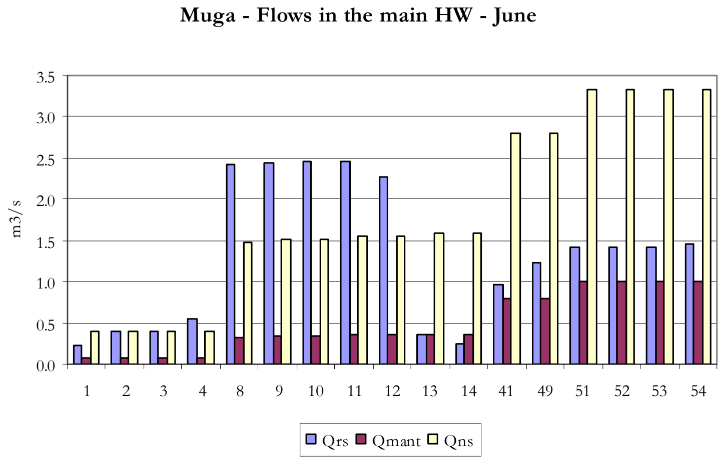


Figure A.6. Flows (real, maintenance and natural) in the main course of the Muga river (June)

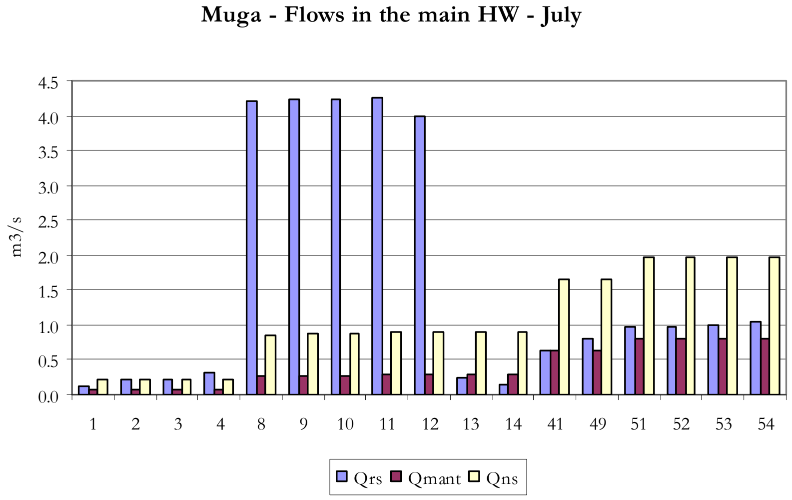


Figure A.7. Flows (real, maintenance and natural) in the main course of the Muga river (July)

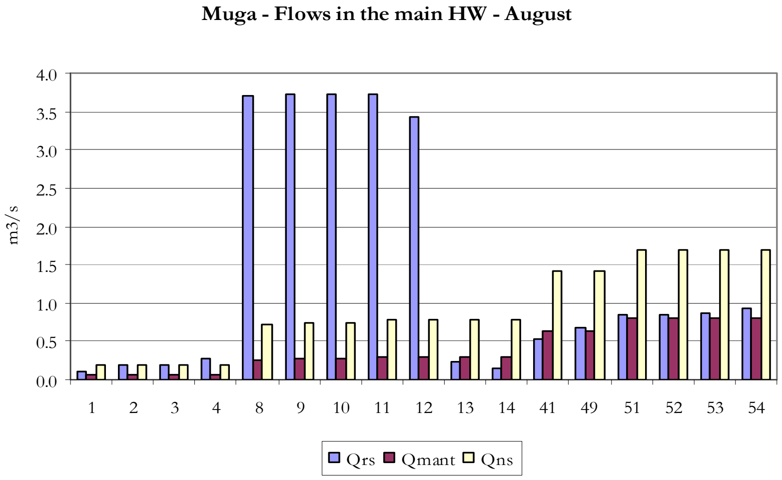


Figure A.8. Flows (real, maintenance and natural) in the main course of the Muga river (August)

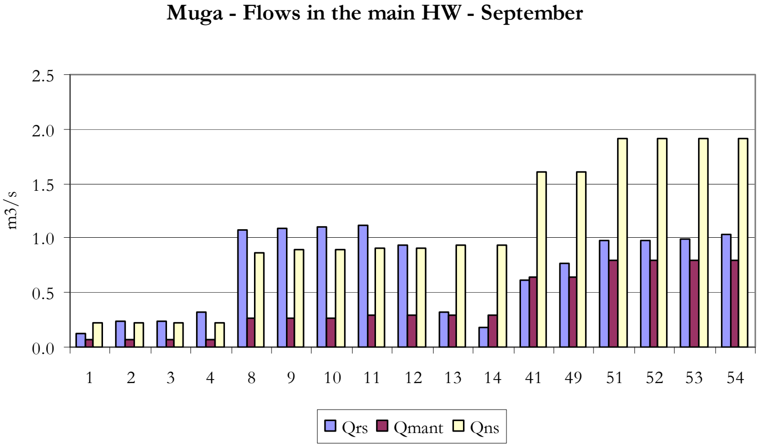


Figure A.9. Flows (real, maintenance and natural) in the main course of the Muga river (September)

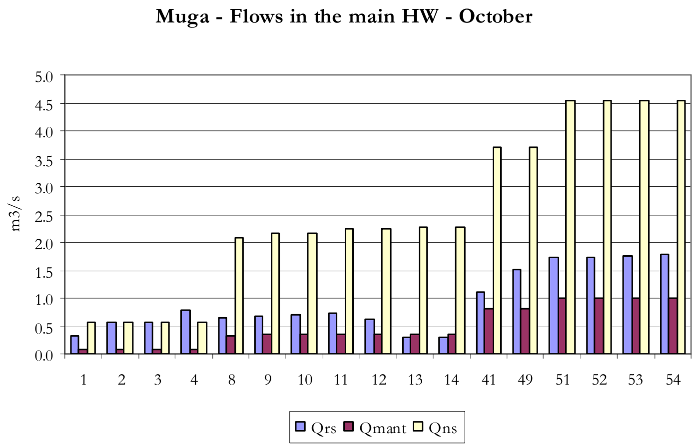


Figure A.10.Flows (real, maintenance and natural) in the main course of the Muga river (October)

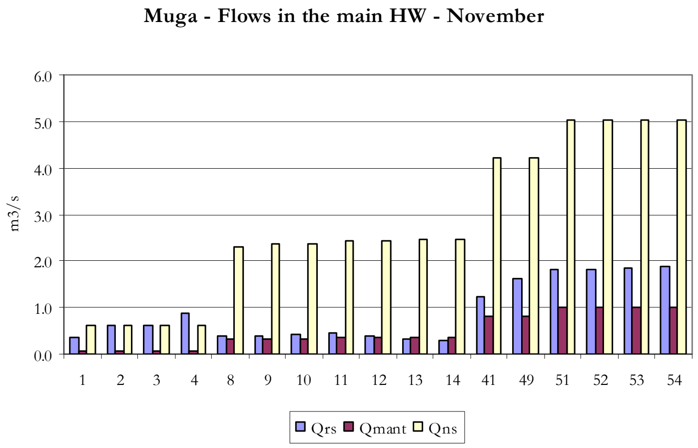


Figure A.11.Flows (real, maintenance and natural) in the main course of the Muga river (November)

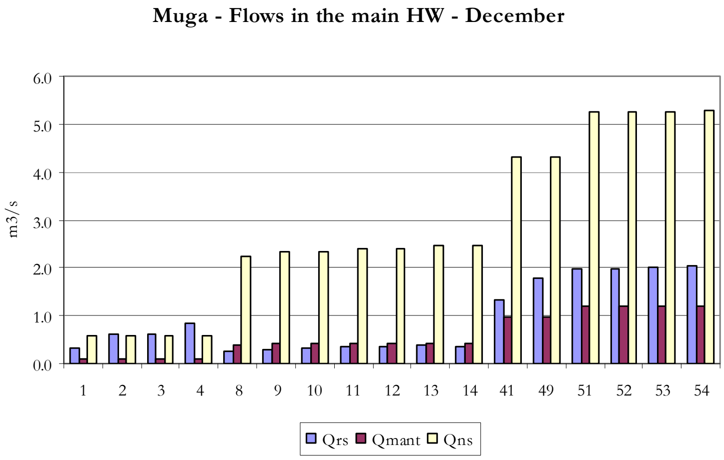


Figure A.12.Flows (real, maintenance and natural) in the main course of the Muga river (December)

A.3. Global exergy value of the Muga watershed

The detailed values of the exergy in the Muga river are given in Table A.1. A summary of these results was provided in Chapter 6.

Bpot (MW)

	ene	feb	mar	abr	may	jun	jul	ago	sep	oct	nov	dic
PS	7.15	5.88	6.00	6.35	4.73	4.30	4.22	3.68	2.37	4.25	4.48	4.52
FS	7.13	5.92	5.99	6.33	4.71	5.27	4.24	3.69	2.34	4.26	4.46	4.51
ES	7.15	5.88	6.00	6.35	4.73	4.30	4.22	3.68	2.37	4.25	4.48	4.52
OS	7.16	5.94	6.03	6.35	4.76	5.33	4.34	3.85	2.44	4.32	4.51	4.63
NS	8.05	7.26	7.51	7.06	6.10	5.69	4.55	3.99	2.64	5.07	5.56	5.67

B_IM (MW)

	ene	feb	mar	abr	may	jun	jul	ago	sep	oct	nov	dic
PS	8.489	6.836	6.803	8.784	5.044	3.622	2.606	2.299	2.570	4.454	4.648	5.065
FS	8.542	7.025	6.873	8.815	5.055	8.871	2.690	2.346	2.559	4.549	4.681	5.107
ES	8.485	6.832	6.800	8.781	5.042	3.618	2.600	2.285	2.565	4.453	4.646	5.063
OS	8.514	6.993	6.838	8.785	5.022	8.853	2.707	2.356	2.558	4.532	4.659	5.085
NS	8.589	7.681	7.815	8.850	6.406	8.906	2.731	2.382	2.591	4.959	5.492	5.747

B_OM (MW)

	ene	feb	mar	abr	may	jun	jul	ago	sep	oct	nov	dic
PS	0.12	0.12	0.12	0.14	0.10	0.08	0.08	0.07	0.07	0.10	0.09	0.08
FS	0.14	0.14	0.14	0.16	0.12	0.15	0.09	0.08	0.09	0.13	0.11	0.10
ES	0.92	1.15	1.03	0.95	0.78	0.69	0.68	0.64	0.76	0.74	0.67	0.64
OS	0.74	0.61	0.60	0.76	0.44	0.77	0.24	0.21	0.22	0.40	0.41	0.44
NS	0.44	0.40	0.40	0.46	0.33	0.46	0.14	0.12	0.13	0.26	0.28	0.30

Table A.1. Global exergy values of the Muga river, by exergy components, for each month

A.4. Exergy profiles for the Muga River

The river profiles in January have been reproduced in section 6.4.3. Those profiles have been elaborated for each month. Here, the graphs for March, July and September are given.

A.4.1. Exergy profile of the PS in the Muga river

A.4.1.1. March

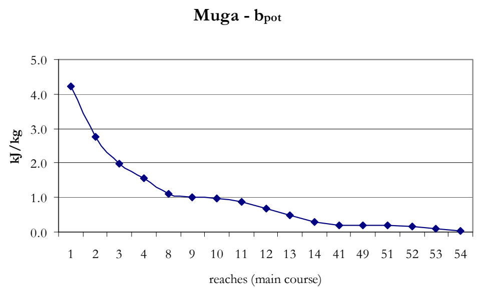


Figure A.13. Specific exergy profile of the potential component (March)

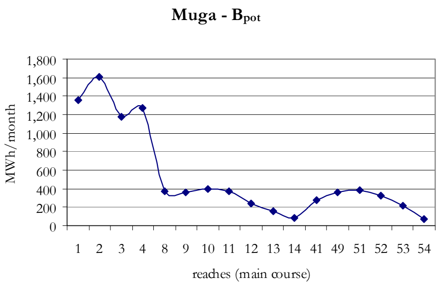


Figure A.14. Exergy profile of the potential component (March)

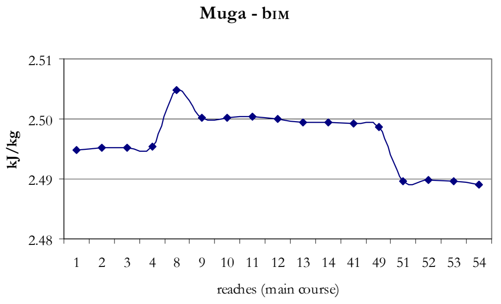


Figure A.15. Specific exergy profile of the IM chemical component (March)

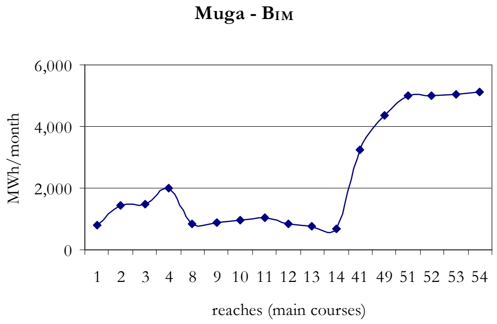


Figure A.16. Exergy profile of the IM chemical component (March)

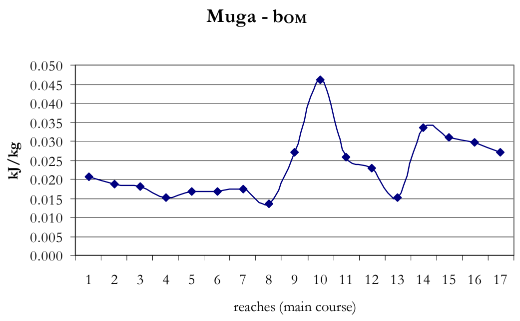


Figure A.17. Specific exergy profile of the OM chemical component (March)

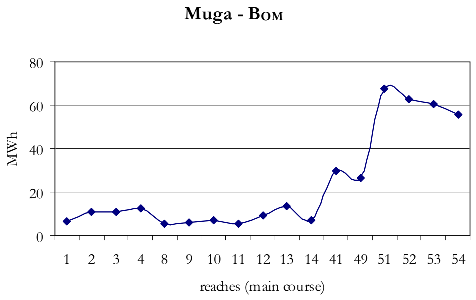


Figure A.18. Exergy profile of the OM chemical component (March)

A.4.1.2. July

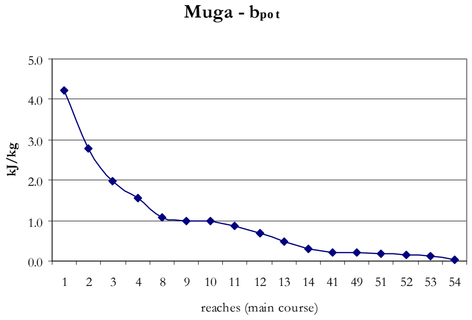


Figure A.19. Specific exergy profile of the potential component (July)

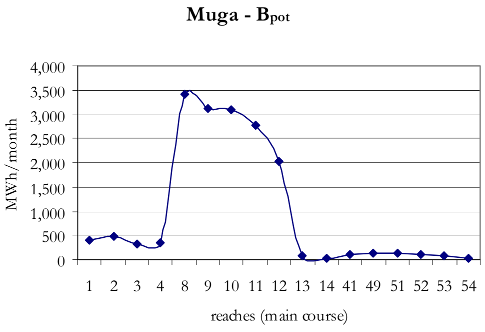


Figure A.20. Exergy profile of the potential component (July)

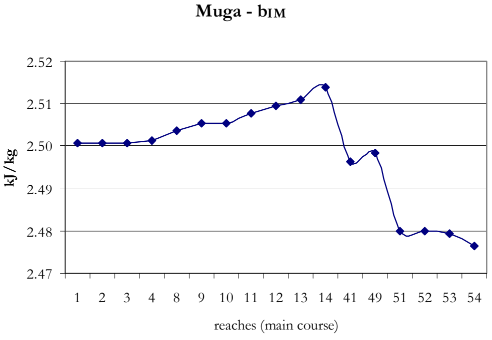


Figure A.21. Specific exergy profile of the IM chemical component (July)

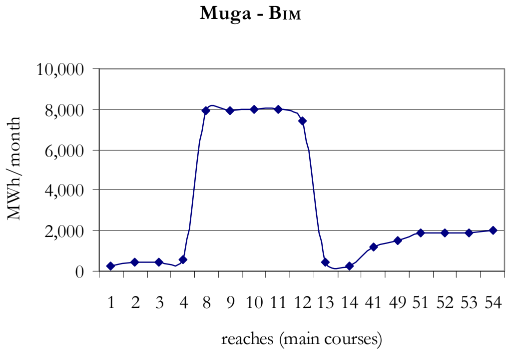


Figure A.22. Exergy profile of the IM chemical component (July)

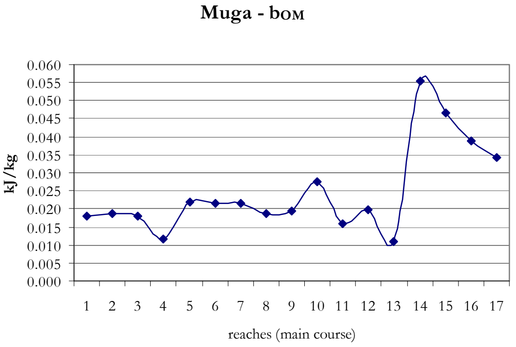


Figure A.23. Specific exergy profile of the OM chemical component (July)

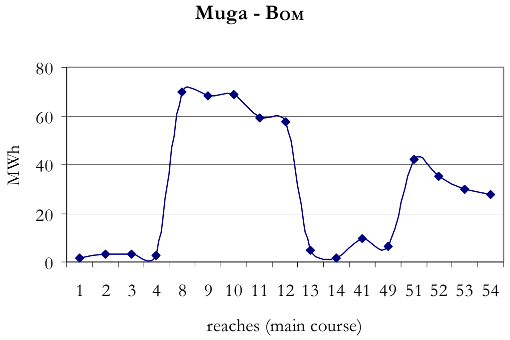


Figure A.24. Exergy profile of the OM chemical component (July)

A.4.1.3. September

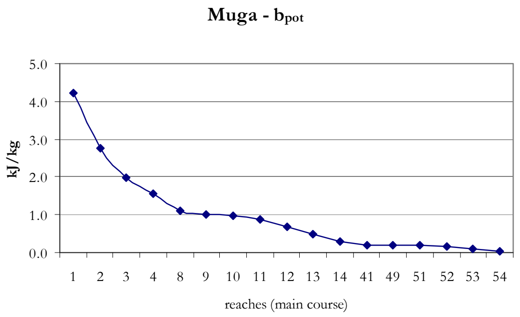


Figure A.25. Specific exergy profile of the potential component (September)

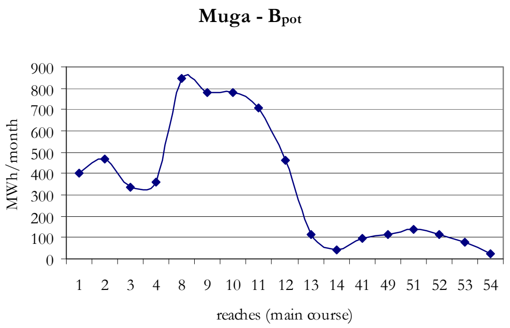


Figure A.26. Exergy profile of the potential component (September)

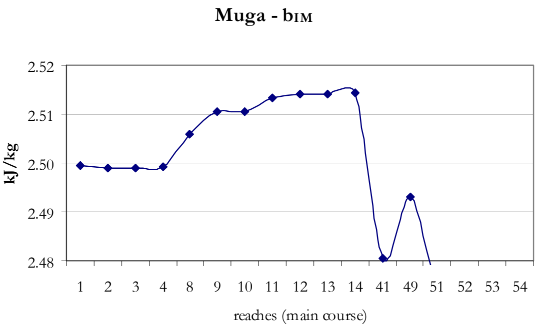


Figure A.27. Specific exergy profile of the IM chemical component (September)

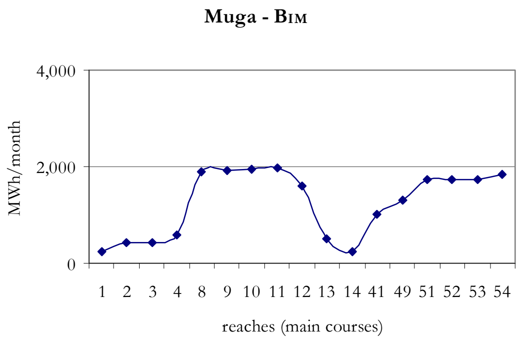


Figure A.28. Exergy profile of the IM chemical component (September)

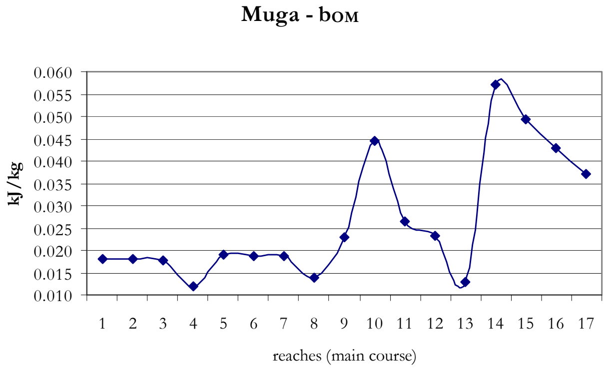


Figure A.29. Specific exergy profile of the OM chemical component (September)

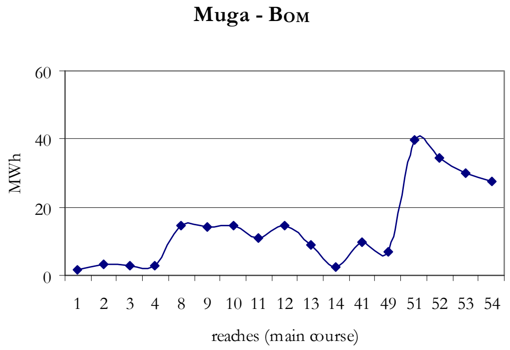


Figure A.30. Exergy profile of the OM chemical component (September)

A.4.2. Exergy profiles (PS, ES and OS) in the Muga river

A.4.2.1. March

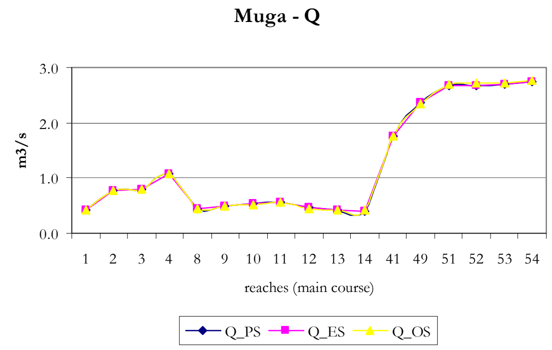


Figure A.31. Flows in the PS, ES and OS in the Muga river in March

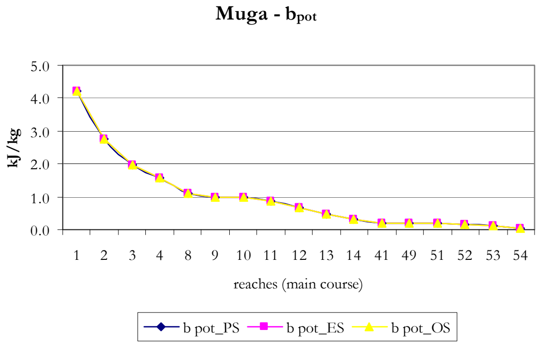


Figure A.32. Specific exergy profile of the potential component in the Muga river in March

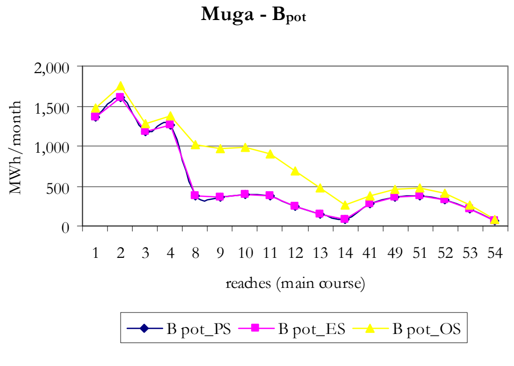


Figure A.33. Exergy profile of the potential component in the Muga river in March

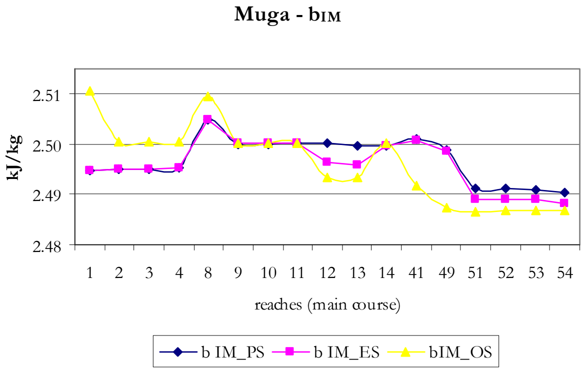


Figure A.34. Specific exergy profile of the IM chemical component in the Muga river in March

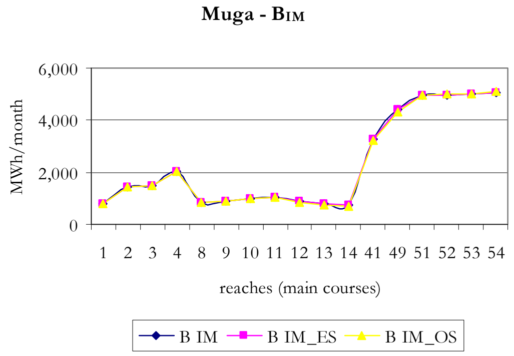


Figure A.35. Exergy profile of the IM chemical component in the Muga river in March

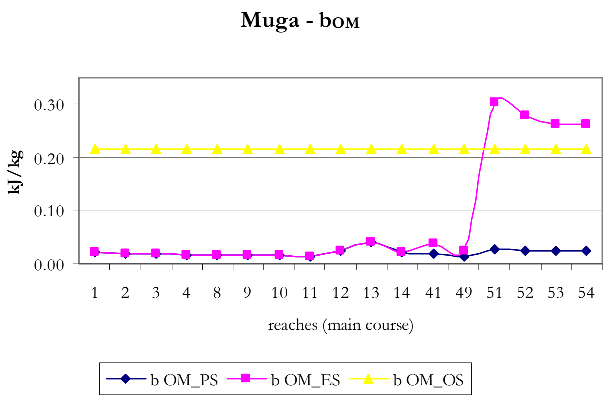


Figure A.36. Specific exergy profile of the OM chemical component in the Muga river in March

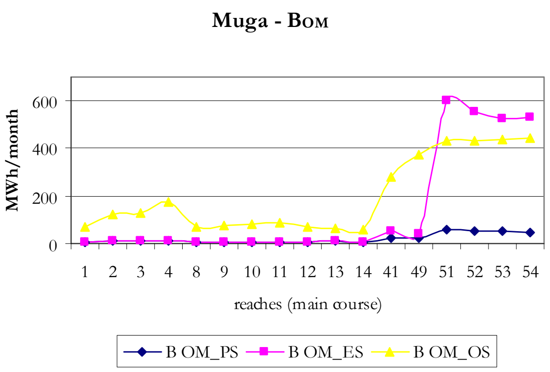


Figure A.37. Exergy profile of the OM chemical component in the Muga river in March

A.4.2.2. July

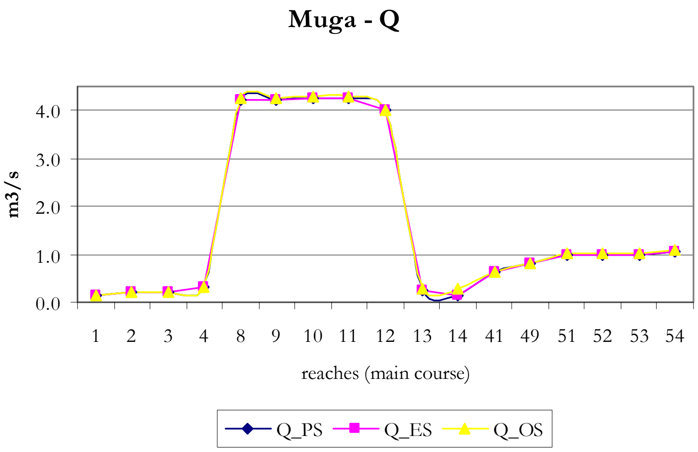


Figure A.38. Flows in the PS, ES and OS in the Muga river in July

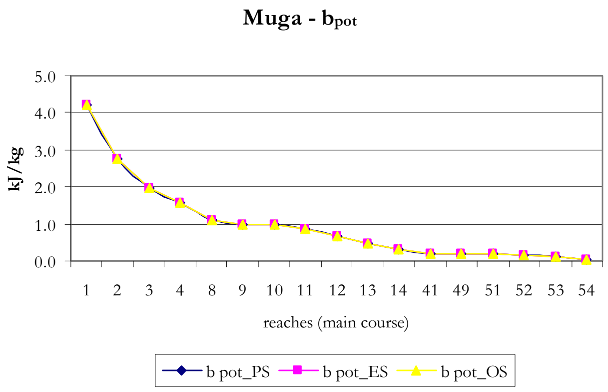


Figure A.39. Specific exergy profile of the potential component in the Muga river in July

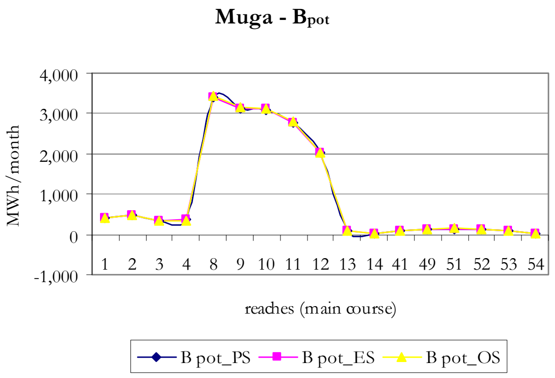


Figure A.40. Exergy profile of the potential component in the Muga river in July

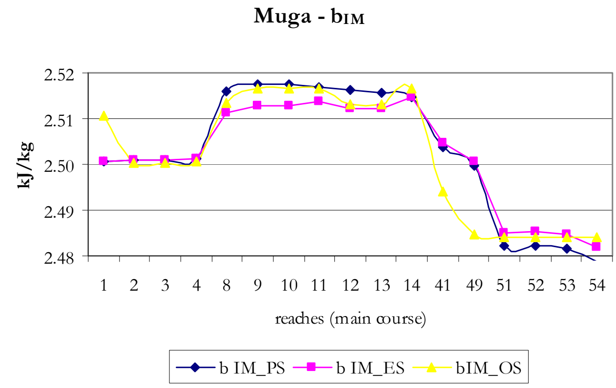


Figure A.41. Specific exergy profile of the IM chemical component in the Muga river in July

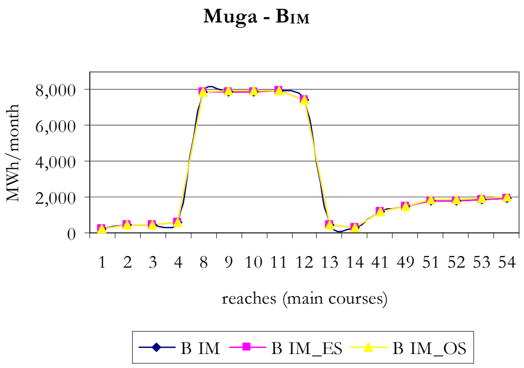


Figure A.42. Exergy profile of the IM chemical component in the Muga river in July

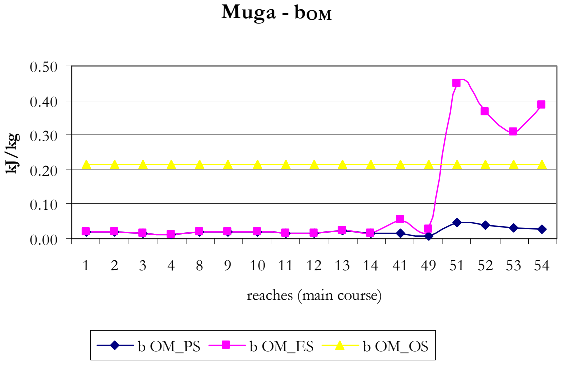


Figure A.43. Specific exergy profile of the OM chemical component in the Muga river in July

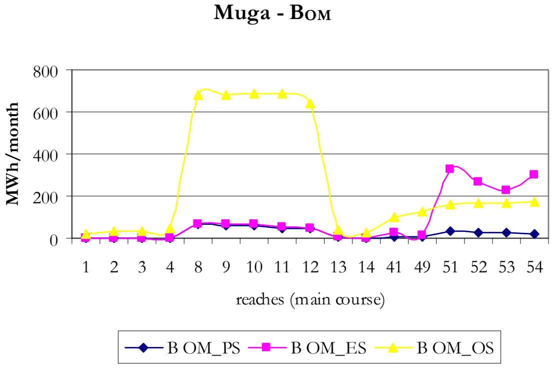


Figure A.44. Exergy profile of the OM chemical component in the Muga river in July

A.4.2.3. September

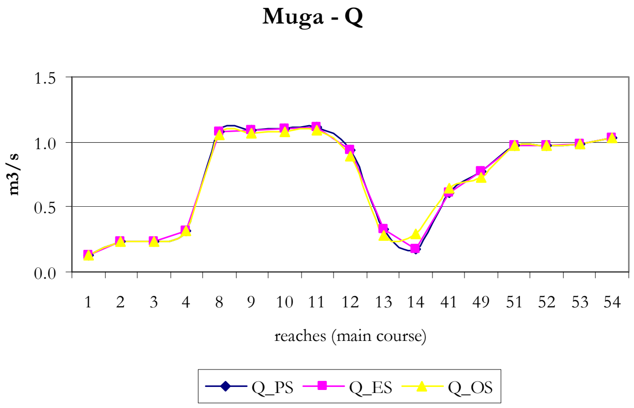


Figure A.45. Flows in the PS, ES and OS in the Muga river in September

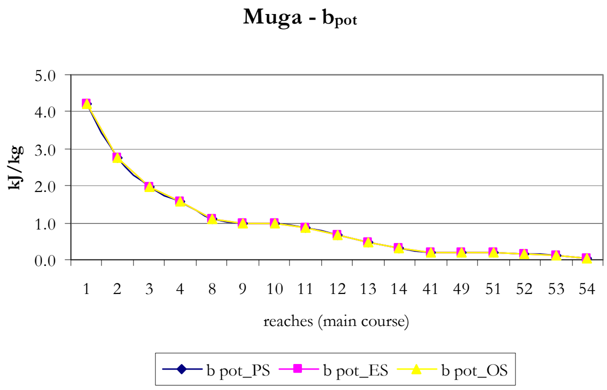


Figure A.46. Specific exergy profile of the potential component in the Muga river in September

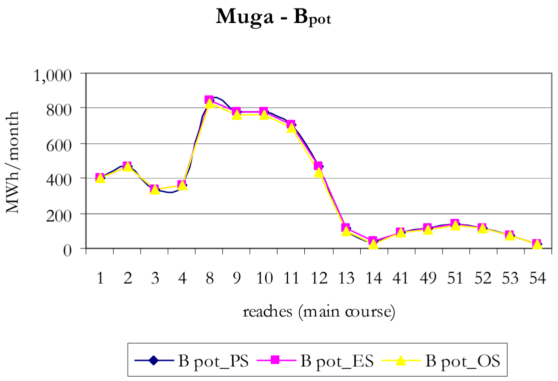


Figure A.47. Exergy profile of the potential component in the Muga river in September

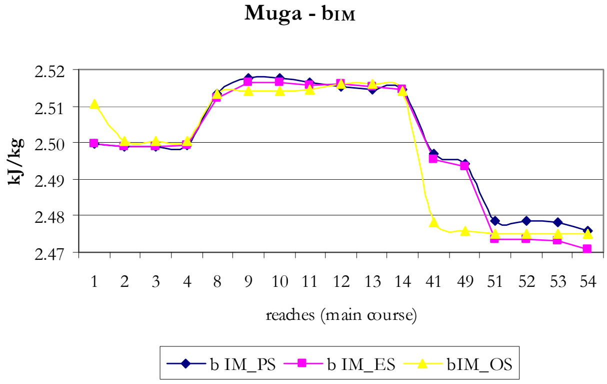


Figure A.48. Specific exergy profile of the IM chemical component in the Muga river in September

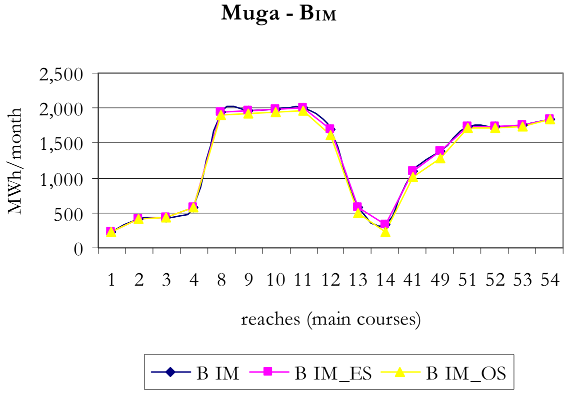


Figure A.49. Exergy profile of the IM chemical component in the Muga river in September

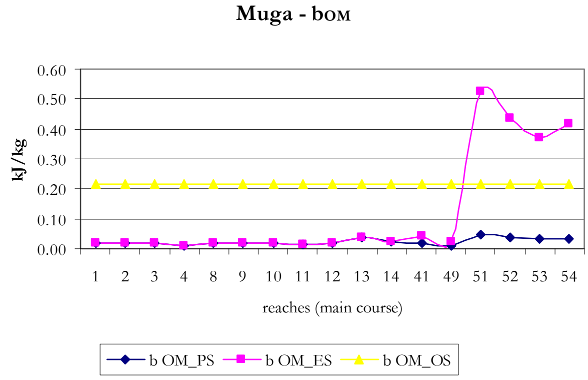


Figure A.50. Specific exergy profile of the OM chemical component in the Muga river in September

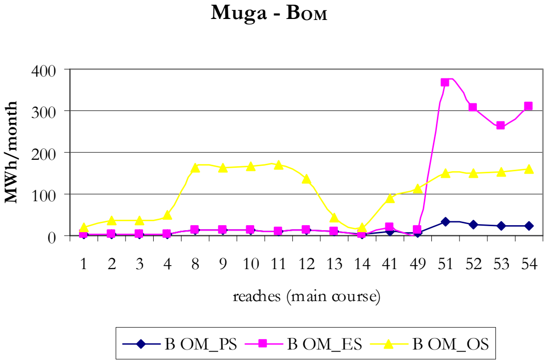
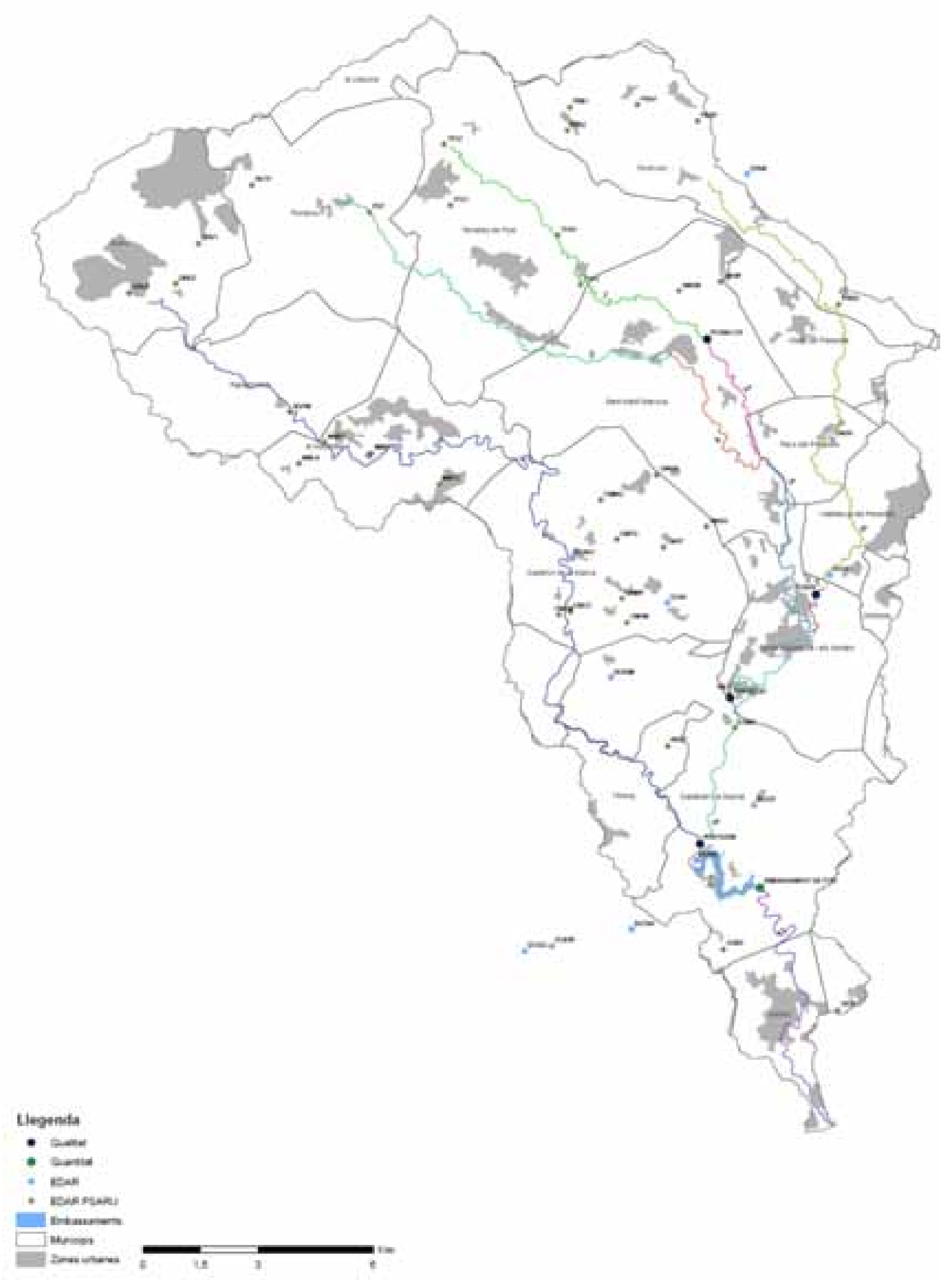


Figure A.51. Exergy profile of the OM chemical component in the Muga river in September

A.5. Foix map


Llegenda
Qualitat
Quantitat
EDAR
EDAR PSARU
Embassaments
Municipis
Zones urbanes
0
1,5
3
6
Km

A.6. Flows in the Foix river

The different flow regimes (real state, maintenance and natural state) in the main headwater of the Foix river are presented (for any month) in this Annex D. This section increase the information given in Chapter 6, where only one of the graphs (January), was included.

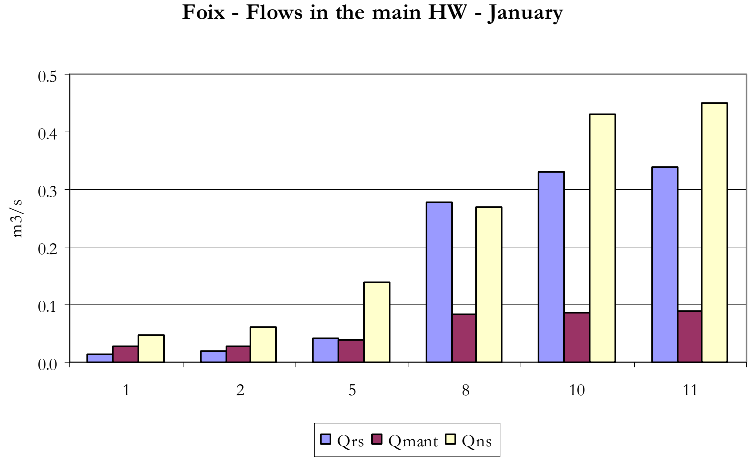


Figure A.52.Flows (real, maintenance and natural) in the main course of the Foix river (January)

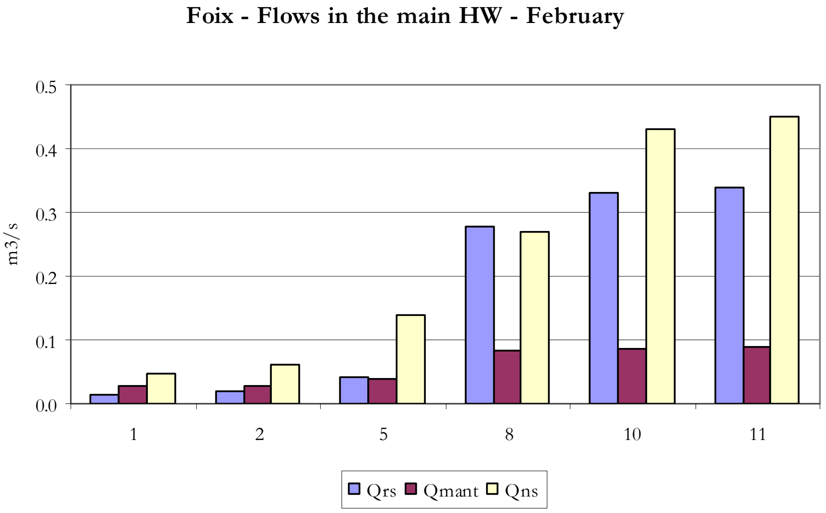


Figure A.53.Flows (real, maintenance and natural) in the main course of the Foix river (February)

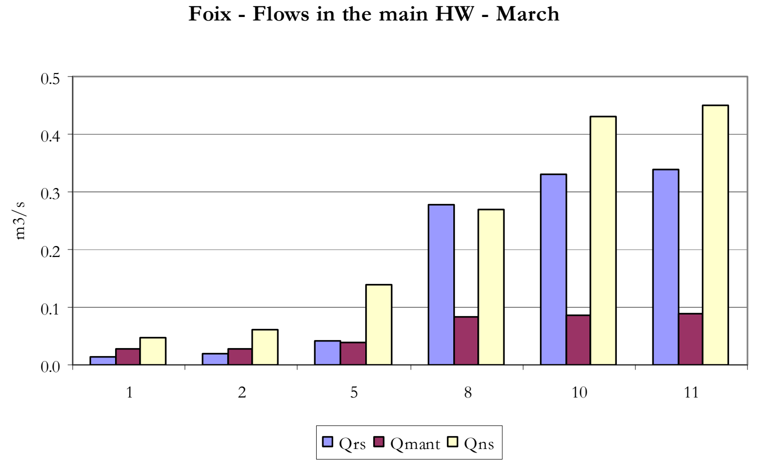


Figure A.54.Flows (real, maintenance and natural) in the main course of the Foix river (March)

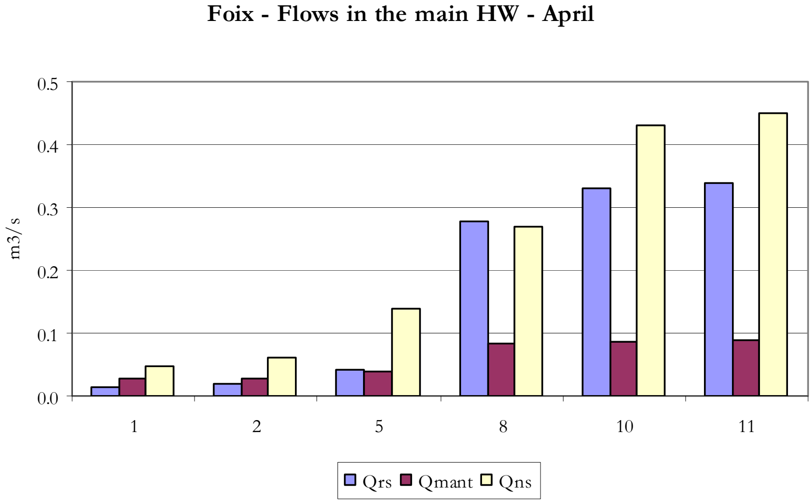


Figure A.55.Flows (real, maintenance and natural) in the main course of the Foix river (April)

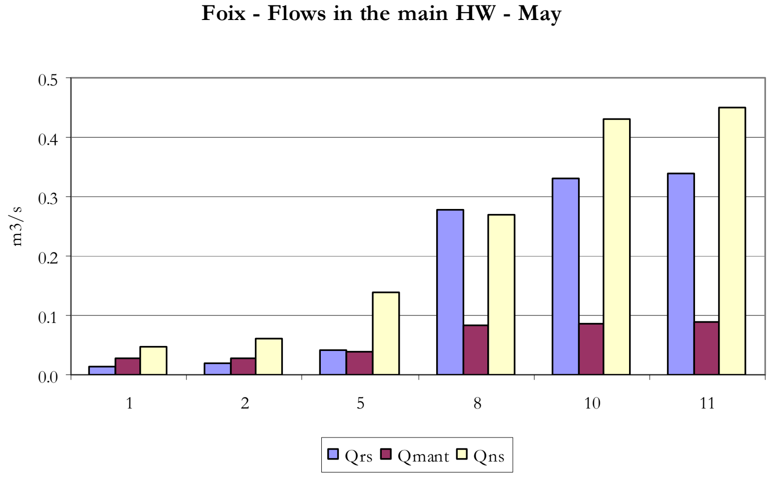


Figure A.56. Flows (real, maintenance and natural) in the main course of the Foix river (May)

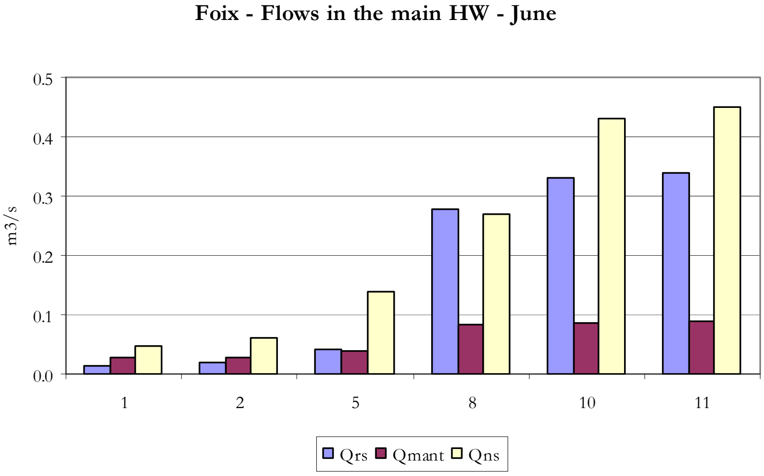


Figure A.57. Flows (real, maintenance and natural) in the main course of the Foix river (June)

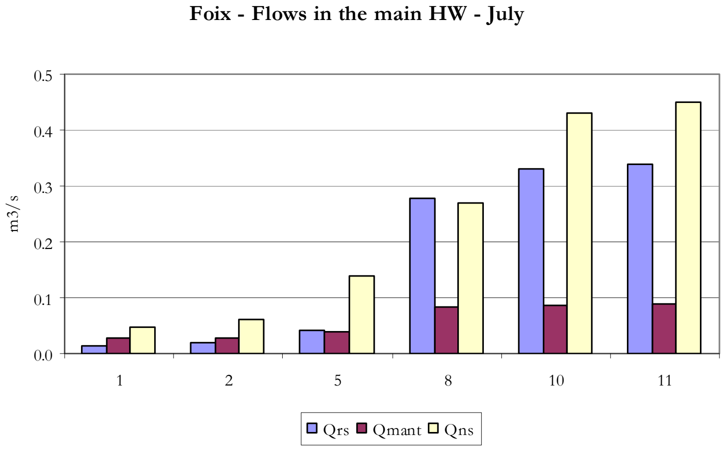


Figure A.58.Flows (real, maintenance and natural) in the main course of the Foix river (July)

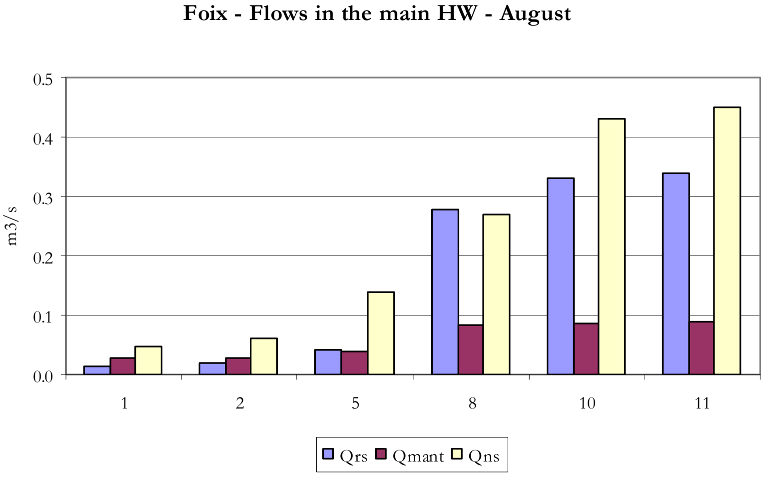


Figure A.59.Flows (real, maintenance and natural) in the main course of the Foix river (August)

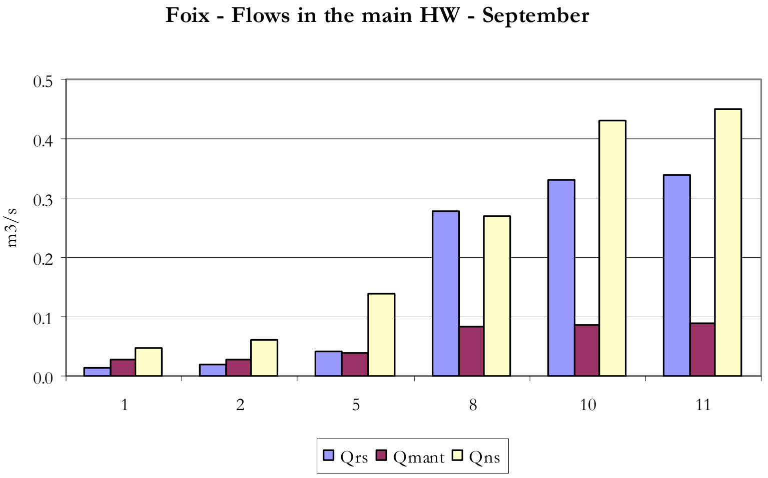


Figure A.60.Flows (real, maintenance and natural) in the main course of the Foix river (September)

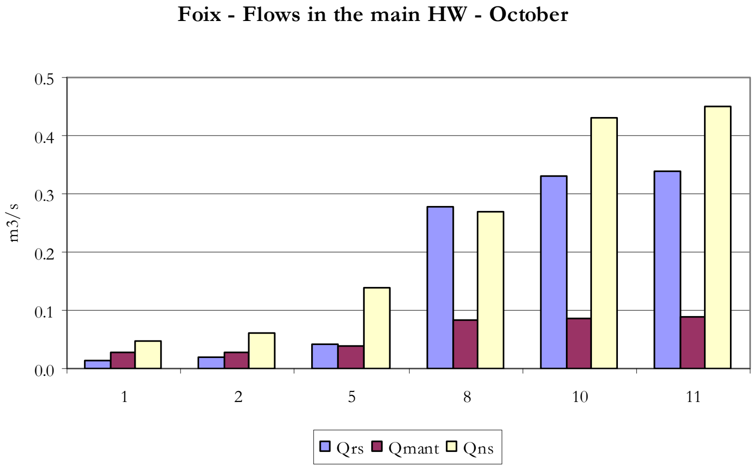


Figure A.61.Flows (real, maintenance and natural) in the main course of the Foix river (October)

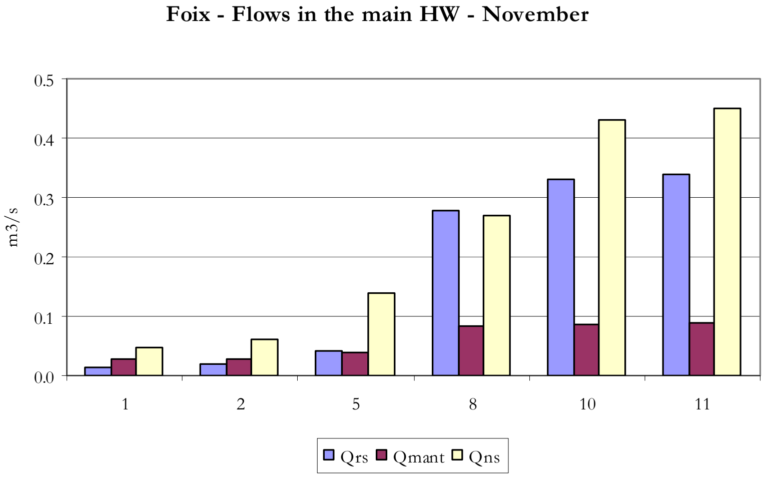


Figure A.62.Flows (real, maintenance and natural) in the main course of the Foix river (November)

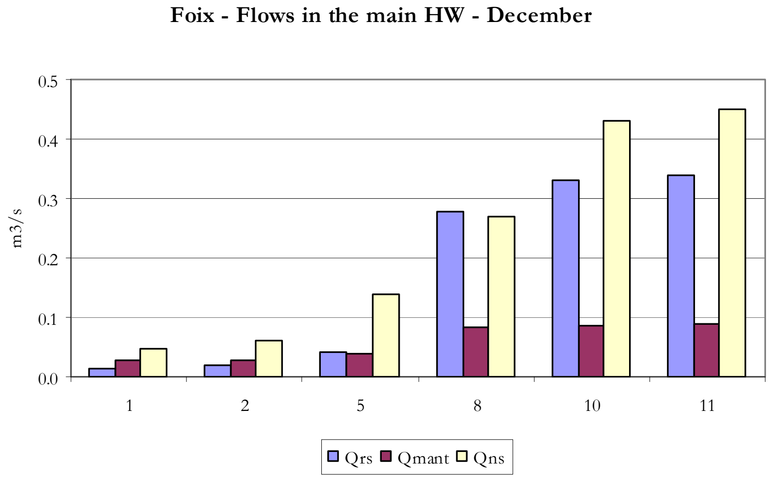


Figure A.63.Flows (real, maintenance and natural) in the main course of the Foix river (December)

A.7. Global exergy value of the Foix watershed

The detailed values of the exergy in the Foix river are given in Table A.2. A summary of these results was provided in Chapter 6.

Bpot (MW)

	ene	feb	mar	abr	may	jun	jul	ago	sep	oct	nov	dic
PS	0.86	0.89	1.11	0.98	0.92	0.73	0.51	0.58	0.64	0.81	0.03	0.99
FS	0.94	0.99	1.20	1.37	1.00	0.82	0.59	0.66	0.73	0.90	0.04	1.08
ES	0.86	0.89	1.11	0.98	0.92	0.73	0.51	0.58	0.64	0.81	0.22	0.99
OS	1.00	1.05	1.30	1.48	1.12	1.00	0.88	0.93	0.92	1.05	0.05	1.20
NS	1.45	1.49	2.11	2.09	1.78	1.22	0.88	0.93	1.16	1.17	0.04	1.82

B_IM (MW)

	ene	feb	mar	abr	may	jun	jul	ago	sep	oct	nov	dic
PS	0.82	0.82	0.72	0.55	0.52	0.40	0.27	0.43	0.18	0.41	0.54	0.65
FS	0.90	0.92	0.78	0.89	0.58	0.46	0.32	0.48	0.25	0.47	0.60	0.71
ES	0.82	0.82	0.71	0.54	0.52	0.40	0.27	0.43	0.18	0.41	0.54	0.64
OS	0.91	0.93	0.80	0.91	0.59	0.47	0.33	0.49	0.25	0.48	0.61	0.72
NS	1.11	1.11	1.12	0.97	0.90	0.51	0.34	0.50	0.46	0.73	0.68	0.92

B_OM (MW)

	ene	feb	mar	abr	may	jun	jul	ago	sep	oct	nov	dic
PS	0.03	0.05	0.04	0.03	0.05	0.04	0.04	0.03	0.02	0.02	0.03	0.03
FS	0.12	0.23	0.07	0.09	0.04	0.03	0.05	0.04	0.03	0.04	0.04	0.03
ES	0.35	0.39	0.25	0.23	0.24	0.23	0.18	0.19	0.21	0.21	0.22	0.25
OS	0.08	0.08	0.07	0.08	0.05	0.04	0.03	0.04	0.02	0.04	0.05	0.06
NS	0.06	0.06	0.06	0.05	0.05	0.03	0.02	0.03	0.02	0.04	0.04	0.05

Table A.2. Global exergy values of the Foix river, by exergy components, for each month

A.8. Exergy profiles for the Foix River

The river profiles in January have been reproduced in section 6.5.4. Those profiles have been elaborated for each month. Here, the graphs for March, July and September are given.

A.8.1. Exergy profile of the PS in the Foix River

A.8.1.1. March

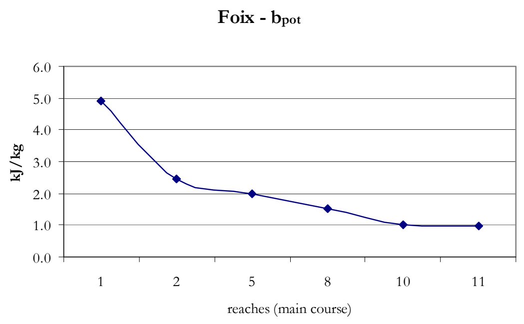


Figure A.64. Specific exergy profile of the potential component (March)

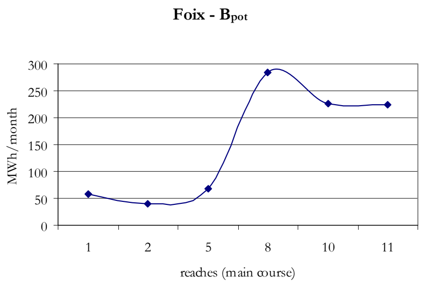


Figure A.65. Exergy profile of the potential component (March)

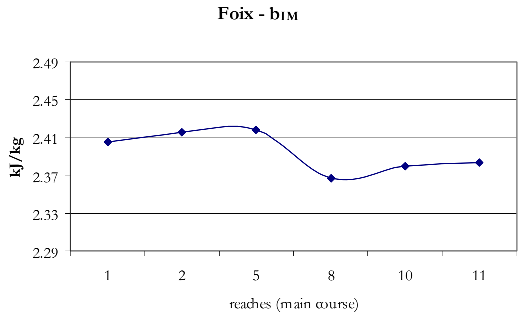


Figure A.66. Specific exergy profile of the IM chemical component (March)

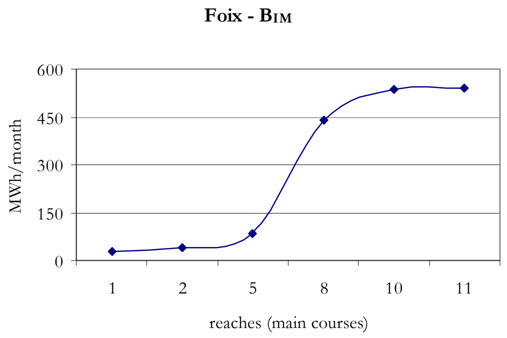


Figure A.67. Exergy profile of the IM chemical component (March)

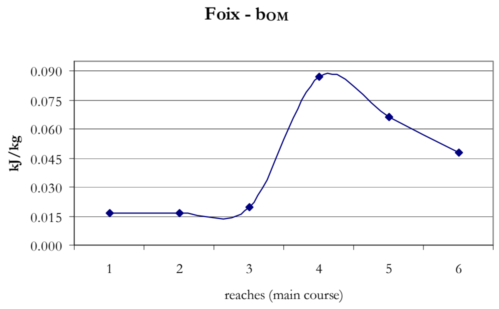


Figure A.68. Specific exergy profile of the OM chemical component (March)

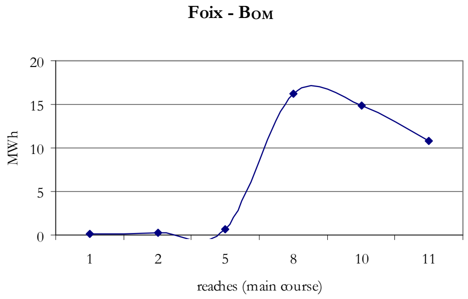
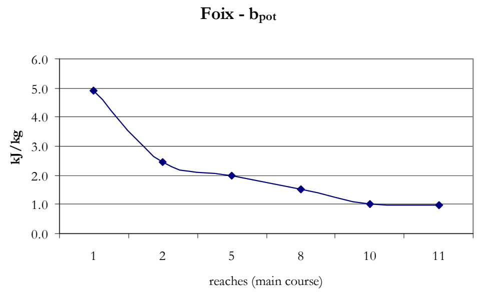


Figure A.69. Exergy profile of the OM chemical component (March)

A.8.1.2. July


Foix - b_{pot}

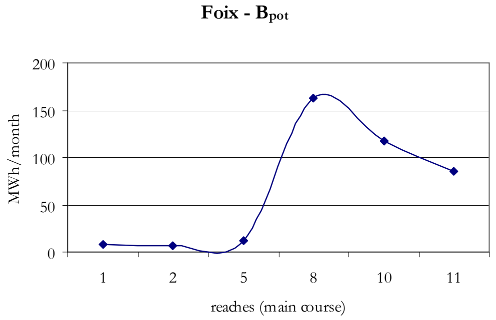
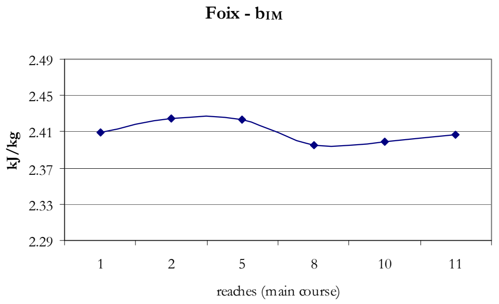

Foix - B_{pot}

Figure A.70. Specific exergy profile of the potential component (July)

Figure A.71. Exergy profile of the potential component (July)


Foix - b_{IM}

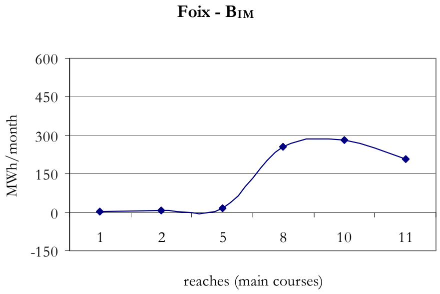
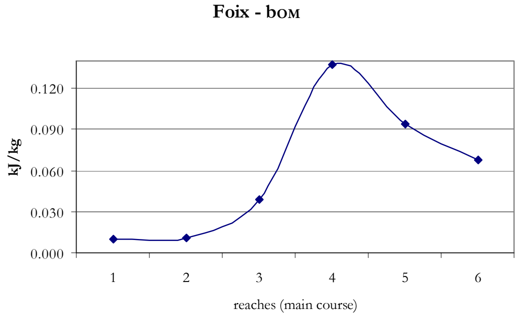

Foix - B_{IM}

Figure A.72. Specific exergy profile of the IM chemical component (July)

Figure A.73. Exergy profile of the IM chemical component (July)


Foix - b_{OM}

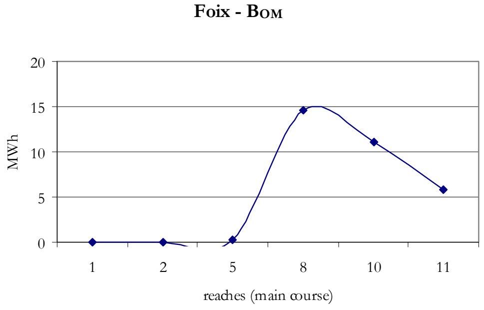

Foix - B_{OM}

Figure A.74. Specific exergy profile of the OM chemical component (July)

Figure A.75. Exergy profile of the OM chemical component (July)

A.8.1.3. September

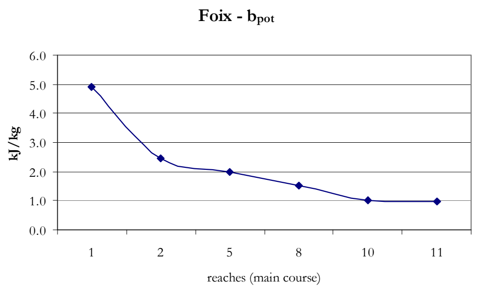


Figure A.76. Specific exergy profile of the potential component (September)

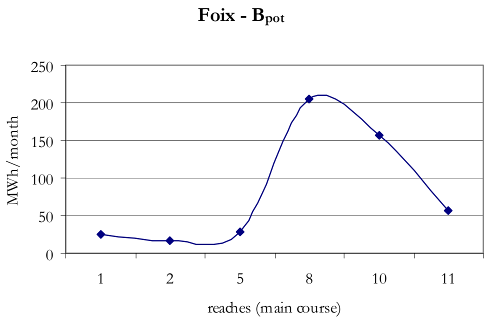


Figure A.77. Exergy profile of the potential component (September)

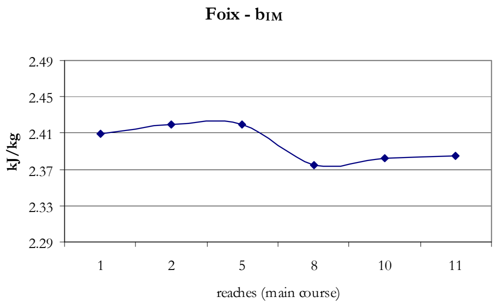


Figure A.78. Specific exergy profile of the IM chemical component (September)

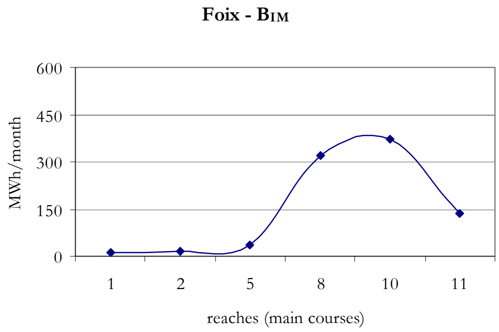


Figure A.79. Exergy profile of the IM chemical component (September)

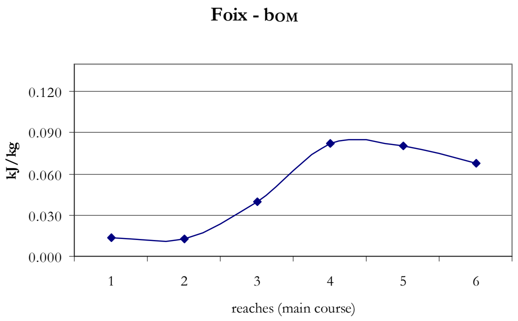


Figure A.80. Specific exergy profile of the OM chemical component (September)

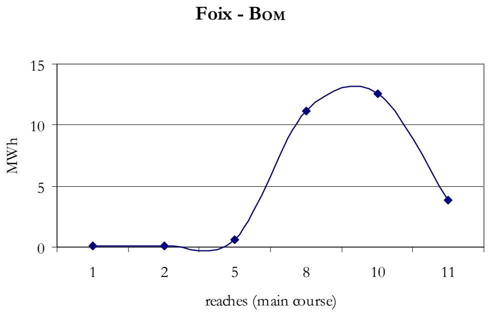


Figure A.81. Exergy profile of the OM chemical component (September)

A.8.2. Exergy profiles (PS, ES and OS) in the Foix river

A.8.2.1. March

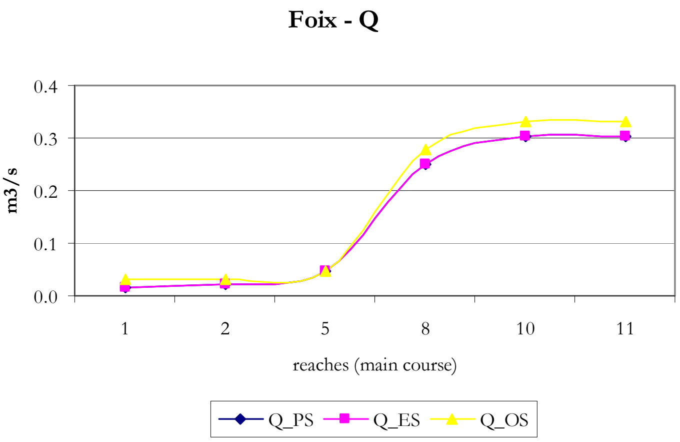
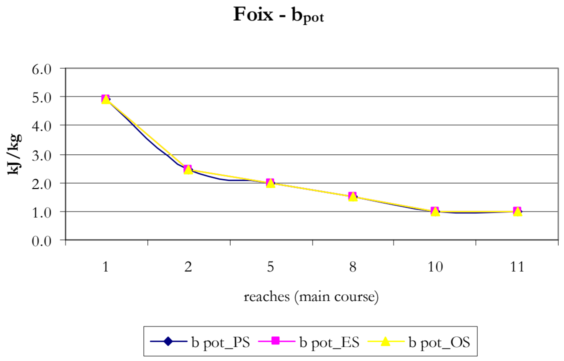


Figure A.82. Flows in the PS, ES and OS in the Foix river in March



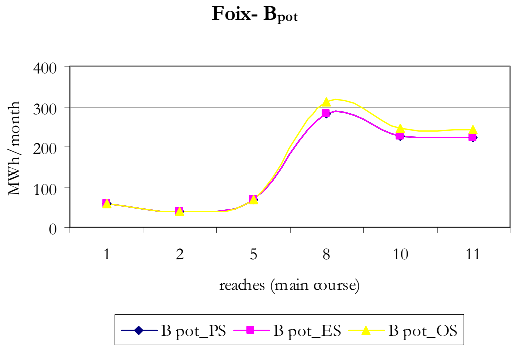
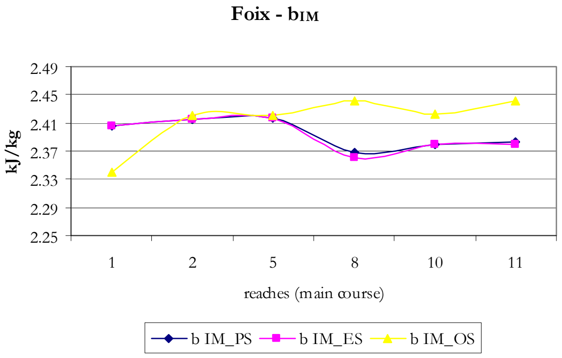


Figure A.83. Specific exergy profile of the potential component in the Foix river in March

Figure A.84. Exergy profile of the potential component in the Foix river in March



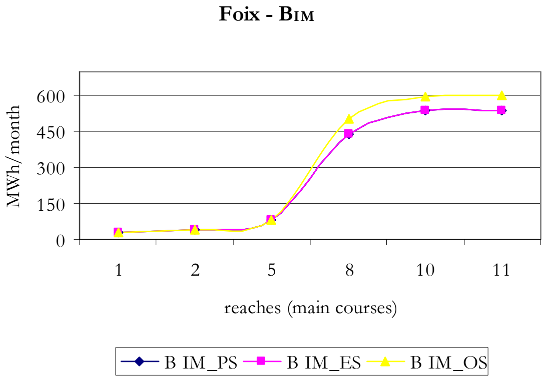


Figure A.85. Specific exergy profile of the IM chemical component in the Foix river in March

Figure A.86. Exergy profile of the IM chemical component in the Foix river in March

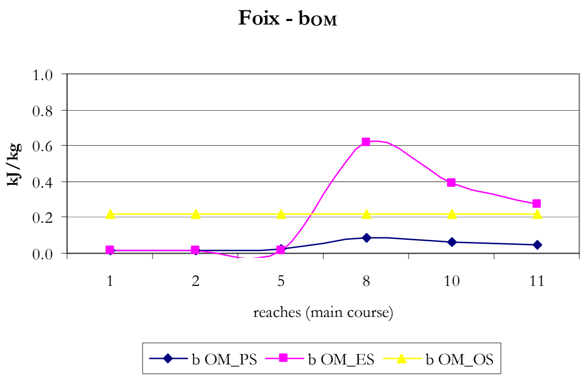


Figure A.87. Specific exergy profile of the OM chemical component in the Foix river in March

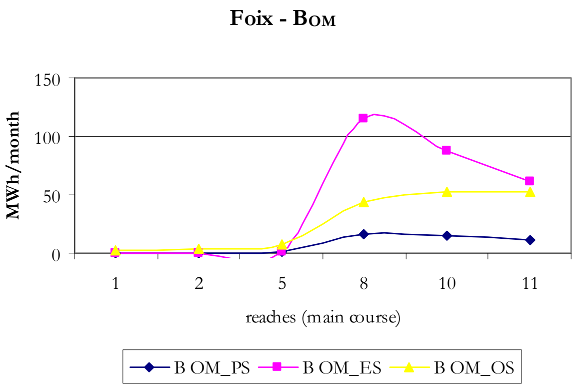


Figure A.88. Exergy profile of the OM chemical component in the Foix river in March

A.8.2.2. July

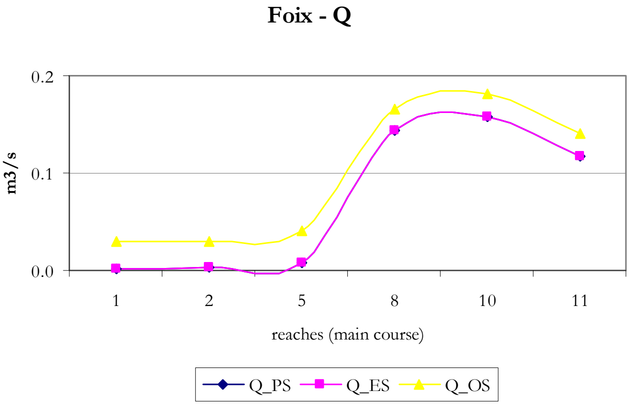


Figure A.89. Flows in the PS, ES and OS in the Foix river in July

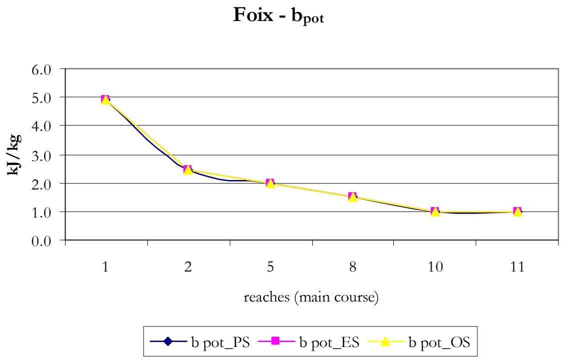


Figure A.90. Specific exergy profile of the potential component in the Foix river in July

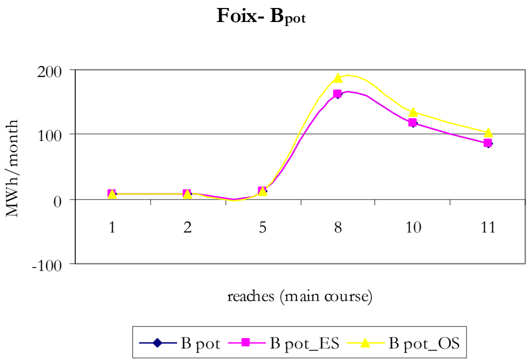


Figure A.91. Exergy profile of the potential component in the Foix river in July

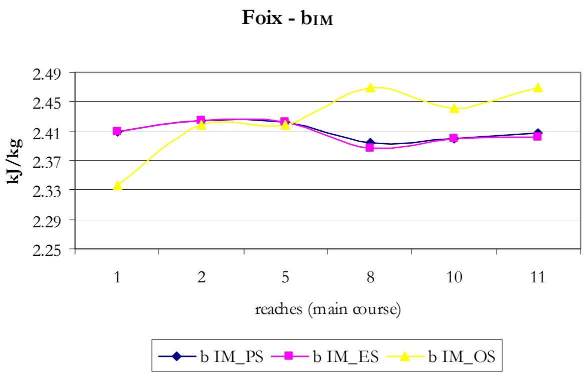


Figure A.92. Specific exergy profile of the IM chemical component in the Foix river in July

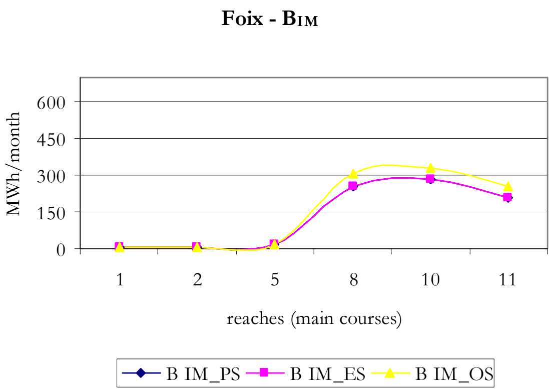


Figure A.93. Exergy profile of the IM chemical component in the Foix river in July

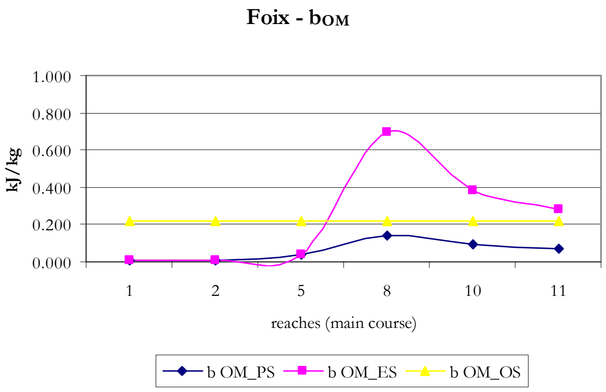


Figure A.94. Specific exergy profile of the OM chemical component in the Foix river in July

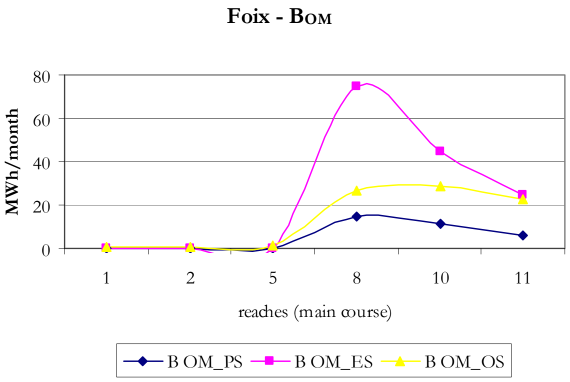


Figure A.95. Exergy profile of the OM chemical component in the Foix river in July

A.8.2.3. September

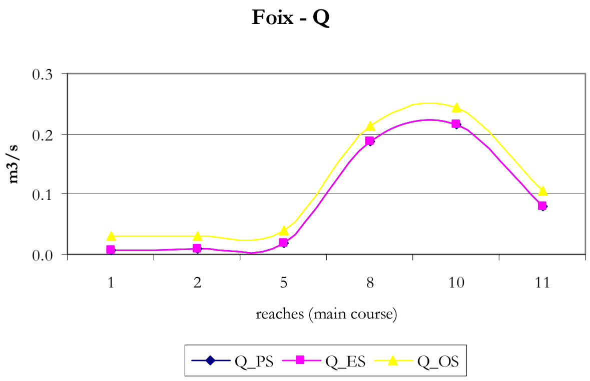


Figure A.96. Flows in the PS, ES and OS in the Foix river in September

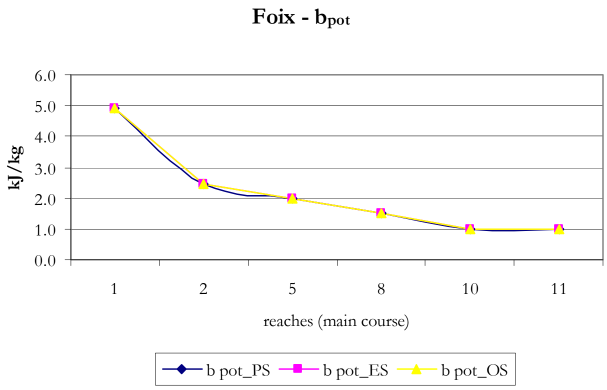


Figure A.97. Specific exergy profile of the potential component in the Foix river in September

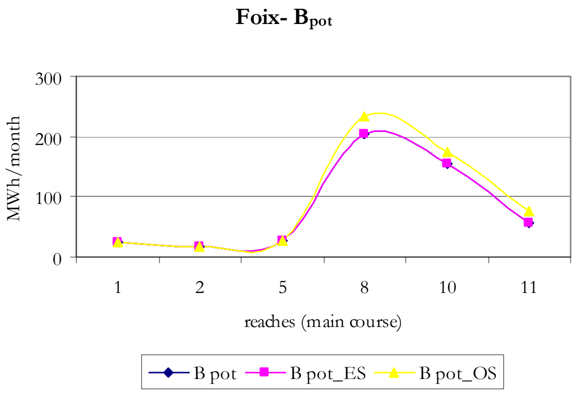


Figure A.98. Exergy profile of the potential component in the Foix river in September

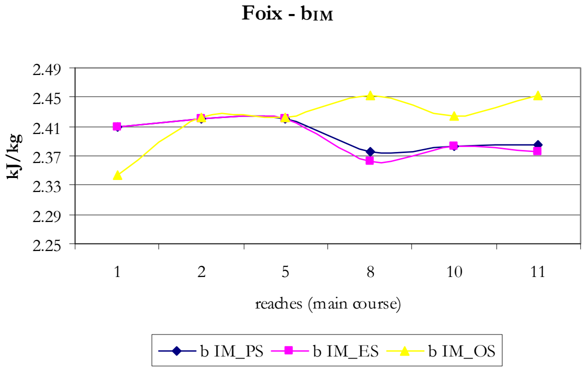


Figure A.99. Specific exergy profile of the IM chemical component in the Foix river in September

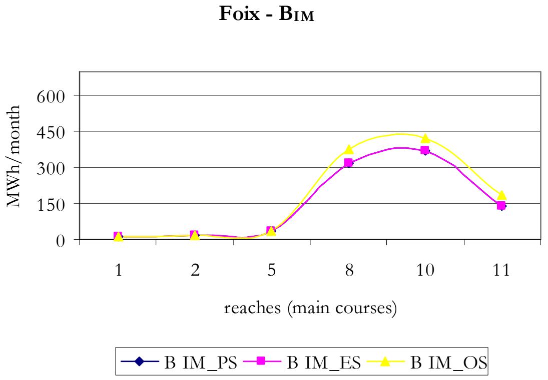


Figure A.100. Exergy profile of the IM chemical component in the Foix river in September

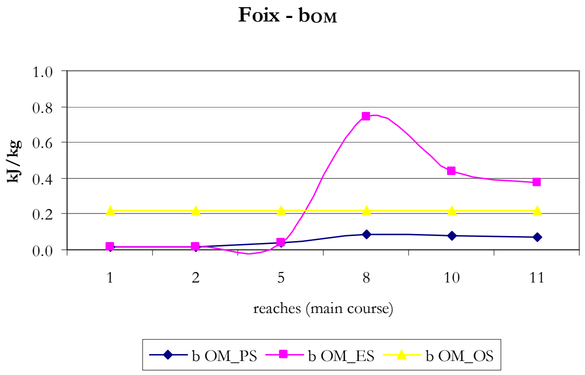


Figure A.101. Specific exergy profile of the OM chemical component in the Foix river in September

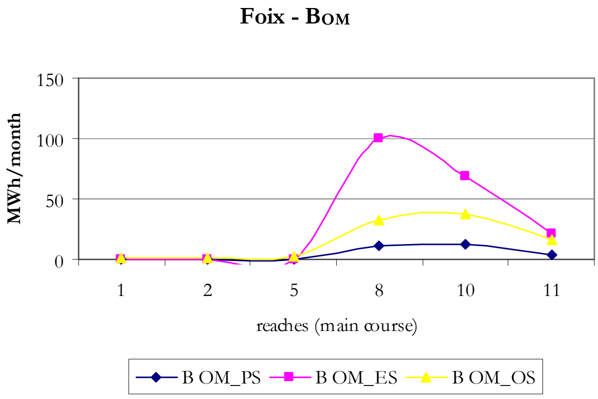


Figure A.102. Exergy profile of the OM chemical component in the Foix river in September

Annex B

Chemical exergy

This Annex is devoted to the development of some of the chemical exergy related concepts, mainly appeared in Chapter 4.

Firstly, the steps for obtaining the general water exergy equation are given. Secondly, the Jorgensen's eco-exergy bases are summarized. In third place, the minimum exergy needed for desalination is detailed and, finally, the calculation procedure to determine the specific chemical exergy of elements is synthesized.

B.1. General water exergy equation

The purpose of this appendix is to clarify the origin of Eq. 4.1 (Eq.B.2 in this appendix). It is obtained from the general specific exergy expression given in Eq.B.1, after applying the Incompressible Substance Model (ISM) and developing the chemical term.

Eq.B.1.

$$B = m\left[\underbrace{(u + Pv - u_0 - P_o v_o) - T_o(s - s_o)}_{b_{ph}} + \underbrace{\frac{C^2}{2}}_{b_k} + \underbrace{gz}_{b_p}\right] + \underbrace{\sum_{i=1}^{N} n_i(\mu_i - \mu_{io})}_{m \cdot b_{ch}}$$

Eq.B.1 is the general expression for exergy, usually reproduced in any Thermodynamic text. However, it is needed to rewrite it to calculate the exergy of water. Then, some basic transformations are introduced to reach Eq.B.2.

Eq.B.2.

$$\underbrace{b_{H_2O}(kJ/kg)}_{Total\ .specific\ .exergy\ ,b} = \underbrace{c_{p,H_20}\left[T - T_0 - T_0 \ln\left(\frac{T}{T_0}\right)\right]}_{Thermal\ .Ex\ ,b_t} + \underbrace{v_{H_2O}\left(p - p_0\right)}_{Mechanical\ .Ex\ ,b_{mch}} +$$

$$\underbrace{\left[\sum_i y_i\left(\Delta G_{f_i} + \sum_e n_e b_{ch,n_e}\right)_i\right]_p}_{Chemical\ .Ex\ ,b_{ch,f}} + \underbrace{RT_0 \sum_i x_i \ln\frac{a_i}{a_0}}_{Concentrat\ ion\ .Ex\ ,b_{ch,f}} + \underbrace{\frac{1}{2}\left(\frac{C^2 - C_0^2}{1000}\right)}_{Kinetic\ .Ex\ ,b_k} + \underbrace{g\left(z - z_0\right)}_{Potential\ .Ex\ ,b_p}$$

Firstly, it is shown that the physical term (b_{ph}) in Eq.B.1contains the thermal (b_t) and mechanical (b_m) ones, as indicated in Eq.B.3 :

Eq.B.3. $b_{ph} = b_t + b_m$

As it is well-known, the ISM states the equivalence between the specific volumes (Eq.B.4), the entropy difference between a given state and the reference as a function of their temperatures ratio and the specific heat of water (Eq.B.5), and the specific internal energy difference (only depending on the temperatures difference and the specific heat, Eq.B.6)

Eq.B.4. $v \approx v_o$

Eq.B.5. $s - s_o = c \ln\frac{T}{T_o}$

Eq.B.6. $u - u_o = c\Delta T = c(T - T_o)$

After introducing these restrictions in the b_{ph} term of Eq.B.1, the equivalence postulated in Eq.B.3is shown: the physical exergy term contains the thermal and mechanical exergy components (Eq.B.7).

Eq.B.7.
$$b_{ph} = (u - u_o) + v(P - P_o) - T_o(s - s_o) = c(T - T_o) - T_o c \ln\frac{T}{T_o} + v(P - P_o) = \\ = c\left[T - T_o - T_o \ln\frac{T}{T_o}\right] + v(P - P_o) = b_t + b_m$$

Secondly, the chemical exergy term for a water flow is disaggregated into the formation and concentration contributions, as follows (Eq.B.8):

Eq.B.8.
$$b_{ch} = b_{ch,f} + b_{ch,c}$$

The chemical potential is defined through the chemical potential in the reference μ_i^0 and the concentration C_i (Eq.B.9). By introducing this definition, the chemical exergy term in Eq.B.1is rewritten as Eq.B.10 indicates

Eq.B.9.
$$\mu_i = \mu_i^0 + RT_0 \ln C_i$$

Eq.B.10.
$$b_{ch} = \sum_i n_i (\mu_i^o + RT_o \ln C_i - \mu_{io}^o - RT_o \ln C_{io}) = \sum_i n_i (\mu_i^o - \mu_{io}^o) + \sum_i n_i RT_o \ln\frac{C_i}{C_{io}} = \\ \sum_i n_i (\mu_i^o - \mu_{io}^o) + RT_o \sum_i n_i \ln\frac{C_i}{C_{io}}$$

According to Klotz and Rossenber (1977), the chemical potential of any component *i* of a mixture could be written as indicated in Eq.B.11.

Eq.B.11.
$$\mu_i^o = h_i^o - T_o s_i^o \\ \mu_{io}^o = h_{io}^o - T_o s_{io}^o$$

In consequence, the searched expression for the chemical exergy, as the addition of its concentration and formation contributions, indicated in Eq.B.8, is obtained (Eq.B.12).

Eq.B.12.
$$b_{ch} = \sum_i n_i \left[(h_i^o - h_{io}^o) - T_c (s_i^o - s_{io}^o)\right] + RT_o \sum_i n_i \ln\frac{C_i}{C_{io}} = \sum n_i (\Delta G_f + \sum n_e b_{chne})_i + RT_o \sum_i n_i \ln\frac{C_i}{C_{io}}$$

The potential and kinetic components do not need any transformation. Finally, by adding all the expressions, Eq.B.2 is completely justified.

B.2. Eco-exergy

This part of Annex B is called to complete the information given in section 4.2.4, specially attending to the relation between entropy and probability.

B.2.1. Exergy and information theory

There is a strong link, in statistical mechanics, between entropy and probability. One of the most important equations describing entropy (Boltzmann, 1886) is expressed by Eq.B.13

Eq.B.13. $$S = k_b \ln W$$

Where k_b is the Boltzmann's constant and W is the number of microstates that will yield one specific macrostate.

W is proportional to the probability p that a particular microstate will occur; in fact, the more microstates there are, the lower is the probability of completely describing the system. A high number of microstates also means a high level of disorder and a low level of information about the real state of the system.

Entropy function grows with the uncertainty about the system, and reaches its highest value exactly when the system reaches its thermodynamic equilibrium. The difference between the entropy level of a system and the entropy level of the same system at thermodynamic equilibrium is a measure of information and order. It can be called negentropy and is associated with the concept of exergy (Wall, 1977).

Eq.B.14. $$I = S_{eq} - S = Negentropy$$

When $S = S_{eq}$ the system has no information, because all its intensive variables are equal to those of its environment, and no more distinction is possible.

Following Shannon's (Shannon and Weaver, 1949) approach, it is possible to calculate information content based on a description of the system through a probability distribution of microstates. If we observe an event that has an a priori probability p, the information I(p) received from the observation is defined as showed in Eq.B.15, and it is here expressed in binary units (bits).

Eq.B.15. $$I(p) = \log_2\left(\frac{1}{p}\right)$$

If a system is unknown, but is described by probabilities distribution p_i for all possible states (i=1, . . ., n), then the maximum quantity of information obtainable is expressed by Eq.B.15. This information allows us to quantify the uncertainty we have about the system before our observation. This uncertainty is called Shannon entropy s and it is defined as Eq.B.16.

Eq.B.16. $$s = \sum_i p_i I(p_i) = \sum_i p_i \log_2 \frac{1}{p_i}$$

The Boltzmann Statistical mechanics entropy (S), defined in Eq.B.13, is proportional to the Shannon entropy defined above (Brillouin, 1956), following this relation:

Eq.B.17. $$S = \kappa_b \sum_i p_i \log_2 \frac{1}{p_i} = \kappa_b s \ln 2$$

To introduce the dependence of exergy on information, we need to introduce the relative information theory proposed by Kullback (1959). This theory shows how to calculate the information gain when, after an observation, we still do not receive full information about the system, but just something more. Even if we do not know the exact microstate, we may replace our original, a priori distribution P(0) with the new one P. The information gained after the observation, called Kullback information, is defined as Eq.B.18.

Eq.B.18. $$K\left[p^{(0)}; p\right] = \sum_i p_i \log \frac{p_i}{p_i^{(0)}}$$

The value of K cannot be negative, but must be at least equal to 0, K≥0, because a new observation can at least let unchanged our knowledge about the system but not reduce it.

As told in previous sections, the ability of a system to perform work depends on its deviation from the thermodynamic equilibrium state. Let us imagine a large system (an environment) described by a probability distribution $p_i(0)$ and a subsystem, included in the environment, that deviates from the equilibrium following a new probability distribution pi.

The relative information of the subsystem can be used to describe the work can be extracted from the subsystem when it is brought to equilibrium with the environment (exergy).

The expression of Kullback information is related to exergy function by

Eq.B.19. $$Ex = k_b T_0 \ln 2K\left[p^{(0)}; p\right] = k_b T_0 \ln 2 \sum_i p_i \log \frac{p_i}{p_i^{(0)}}$$

Where k_b is the Boltzmann constant, and T_0 is the temperature of the environment.

Following Eq.B.19, the exergy embodied in one bit of information is, at 27 °C, about 3×10^{-21} J. The cost, from an exergetic point of view, of building information is usually much higher than the exergetic content of information itself (Wall and Gong, 2001; Lindgren, 2003). This rule is not respected by living systems that bring with them an incredible amount of information in their bodies, in the form of complex chemical and biological structures, such as DNA (Jørgensen, 2000). The basic idea behind Jørgensen's eco-exergy is to take into account both physical and informational exergy.

B.2.2. Definition of eco-exergy

Exergy (Ex) is directly derived from the second law and is expressed by Eq.B.20:

Eq.B.20. $$Ex = U + P_0 V - T_0 S - \sum_i \mu_{i0} n_i$$

Where U, V, S and n_i (internal energy, volume, entropy and number of moles) are the extensive variables of the system and P_0, T_0 and μ_{i0} (pressure, temperature and chemical potential) are the intensive variables of the environment. If the function U in Eq.B.20 is developed, it can be written:

Eq.B.21. $$Ex = S(T - T_0) - V(P - P_0) + \sum_{i=0}^{n} (\mu_i - \mu_{i0}) n_i$$

Assuming, as indicated in Chapter 4, constant temperature and pressure and introducing the chemical potential definition (Eq.B.22),

Eq.B.22. $$\mu_i = \mu_i^{eq} + RT \ln \frac{c_i}{c_i^{eq}}$$

the general exergy expresion becomes (Jørgensen and Mejer, 1977):

Eq.B.23. $$Ex = RT_0 \sum_{i=0}^{n} c_i \ln \frac{c_i}{c_i^{eq}}$$

Where:

R	is the gas constant
T_0	the temperature of the environment
C_i	the concentration of the ith chemical component of the system
c_i^{eq}	the concentration of the ith component at the equilibrium

B.2.3. Basic problema: c_{io} measurement.

The concentrations of each organism can be measured, but the concentrations in the reference state (thermodynamic equilibrium) are based on the usual chemical equilibrium constants. If we presume the reaction to form organism A as *OrganismA* <-> *inorganic decomposition products*, there is a chemical equilibrium constant, K:

Eq.B.24. $$K = \frac{[inorganic\_decomposition\_products]}{[component\_A]}$$

The concentration of component A at thermodynamic equilibrium is very low so K has a very high value. K is defined as indicated in Eq.B.25, and its graph can be seen in Figure B.1.

Eq.B.25. $$K = e^{\frac{-\Delta G_0}{RT}}$$

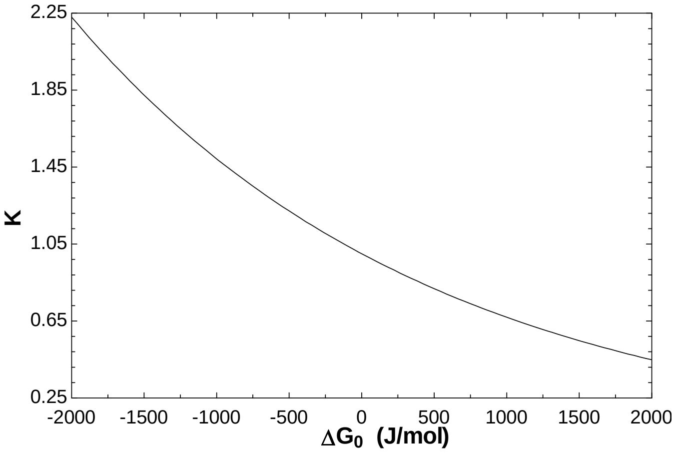


Figure B.1. Chemical equilibrium constant versus its formation energy

It can be easily seen that the lower the probability of formation of a complex structure, the higher its exergy content expressed in Eq.B.25 by $-\Delta G_0$. A very complex structure has a high level of information content and a low probability of existence.

To calculate the exergy content due to information, the Kullback's information formula (Kullback, 1959) can be used. If the probability of the i^{th} component, p_i, is defined according to Eq.B.26, where A is given by Eq.B.27 and represents the total amount of matter in the system, exergy can be defined as a function of both biomass and information (Eq.B.28).

Eq.B.26. $$p_i = \frac{c_i}{A}$$

Eq.B.27. $$A = \sum_{i=0}^{n} c_i$$

Eq.B.28. $$Ex = ART_0 \sum_i p_i \ln \frac{p_i}{p_i^{(0)}} + A \ln \frac{A}{A^{(0)}}$$

as $A \approx A_{eq}$, exergy becomes a product of the total biomass A (multiplied by RT_0) and the Kullback measure defined in Eq.B.18:

Eq.B.29. $$Ex = ART_0 K\left[p^{(0)}; p\right]$$

Where A is physical biomass contribution and K is the informational contribution.

The a posteriori probability (p_i) of each component is equal to 1 if we know exactly the system and Eq.B.28 becomes:

Eq.B.30. $$Ex = -RT_0 \sum_i c_i \ln p_i^{(0)}$$

starting from i = 1 because $p^{eq}_0 \approx 1$.

For biological components, the probability p_e^{qi} consists at least of the probability of producing the organic matter (detritus) p_1 and the probability p_i of finding a correct composition of the nucleotides determining the biochemical processes in the organisms. A clear correlation between the number of genes and complexity has been shown by many authors (Li and Grauer, 1991).

Eq.B.31. $$p_i^{(0)} = p_1 p_i$$

Living organisms use 4 different nucleotides which are responsible for coding amino-acids and their proteins. Each organism has, in its DNA, a given number of nucleotides (ai) structured in genes and a given percentage of repeating genes (g_i). p_i can be found as the number of permutations among the four characteristic nucleotides sequences for the considered organism genome, taking into account only the non-repeating genes present in the DNA chain. From that, Eq.B.32 is derived.

Eq.B.32. $$p_i = 4^{-a_i(1-g_i)}$$

$p_{eq}^{\ i}$ value is given by the classical exergy theory:

Eq.B.33. $$p_i = \frac{c_i}{c_o^{\ eq}} e^{-\left(\frac{\mu_1 - \mu_1^{eq}}{RT}\right)}$$

where the specific free energy of detritus $\left(\mu_1 - \mu_1^{eq}\right)$ is known (18.7 kJ/g).

Organisms	**β**	**Specific exergy (KJ/g)**
Detritus	1	18.70
Bacteria	12	224.40
Algae	28	523.60
Plant	437	8,171.90
Insect	446	8,340.20
Fisch	689	12,884.30
Reptile	1150	21,505.00
Bird	1150	21,505.00
Mammal	2935	54,884.50
Human	2967	55,482.90

Table A.1. β and specific exergy values of different organisms based on their genetic patrimonies. (Source: Jørgensen et al., 2005)

By Combining Eqs. (16) and (17), Eq.B.34 is obtained:

Eq.B.34. $$Ex = -RT_0 \sum_{i=1}^{n} c_i \left[\ln p_i - \left(\frac{\mu_1 - \mu_1^{eq}}{RT_0} \right) + \ln \frac{c_1}{c_0^{\ eq}} \right]$$

As $\ln c_1 / c_0^{\ eq}$ is negligible compared to the rest we can write

Eq.B.35. $$Ex = \left(\mu_1 - \mu_1^{eq}\right)\sum_{i=1}^{n} c_i - RT_0 \ln 4 \sum_{i=2}^{n} c_i a_i \left(1 - g_i\right)$$

starting from i = 2 in the second term because detritus has no genetic structures.
(For i=1, firs term of eq 21 is equal to detritus exergy, 18.7 kJ/g).

The Eq. (21) now has two terms, one describing classical exergy and another one describing informational exergy. Using the known specific free energy value of detritus (18.7 kJ/g) and ci expressed in grams, we can calculate the exergy value of a generic compound of our system as T_0 = 300K expressed in kJ (Jørgensen et al., 2005):

Eq.B.36. $$Ex_i = c_i\left[18.7 + 3.54x10^{-5} a_i \left(1 - g_i\right)\right]$$

and the useful β value expressed by the following formula:

Eq.B.37. $$\beta = \frac{ex^{eco}}{ex^{phys}} = 1 + \frac{ex^{\inf o}}{ex^{phys}}$$

Where:

Eq.B.38. $$ex^{eco} = ex^{phys} + ex^{\inf o}$$

B.3. Minimum energy required for desalination.

A desalination plant can be considered a black box with water and energy flows Figure B.2. Normally there is only one source of sea water and two outputs, drinking water and concentrated brine. There is also an energy flow which enters as high quality energy and exits as low quality (Hanbury et al., 1993).

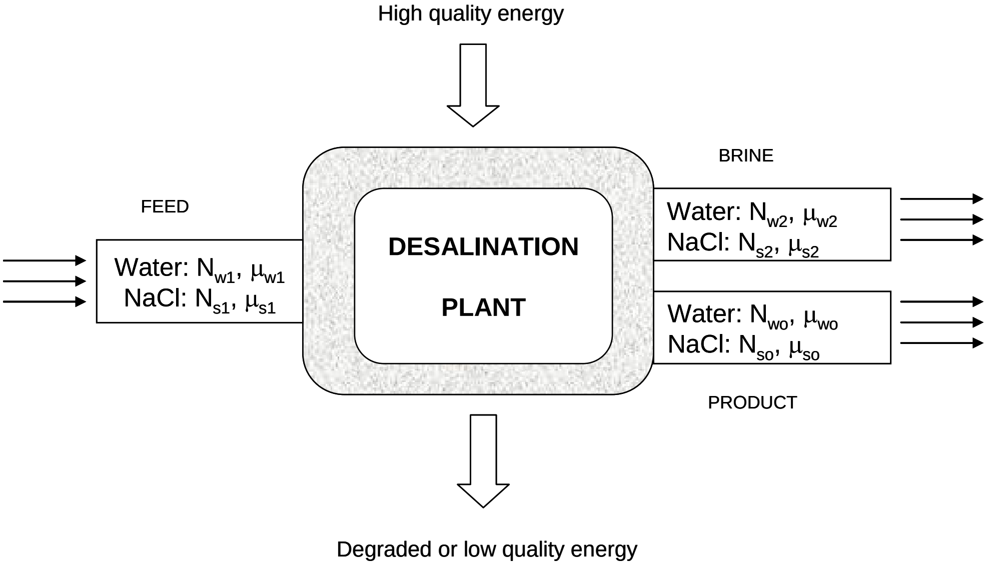


Figure B.2. Characterization of the flows in a desalination plant.

The minimum desalination energy is the difference between the free energy of the input flow (salt water) and the output water flows (desalted water and concentrated brine), Eq.B.39.

Eq.B.39. $$dG = VdP - SdT + \sum \mu_i dN_i$$

At a constant pressure and temperature, the change in free energy can be expressed as indicated in Eq.B.40:

Eq.B.40. $$\Delta G = \sum \mu_i \Delta N_i = \sum \mu_s N_s - \sum \mu_e N_e$$

For N_1 moles of water entering the plant, N_0 moles of water in product, N_2 moles of water in the concentrated brine, N_{s1} moles of salt entering the plant, N_{s0} moles of salt in product and Ns_2 moles of salt in brine, equation Eq.B.40 can be written as:

Eq.B.41. $$\sum \mu_i \Delta N_i = -\mu_1 N_1 + \mu_2 N_2 + \mu_o N_o - \mu_{s1} N_{s1} + \mu_{s2} N_{s2} + \mu_{so} N_{so}$$

The mass balance for the water and salt implies that $N_1 = N_2 + N_o$ and $N_{s1} = N_{s2} + N_{s0}$. The recuperation ratio can be defined as $R_c = N_0/N_1$, the molar fraction of the salt in the entry flow as $x_1 = N_{s1}/(N_1 + N_{s1})$ and if the water produced is very pure $N_{s0} \approx 0$, so the minimal energy per unit of water produced can be expressed using the Eq.B.41.

Eq.B.42. $$\frac{\Delta G}{N_o} = \left[\frac{1}{R_c} - 1\right](\mu_2 - \mu_1) + (\mu_o - \mu_1) + \frac{1}{R_c}\frac{x_1}{1 - x_1}(\mu_{s2} - \mu_{s1})$$

Expressing the chemical potentials in relation to the molar concentrations in the input and output, we obtain the expression to calculate the desalination exergy in function of the recovery ratio (R_c) and the molar salt fraction at the input flow of the plant:

Eq.B.43. $$b_{des} = \frac{\Delta G}{N_o} = \frac{vRT}{R_c}\frac{x_1}{1 - x_1}\ln\left[\frac{1}{1 - R_c}\right]$$

According to equation Eq.B.43, the minimal desalination energy varies between 2.6 MJ/m^3 and 6.5 MJ/m^3 for a plant input of sea water with a salt concentration of 35,000 ppm and a recuperation ratio (R_c) that varies between 0.1 and 0.9 respectively.

B.4. Calculation methodology: standard chemical exergy of the chemical elements

Chemical exergy expresses the exergy of a substance at ambient temperature and pressure. It is defined as a maximum work which can be obtained when the considered substance is brought in a reversible way to the state of reference substances present in the environment, using the environment as a source of heat and of reference substances necessary for the realization of the described process. The RE most common in the environment are accepted separately for every chemical element, and are mutually independent. Hence, the problem of equilibrium between the reference substances does not exist. It is impossible to formulate a chemical reaction in which only the reference substances take part.

B.4.1. Standard Chemicals exergy of Chemicals compounds

Standard chemical exergy results from a conventional assumption of a standard ambient temperature and pressure and standard concentration of reference substances in the natural environment. The standard chemical exergy of any chemical compound can be calculated by means of the exergy balance of a reversible formation reaction;

Eq.B.44. $$b_{chn} = \Delta G_f + \sum_e n_e b_{chne}$$

where:

ΔG_f	formation Gibbs energy
n_e	amount of kmol of the element $_e$
b_{chne}	standard chemical exergy of the element.

If the chemical element does not belong to the reference substances, its standard chemical exergy can also be calculated from Eq.B.44, however, a reference reaction of this element should be formulated. This reaction contains only reference substances, additional as reactants and final as products. For example, following reference reaction holds for the element $C : C + O_2 = CO_2$, where O_2 is the additional and CO_2 the final reference substance. The standard chemical exergy of the reference substances are calculated prior to the standard chemical exergy of the element.

B.4.2. Gaseous reference substances

Free chemical elements present in the atmospheric air $(O_2, N_2, Ar, He; Ne, Kr, Xe)$ and the compounds H_2O, CO_2 are assumed as reference substances. Their standard chemical exergy results from the conventional standard concentration in the atmosphere;

Eq.B.45. $$b_{chn} = -RT_0 \ln \frac{P_{0n}}{P_n} = -RT_0 \ln z_0$$

Where:

R	gas constant,
T_0	standard ambient temperature (298,15 K),
P_{0n}	conventional mean ideal gas partial pressure in the atmosphere (kPa),
P_n	standard pressure (101,325 kPa),
z_0	conventional standard molar fraction in the environment.

The values of standard chemical exergy of gaseous reference substances O_2, H_2O, CO_2, N_2 are calculated before other values because they are necessary in the calculation of standard chemical exergy of non-gaseous reference substances.

B.4.3. Solid reference substances

For a prevailing part of chemical elements, solid R.S. commonly appearing in the external layer of the continental part of Earth's crust, have been assumed. However, the Earth's crust is a very complicated mixture of solid solutions and an exact calculation of the chemical exergy of its components is impossible. We can only approximately evaluate that exergy, assuming that the reference species behave as components of an ideal solution. Hence, Eq. 2 can be applied also in this case. The evaluation of the standard molar concentration of solid R.S. in the external layer of the Earth's crust is difficult. In past geochemical publications we can only find a mean mass concentration of particular chemical elements and some information about the chemical compounds containing the considered elements.
Hence, the best considered way so far to obtain the standard molar concentration of R.S. in the solid environment, has been with following equation suggested by Szargut in [12]:

Eq.B.46. $$z_{0i} = \frac{1}{l_i} n_{0i} c_i M_o$$

where:

n_{0i} mean molar concentration (in mol/kg) of the i-th element in the continental part of the Earth's crust,

l_i number of the atoms of i-th element in the molecule of the reference species,

c_i fraction of the i-th element appearing in the form of reference species,

M_0 mean molecular mass of the upper layer of the continental part of Earth's crust.

The reference reactions of the elements having solid R.S. contain usually the gaseous R.S. Sometimes appear also solid reference species. For example, the solid R.S. of Mg is Mg3Si4O10(OH)2 the reference reaction for the element Mg has a form:
3 Mg+4 SiO2 + 1,5 O2 + H2O = Mg3Si4O10(OH)2 In such case the standard chemical exergy of the appearing solid reference substance should be calculated prior to the calculation of the chemical exergy of the considered element (Szargut, 2005).

B.4.4. Reference substances dissolved in seawater

Assumption of ionic or molecular R.S. dissolved in seawater ensures in many cases more exact determination of standard chemical exergy of chemical elements when compared with solid RE. The calculation methods of thermodynamic functions of monocharged and bicharged ions are relatively exact. This is the case also when the reference substance is dissolved in molecular form with a very small degree of ionization.

The method of calculation of standard chemical exergy of elements with R.S. dissolved in seawater has been developed by Morris [32]:

Eq.B.47. $$b_{chn} = j\left(-\Delta G_f + 0.5zb_{chH2} - \sum_k v_k b_{chk} - RT_n\left[2.303z(ph) + \ln m_n \gamma\right]\right)$$

where:

j	number of reference ions or molecules derived from one molecule of the element under consideration,
ΔG_f	formation Gibbs energy of the R.S., z number of elementary positive charges of the reference ion,
v_k	number of molecules of additional elements present in the molecule of reference substance,
b_{chH2}, b_{chk}	standard chemical exergy of hydrogen gas and of the k-th additional element.
m_n	conventional standard molarity of the reference substance in seawater,
γ	activity coefficient (molarity scale) of the reference substance in seawater,
pH	exponent of the concentration of hydrogen ion in seawater (=8,1)

The activity coefficient of single ion can be calculated
by means of the Debye-Huckel equation:

Eq.B.48. $$-\log y_i = \frac{Az_i^2\sqrt{I}}{1 + a_i B\sqrt{I}}$$

where:

A	= 0,51 kg1/2 mol−1/2 for water at 25oC,
B	= 3,287 * 109 kg1/2 m−1 mol−1/2 for water at 25oC,
a_i	effective diameter of the ion,
I	ionic strength of the electrolyte.

The ionic strength of the electrolyte results from the
following equation:

Eq.B.49. $$I = \frac{1}{2}\sum_i m_i z_i^2$$

where:

m_i	molarity of the ion, mol/kgH2O,
z_i	number of elementary electric charges of the ion.

The ion Cl^- prevails among the negative ions in seawater. Therefore, the data of chlorides can be assumed for activity coefficients of the positive ions Na^+, K^+. The activity coefficients of the negative ions Cl^- and SO_4^{-2} can be estimated in reference to the predominant positive ion Na^+.

Annex C

Water Framework Directive, water-related organizations and Spanish water accounts methodology

Different subjects related to Chapter 1 and Chapter 3 are presented in this Annex, aimed to complete the provided information.

Firstly, some general aspects of the WFD are summarized: from its structure to its basic principles. Secondly, national and international water-related organization are briefly described. Finally, the background of the Spanish water accounts is given.

C.1. General contents of the Water Framework Directive (2000/60/EC)

The WFD is structured in 26 articles and 5 annex, in addition to its corresponding preamble.

Article 1: Purpose
Article 2: Definitions
Article 3: Coordination of administrative arrangements within river basin districts
Article 4: Environmental objectives
Article 5: Characteristics of the river basin district, review of the environmental impact of human activity and economic analysis of water use.
Article 6: Register of protected areas.
Article 7: Waters used for the abstraction of drinking water.
Article 8: Monitoring of surface water status, groundwater status and protected areas.
Article 9: Recovery of costs for water services.
Article 10: The combined approach for point and diffuse sources.
Article 11: Programme of measures.
Article 12: Issues which can not be dealt with at Member State level.
Article 13: River basin management plans.
Article 14: Public information and consultation.
Article 15: Reporting.
Article 16: Strategies against pollution of water.
Article 17: Strategies to prevent and control pollution of groundwater.
Article 18: Commission report.
Article 19: Plans for future Community measures.
Article 20: Technical adaptations to the Directive.
Article 21: Regulatory committee.
Article 22: Repeals and transitional provisions.
Article 23: Penalties.
Article 24: Implementation.
Article 25:Entry into force.
Article 26: Addresees.

Annex I: Information required for the list of competent authorities.
Annex II: Waters characterization.
Annex III: Economic analysis.
Annex IV: Protected areas.
Annex V: Waters statuses.

The main purpose of the Directive is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater. There exist four basic principles extracted from the text:

The principle of non-deterioration and achievement of good overall status of surface water and groundwater masses.
The need to limit uses, discharges or activities that directly or indirectly affect the water environment, in accordance with the recipient system and its capacity to withstand said impacts, with constant consideration for the structure and operation of the altered water ecosystems. Water systems must therefore be defined and classified for better

adaptation of the programme of control and diagnosis and the system's management model.

The principle of a combined approach to pollution and the integrated management of the resource.
The Directive covers the objectives and aims of previous Directives and includes all these within a global approach of the systems to be analysed (which in this case are water systems), with a combined focus and from an ecosystemic perspective. Limitation of the use of water, discharges or activities that could affect water ecosystems is based on an integrated analysis of the environment and both considers the appropriate physiochemical elements for the maintenance of good quality and also contemplates the use of the main natural elements that comprise it (biological communities) and the quality of the structure that sustains it (the habitat). The unit (part of the water system) that provides the basis for the integrated management, the programme of control, and the programme of measures for the achievement or maintenance of good ecological status is known as the water mass.

The principle of full recovery of the costs associated with water services and the use of aquatic areas.
The new directive introduces the concept of full recovery and internalisation of both the environmental and resource costs (opportunity cost) that arise from services associated with the use of the water and from sustainable maintenance of associated ecosystems in a good state of health. The cost of the sustainable use of the water and of the river area must be assumed by the beneficiary or operator of the activity that generates the cost.

The principle of public participation and transparency in water policies.
The management of resources, and the programmes of measures and control, which must be included in the new Management Plan (new Hydrological Plan) to ensure the good ecological status of the river systems, must involve social participation and consensus based on mechanisms for citizen participation and must be totally transparent to the public.

In general terms, the WFD suggests a framework for the protection of all water, including continental surface water, transition water and seawater, as well as groundwater, with the following objectives:

- To prevent further deterioration, to protect and improve the condition of aquatic systems in terms of their water needs.
- To promote sustainable use of water, based on the long-term protection of available water resources.
- To achieve greater protection and improve the aquatic environment with specific measures for the progressive reduction of discharges, emissions or losses of priority hazardous substances, halting or gradually eliminating them.
- To ensure the gradual reduction of the pollution of groundwater and to prevent new pollution.
- To contribute towards relieving the effects of floods and droughts.

Specifically, the objectives of achieving good water status involves a set of measures in all areas concerned with the water environment, from the natural aspects (hydrology, ecology, geodynamics...) to its economic and social nature.

In this sense, the WFD defines the methods, procedures and indicator parameters necessary for characterising the condition of water and the strategies and instruments needed to protect this condition and to regenerate it, if necessary. In this context, the most important aspects of the WFD are:

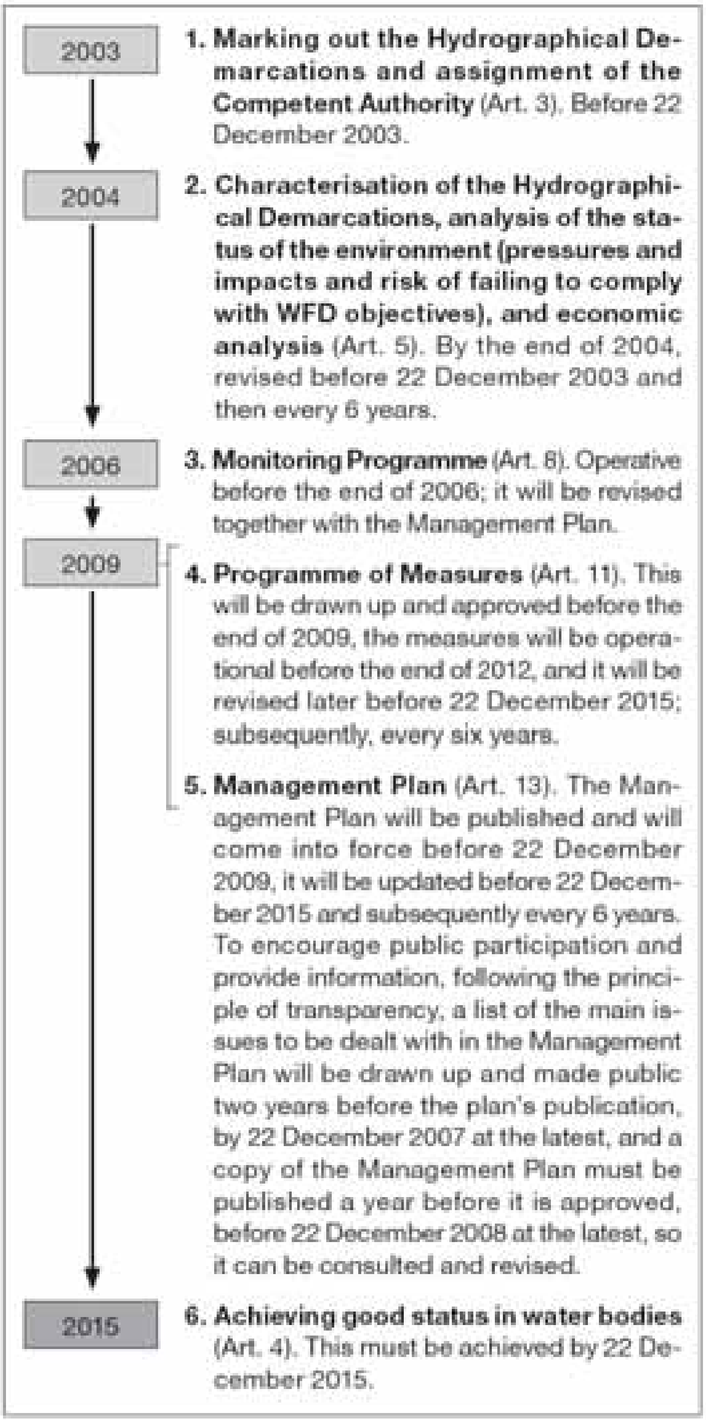
- Evaluating the condition of the water resources of all water bodies, using quantitative and qualitative parameters.
- Determining the ecological status of these water bodies, and identifying the associated pressures, impacts and risks that condition it.
- Creating economic instruments for water management based on the principle of recovery of costs.
- Promoting public participation in decisions related to water management.
- Drawing up river basin water plans including the water and ecological information required by the Directive, the description of the water bodies identified and their ecological status, the programmes of measures necessary for achieving the environmental objectives already mentioned, and all the exceptions or difficulties making compliance impossible.

In general terms, the key concept of this Community directive is the *transversal integration* of factors and agents involved in water management and in the protection of its values. Specifically, it includes the integration of environmental objectives, combining water-related and ecological objectives in order to ensure the good condition of all water and the protection of aquatic systems, the integration of all water resources at the level of a river basin and the integration of all uses, functions and values of water including environmental, health, economic and social aspects, in a single policy framework.

The integration of all fields of knowledge and expertise to provide advice on the condition of water bodies, the pressures and impacts they are subject to, in order to achieve the established objectives, as well as the the integration of water legislation into a common, coherent framework in all European Union member states are also needed.

Finally, the integration of all aspects related to water planning based on sustainability, financial and economic instruments for achieving the environmental objectives and the integration of managers and civil society into decision-making offering access to information, transparency and opportunities for participation, are included.

The ultimate objective is to achieve good water status by 2015. For this reason, the Directive has been provided with a calendar for application. The main tasks it involves and the deadlines by which they must be carried out as indicated in Figure A.1.



2003

1. Marking out the Hydrographical Demarcations and assignment of the Competent Authority (Art. 3). Before 22 December 2003.

2004

2. Characterisation of the Hydrographical Demarcations, analysis of the status of the environment (pressures and impacts and risk of failing to comply with WFD objectives), and economic analysis (Art. 5). By the end of 2004, revised before 22 December 2003 and then every 6 years.

2006

3. Monitoring Programme (Art. 8). Operative before the end of 2006; it will be revised together with the Management Plan.

2009

4. Programme of Measures (Art. 11). This will be drawn up and approved before the end of 2009, the measures will be operational before the end of 2012, and it will be revised later before 22 December 2015; subsequently, every six years.

5. Management Plan (Art. 13). The Management Plan will be published and will come into force before 22 December 2009, it will be updated before 22 December 2015 and subsequently every 6 years. To encourage public participation and provide information, following the principle of transparency, a list of the main issues to be dealt with in the Management Plan will be drawn up and made public two years before the plan's publication, by 22 December 2007 at the latest, and a copy of the Management Plan must be published a year before it is approved, before 22 December 2008 at the latest, so it can be consulted and revised.

2015

6. Achieving good status in water bodies (Art. 4). This must be achieved by 22 December 2015.

Figure A.1. Schematic summary of the schedule of the main actions to be implemented under the WFD (2000/60/EC). (Source: Castañón, 2007))

However, the possibility that not all masses of water will achieve the good condition by 2015 is considered, either because of technological capability, disproportionate costs or natural circumstances. All these circumstances must be explicitly specified in the river basin management plans. The Directive offers the opportunity to develop two more six-year cycles for the planning and implementation of the appropriate measures.

C.2. Water-related organizations

Many references to organizations, research groups, universities and institutions appear along this dissertation. All of them have been collected in the references section. In this part of the Annexes, some of them are widely described. Because of the huge amount of interdisciplinary information sources, maybe not all of them that should be here have been reported.

C.2.1. International water-related organizations

In this section, the most representative international water organizations are briefly described.

C.2.1.1. United Nations Organisation for Education, Science and Culture (UNESCO)

UNESCO was created on 16 November 1945. Currently it is laboratory for ideas that sets standards in establishing agreements at a global level on questions related to ethical principles as they are needed. The organisation also plays a role as a centre for exchange of information and knowledge. At the same time, it helps Member States to construct their human and institutional capacities in different spheres of activity. In Short, UNESCO promotes international cooperation on education, science, culture and communication among its 193 Member States and six Associate Members. Through its strategies and activities it promotes the United Nations Millennium Development Goals.

UNESCO has a number of tools related to water management.

The World Water Assessment Programme (WWAP), set up in 2000, is the flagship UN water programme. WWAP supervises questions related to fresh water and offers recommendations, develops case studies, reinforces the ability to evaluate at a national level and inform on the decision-making process. Its main product, the Report on the World Water development Report (WWDR) is a wide-ranging periodic report offering a reliable view of the current situation of the planet water resources. Its third edition has just been published under the title W*ater, a shared responsilibity.*

The International Hydrological programme (IHP) is the UNESCO inter-governmental scientific cooperation programme on water resources. It helps Member States aim to improve their knowledge of the water cycle and increase their capacity to administer and exploit their water resources. The IHP aims to improve scientific and technological foundations in order to develop methods of rational management of water resources, including environmental protection.

The Institute of Water Education, (IWE) was established in 2003. It carries out research, education and capacity-building activities in the fields of water, environment and infrastructure. There are also Water Centres, which cover specific subjects at international and regional level and Water Chairs in various Universities around the world.

C.2.1.2. The international network of basin organisations (INBO)

The International Network of Basin Organisations (INBO) was created in 1994 at the *Aix les Basins* assembly in France by various organisations whose common aim was the basin-based implementation of the Integrated Water Resources Management (IWRM). They voluntarily signed the charter accepted at the assembly in Morelia (Mexico) in 1996, which was subsequently confirmed at the following assemblies in Valencia (Spain) in 1997 and Salvador (Brazil) in 1998. Currently it groups together 134 organisations in 51 countries.

The goal of INBO is to promote a basin-based global management to water resources as an essential tool for sustainable development. With this goal in mind, INBO to achieve the following objectives:

- To develop lasting relations between the organisations interested in such a comprehensive management, and favour exchanges of experiences and expertise among them;
- To facilitate the implementation of tools suitable for institutional and financial management, for knowledge and follow up of water resources, for the organisation of data banks, for the concerted preparation of master plans and action programs in the medium and long term:
- To develop information and training programmes for local elected officials, for users representatives and for the different stakeholders involved in water management as well as for the executives and staff of the organisations in charge of water management at the river basin level:
- To encourage education of the population regarding these issues:
- To promote these principles in international cooperation programmes:
- To evaluate ongoing actions initiated by the member organisations and disseminate their results.

The INBO is a flexible structure based on its members´ willingness to work together. It does not have its own legal personality or international organisation bye-laws, and is simply governed by a Charter of Organisation and Operation. The last assembly was held in Debrecen (Hungary) in June 2007.

The declaration of Debrecen, based on the acquired experience, stated that the management of water resources on a basin scale offers obvious advantages in terms of governance. The management of water resources should be tackled as follows:

On the scale of local, national or transboundary basins of rivers, lakes and aquifers:

- Based on integrated information systems, allowing knowledge on resources and their uses, polluting pressures, ecosystems and their functioning, the follow-up of their evolutions and risk assessment. These information systems will have to be used as an objective basis for dialogue, negotiation, decision-making and evaluation of undertaken actions, as well as coordination of financing from the various donors.

- Based on management plans or master plans that define the medium and long-term objectives to be achieved.

Through the development of Programs of Measures and successive multiyear priority investments:

- With the mobilization of specific financial resources, based on the polluter-pays principle and user-pays , systems
- With the participation in decision-making of the concerned Governmental Administrations and local Authorities, the representatives of different categories of users and associations for environmental protection or of public interest. Indeed, this concerted participation will ensure the social and economic acceptability of decisions taking into account the real needs, the provisions to be acted upon and the contribution capabilities of the stakeholders in social and economic life. Decentralisation is the basis for effectiveness in water policies.

C.2.1.3. Global Water Partnership (GWP)

Although it is widely understood that water should be holistically managed, it was not until the Dublin and Rio de Janerio conferences in 1992 that a more comprehensive approach to water management was judged necessary for sustainable development. This awareness, together with the need for participatory institutional mechanisms related to water, called for a new coordinating organisation. In response to this demand, the World Bank, the United Nations Development Programme and the Swedish International Development Agency created the GWP in 1996.

The GWP is a working partnership between all those involved in water management: government agencies, public institutions, private companies, professional organisations, multilateral development agencies and other committed to the Dublin-Rio principles.
Today, this partnership actively identifies critical knowledge needs at global, regional and national levels, helps design programmes for meeting these needs, and serves as a mechanism for alliance building and information exchange on integrated water resources management.

The mission of the GWP is to support countries in the sustainable management of their water resources. Its objectives are to:

- Clearly establish the principles of sustainable water resource management and support initiatives responding to these principles at a local, national, regional or river-basin level.
- Identify gaps and motivate partners to meet critical needs within their available human and financial resources:
- Help match needs to available resources.

This initiative was based on promoting and implementing IWRM through the development of a worldwide network that could pull together financial, technical, policy and human resources to address the critical issues of sustainable water management.

C.2.1.4. World Water Council (WWC)

The World Water Council is an international multi-stakeholder platform. It was established in 1996 on the initiative of renowned water specialists and international

organisations in response to an increasing concern about world water issues from the global community.
Its mission is to promote awareness, build political commitment and trigger action on critical water issues at all levels, including the highest decision-making levels, to facilitate the efficient conservation, protection, development, planning, management and use of water in all its dimensions (on an environmentally sustainable basis for the benefit of all life on earth).

By providing a platform to encourage debate and the exchange of experiences, the WWC aims to reach a common strategic vision on water resources and water services management amongst all stakeholders in the water community. In the process, the Council also catalyses initiatives and activities, whose results converge towards its flagship product, the World Waster Forum (WWF).

The WWC is financed primarily through membership fees and additional support is provided by the host city of Marseilles. Specific projects and programmes are financed through donations and grants from governments, international organisations and NGOs

C.2.1.5. The World Bank.

The World Bank is a source of financial and technical assistance for developing countries around the world. It is an international organisation that is owned by 185 member countries and formed by two unique development institutions: the International Bank for Reconstruction and Development (IBRD) and the International Development Association (IDA). (This last institution should not be confused with the International Desalination Association, with the same acronym, IDA). Each institution plays a different but supportive role in the mission of global poverty reduction and the improvement in standards of living. The IBRD focuses on middle- income and creditworthy poor countries, while the IDA focuses on the poorest countries in the world. Together, they provide low-interest loans, interest-free credit and grant to developing countries for education, health, infrastructure, communications and many other purposes.

Among its main lines of research, there exist annual publications. The W*orld development report*; the G*lobal monitoring report* analysing compliance with the Millennium Development goals; and the *World development indicators*. In recent years it has worked actively on the study and analysis of decentralised management of River Basins.

C.2.1.6. The International Water Management Institute (IWMI)

The International Water Management Institute (IWMI) is one of fifteen international research centres supported by a network of 60 governments, private foundations and regional organisations known collectively as the Consultative Group on International Agricultural Research, (CGIAR). It is a non-profit organisation with a staff of about fifty members, and offices in over ten countries across Asia an Africa, with its headquarters in Colombo, Sri Lanka.

The IWMI Mission is to improve the management of land and water resources for food, livelihoods and nature. Its vision is to be a world-class knowledge centre on water, food

and the environment. The IWMI targets water and land management challenges faced by poor communities in the developing world and through this contributes towards the achievement of the UN Millennium Development Goals (MDG) of reducing poverty, hunger and maintaining a sustainable environment.
Research is the core activity of the IWRI. The priority themes are: basin water management; land; water and livelihoods; agriculture, water and cities; and water management and the environment. The work involves collaboration with numerous partners in the North and South and targets policymakers, development agencies, farmers and private-sector organisations.

C.2.1.7. World Resources Institute (WRI)

The World Resources Institute (WRI) is an environmental think tank that goes beyond research to find practical ways to protect the Earth and improve people´s lives. Its mission is to move human society to live in ways that protect the Earth´s environment and its capacity to provide for the needs and aspirations of current and future generations.

Because people are inspired by ideas, empowered by knowledge, and moved to change by greater understanding, WRI provides- and helps other institutions provide-objetive information and practical proposals for policy and institutional change that will foster environmentally sound and socially equitable development. The WRI publishers regular reports on resources at a global level. The most recent of them is *World resources 2005- the wealth of the poor: managing, ecosystems of fight poverty*, with the collaboration of the Development and Environment programmes of the United Nations and the World Bank.

C.2.1.8. The Stockholm International Water Institute (SIWI)

The Stockholm International Water Institute (SIWI) is a policy institute that seeks sustainable solutions to the world escalating water crisis. SIWI advocates future-orientated, knowledge integrated water views in decision making (nationally and internationally), that lead to sustainable use of the world water resources, sustainable development, of societies and reduced poverty.

By creating opportunities for dialogue and collaboration between water experts and decision makers, SIWI stimulates the development of innovative policies and scientifically-based solutions to water-related problems. This is necessary in order to achieve the MDGs and the water related targets which were agreed upon at the Johannesburg Summit.

SIWI stresses that water is a key to socio-economic development and quality of life, and that through IWRM barriers which hinder increased food production, pollution prevention and poverty reduction can be overcome. SIWI organises the World Water Week (WWW) in Stockholm, manages the Swedish Water House (SWH) and hosts the UNDP Water Governance Facility, working on a variety of international projects related to water, particularly on the question of developing policies and training capacities through various working committees. It has published the report *Health, dignity and* *development; what will it take?* with the collaboration of the Working Group on Water and Sanitation from the United Nations Millennium Project.

C.2.2. National water-related organizations

C.2.2.1. Fundación Nueva Cultura del Agua (FNCA)

The New Water Culture Foundation started as the result of the "Iberic Congress about Water Management and Planning", celebrated every two years since 1998 with the support of more than 70 Spanish and Portuguese Universities. The Foundation has about 100 founder members, with outstanding specialists in every area related to the water management, most of them coming from the academic field.

The basic idea of the Foundation is that traditional water policies are enough neither to incorporate the needs and worries of our society nor to give proper answers to the challenges of a new model based on sustainability. In order to harmonize social welfare improvement with environment limits, guaranteeing its conservation, it is necessary to switch.

C.2.2.2. Coordinadora de Afectados por Grandes Embalses y Trasvases (COAGRET).

This organization was born in1995, with the purpose of creating a group of people and areas affected by the construction of big hydraulic buildings within the Spanish territory. COAGRET tries to combine a range of willpowers and knowledge, searching a change in the water policy towards rationality and respect. The actively participate in all the hydraulic discussions in Spain. It is composed by an important amount of associations, but also by individual members.

C.2.2.3. Instituto Tecnológico del Agua (ITA) – Universidad Politécnica de Valencia

ITA is a research center located at the Universidad Politecnica de Valencia, and also dependant from the Generalitat Valenciana (the regional government). Its activity is focused on research and development, dealing with urban water engineering and management. The ITA is formed by a group of water professionals consolidated over the last thirty years in Valencia and which originated around the Fluid Mechanics Chair at the Universidad Politécnica de Valencia.

C.3. Spanish water accounts methodology

C.3.1. Spanish water accounts: quantity

As suggested by the *Group on the State of the Environment* of the OECD (1990, 1993), an average year accounting model was calculated for each administrative water basin of Spain. A PIOT analysis evaluates the origin and final uses of water resources for each water subsystem, and the total resources and their availability. According to a et al. (2005b), the physical input-output table (PIOT) to determine water resources and their availability for an average year in a determined area, generally a country, a region or a watershed is subdivided in three parts:

- a total water resources table with the origin of the water;
- an internal transfers matrix with water-flows between various hydrological subsystems; and
- a primary withdrawals and final uses table.

This PIOT allows the calculation of the total water resources and their availability. Before completing a PIOT analysis, the following should be defined: a unit of account, a measurement unit, a reference period, statistical units, a reference area, areas of hydrological elements, and water transfers.

The unit of account is the water. The measurement unit is the cubic kilometer per year. The reference period is the average year, which has the advantage of providing an estimation in order to define a statistical normal year. The average year has the disadvantage of eliminating events such as severe floods or droughts, which may be short-lived but cause severe management problems. Subannual, seasonal, or monthly time periods should also be considered (Gascó et al., 2005b).

The statistical units were subsystems of the inland water resource system (RS). These subsystems are classified as follows (the nomenclature is due to the correspondence with the originals OECD quantity accounts tables):

RS9: Atmosphere;
RS6+RS5: Ground (soil) and vegetation cover;
RS44: Rivers (natural) and channels (artificial);
RS43: Lakes (natural) and water reservoirs (artificial);
RS42: Snow and glaciers; and
RS41:, Groundwater.

Because artificial water reservoirs are closely connected with the natural environment, they are included in RS and not in the utilization system (US). Channels are closely integrated within the hydrological system, and they are classified together with rivers in the RS instead of in the US. The average infrastructure of dams and channels has to be maintained during the time of reference.

The area of land–atmosphere interface must coincide with the sum of the surfaces of all elements, except groundwater, as indicated by Eq. A.1:

Eq. A.1. $$\mathrm{RS9} = \mathrm{RS6} + \mathrm{RS5} + \mathrm{RS44} + \mathrm{RS43} + \mathrm{RS42}$$

Raw data include initial and final stocks, and natural and artificial inputs and outputs for each hydrological element. The RS is bounded by its interfaces with the atmosphere and the sea. Atmospheric precipitation is a primary input while evapotranspiration and flow into the sea are outputs from the system.

C.3.1.1. Total Resources and Gross Annual Availability

Total water resources (TR) and total water uses (TU) in hm^3/yr are transfers that follow the following conservation principle:

Eq. A.2. $TR = TU$

Eq. A.2 can also be applied to each subsystem integrating the resource system in each of the hydrographical basins that are used for water resource management within a specific reference territory, as shown in France (Margat 1983; Weber 1984; INSEE 1986), Spain (Naredo and Gasco´ 1994), and other countries (OECD 1990, 1993). The defining equations for total resources are as follows:

Eq. A.3. $TR = PI + SI$

Eq. A.4. $PI = AP + IFO$

Eq. A.5. $SI = ITI + NIBF + IBF$

Eq. A.6. $TR = AP + IFO + ITI + NIBF + IBF$

where PI is primary inputs, SI is secondary inputs, AP is atmospheric precipitation, IFO is influents from outside, ITI is internal transfer inflows, NIBF is nonirrigation backflows on underground waters and rivers, and IBF is irrigation backflows on underground waters and rivers. Total resources are not all available because natural and artificial elements of the resource systems need a minimum quantity of water for internal transfers between them. Gross annual availability (GAA) is obtained as follows:

Eq. A.7. $GAA = TR - TIO$

Where total internal outflows derive from the internal transfers matrix, which describes water flow relations between various subsystems.
Internal Transfers Matrix and Water Environment

According to the physical continuity principle, total internal outflows (TIO) and total internal inflows (ITI) are equal.

Eq. A.8. $TIO = ITI$

An internal transfers matrix describes inputs and outputs for each subsystem. Values of ITI and TIO change according to the properties of natural–artificial water cycles into resource systems, which may be modified by resource development, management, and use. In general, civil works for temporal (dams) and spatial (aqueducts) regulations increase the availability of water resources. Nevertheless, primary withdrawals sometimes increase more than water availability, and a drastic negative net accumulation may occur. The decrease of spontaneous natural outflows from a specific reference territory is symptomatic of its environmental degradation.

C.3.1.2. Total uses and Net Accumulation

Total uses in the right side of Eq. A.2 include total internal outflows, total withdrawals and final uses (TWFU), and net accumulation (NA). The defining equations are as follows:

Eq. A.9. $$TU = TIO + TWFU + NA$$

Eq. A.10. $$TWFU = PW + NO + RE$$

Eq. A.11. $$NO = NO_s + NO_t$$

where PW is primary withdrawals, NO is natural outflows, RE is real evaporation, NO_s is natural outflows to the sea, and NO_t is natural outflows to the outside territory. NA defines the difference between final stocks and initial stocks in the hydrological subsystems of the continental water resource system. Net accumulation can also be calculated using Eq. A.7 and Eq. A.9:

Eq. A.12. $$NA = GAA - TWFU$$

Total withdrawals and final uses may exceed the gross annual availability (GAA), thus triggering a negative value of NA. In this case, water stocks and flows in the resource system would decrease year after year, making the water resources unsustainable.

C.3.1.3. Example: Inland Basins of Catalonia

The described PIOT methodology was applied to the Inland Basins of Catalonia by Gascó et al. (2007). Their results were partially presented in the *Seminario sobre Cuentas y Costes del Agua en Cataluña*, celebrated in Barcelona, June 18-19, 2007 and organizad by the CWA. Those figures have been adapted and reorganized here in order to illustrate the followed methodology.

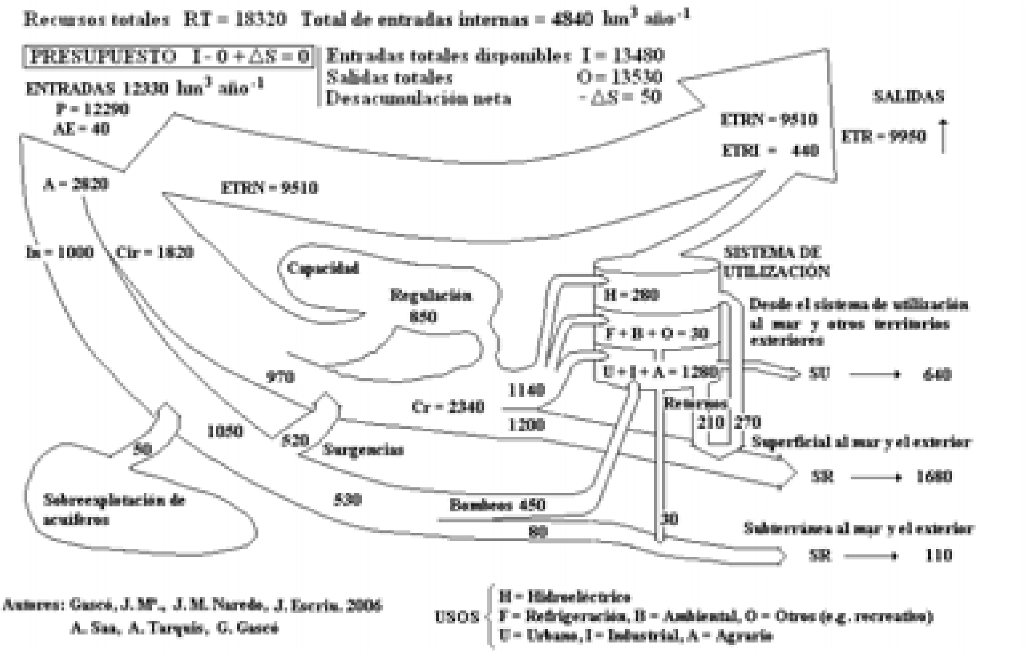


Figure A.1. Average hydrologic cycle in the Inland Basins of Catalonia (source: Gascó et al., 2007)

In this case, the reference territory is not a complete and isolated catchment, so primary inputs increase by natural and artificial inflows from the outside (river diversions), and outputs increase by downstream flows to other territories and artificial outputs such as flows through emissaries into the sea. Water flows for a specific reference territory are divided in two categories: outside flows in relation to water flowing between the reference area and other regions, and internal flows within the reference area between various continental water subsystems.

Internal flows are divided into spontaneous transfers, and transfers induced by economic agents. Internal transfer inflows in Table A.1 include spontaneous and engineering transfers.

Spontaneous internal transfers include surface and underground transfers. Surface transfers: run-off (RS9 → RS44), flow-off (RS43 → RS44, RS42 → RS6 +RS5, and RS42 → RS44), surface storage (RS44 → RS43), and overflow (RS44 → RS9). Underground transfers: seepage (RS9 → RS6 + RS5 → RS41, and RS44 → RS41), discharge point (RS41 → RS44, and RS41 → RS9), and rise (RS41 → RS6 + RS5).

Internal engineering transfers are subdivided into direct and induced. Direct internal engineering transfers are the following: drainage (RS6 + RS5 → RS44, RS6 + RS5 → RS41), pumping (RS41 → RS44), spatial flow regulation (RS43 → RS44), and temporal flow regulation (RS44 → RS43, and also RS43 → RS41).

Induced internal engineering transfers are the following: indirect impacts due to alterations of the vegetation cover, sealing effect due to urbanization, and transfers caused by primary withdrawals (RS41 → RS44, and RS44 → RS41), artificial inflows (RS6 + RS5 → RS41 → RS44), and backflows (in particular RS41 → RS43). Nonirrigation backflows include losses and leaks (US → RS6 + RS5, US → RS41, and US → RS9), and returns or discharges into the environment after use (US → RS6 + RS5), (US → RS41), (US → RS44). Finally, irrigation backflows include water distributed for irrigation (US → RS6 + RS5), and exclude losses and leaks (US → RS6 + RS5).

Total internal outflows and internal transfer inflows are shown in Table 7(B). Internal transfers inside each administrative hydrographical basin are linked by an internal transfers matrix that defines water flows between different resource subsystems. This matrix derives from figures showing all transfers of water within the resource system and between the resource system and the utilization system Figure A.2.

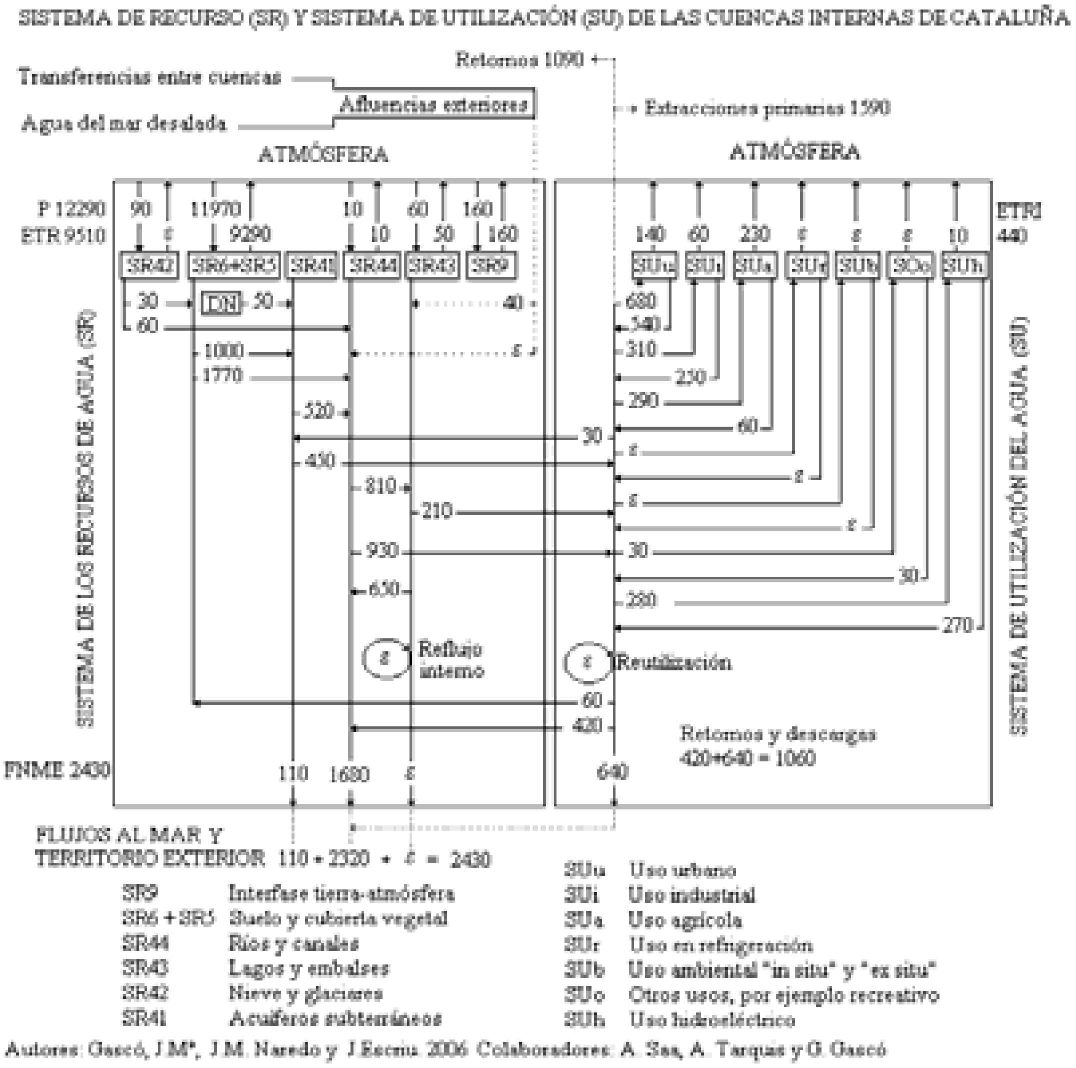


Figure A.2. Average year water transfers in the IBC (source: Gascó et al., 2007)

The model by Newhall (1972) was used to calculate soil moisture regimens according to Soil Survey Staff (1998) and to estimate real evapotranspiration. The Newhall model was modified to include natural and artificial inputs for the estimation of induced real evapotranspiration in irrigated lands. Meteorological observatories and water-flow stations were classified according to temperature and altitude to get the transfers of RS42. Seasonal low flows were used to calculate transfers from RS41. Data registered in dams were used to estimate internal engineering transfers from RS43. The balance in groundwater was corrected with information from registered water level depths.

In the IBC, average primary inputs were 12,249 hm^3/yr, 40 of which are influents from outside in the different water basins, and 12,209 come from atmospheric precipitation. Natural real evapotranspiration reached 9,510 hm^3/yr, whereas the one induced by the utilization system reached 440 hm^3/yr, 230 of which came from agriculture (land irrigation). Induced real evapotranspiration (440 hm^3/yr) is included as a part of primary withdrawals (1,590 hm^3/yr). Average backflows from the utilization system reached 1,090 hm^3/yr.

Natural outflows to the sea and outside territory reached 2,430 hm^3/yr. There was a negative net accumulation of 50 hm^3/yr.

The part of intercepted precipitation that dropped from the leaves or slipped down the trunks of the trees was considered as inputs into the soil (Gascó et al., 2005b). In RS9, only the part directly evaporated was considered as input or output. Thus, atmospheric precipitation and real evapotranspiration were considered the same in RS9. If trees are cut down, net interception will be zero, so the input into the continental water resource system will coincide with the value registered in pluviometers.

Primary withdrawals by the utilization system (RS → US) may be for different types of supplies: urban (USu), industrial (USi), agricultural (USa), refrigeration (USr), "in situ" and "ex situ" environmental (USe), hydroelectrical (USh), and others such as recreational (USo). Real evapotranspiration is a transfer involving a change of phase from liquid, snow, or ice to vapor (RS → RS9). Total withdrawals and final uses include primary withdrawals without a change of phase to vapor, spontaneous natural outflows, and real evapotranspiration.

Spatial and temporal distribution of the atmospheric precipitation/potential evapotranspiration ratio defines the spatial and temporal imbalance in the IBC. All water basins present a water excess in winter and a deficit in the summer. Temporal and spatial imbalances were used by Gascó et al. (2006) for justifying new infrastructures of dams for reserving water, and channels for transporting water to arid zones (Gasco´ and Saa 1992, Maestu and others 2001), where some unconventional sources of supply are being used, e.g., desalting brackish water or seawater (Gascó, 2004).

		Inputs in subsystems (hm^3/yr)						
Inputs	**Origin of water resources**	**RS9**	**RS6+RS5**	**RS44**	**RS43**	**RS42**	**RS41**	**Total input**
PI	AP	160	11,970	10	60	9.40	_	12,209
	IFO	e	_	E	40	e	e	40
SI	ITI	e	30	107,370	810	e	1,000	108,210
	NIBF	e	e	420	e	e	30	420
	IBF	e	60	_	_	_	_	60
Total resources TR (km^3 y^{-1})		160	12,060	107,800	910	9	1,030	120,939

Table A.1.   Total resources in the IBC.

Where:

PI, Primary inputs,
SI Secondary inputs,
TR, Total resources.
AP, Atmospheric precipitations,

IFO Influents from the outside, including: natural influents, inflows induced by economic agents, and backflows from the outside,
TI, Internal transfers inflows, including spontaneous internal transfers and internal inflows induced by economic agents, and backflows from the outside, engineering transfers (surface transfers and underground transfers),
NIBF, Non-irrigation backflows,
IBF, Irrigation backflows.
RSP, Land-atmosphere interface

		Internal transfers(hm^3/yr)					
		Receiving subsystems					
		RS6+RS5	**RS44**	**RS43**	**RS42**	**RS41**	**TIO**
Supplying subsystems	**RS6+RS5**	_	1,770	e	e	1000	2,770
	RS44	e	_	810	e	e	810
	RS43	e	650	_	e	e	650
	RS42	30	60	e	_	e	90
	RS41	e	520	e	e	_	520
Internal trasnfer inflows ITI		30	3,000	810	0	1,000	4,840
Input-Output balance		-2,740	2,190	160	-90	480	0

Table A.2. Internal transfers matrix

TIO Total internal outflows, including spontaneous internal transfer and internal engineering transfers (surface transfers and underground transfers).

	(hm^3/yr)							
				NO				
Subsystems	**GAA**	**PW**	**RE**	**Nos**	**Nos+Not**	**TWFU**	**NA**	**TU**
RS9	160	_	160	_	_	160	0	160
RS6+RS5	9,290	_	9290	_	_	9,290	0	12,060
RS44	106,990	930	10		2,320	3,260	103,730	107,800
RS43	260	210	50	e	E	260	0	910
RS42	-81	e	E	e	e	0	-81	9
RS41	510	450	_		110	560	-50	1,030
Total	117,129	1590	9510	0.00	2,430	13,530	103,599	121,969

Table A.3. Internal trasnfers matrix

GAA, Gross annual availability,
PW, Primary withdrawals,
RE, Real evapotranspiration;
NO, Natural outflow,
Nos, Natural outflow to the sea,
Not, Natural outflow to the outside territory,
TWFU, Total withdrawals and final uses,
NA, Net accumulation,
TU, Total ises,

C.3.1.4. Spanish water accounts: quality

In line with the previously outlined methodological proposal, the system of Water Quality Accounts approaches the subject of quality from the perspective of both the resources and the requirement of the different uses, ordering the analytical information provided by the national network of streamflow measurement stations.

Water generally looses its quality as it moves through the hydrological cycle, from the source (the rain or the flow spring) to the final drain (the sea), and that this loss of quality is greater and takes place earlier in arid-climate territories. The aridity that characterises most of the Spanish territory gives rise to the frequently observed bad water quality-water scarcity binomial, superimposing on the water quantity imbalances other pronounced quality imbalances, the consideration of which is essential for the design of a sound water management policy (Naredo, 1997). Thus, salt content can be regarded as the most relevant indicator of the natural quality of water.

Salt content, which is usually expressed in milligrams per litre (mg/l) or in parts per million (ppm), is directly related to the electric conductivity of water. One of the most widely used water quality classifications is that of the laboratory of Salinity of the United States, which divides water into different groups according to degree of salinity and potential soil deterioration effect. This classification separates water into four classes (C1, C2, C3, C4) in which salinity levels range from 0 to 0,25 dS/m; from 0.25 to 0.75 dS/m, from 0.75 to 2.25 dS/m; and over 2.25 dS/m. Water containing up to 0.75 dS/m (nearly 500 mg/l) is considered to be prepotable (i.e., although it has organic contamination, it can be made potable if treated correctly).

In another line, to solve the problem of adding and comparing the water quality information of the different basins, the French Water Account methodology proposes the use of the Kilometre of standard river (klm.s.r.) as the common unit of calculation, understanding this to mean a river bed that is one kilometre long and that carries a flow of one cubic metre per second (m^3/s). The AQUAL model is capable of expressing the totality of the measured water network in Kilometres of standard river.

The first and foremost conclusion that can be drawn from the quality tables presented in the Spanish water accounts is that in the annual mean, most of the km.s.r. of all basins, save for those of the Norte and Duero basins, contain poor-quality water which their salt content places them beyond the limit of non potability. The weight of poor-quality waters becomes much more apparent during the summer months, when water flows decrease. The poor quality of these waters cannot be attributed to urban-industrial contamination, on which community regulations place so much stress, but rather to the determining factors of the natural environment, which are party heightened by anthropogenic land uses and farming practices (mainly affecting ground water quality, as the draft for the Hydrological Plan correctly points out). Consequently, this map of hostile water quality cannot be changed through the installation of water treatment plants. The problem presented by the discharges of urban-industrial precedence (also heightened in the summer), leading to the loss of potability of many of the class 1 and 2 km.s.r., must certainly be dealt with in order to avoid further deterioration of the already precarious water situation. But the only way to mitigate the underlying water quality problem is through the establishment of sound water management policies that take water quality into account, (avoiding unfortunate combinations, for example) and that have an effect on land use and farming practice (installing "green filters", improving irrigation efficiency to lower salt and fertiliser lixiviation without deteriorating the soil, etc)

Having introduced the subject of the natural quality of water, the theory sustaining the Spanish quality water accounts means the introduction of the available energy (or exergy) concept, that can be liberated by water, or to the energetic cost (of desalinating and pumping) that would have to be incurred in order to situate it at the desired quality level if it were taken from the final "drain" (the sea). The power (in kW) of a specific quantity of water in any point of the territory can be determined by measuring two of its aspects: its hydraulic power, which depend on the altitude, and its osmotic power, which is related to its dilution capacity. Both aspects take sea water as the point of reference for altitude and chemical composition (Naredo, 1997).

C.3.1.5. Hydraulic power (HP)

According to mass-energy relationship, the HP (MW) of a river basin in the earth gravitational field (g) and for a water density (ρ_w) can be evaluated by integration of a volume flow- height graph according to Eq. A.13:

Eq. A.13. $$HP = \int_{H=0;h=h_o}^{H=h;h_o=0} 10^{-3} \cdot 9.8 \cdot Q(H) \cdot dH$$

Where *H(m)* is the height difference between a river course position at height *h (m)* and the reference level placed at height h_o *(m)* over sea level, and *Q(H)* is the water flow (m^3/s) measured in a river course at the position *H (m)*.

The water resources of a hydrographical basin can be exploited as an energy resource for hydroelectric production and HP (MW) can be evaluated by integration of a mass flow-length graph (Figure A.3 and Figure A.4). Therefore, HP is the minimum power value necessary to transport natural water flow Q from sea level to position H (m) in a river course.

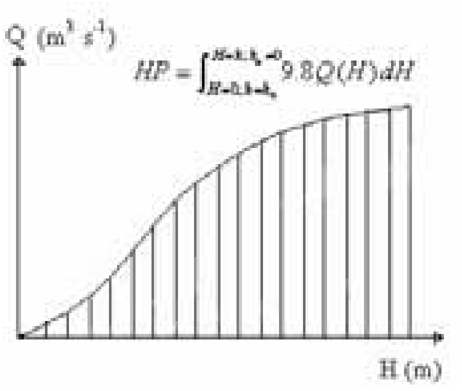


Figure A.3. Flow-height graph and hydraulic power (source: Gascó et

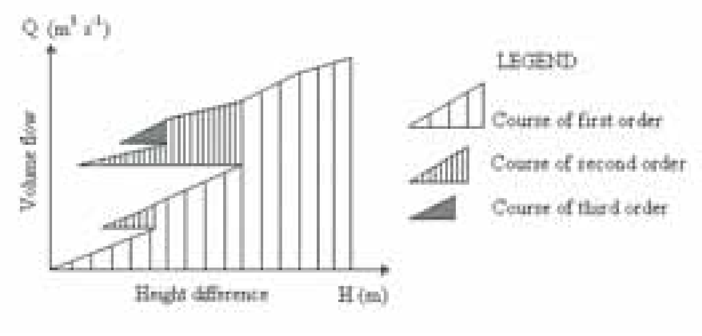


Figure A.4. Flow-height graph of an elemental hydrographical basin with courses of different orders source: Gascó et al.,

al., 2005a)	2005a)

Tributaries of all orders can be integrated by using their flow-height graphs (Fig.3). In general, height and water-volume flow can be approximately considered as object with additive properties. Therefore, an HP value can be useful when classifying hydrographical basins according to their hydroelectric power production capacity (Gascó et al., 2005a).

C.3.1.6. Osmotic power (OP)

Water salt concentration defines a water property linked to water desalination. The system most used to desalinate water is reverse osmosis (RO). OP could be evaluated by the integration of an osmotic pressure –volume flow where Q (m^3/s) (KPa) of the water□ is the water flow, which depends on the osmotic pressure solution. OP can be calculated for both pure and sea water as follows:

For pure water

Eq. A.14. $$OP = 10^{-3} \cdot \int_{\pi=0}^{\pi} Q(\pi) \cdot d\pi$$

For sea water

Eq. A.15. $$OP = 10^{-3} \cdot \int_{\pi=\pi}^{\pi=\pi_s} Q(\pi) \cdot d\pi$$

is osmotic pressure□ Where of water solution and □$_s$ stands for the osmotic pressure of sea-water solution.

Osmotic pressure can be estimated with electrical conductivity EC (dS/m, at 25° C) whose value depends on the ionic properties of water solutions. Gascó (2005a) uses the relationship given by Richards (1954) for natural water solutions:

Eq. A.16. $$\pi \approx 36.48\,\mathrm{EC}$$

Applying Eq. A.16 to rainfall (EC ≈0.046 dS/m according to Honotoria (2003) and seawater (EC≈54 dS/m), osmotic pressures result 1.7 kPa and 1970 kPa respectively. Therefore, the osmotic pressure of rainwater can be considered negligible with respect to seawater.

The OP needed to desalinate a water volume flow Q (m^3/s), with the sea-water salt concentration (54 $dS\cdot m^{-1}$) equal to the natural water salt concentration at a given point in the river course, can be calculated by the following equation:

Eq. A.17. $$OP(MW) = 10^{-3} \cdot Q \cdot (1970 - 36.48 \cdot EC)$$

Total power (TP), obtained by adding OP to HP, can give an idea of the total power to of a basin. Currently, this fact is very important as an increase in the price of energy can affect the short-term implementation of water policy (water transfer or water desalination) in the countries where water is a scarce resource.

To sum up, it is possible to calculate OP, HP and TP for the assessment of the WRQ at the hydrographical basin level as the basis for water resource planning and management, and as a first step in the design of water resource accounts based on quality.

Annex D

Emergy accounting

An extensive introduction about the Emergy approach is provided in Chapter 7. The aim of this Annex is to proportionate a wider perspective of the Emergy methodology. A summary of the most representative aspects of the methodology has been elaborated.

Because of its importance within the Emergy concept, a first section is devoted to *Transformities*. Secondly, flows maintaining order on Earth are analyzed and the emergy baseline is justified by reproducing its calculation. In a third step, the emergy calculation procedure is summarized and, finally, the commonly used emergy index are explained.

A quick review on Emergy main concepts has been done. However, much more interesting aspects could have been included.

There exists a nourished literature on Emergy. The reference website is *EmergySystems.org* (http://www.emergysystems.org/), developed in response to a demand expressed by the community of scientists, students, and friends for a central location of materials, information and news related to Emergy. The site is designed to aid in the research and teaching of emergy systems theory, with the mission of providing a locus for those interested in obtaining information about the theory, concepts and principles of emergy systems and systems ecology.

D.1. Transformity

The amount of input emergy dissipated (availability used up) per unit output exergy is called solar transformity It represents the emergy investment per unit product, and as such it is a measure of the way solar exergy is transformed and degraded. It may therefore be considered a 'quality' factor, which functions as a measure of the 'intensity of the biosphere support' to the product under study. The total solar emergy, U, driving a production process of a product, P, may be expressed as

$$\text{Eq.E.1.} \qquad E_m = \sum_i E_i \times Tr_i = E_I \times Tr_I \, ; i = 1,\ldots,n$$

where E_i is the exergy and Tr_i is the solar transformity of the ith input flow Pi, E_m is calculated over all the independent input flows (i.e. flows that are not originated by the same source) and E_I and Tr_I are n-dimensional vectors depending on the inputs to the process. The solar transformity Tr_i of the input P_i is in turn defined as follows:

$$\text{Eq.E.2.} \quad Tr_i = \frac{E_m}{E_{\ i}} = \sum_j E_{ij} \times \frac{Tr_{ij}}{E_i} = E_J \times \frac{Tr_J}{E_i} \, ; j = 1,\ldots,m$$

In Eq.E.2, U_i is the solar emergy driving the production of P_i, while E_{ij} is the exergy and Tr_{ij} the solar transformity of the j^th^ input flow contributing to P_i. This apparently circular definition is made operational by putting Tr_s, the solar transformity of direct solar radiation, equal to 1. Substitution of Eq.E.1 yields:

$$\text{Eq.E.3.} \quad U = \sum_{ij} E_{ij} \times Tr_{ji} = E \times Tr, i = 1,\ldots,n, j = 1,\ldots,m$$

where E is the matrix of all indirect exergy inputs supporting the production process and Tr the matrix of transformities that link each flow to the total emergy E_m.

The inputs E_i to a process can be locally renewable (R_i), locally non-renewable (N_i), or imported from outside the system (F_i; feedbacks supplied from outside to reinforce the process). Therefore, an equivalent form for (Eq.E.3) is:

$$\text{Eq.E.4.} \qquad E_m = \sum_i Tr_i R_i + \sum_j Tr_j N_j + \sum_k Tr_k F_k \, ; i = 1,\ldots,n, j = 1,\ldots,1', k = 1,\ldots,n''$$

The total solar emergy, E_m, driving a process is assigned to the output as a measure of the resource investment required.

Figure E.1 shows the parameters needed to calculate transformities. Symbols are explained at the end of this annex. R, N, and F indicate, respectively, renewable, non-renewable and purchased emergy flows into a process. E_{out} is the energy content of the output(J). Y=R+N+F is the total emergy assigned to the output as a measure of the environmental support needed (seJ). Finally, Tr = Y/E_{out} is the transformity of the output (seJ/J).

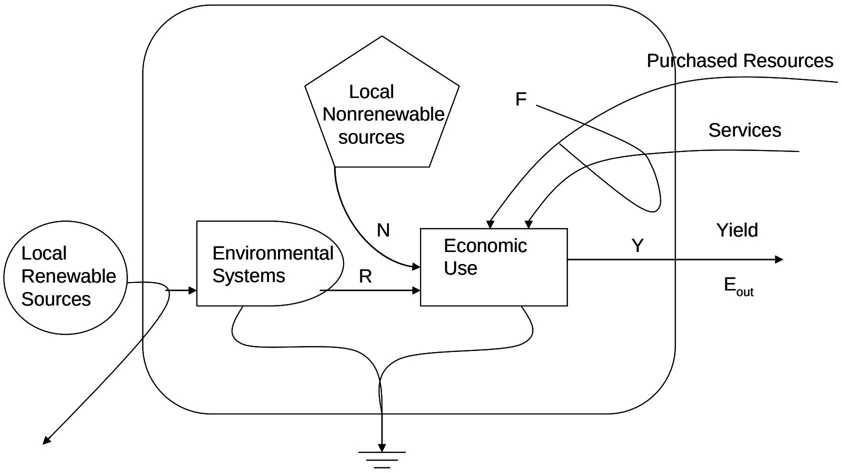


Figure E.1. Diagram for the calculation of transformities.

The transformity of the output flow is, therefore (Figure E.1):

$$Tr_{out} = \frac{total\_emergy\_U\_driving\_the\_process}{available\_energy\_of\_the\_output} = \frac{\sum_i Tr_i R_i + \sum_j Tr_j N_j + \sum_k Tr_k F_k;}{E_{out}}$$

Eq.E.5.

$$i = 1,...,n,\ j = 1,...,n',k = 1,...,n''$$

The solar transformity is measured as solar emergy joules per exergy joule of product (seJ/J). Some flows cannot be easily expressed as exergy and therefore other emergy intensity factors are used (seJ/g, seJ/$, seJ/h, etc) instead of solar transformity. In so doing, all kinds of flows to a system are converted to the same unit (seJ of solar emergy).

According to the process efficiencies along a given pathway, more or less emergy might have been required to reach the same result. The second law of thermodynamics dictates that there is a lower limit below which a product cannot be made. There is also some upper limit above which the process would not be feasible in practice although, in principle, an infinite amount of fuel could be invested in a process and thus have an infinitely high transformity.

Average transformities are used whenever the exact origin of a resource or commodity is not known or when it is not calculated separately. According to (Sciubba and Ulgiati, 2003), it follows that *transformities are not constant nor have they the same value for the same product everywhere, since many different pathways may be chosen to reach the same end state.*

Emergy is not a point function in the way energy and other thermodynamic state functions are. Its value depends upon space and time convergence, since more emergy is used up over a pathway requiring a higher level of processing for the same product. The emergy value is a 'memory' of resources invested over all processes leading to a product. While the exergy content of a given resource indicates something that is still available, the emergy assigned to a given item means something that has already been used up and depends on the characteristics of processes converging to the product.

Optimum performance for specified external constraints may be exhibited by systems that have undergone natural selection during a long 'trial and error' period and that have therefore selforganized their feedback for maximum power output. Their performance may result in optimum (not necessarily minimum) transformity.

Transformities are a very central concept in emergy accounting. Basic transformities of biosphere processes and primary resource formation have been calculated by different author (see, for example, Odum,2000, Brown and Bardi, 2001, Kangas, 2002, Brandt-Williams, 2002). Transformities of manufactured products are available in the scientific literature on emergy.

When a large set of transformities is available, other natural and economic processes can be evaluated by calculating input flows, throughput flows, storages within the system, and final products in emergy units. After emergy flows to and storages in a process or system have been evaluated, it is also possible to calculate a set of indices and ratios that may be suitable for system design and policy making.

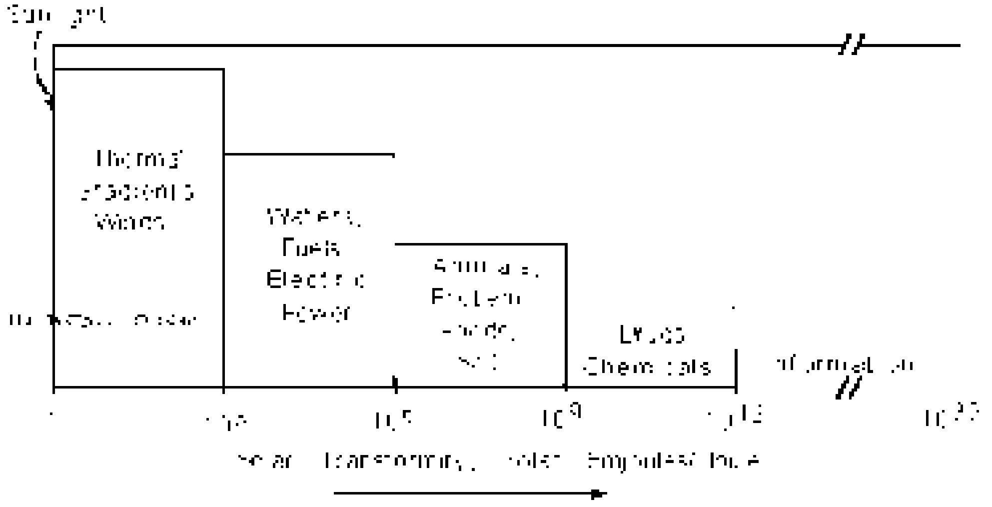


Figure E.2. Solar transformities scale (Adapted from Odum, 1996)

Transformities provide a quality factor as they account for the convergence of biosphere processes required to produce something. Embodied in the emergy value are the services provided by the environment, which are 'free' and outside of the money-based economy. By accounting for quality and free environmental services, resources are not valued by their money cost or society's willingness to pay, which often are very misleading.

D.2. Emergy evaluation of the biosphere and its processes

Flows of energy maintain order. The biosphere is driven by the flux of renewable energies in sunlight, tidal momentum, and deep earth heat each contributing to geologic, climatic, oceanic, and ecologic processes that are interconnected with flows of energy and materials and non-renewable energies contained in vast storages that are explited and released by society (Figure E.3).

Useful work means using inflowing emergy in reinforcement actions that ensure and, if possible, increase inflowing emergy. Energy dissipation without useful contribution to increasing inflowing emergy is not reinforcing, and thus cannot compete with systems that use inflowing emergy in self-reinforcing ways.

Figure E.3 shows an aggregated system diagram of the energy transformation network of the biosphere arranged with decreasing energy from left to right. It can be seen that all components interact and are required by the others.

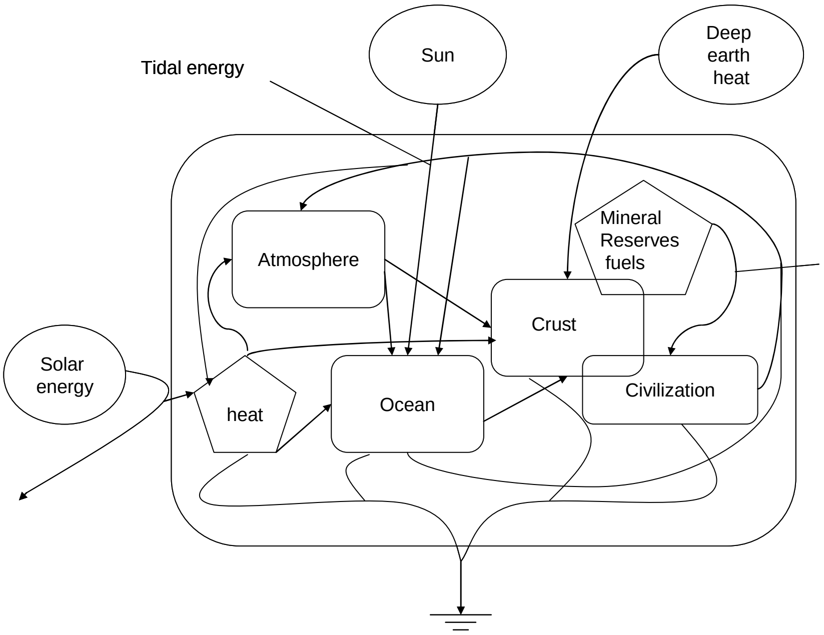


Figure E.3. Flows in the Biosphere

As a result, the total emergy driving the biosphere (the sum of solar, tidal and deep heat) is required by all processes within, and thus the emergy assigned to each of the internal pathways is the same. After millions of years of self-organization, the transformations of the driving energies by the atmosphere, ocean, and land are organized simultaneously to interact and contribute mutual reinforcements. Therefore, the energy flow of each jointly necessary process is the sum of the emergy from the three sources.

D.2.1. Annual budget of emergy flow supporting the Geobiosphere

The annual budget of emergy flow (empower) supporting the geobiosphere (atmosphere, ocean, and earth crust) includes solar energy, tidal, energy, and heat energy from the deep earth. Other inputs from space, such as the high-energy radiation of solar flares, cosmic rays, meteorites and stellar dust are not evaluate. All of these vary with oscillations and pulses, and their emergy values vary with their intensities.

The solar emergy is defined as the sum of all inputs of solar energy directly or indirectly required in a process (Odum, 1971). Input flows that are not from solar source (like geothermal and gravitational flows) are expressed as solar equivalent exergy by means of suitable transformation coefficients (Odum, 1988). The commonly used emergy unit is therefore the solar equivalent joule (seJ).

An emergy equation sets the empower of inputs into an energy transformation process equal to the empower of an output, where each term contains a flow multiplied by its emergy/unit. In the first equation, *Solar emergy+tidal emergy* equals to the *emergy of the heat generated by the surface processes* (Eq.E.6).

Eq.E.6. $$(3.93*10^{24} J/yr)\ (1 sej/J) + (0.52*10^{20} J/yr)\cdot Tr_t = (6.49*10^{20} J/yr)\cdot Tr_b$$

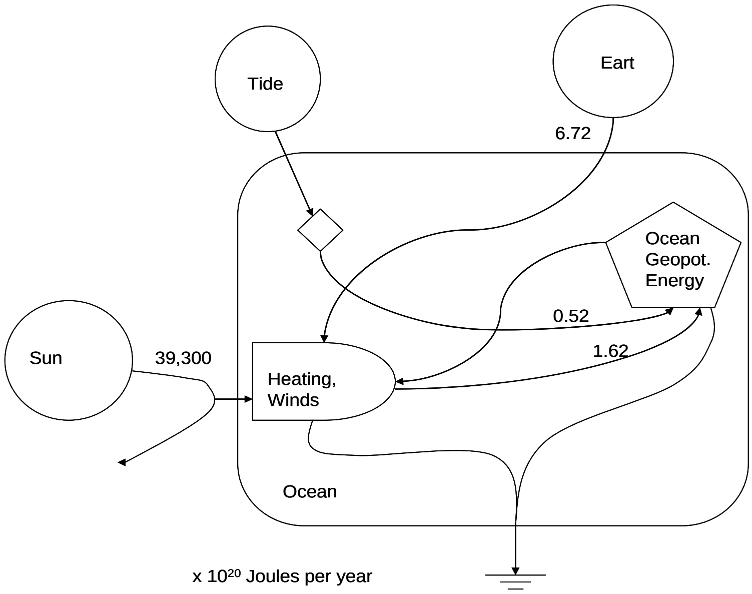


Figure E.4. Emergy diagram representing by Eq.E.6

In addition to that, a second equation establishes the equality between *Solar emergy+tidal emergy+deep earth emergy*, and the *oceanic geopotential energy* (Eq.E.7).

Eq.E.7. $$(3.93*10^{24} J/yr)(1sej/J)+(0.52*10^{20} J/yr)\cdot Tr_t + (6.72*10^{20} J/yr)\cdot Tr_b = (2.14*10^{20} J/yr)\cdot Tr_t$$

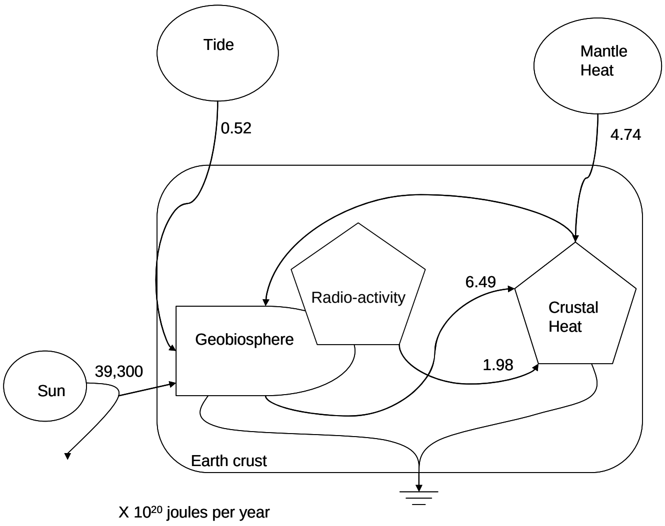


Figure E.5. Emergy diagram representing Eq.E.7

Total emergy contributions to the geobiosphere are about 15,83*10^{24} sej/year based on a reevaluation and subsequent recalculation of energy contributions dome in the year 2000.

Prior to that date, the total emergy contribution to the geobiosphere that was used in calculating unit emergy values was 9,44*10^{24} sej/year. The increase in global emergy reference base to 15.83*10^{24} sej/year changes all the unit emergy values that directly and indirectly were derived from the value of global annual empower. Thus, unit emergy values calculated prior to that year are multiplied by 1,68 (the ratio of 15,83/9,44).

It takes emergy (resources used up) to drive processes and make things. This also applies to processes that are apparently out of the realm of Thermodynamics, like generation of labor, Gross National Product, culture and information. These 'products' are not explicitly expressed in terms of thermodynamic quantities, but they require an investment of resources to be generated and operated. This production cost is adequately measured in emergy terms.

This new point of view accounts for energy concentration through a hierarchy of processes, most of them not under human control, which may therefore follow a different optimization pattern than the one that humans would choose. Human societies try to maximize efficiency, short time-scale return on investment, employment, profit, one-product output. Quite on the opposite, natural processes are stochastic and system-oriented and seem to maximize the utility of the total flow of resources processed through optimization of efficiencies and feedback reinforcement. As environmental conditions change, it appears that the response of the system adapts so that maximum power output can be maintained. In this way, systems tune their thermodynamic performance to the changing environment.

Accounting for required inputs over a hierarchy of levels gives rise to a *donor system of value*, while any purely exergetic analysis and economic evaluation are *receiver systems of value*, where something has a value according to its usefulness to the end user. It is useful to recall that emergy is not energy and, therefore, it is not conserved in the way energy is. Similarly to any other cost measure, the emergy used up is no longer available to drive further transformations. It is embodied in the product, generally in the form of upgraded quality and hierarchical role.

The emergy of a given flow or product is, by definition, a measure of the work of self-organization of the planet in making it. Nature supplies resources by cycling and concentrating matter through interacting and converging patterns. Some resources require a larger environmental work than others, and their use means a larger appropriation of environmental support and services. The emergy content may be therefore assumed as a measure of sustainability and/or pressure on the environment by the system.

D.2.2. Average Emergy Unit Values for Main Global Processes

Inputs of energy into the biosphere can be classified as renewable, non-renewable and slowly renewable. Within the last several hundred years, the total inputs of energy released by society to the biosphere from slowly renewable storages and non-renewable storages have grown to exceed the renewable ones. Table E.1 lists the overall emergy values of the flows of emergy driving the biosphere, including those released by society. Wood is sometimes considered a renewable energy input, however rates of deforestation and cutting exceed regrowth. The net loss of wood biomass is included in the analysis. Soil erosion has become a serious global problem. It is estimated that over 1/3 of all agricultural land is suffering erosional losses that threaten their productive capacity (Brown and Ulgiati, 1999)]. Eroded soil is included as a slowly-renewable energy "released" by society, since it is lost to agricultural production in the future.

Total emergy driving the biosphere, including human society, is about $3.23 \cdot 10^{25}$ seJ, composed of 1.58·1025 from renewable inputs and $1.65 \cdot 10^{25}$ sej from slowly- renewable and non-renewable sources. Of the total emergy inputs to the *global economy*, 51% are from slowly and non-renewable sources, while 49% are renewable (Table E.1).

In conclusion, the total emergy input to the geobiosphere in solar emergy ($15,83 * 10^{24}$ seJ/year). For the calculations, it is divided by each of the global product's ordinary measure (number of joules or grams). The unit values that result are useful for other emergy evaluations where global averages can be used.

Note	**Name**	**Unit**	**Energy flux (unit/yr)**	**Transformity (seJ/unit)**	**Emergy (sej)**	**Emdollars (Em$,US)**
	Global Renewable Energies					
1	Solar insolation	J	3.94E+24	1	3.937E+24	3.58E+12
2	Deep earth heat	J	6.72E+20	1.20E+04	8.064E+24	7.33E+12
3	Tidal energy	J	5.20E+19	7.40E+04	3.848E+24	3.50E+12
	Subtotal				**1.58E+25**	1.44E+13
	Society Released Energies (non-renewables and slowly renewables)					
4	Oil	J	1.38E+20	5.40E+04	7.46E+24	6.78E+12
5	Natural gas	J	7.89E+09	4.80E+04	3.79E+14	3.44E+02
6	Coal	J	1.09E+20	4.00E+04	4.36E+24	3.96E+12
7	Nuclar energy	J	8.60E+18	2.00E+05	1.72E+24	1.56E+12
8	Wood	J	4.10E+19	1.10E+04	4.51E+23	4.10E+11
9	Soils	J	1.38E+19	7.40E+04	1.02E+24	9.28E+11
10	Phosphate	J	4.77E+16	7.70E+06	3.67E+23	3.34E+11
11	Limestone	J	7.33E+16	1.62E+06	1.19E+23	1.08E+11
12	Metals	g	9.93E+14	1.00E+09	9.93E+23	9.03E+11
	Subtotal				**1.65E+25**	1.50E+13
	TOTAL				**3.23E+25**	
	Transformities and specific emergies from Odum (1996)					
	Emdollars obtained by dividing Emergy by		1.10E+12	sej/$		
1	Solar constant	2	cal/cm2/min			
		70%	absorbed			
	Earth cross section facing the sun=	1.28E+14	m2			
		5.26E+05	min/yr			
	Energy flux=			3.94E+24	J/yr	

2	Deep earth heat				
	heat to the earth's crust (Sclater et al., 1980)	1.32E+21	J/yr		
	radioactivity generation	1.98E+20	J/yr		
	heat flux up from the mantle	4.74E+20	J/yr		
	remaining (drive atmosphere, ocean, hydrological and sedimentry cycles)	6.49E+20	J/yr		
	Energy flux=			6.72E+20	J/yr
3	Tidal energy				
	Tidal contribution to oceanic geopotential flux	5.20E+19	J/yr		
	Energy flux=			5.20E+19	J/yr
4	Oil				
	total production	3.30E+09	Mt oil equivalent		
		4.19E+10	J/t oil eq		
	Energy flux=			1.38E+20	J/yr
5	Natural gas				
	total production	2.09E+09	m3		
		3.77	J/m3		
	Energy flux=			7.89E+09	J/yr
6	Coal				
	total production (soft)	1.22E+09	t/yr		
		1.39E+10	J/t		
	total production (hard)	3.30E+09	t/yr		
		2.79E+10	J/t		
	Energy flux=			1.09E+20	J/yr
7	Nuclear				
	total production	2.39E+12	kWh/yr		
		3.60E+06	J/kWh		
	Energy flux=			8.60E+18	J/yr
8	Wood				
	Annual net forest area loss	1.127E+07	ha/yr		
	biomass	40	kg/m3		
		30%	moisture		
		1.3E+07	J/kg		
	Energy flux=			4.10E+19	J/yr
9	Soil erosion				
	total soil erosion	6.10E+10	t/yr		
	assume soil loss estimate of 10 t/ha/yr and 6,1*E9 ha agricultural land	6.10E+16	g/yr		
	organic matter	1%			
		5.40E+00	kcal/g		
	Energy flux=			1.38E+19	J/yr
10	Phosphate				
	total global production	1.37E+14	t/yr		
	Gibbs free energy phosphate rock	3.48E+02	J/g		
	Energy flux=			4.77E+16	J/yr
11	Limestone				
	total production	1.20E+14	t/yr		
	gibbs free energy limestone	611	J/kg		

	Energy flux=			7.33E+16	J/yr
12	Metals				
	total production	9.93E+08	t/yr		
				9.93E+14	g/yr

Table E.1. Flux of renewable and non-renewable energies driving global processes (source: Adapted from Brown and Ulgiati, 1999)

In addition to the flows running the Economy, an emergy evaluation of global natural capital is summarized in Table E.2. Environmental resources (rows 1 - 4) are considered slowly-renewable resources. The non-renewable, fossil fuel resources, metals, and phosphorus are also included as natural capital and they are given in the table for comparison.

Note	**Name**	**Unit**	**Amount**	**sej/unit**	**Emergy (sej)**	**Emdollars (Em$,US)**
1	Fresh water	J	1.64E+23	1.82E+04	2.98E+27	2.71E+15
2	Soil organic matter	J	3.10E+22	7.40E+04	2.29E+27	2.09E+15
3	Plant biomass	J	4.16E+22	1.00E+04	4.16E+26	3.78E+14
4	Animal biomass	J	4.55E+19	1.00E+06	4.55E+25	4.14E+13
	Subtotal				5.74E+27	5.22E+15
5	Coal	J	2.16E+22	4.00E+04	8.64E+26	7.85E+14
6	Crude oil	J	5.82E+21	5.40E+04	3.14E+26	2.86E+14
7	Natural gas	J	5.28E+21	4.80E+04	2.53E+26	2.30E+14
8	Metals	g	1.74E+17	1.00E+09	1.74E+26	1.58E+14
9	Uranium	J	8.35E+20	1.79E+03	1.49E+24	1.36E+12
10	Phosphate rock	g	1.10E+16	3.90E+09	4.29E+25	3.90E+13
	Subtotal				1.65E+27	1.50E+15
	TOTAL				7.39E+27	6.72E+15

Transformities and specific emergies from Odum (1996)
Emdollars obtained by dividing
Emergy by 1.10E+12 sej($

1 Fresh water	Total freshwater including ice caps=		3.33E+07	km3
	Gibbs free energy of water=		4.94E+06	J/m3
	Energy=		1.64E+23	J
2 Soil organic matter	1.11E+10	ha	in woodland, crops, pasture, grassland	
	Assume:	1	m dep	
		1%	organic matter	
		5.4	kcal/kg	
		1.47	g/cm3	
	Energy=		3.6717E+22	J
3 Plant biomass	Total biomass=	1.841E+12	t dry wt.	
		5.4	kcal/kg	

		Energy=			4.161E+22	J		
4	Animal biomass	Total biomass=	2.01E+09	t dry wt.				
		(	1.02E+09	t on land,			9.98E+08	t in ocean)
			5.4	kcal/g				
		Energy=			4.55E+19	J		
5	Coal	Recoverable reserves=	5.19E+11	t coal eq. (hard coal)				
			2.79E+10	J/t				
			5.12E+11	t coal eq. (soft coal)				
			1.39E+10	J/t				
		Energy=			2.16E+22	J		
6	Crude oil	Recoverable reserves=	1.39E+11	t oil				
			4.19E+10	J/t oil eq				
		Energy=			5.82E+21	J		
7	Natural gas	Recoverable reserves=	1.40E+14	m3				
			3.77E+07	J/m3				
		Energy=			5.28E+21	J		
8	Metals	Total recoverable reserves=	1.74E+11	t				
		Energy=	1.74E+17	g				
9	Uranium	Recoverable reserve=	1.50E+06	t				
			7.95E+10	J/g				
			0.70%					
		Energy=			8.35E+20	J		
10	Phosphate	Recoverable reserves=	1.10E+10	t				
		Energy=			1.10E+16	g		

Table E.2. Global storages of natural capital (source: Adapted from Brown, 2000)

Total emergy value of natural capital is $7.39 \cdot 10^{27}$ seJ (78% renewable). The largest storage of natural capital is fresh water (40%) that includes the polar ice caps, ground water and lakes, rivers, soil moisture etc. Soil organic matter is the next largest storage of natural capital (31%). Plant biomass and animal biomass are valued at about 6% and 1% of the total natural capital respectively. The storages of non-renewable account for 22% (coal 12%, oil 4%, natural gas 3% and metals 2%).

It is important to note that the unit emergy values given in Table E.1 and Table E.2 are average values for global processes. It is well understood that there is no single unit emergy value for any given product, since no two processes are alike. This also holds for the processes of the biosphere. For instance, there are many transformities for rain depending on location and even time of year. Precipitation vvaries with altitude, is affected by mountains, and depends on the weather systems in complex ways. The evaluations are for the whole earth with 70% ocean. If the land is regarded as a higher level in the hierarchical organization of the geobiosphere, then rain over the land represents a convergence of oceanic resources as well as those of the continents, and calculation of continental rain transformiy includes all geobiosphere driving energy. As a result, continental rainfall has a higher transformity compared to the global average. To carry this idea even farther, the rainfall in any particular location may have a higher or lower transformity depending on the source area and intensity of the solar energy driving the cycles that produce it.

D.3. Emergy evaluation procedure: Emergy Synthesis

This evaluation process has been termed *emergy synthesis*. Synthesis is the act of combining elements into coherent wholes. Rather than dissect and break apart systems and build understanding from the pieces upward, emergy synthesis strives for understanding by grasping the wholeness of systems. Emergy is a systems concept, context driven, and cannot be fully understood or utilized outside of systems. By evaluating complex systems using emergy methods, the major inputs from the human economy and those coming "free" from the environment can be integrated to analyze questions of public policy and environmental management holistically.

Emergy accounting uses the thermodynamic basis of all forms of energy, materials, and human services but converts them into equivalents of one form. Emergy accounting is organized as a top-down approach where first a system diagram of the process is drawn to organize the evaluation and account for all inputs and outflows

Emergy accompanying a flow of something (energy, matter, information...) is easily calculated if the unit emergy value is known. The flow expressed in its usual units is multiplied by the emergy per unit of that flow. For example, the flow of fuels in joules per time can be multiplied by the transformity of that fuel (emergy per unit energy in solar emjoules/joule), or the mass of a material input can be multiplied by its specific emergy. The emergy of storage is readily calculated by multiplying the storage quantity in its usual units by the emergy per unit.

Unit emergy values are a kind of efficiency measure, since they relate all the inputs to an output. The lower the transformity or specific emergy, the more efficient the conversion. It follows from the second law of thermodynamics that there are some minimum unit emergy values for processes, which are consistent with maximum power operations. While there is no way to calculate them directly, the lowest transformity found in long-operating systems is used as an approximation. When estimating a theoretical potential of some system, it is appropriate to use the best (lowest) transformity known. Emergy flows are usually expressed in units of solar empower (solar emjoules per time).

Tables of the actual flows of materials, labor, and energy are constructed from the diagram and all flows are evaluated. The final step of an emergy evaluation involves interpreting the quantitative results. In some cases, the evaluation is done to determine fitness of a development proposal. In others, it may be a question of comparing different alternatives. The evaluation may be seeking the best use of resources to maximize economic vitality. So the final step in the evaluation is to calculate several emergy indices that relate emergy flows of the system being evaluated with those of the environment and larger economy within which it is embedded and that allow the prediction of economic viability, carrying capacity, or fitness.

D.3.1. Energy Systems Diagram

Systems diagrams are used to show the inputs that are evaluated and summed to obtain the emergy of a resulting flow or storage. The purpose of the system diagram is to conduct a critical inventory of processes, storages, and flows that are important to the system under consideration and are therefore necessary to evaluate. Components and flows within diagrams are arranged from left to right reflecting more available energy flow on the left, decreasing to the right with each successive energy transformation. For example, abundant solar energy is utilized in successive transformations in ecological, agricultural, and technoeconomic subsystems to support a small amount of high-quality energy of humans, their government, and information. A simple diagram of the global system including humans is shown in The left-to-right organization also corresponds to increasing scale of territory and turnover time. As illustrated, every energy transformation box has more than one input, including larger energy flows from the left, lesser amounts from units in parallel, and small but important controlling energies feeding back from the right.

D.3.2. Emergy Evaluation Table

Tables of the actual flows of materials, labor, and energy are constructed from the diagram. Raw data on flows and storage reserves are converted into emergy units and then summed for a total emergy flow to the system. Inputs that come from the same source are not added, to avoid double counting. Only the larger input is accounted for. If the table is for the evaluation of a process, it represents flows per unit time (usually per year). If the table is for the evaluation of reserve storages, it includes those storages with a turnover time longer than a year.

D.3.3. Procedure for emergy accounting

The general methodology for emergy analysis is a ‘top-down’ systems approach. It can be organized in three steps, as described below. Case studies with numerical examples can be found in [12,30,33,43].

The first step is drawing a detailed energy systems diagram, to gain an initial network overview, combine information, and organize data-gathering efforts. Diagrams must be considered as a ‘guide’ to organizing one’s thinking of the relationships between components and pathways of exchange and resource flow. According to Uligiati (20XX) This is achieved by:

a. Defining the boundary of the system for a correct inclusion of input flows
b. Listing the main components believed important on the investigated scale.
c. Knowing as many possible details about the processes occurring within the boundary (flows, relationships, interactions, production and consumption processes, etc.). Included in these are flows and transactions of money and labor believed to be important.
d. Drawing the system diagram of the whole system, by means of the symbols described in section D.5 (flow addition, interaction, positive or negative feedback, depreciation, etc.). A second system diagram is often drawn that represents an aggregated overview of the system under study. Processes and

storages are aggregated to reduce complexity, while retaining overall system integrity and aggregation

The second step is to construct emergy evaluation tables directly from the diagrams, to facilitate calculation of flows to and from the system. This also permits the identification of the flows of coproducts from each phase, some diverging, feeding back and converging within the process, and helps avoid double-counting. Raw data from preliminary material and energy flow accounting are entered as input flows. They are usually expressed as joules of exergy then they are multiplied by suitable transformities and converted to emergy units. Finally they are summed into a total emergy inflow driving the system. A table for storage reservoirs is also often constructed to place in perspective the emergy content of major system components.

An emergy analysis table usually has the following column headings (Table E.3).

A	B	C	D	E	F	G
Note	item	Unit	Amount	Transformity (seJ/J)	Ref.for transformity	Emergy (seJ/yr)
1	CH_4	Joule	...	54,000	[42]	=D1*E1

Table E.3. A typical emergy accounting table

If the table is for flows, it represents flows per unit time (usually per year). If the table is for reserve storages, it includes those storages with a turnover time longer than one year. Dynamic models for storage variation may also be constructed and run [44].

- Column A is the line item number, which is also the number of the footnote in the table where raw data source is cited and calculations shown.
- Column B is the name of the item, also shown on the aggregated diagram.
- Column D is the raw data in joules, grams, dollars or other units, that are shown in column C. Labor inputs are usually given in working time units (years, hours), while services (previous work done to deliver the input flow) are evaluated through the money cost of each flow.
- Column E is the transformity, or the emergy per unit, used for calculations, in solar emergy joules per unit of raw input (seJ/J; seJ/g). These are obtained from previous studies cited in literature or calculated for the system under study. Converting labor and services into emergy units requires conversion coefficients, C_{lab}, C_{econ}, calculated by means of a previous emergy analysis of a country's economy, for a given year (C_{lab}=U/work force; C_{econ}=U/GNP). If transformities from other authors are used, source reference should be shown in column F.
- Column G is the solar emergy of a given flow, calculated as raw input times its transformity (column D times column E).

Finally, when the emergy tables have been completed, a third step involves calculating several emergy indices that relate emergy flows of the process or economy with those of the environment, and allow the evaluation of a system's performance as well as predictions of economic viability and carrying capacity.

D.4. Emergy based indices of sustainability

Transformity only measures how much emergy it takes to generate one unit of output, regardless of whether or not the input is renewable. It is a measure of efficiency on the global spatial and timescale of the biosphere. It indicates the hierarchical position of an item in the thermodynamic scale of the biosphere and can be regarded as a quality factor from the point of view of biosphere dynamics.

A definition of sustainability must include time. What is sustainable in one period, may not be sustainable in the long run. Emergy provides indicators that expand the evaluation process to the larger space and time scales of the biosphere While the emergy approach is unlikely to be of practical use in making decisions about the price of food at the grocery store or about the way a process should be improved to maximize exergy efficiency at the process scale, its ability to link local processes to the global dynamics of the biosphere provides a valuable tool for adapting human driven processes to the oscillations and rates of natural processes. This may be a useful step towards developing sustainable patterns of human economies. Emergy measures thermodynamic and environmental values of both energy and material resources within a common framework. Several emergy indices are defined to illuminate these different aspects of sustainability.

The systems diagram shows nonrenewable environmental contributions (N) as an emergy storage of materials, renewable environmental inputs (R), and inputs from the economy as purchased (F) goods and services. Purchased inputs are needed for the process to take place and include human service and purchased nonrenewable energy and material brought in from elsewhere (fuels, minerals, electricity, machinery, fertilizer, etc.). Several ratios or indices are defined to evaluate the global performance of a process.

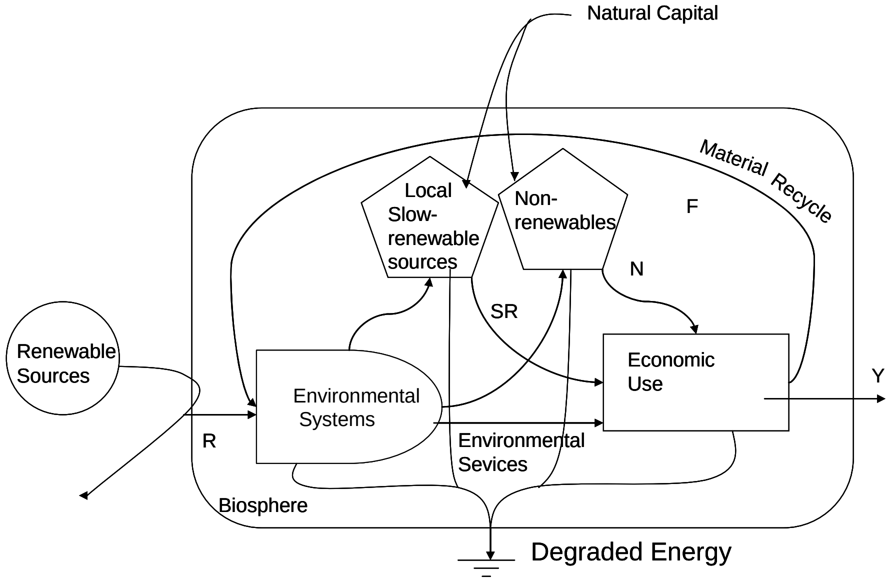


Figure E.6. Simplified systems diagram of the biosphere

D.4.1. Percent Renewable (%Ren)

The percent of the total energy driving a process that is derived from renewable sources. In the long run, only processes with high %Ren are sustainable.

Eq.E.8. $$\%\mathrm{Re}n = \frac{R}{R + SR + N}$$

D.4.2. Emergy Yield Ratio (EYR)

At the scale of the biosphere, the EYR is the ratio of the emergy of the output (Y=R+SR+N) divided by the emergy of non-renewable inputs that are used.

Eq.E.9. $$EYR = \frac{Y}{N}$$

D.4.3. Environmental Loading Ratio (ELR)

At the scale of the biosphere, it is the ratio of non-renewable and slowly-renewable emergy (imported emergy) to renewable emergy. The ELR is an indicator of the load on the environment and might be considered a measure of stress due to economic activity. In the absence of investments from outside, the renewable emergy that is locally available would have driven the growth of a mature ecosystem consistent with the constraints imposed by the environment and would be characterized by an ELR=0.

Eq.E.10. $$ELR = \frac{N + SR}{R}$$

In some ways, the ELR is a measure of the disturbance to the local environmental dynamics, generated by the development driven from outside. The ELR is clearly able to make a difference between nonrenewable and renewable resources, thus complementing the information that is provided by the transformity. Low ELRs (arround 2 or les) are indicative of relatively low environmental impacts (or processes that can use large areas of a local environmento to "dilute impacts"). ELRs between 3 and 10 are indicative of moderate environmental impacts, while ELRs ranging from 10 up to extremely high values indicate much higher environmental impacts due to large flows of concentrated nonrenewable emergy in a relatively small local environment

D.4.4. Emergy Sustainablility Index (ESI)

An index that accounts for yield, renewability and environmental load. It is the incremental emergy yield compared to the environmental load and is calculated as the ratio of emergy yield to environmental load. It measures the potential contribution of a resource or process to the economy per unit of environmental loading.

Eq.E.11. $$ESI = \frac{EYR}{ELR}$$

EISs lower than 1 appear to be indicative of consumer products or processes and those greater than 1 indicative of products that have net contributions to society without heavily affecting its environmental equilibrium. As it relates to economies, an EIS lower than 1 is indicative of highly developed consumer-oriented systems, EISs between 1 and 10 have been calculated for what have been termed "developing economies", while EISs greater than 10 indicate economies that have not yet significantly started any industrial development.

D.4.5. Emergy yield ratio

The emergy yield ratio is a measure of the ability of a process to exploit and make available local resources by investing outside resources. It provides a measure of the appropiation of local resources by a process, which can be read as a potential additional contribution to the economy, gained by investing resources already available.

$$\text{Eq.E.12.} \qquad EYR = Y / F$$

The lowest possible value or the EYR is 1, which indicates that a process delivers the same amount of emergy that was provided to drive it, and that it is unable to usefully exploit any local resource. Therefore, processes whose EYR is 1 or only slightly higher do not provide significant net emergy to the economy and only transform resources that are already available from previous processes. In so doing, they act as consumer processes more than creating new opportunities for system's growth. Primary energy sources (crude oil, oil, natural gas, uranium,...) usually show EYRs greater than 5, since they are exploited by means of a small input from the economy and return much greater emergy flows, which have been generated by previous geologic and ecological activities that accumulated these resources over past millennia. Secondary energy sources and primary materials like cement and steel show EYRs in the range from 2 to 5, indicating moderate contribution to the economy (Brown and Ulgiati, 1997).

D.4.6. Emergy Investment Ratio (IR)

The ratio of emergy fed back from outside a system to the indigenous emergy inputs (both renewable and non renewable). It evaluates if a process is a good user of the emergy that is invested, in comparison with alternatives.

$$\text{Eq.E.13.} \qquad IR = \frac{F}{R + N}$$

D.4.7. Empower density

The ratio of total emergy use in the economy of a region or nation to the total area of the region or nation. Renewable and non-renewable emergy density are also calculated separately by dividing the total renewable emergy by area and the total nonrenewable emergy by area, respectively.

$$\text{Eq.E.14.} \qquad empower\_density = \frac{R + N + F}{area}$$

D.4.8. Emprice

The emprice of a commodity is the emergy one receives for the money spent. Its units are sej/$.

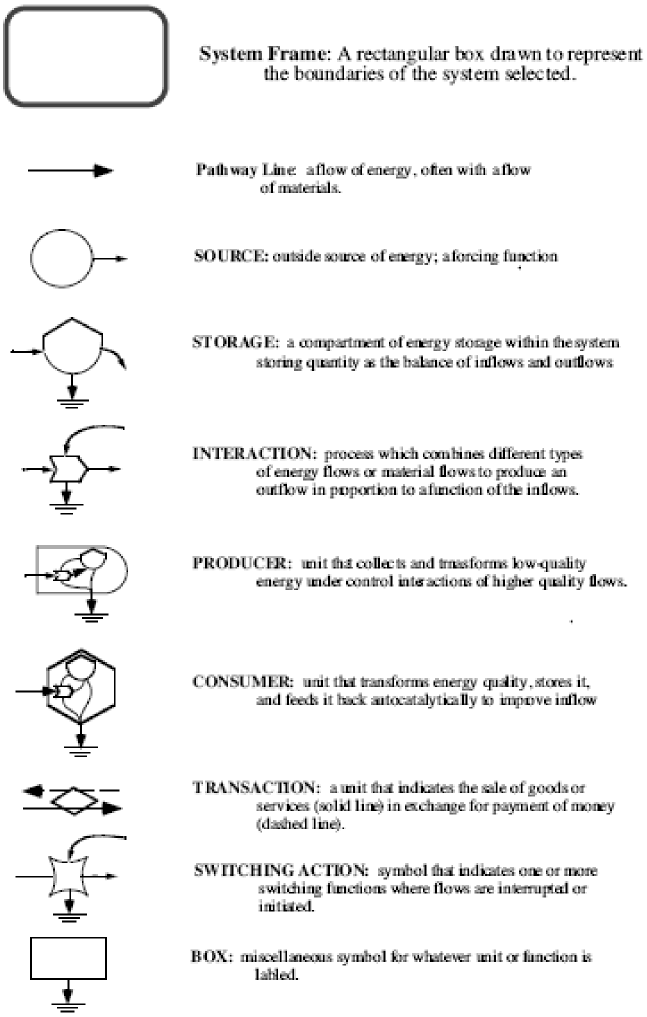
D.4.9. Emergy exchange ratio

The ratio of emergy exchanged in a trade or purchase (what is received to what is given). The ratio is always expressed relative to one or the other trading partners and is a measure of the relative trade advantage of one partner over the other.

D.4.10. Emergy per capita

The ratio of total emergy use in the economy of a region or nation to the total population. Emergy per capita can be used as measure of potential, average standard of living of the population.

D.5. Energy Systems symbols



System Frame: A rectangular box drawn to represent the boundaries of the system selected.

Pathway Line: a flow of energy, often with a flow of materials.

SOURCE: outside source of energy; a forcing function

STORAGE: a compartment of energy storage within the system storing quantity as the balance of inflows and outflows

INTERACTION: process which combines different types of energy flows or material flows to produce an outflow in proportion to a function of the inflows.

PRODUCER: unit that collects and transforms low-quality energy under control interactions of higher quality flows.

CONSUMER: unit that transforms energy quality, stores it, and feeds it back autocatalytically to improve inflow

TRANSACTION: a unit that indicates the sale of goods or services (solid line) in exchange for payment of money (dashed line).

SWITCHING ACTION: symbol that indicates one or more switching functions where flows are interrupted or initiated.

BOX: miscellaneous symbol for whatever unit or function is labled.

Annex E

Water simulation softwares

E.1. Water quality models

Information related to different simulation software alternatives, as complement to the information given in Chapter 5, is provided here. In addition, a wide summary about the Qual2k simulator is given in the second part of the Annex.

E.1.1. Group 1

The general water quality models are presented in this first group.

E.1.1.1. WASP7

The Water Quality Analysis Simulation Program, WASP7, is an enhancement of the original WASP (EPA, 2009). It helps users to interpret and predict water quality responses to natural phenomena and manmade pollution for pollution management decisions. WASP is a dynamic compartment-modelling program for aquatic systems, including both the water column and the underlying benthos. WASP allows the user to investigate 1, 2, and 3 dimensional systems, and a variety of pollutant types. The time varying processes of advection, dispersion, point and diffuse mass loading and boundary exchange are represented in the model. WASP can also be linked with hydrodynamic and sediment transport models that can provide flows, depths velocities, temperature, salinity and sediment fluxes.

When linking WASP with hydrodynamic models is searched, it is as simple as pointing to the hydrodynamic linkage file. The main features of the programme are:

- Import time series from WRDB (spreadsheet, text files)
- Automatically import hydrodynamic model interface information
- Multi-session capable

- Run time diagnosis

The data preprocessor allows for the rapid development of input datasets. The ability to bring data into the model is as simple as cut and paste or queried from a database. The preprocessor provides detailed descriptions of all model parameters and kinetic constants.

The Post-Processor (MOVEM) provides an efficient method for reviewing model predictions and comparing them with field data for calibration. MOVEM has the ability to display results from all of the WASP models as well as others. MOVEM allows the modeller to display the results in two graphical formats:

1. Spatial Grid, a two dimensional rendition of the model network is displayed in a window where the model network is color shaded based upon the predicted concentration.
2. x/y Plots -- generates an x/y line plot of predicted and/or observed model results in a window.

There is no limit on the number of x/y plots, spatial grids or even model result files that the user can utilize in a session. Separate windows are created for each spatial grid or x/y plot created by the user.

For example, WASP has been used to examine eutrophication of Tampa Bay in Florida and in the Neuse River Estuary in North California; and to the phosphorus loading in the Lake Okeechobee, also in Florida.

E.1.1.2. QUAL2K

QUAL2K (or Q2K) is a river and stream water quality model that is intended to represent a modernized version of the QUAL2E (or Q2E) model (Brown and Barnwell 1987).

It is briefly described in Chapter 5 and a complete description can be found in the second part of this Annex C, since it has been chosen as the simulation software for this dissertation.

E.1.1.3. EPD-RIV1

EPD-RIV1 is a system of programs to perform one-dimensional dynamic hydraulic and water quality simulations. The computational model is based upon the CE-QUAL-RIV1 model developed by the U.S. Army Engineers Waterways Experiment Station (WES). This modelling system was developed for the Georgia Environmental Protection Division of the Georgia Department of Natural Resources. Program Manager and the U.S. Environmental Protection Agency, Region IV.

EPD-RIV1 consists of two parts: a hydrodynamic code which is typically applied first, and a quality code. The hydraulic information, produced from application of the hydrodynamic model, is saved to a file which is read by, and provides transport information to, the quality code when performing quality simulations.

The quality code can simulate the interactions of 16 state variables, including water temperature, nitrogen species (or nitrogenous biochemical oxygen demand), phosphorus species, dissolved oxygen, carbonaceous oxygen demand (two types), algae, iron, manganese, coliform bacteria and two arbitrary constituents. In addition, the model can simulate the impacts of macrophytes on dissolved oxygen and nutrient cycling.

The model was designed for the simulation of dynamic conditions in rivers and streams for the purpose of analyzing existing conditions and performing waste load allocations, including allocations of Total Maximum Daily Loads (TMDLs). This system provides the user a unique set of tools to aid in the analysis of environmental data, preparation of data for a model application, simulating the impact of time-varying point and non-point sources on the hydrodynamics and water quality of a stream or river, and analyzing the model results.

The PreRiv1 preprocessor is organized about the project concept, in which all the files associated with a hydrodynamic and water quality simulation are identified and stored. Input data files are saved in the standard model input format, but can be edited with user-friendly forms especially designed to input modelling data; the on-line help explains the required input and offers suggestions for reasonable values for kinetic parameters.

Time series data can be manually introduced, or imported from WRDB or any other data sources, mapping one or more stations to model cross-sections. The user can interpolate missing values if appropriate, and apply scale and conversion factors during the "build"operation.

PreRiv1 also acts as the control center for viewing data files, running the hydrodynamic and water quality simulation models, examining modelling results using the postprocessor, and running WRDB. When the simulation model is running, intermediate results are displayed in an "interactor" screen.

The postprocessor is capable of graphically displaying huge (100s of Mb) modelling output files and comparing simulation results with observed data stored in a variety of data sources (usually WRDB). Several graphic formats are available including: time series; longitudinal. Depth, and width profiles; frequency histograms and probability plots, and scatter plots. Statistics can be instantly displayed to help the modeller compare various modelling runs or observed data.

PreRiv1 also acts as the control center for viewing data files, running the hydrodynamic and water quality simulation models, examining modelling results using the postprocessor, and running WRDB. When the simulation models are running, intermediate results are displayed in an "interactor" screen; the user can cancel lengthy computations if it apparent that computed results are inappropriate.

E.1.1.4. EFDC Hydro

The Environmental Fluid Dynamics Code (EFDC Hydro) is hydrodynamic model that can be used to simulate aquatic systems in one, two, and three dimensions. It has evolved over the past two decades to become one of the most widely used and technically defensible hydrodynamic models in the world. EFDC uses stretched or sigma vertical coordinates and Cartesian or curvilinear, orthogonal horizontal coordinates to represent the physical characteristics of a water body. It solves three-dimensional, vertically hydrostatic, free surface, turbulent averaged equations of motion for a variable-density fluid. Dynamically-coupled transport equations for turbulent kinetic energy, turbulent length scale, salinity and temperature are also solved. The EFDC model allows for drying and wetting in shallow areas by a mass conservation scheme. The physics of the EFDC model and many aspects of the computational scheme are equivalent to the widely used Blumberg-Mellor model and U. S. Army Corps of Engineers' Chesapeake

In order to facilitate the setup and application of EFDC, a preprocessor is being developed. The preprocessor will be composed of two major components: the Curvilinear Grid Generator and the EFDC Model Interface. Tthese components will together enable users to generate curvilinear-orthogonal grids or simulate aquatic systems in 1, 2 or 3-dimensions, link 2-D grids to 1-D grids in a quickly and easily set, and change critical modelling parameters, as well as make use of watershed loading model results and monitoring data for boundary conditions.

. It will. Grid generation will significantly decrease the repetitive effort typically required through manual grid generation methods, and it will be conducted interactively and intuitively through the interface and associated controls. Key features of the tool will include:

- GIS interface
- Model domain designation through user control point designation
- Automatic insertion of grid boundary points based on control point designation
- Automatic curvilinear-orthogonal grid generation
- Model grid conversion to GIS shape file format
- Cell mapping between EFDC and WASP

Once a grid has been generated, it's necessary to set and calibrate pertinent modelling parameters. The EFDC interface will simplify the setup and application of EFDC through a user-friendly graphical interface and associated windows. It will support input of EFDC model run control and model parameter designation, and it will link directly to boundary condition/source data. e.g. watershed model output and point source contributions. Key features of the tool will include

- Database-oriented interface
- Visual linkage to the model grid
- Visual linkage to point and nonpoint source inputs
- New model parameter addition and accommodation
- Direct linkage to WRDB for boundary condition designation/generation

Watershed models play an important role in linking sources of pollutants to receiving waterbodies as nonpoint source loads. Watershed models are driven by precipitation. Landuse, impervious area, slope, soil types and drainage area. GIS programs like BASINS and WCS provide the data which are needed for water models to predict both water and pollutant runoff from a watershed.

E.1.1.5. AQUATOX

AQUATOX is a simulation model for aquatic systems that predicts the fate of various pollutants, such as nutrients and organic chemicals, and their effects on the ecosystem, including fish, invertebrates, and aquatic plants. This model is a valuable tool for ecologists, biologists, water quality modellers, and anyone involved in performing ecological risk assessments for aquatic ecosystems.

AQUATOX is a PC-based ecosystem model that predicts the fate of nutrients and organic chemicals in water bodies as well as their direct and indirect effects on the resident organisms. It simulates the transfer of biomass and chemicals from one compartment of the ecosystem to another, by simultaneously computing important chemical and biological processes over time. AQUATOX simulates multiple environmental stressors (including nutrients. organic loadings. toxic chemicals. and temperature) and their effects on the algal. Macrophyte, invertebrate, and fish communities, AQUATOX can help identify and understand the cause and effect relationships between chemical water quality, the physical environment, and aquatic life. It can represent a variety of aquatic ecosystems, including vertically stratified lakes, reservoirs and ponds, as well as rivers and streams.

AQUATOX can be used to address a wide variety of issues requiring a better understanding of the processes relating the chemical and physical environment to the biological community. Possible applications of AQUATOX include:

- Developing numeric nutrient targets based on desired biological endpoints.
- Evaluating which are the stressors causing the observed biological impairment.
- Predicting effects of pesticides and other toxic substances on aquatic life.
- Evaluating potential ecosystem responses to invasive species.
- Determining effects of land use changes on aquatic life by using the linkage with BASINS.
- Estimating time to recovery of fish or invertebrate communities after reducing pollutant loads.

E.1.1.6. WAM

WAM (Water Assessment Model) is a tool that has been shown to be useful in the assessment of watershed-related properties. It was developed to allow engineers and planners to assess the water quality of both surface water and groundwater based on land use, soils, climate and other factors. The model simulates the primary physical processes important for watershed hydrologic and pollutant transport. The WAM GIS-based coverage includes land use, soils, topography, hydrography, basin and sub-basin boundaries, point sources and service area coverage, climate data, and land use and soils description files.

The coverages are used to develop data that can be used in the simulation of a variety of physical and chemical processes. The advantage of this model is its ability to:

- Use a grid-based system to assess the spatial impact of existing and modified land uses on water quality and quantity for tributaries within a watershed;

- Develop phosphorus (P) load allocations for total maximum daily loads (TMDLs) that will be acceptable to Florida Department of Environmental Protection (FDEP);
- Identify P and flow "hot spots";
- Rank P loadings by source, sub-basin, and sub-watersheds

The model can be used to assess P load strategies including the use of stormwater treatment areas (STAs) and reservoir assisted stormwater treatment areas (RASTAs). WAM also has the ability to aid in the assessment of the impact of growth changes in the watershed.

WAM was developed on the base of a grid cell representation of the watershed. The grid cell representation allows for the identification of surface and groundwater flow and phosphorus concentrations for each cell. The model then "routes" the surface water and groundwater flows from the cells to assess the flow and phosphorus levels throughout the watershed. Thus, the model simulates the following elements:

- Surface water and ground water flow, allowing the assessment of flow and pollutant loading for a tributary reach.
- Water quality including particulate and soluble phosphorus, particulate and soluble nitrogen (NO_3, NH_4, and organic N), total suspended solids, and biological oxygen demand. WAM can be linked to WASP (SWET. 2003), which enables the simulation of dissolved oxygen and chlorophylla.
- Time-series outputs at the source cells. Sub-basins, and individual tributary reaches including: source load maps (surface water and groundwater), attenuated sub-basin and basin loads, ranking of land uses by load source, daily time series of flows and pollutants, and comparative displays of different BMP/Management Scenarios.

Dynamic routing of flows is accomplished through the use of an algorithm that uses a Manning's flow equation based technique (Jacobson et al.. 1998). Attenuation is based on the flow rate, characteristics of the flow path, and the distance of travel. The model provides many features that improve its ability to simulate the physical features in the generation of flows and loadings including:

- Flow structures simulation
- Generation of typical farms
- BMPs
- Rain zones built into unique cells definitions
- Full erosion/deposition and in-stream routing (used with pond and reservoirs)
- Closed basins and depressions are simulated
- Separate simulation of vegetative areas in residential/urban
- Simulation of point sources with service areas
- Urban retention ponds
- Impervious sediment buildup/washoff
- Shoreline reaches for more precise delivery to rivers/lakes/estuaries
- Wildlife diversity within wetlands
- Spatial map of areas having wetland assimilation protection
- Indexing sub-models for BOD, bacteria, and toxins

E.1.1.7. WARMF

To facilitate TMDL analysis and watershed planning, WARMF was developed under the sponsorship of the Electric Power Research Institute (EPRI) in order to provide a decision support system for watershed management. The system provides a road map to calculate TMDLs for most conventional pollutants (coliform, TSS, BOD, nutrients). It also provides a road map to guide stakeholders to reach consensus on an implementation plan. The scientific basis of the model and the consensus process have undergone several peer reviews by independent experts under EPA guidelines. WARMF is now compatible with data extraction and watershed delineation tools of EPA BASINS. WARMF is organized into five linked modules under one, the GIS-based graphical user interface. It is a very user- friendly tool, suitable for expert modellers as well as general stakeholders.

The *Engineering Module* is a GIS-based watershed model that calculates daily runoff, shallow ground water flow, hydrology and water quality of a river basin. A river basin is divided into a network of land catchments (including canopy and soil layers), stream segments, and lake layers for hydrologic and water quality simulations. Land surface is characterized by land use / land cover, and precipitation is deposited on the land catchments to calculate snow and soil hydrology, and resulting surface runoff and groundwater accretion to river segments. Water is then routed from one river segment to the next, from river segments to reservoirs, and then from a reservoir to river segments, until watershed terminus is reached. Instead of using export coefficients, a complete mass balance is performed starting with atmospheric deposition and land application as boundary conditions. Pollutants are routed with water in throughfall, infiltration, soil adsorption, exfiltration, and overland flow. The sources of point and nonpoint loads are routed through the system with the mass so the source of nonpoint loading can be tracked back to land use and location. WARMF provides several options for modelling reservoirs using 1D or 2D approaches.

The *Data Module* contains meteorology, air quality, point source, reservoir release, and flow diversion data used to drive the model. It also contains observed flow and water quality data used for calibration. The data is accessed through the map-based interface and can be viewed and edited in both graphical and tabular format. The *Knowledge Module* stores supplimental watershed data. Documents, case studies, or reports of past modelling activities can be easily accessed by model users.

At the center of WARMF there are the two watershed approach modules for Consensus building and TMDL calculation. These two modules are roadmaps that provide guidance for stakeholders during the decision making process. The *Consensus Module* of WARMF provides information in a series of steps for stakeholders to learn about the issues, formulate and evaluate alternatives, and negotiate a consensus. Outputs are displayed in coloured maps and graphs. A GIS map is used to show the bar charts of pollution loads from various sub regions of the river basin. Another GIS map is used to show the consequence of the pollution loads, in which water bodies suitable for a selected use are shaded green and those not suitable are shaded red. Through the TMDL Module, calculations are made for a series of control points from the upstream to the downstream of a river basin. A road map is provided for the step-by-step procedure. An iterative set of simulations are performed to calculate various combinations of point and nonpoint loads that the water body can accept and meet the water quality criteria of the designated uses. The water quality criteria can be specified for multiple parameters and based on percent compliance.

WARMF can help answer water resource and water quality questions such as:

- What are the cumulative water quality impacts under various watershed management scenarios?
- What are the trade-offs with sewer extension vs. onsite wastewater systems?
- How will regional growth affect water quality?
- How will increased water diversions affect hydrology and water quality?

The advantages of WARMF include:

- Integrates models, databases, and graphical software into a map-based stand alone tool that does not require ArcView
- Links catchments, river segments, and lakes to form a seamless river basin model which computes soil and surface hydrology, pollutant build up and washoff based on physical principles instead of SCS curve numbers and run off coefficients
- Contains a user friendly GUI and unique decision support tools that allow a variety of stakeholders (including modelers and lay persons) to run the model and to take ownership of their watershed by learning about the science behind their water quality issues
- Calculates TMDLs to meet water quality criteria for beneficial uses
- Uses readily available data from NOAA, EPA, and USGS to predict hydrology and water quality of rivers and lakes
- Models flow, temperature, nutrients, bacteria, dissolved oxygen, sediment transport, periphyton, phytoplankton, and loading from onsite wastewater systems
- Displays sources of point and nonpoint loading using easy-to-understand GIS maps
- Displays water quality status in terms of suitability for fish habitat, swimming. water supply, and other uses with red and green color codes
- Evaluates cost sharing schemes for pollution trading and determines the failure risk of a management plan

WARMF has been applied to over 15 watersheds in the United States. The studies have addressed the TMDLs of nutrients, sediment, fecal coliform, and the impact of onsite wastewater systems on a watershed scale. The size of river basin applications ranges from the small Mica Creek research watershed in Idaho (10.8 mi^2) to the large San Juan Basin of Colorado and New Mexico (16.000 mi^2). There is no limit on the size or scale of a potential WARMF application as long as adequate topography data are available.

E.1.1.8. LSPC

LSPC is the Loading Simulation Program in C++, a watershed modelling system that includes streamlined Hydrologic Simulation Program Fortran (HSPF) algorithms for simulating hydrology, sediment, and general water quality on land as well as a simplified stream transport model. LSPC is derived from the Mining Data Analysis System (MDAS), which was developed by EPA and has been widely used for mining applications and TMDLs. A key data management feature of this system is that it uses a Microsoft Access database to manage model data and weather text files for driving the simulation. The system also contains a module to assist in TMDL calculation and source allocations.

For each model running, it automatically generates comprehensive text-file output by sub-basin for all land-layers. Reaches and simulated modules can be expressed on hourly or daily intervals. Output from LSPC has been linked to other model applications such as EFDC, WASP, and CE-QUAL-W2. LSPC has no inherent limitations in terms of modelling size or model operations. The Microsoft Visual C++ programming architecture allows for seamless integration with modern-day, widely available software such as Microsoft Access and Excel.

LSPC was designed to handle very large-scale watershed modelling applications. The model has been successfully used to model watershed systems composed of over 1.000 sub-basins. Using the WCS extension increases the efficiency of model setup and execution by eliminating unnecessary, repetitive user-input, hence minimizes the chance of human error. The system is tailored for source representation and TMDL calculation. The highly adaptable design and programming architecture allows for future modular additions and/or improvements. Furthermore, the entire system is designed to simplify transfer of information between models and users. The LSPC GIS interface, which is compatible with ArcView shape files, acts as the control center for launching watershed model scenarios. This stand-alone interface easily communicates with both shape files and the microsoft access database, but does not directly rely on the main programs. Therefore, once a watershed application is created, it is easily transferable to users who may not have ArcView or MS Access installed on their computers.

There are seven basic components of the LSPC system. They include: (1) a WCS extension for efficient model setup; (2) an interactive, stand-alone GIS control center; (3) data management tools; (4) data inventory tools; (5) data analysis tools; (6) a dynamic watershed model tailored for TMDL calculation; and (7) model results analysis.

E.1.2. Group 2. Particular water problems contexts simulation models

Simulation models covering particular water problems are presented in this section.

E.1.2.1. ADIOS2

ADIOS2 (Automated Data Inquiry for Oil Spills) is an oil weathering model that runs both on Macintosh computers and in Windows. ADIOS2 incorporates a database containing more than a thousand crude oils and refined products, and provides quick estimates of the expected characteristics and behaviour of oil spilled into the marine environment. The predictions it makes, presented as both graphics and text, are designed to help answer questions that typically arise during spill response and cleanup. For example:

- By predicting change in an oil's viscosity (resistance to flow) over time, ADIOS2 offers an answer to the question: Can the oil still be dispersed with chemical dispersants?
- By predicting the rate of increase in an oil's water content over time, ADIOS2 offers an answer to questions like: If 1,000 litres of crude oil has spilled, will more than 1,000 litres of oil-and-water mixture need to be cleaned up and disposed of? How much more?

ADIOS2 includes new models to estimate the effects of common cleanup techniques such as chemically dispersing, skimming, or burning the oil, and it accounts for environmental processes not included in the previous version, such as sedimentation. It also includes an expanded online help and electronic manual.

The ADIOS2 database includes estimations of the physical properties of oils and products. ADIOS uses this information to predict changes in an oil's properties once it has spilled. The database was compiled from different sources, including the U.S. Department of Energy and Industry.

ADIOS uses mathematical equations and information from the database to predict changes along the time in density, viscosity, and water content of an oil or product, the rates at which it evaporates from the sea surface and disperses into the water, and the rate at which an oil-in-water emulsion may form. It was designed to make use of as little information as possible, and to use information that can quickly be estimated or obtained in the field. such as wind speed(s), wave heights, water temperature, and salinity or density, the type and amount of oil or product spilled, and the rate and duration of the spill.

E.1.2.2. GNOME

GNOME (General NOAA Operational Modelling Environment) is the oil spill trajectory model used by OR&R Emergency Response Division (ERD) responders during an oil spill. ERD trajectory modelers use GNOME in Diagnostic Mode to set up custom scenarios quickly. In Standard Mode, anyone can use GNOME (with a Location File) to:

- predict how wind, currents, and other processes might move and spread oil spilled on the water.
- learn how predicted oil trajectories are affected by inexactness ("uncertainty") in current and wind observations and forecasts.
- see how spilled oil is predicted to change chemically and physically ("weather") during the time that it remains on the water surface.

To use GNOME, you describe a spill scenario by entering information into the program; GNOME then creates and displays an oil spill "movie" showing the predicted trajectory of the oil spilled in your scenario. Along with GNOME, most users also could download the Location Files for their regions of interest. Location Files contain prepackaged tide and current data and make it easier to work with GNOME.

GNOME was developed by the Emergency Response Division (ERD) (formerly the Hazardous Materials Response Division [HAZMAT]) of NOAA's Office of Response and Restoration (OR&R) in USA. The latest version is GNOME 1.3.0.

Finally, GNOME does not run on Macintosh computers with Intel microprocessors, although this problem is trying to be solved.

E.1.2.3. BIOPLUME III

BIOPLUME III is a 2D finite-difference model to simulate the natural attenuation of organic contaminants in ground-water due to the processes of advection, dispersion, sorption, and biodegradation. Bio-Transformation processes are potentially important in the restoration of aquifers contaminated with organic pollutants. As a result, these processes require evaluation in remedial action planning studies associated with hydrocarbon contaminants. It is based on the USGS solute transport code MOC and solves the solute transport equation six times in order to determine the fate and transport of the hydrocarbons and the electron acceptors (O_2, NO_3^-, Fe^{3+}, SO_4^{2-}, and CO_2) and the by-products generation (Fe^{2+}). A number of aerobic and anaerobic electron acceptors such as oxygen, nitrate, sulphate, iron (III) and carbon dioxide have been considered in this model to simulate the biodegradation of organic contaminants.

Three different kinetic expressions can be used to simulate the aerobic and anaerobic biodegradation reactions. These include: first-order decay, instantaneous reaction and kinetics. The principle of superposition is used to combine the hydrocarbon plume with the electron acceptor plumes. The model has been integrated with a sophisticated ground-water modelling platform, known as EIS. A graphical user platform allows the user to create, enter and edit data for model simulation. Discretization of time and space, hydrogeologic characteristics of the aquifer, initial and boundary conditions, sources and sinks, sorption, source decay, radioactive decay, ion-exchange and biodegradation variables are the different input parameters of the model. The model generates a standard output file that lists the results from a specific model run. This output file lists the input data for the run followed by computed head and concentration maps. Simulation results are also shown graphically. Data can be extracted and used in conjunction with a graphics generation software program to generate graphical results from the model.

E.1.2.4. SWMM

The EPA Storm Water Management Model (SWMM) is a dynamic rainfall-runoff simulation model used for single event or long-term (continuous) simulation of runoff quantity and quality from primarily urban areas. The runoff component of SWMM operates on a collection of subcatchment areas on which rain falls and runoff is generated. The routing portion of SWMM transports this runoff through a conveyance system of pipes, channels, storage/treatment devices, pumps, and regulators. SWMM tracks the quantity and quality of runoff generated within each subcatchment, and the flow rate, flow depth, and quality of water in each pipe and channel during a simulation period comprised of multiple time steps.

SWMM was first developed back in 1971 and has undergone several major upgrades since then. The current edition, Version 5, is a complete re-write of the previous release. Running under Windows, EPA SWMM 5 provides an integrated environment for editing drainage area input data, running hydraulic and water quality simulations, and viewing the results in a variety of formats. These include color-coded drainage area maps, time series graphs and tables, profile plots, and statistical frequency analyses.

This latest version of EPA SWMM was produced by the Water Supply and Water Resources Division of the U.S. Environmental Protection Agency's (National Risk Management Research Laboratory) with assistance from the consulting firm of CDM. Inc.

E.1.3. Comparative

Main features of the softwares summarized in groups 1 and 2 are given in Table E.1

Model	Simulation field	system dimension range	Underground water simulation availability	informatic environment	External linkages	taxes	Available download source
WASP7	general	1,2 and 3 dimen.	yes	MOVEM/Spatial Grid	Loading models, hydrodinamic models	free	EPA
QUAL2K	general	One dimens.	no	windows-VBA-/excel	Undergorund simulation models, Loading models, hydrodinamic models	free	EPA
EPD-RIV1	general	One dimens.	no	PreRiv1/WRDB		free	EPA
EFDC Hydro	general	1,2 and 3 dimen.	no	GIS	yes (with model grid and non-point souces)	free	EPA
AQUATOX	general	One dimen.	no	Aquatox ecosystem		free	GDNR
WARMF	general	1,2 dimen.	no	GIS, grid cell based	yes (with gubernament organizations data)	free	EPA
LSPC	general (stream-lined hydro.prog.)	One dimens.	yes	C++ (availability of ArcView and MSAcces)	WCS extension	free	EPA
ADIOS2	Oceanic Oil Spills (Characteristics and behaviour)	One dimens.	no	Macintosh/Windows	Database compiled from different gubernament.sources	free	OSORR
GNOME	Oceanic Oil spills (Trayectory)	One dimen.	no	Macintosh/Windows		free	OSORR
BIOPLUME III	Organic contaminants in ground water	Two dimens.	yes	ISGS (solute transport code MOC)/ EIS (ground-water modelling platform)		free	EPA
SWMM	Dynamic rainfall-runoff sim.model(storma water management)	One dimens.	no	Windows			EPA

Table E.1. Main features of the summarized water simulation programmes. (Note: EPA, Environmental Protection Agency – US; GDNR, Governmental Department of Natural Resources - US; OSORR, Office Service of Resources Research – US)

E.2. Simulation model used in this work: Qual2KW

In order to provide some additional information to the summary given in Chapter 5, Qual2k software is described here. Much more information can be found in the manual of the program, available in the EPA website (http://www.epa.gov/).

E.2.1. Introduction

Computer models are used extensively for water-quality management of rivers and streams (see Thomann and Mueller, 1987; Chapra, 1997 for reviews). These models must typically be calibrated by adjusting a large number of parameters to attain optimal agreement between model output and field measurements. Such calibration is often performed by the time-consuming process of manual trial-and-error. The model chosen in this work is a model that includes automatic calibration.

There are several models for Total Maximum Daily Load Studies supported by the US Department of Ecology. A TMDL or Total Maximum Daily Load is a calculation of the maximum amount of a pollutant that a waterbody can receive and still meet water quality standards. Computer models are used extensively for water quality management and TMDLs. Models are used to predict the water quality in a water body in response to changes in pollutant loading and various allocation strategies.

QUAL2Kw is a modelling framework that is intended to represent a modernized version of the U.S. Environmental Protection Agency's standard river water-quality model: QUAL2E (Brown and Barnwell, 1987). In addition to incorporating more current science, the frame work also includes several new features that allow it to be applied to shallow, upland streams.

As with QUAL2E, QUAL2Kw simulates the transport and fate of conventional (i.e., non-toxic) pollutants. The framework represents the river as a one-dimension al channel with non-uniform, steady flow, and simulates the impact of both point and non-point pollutant loadings. The model simulates changes within the daily cycle with a user-selected time step of less than 1 h.

The model simulates the transport and fate of a number of constituents such as temperature, carbonaceous biochemical oxygen demand, dissolved oxygen, phytoplankton and several forms of the nutrients phosphorus and nitrogen (Table 1). It also simulates several other constituents that are not typically included ingenerally-available software. In particular, the model simulates pH, alkalinity, inorganic suspended solids, pathogenic bacteria, and bottom algae. The inclusion of bottom algae is essential for simulating shallow streams. These algae have the novel feature of variable stoichiometry of the nutrients nitrogen and phosphorus.

The model has two other features that distinguish it from other frameworks. First, sediment-water fluxes of dissolved oxygen and nutrients are simulated internally rather than being prescribed. That is, oxygen and nutrient fluxes are computed as a function of settling particulate organic matter, reactions within the sediments, and the concentrations of soluble forms in the overlying waters. Second, the hyporheic zone is modeled. This is the area below the streambed where water percolates through spaces between the rocks and cobbles. This is another feature that is necessary in order to simulate shallow streams.
QUAL2Kw is implemented within Microsoft Excel. It is programmed in Visual Basic for Applications(VBA). Excel is used as the graphical user interface forinput, running the model, and viewing of output. The numerical integration during a model run is performedby a compiled Fortran 95 program that is run by the Excel VBA program.

One of them is the QUAL2Kw, a modelling framework written in Excel/VBA for simulating river and stream water quality. It is intended to represent a modernized version of the QUAL2E model (Brown and Barnwell, 1987). QUAL2Kw is related to the QUAL2K model that was developed by Dr. Steven Chapra (Chapra and Pelletier, 2003).

The QUAL2Kw framework has the following characteristics:

- One dimensional. The channel is well-mixed vertically and laterally.
- Steady flow. Non-uniform, steady flow is simulated.
- Diel heat budget. The heat budget and temperature are simulated as a function of meteorology on a diel time scale.
- Diel water-quality kinetics. All water quality state variables are simulated on a diel time scale for biogeochemical processes.
- Heat and mass inputs. Point and non-point loads and abstractions are simulated.
- Phytoplankton and bottom algae in the water column, as well as sediment diagenesis, and heterotrophic metabolism in the hyporheic zone are simulated.
- Variable stoichiometry. Luxury uptake of nutrients by the bottom algae (periphyton) is simulated with variable stoichiometry of N and P.
- Automatic calibration. Includes a genetic algorithm to automatically calibrate the kinetic rate parameters

Its main novelties are:

- Software environment and interface. Excel is used as the graphical user interface.
- Model segmentation. QUAL2E segments the system into river reaches comprised of equally spaced elements. In contrast, Q2K can use unequally-spaced reaches. In addition, multiple loadings and abstractions can be input to any reach.
- Carbon speciation. Q2K uses two forms of carbon, rather than BOD, to represent organic carbon. These forms are a slowly oxidizing form (slow dissolved organic carbon) and a rapidly oxidizing form (fast dissolved organic carbon). In addition, non-living particulate organic matter (detritus) is simulated. This detrital material includes particulate organic carbon, nitrogen, and phosphorus.
- Anoxia. Q2K accommodates anoxia by reducing oxidation reactions to zero at low oxygen levels. In addition, denitrification is modeled.
- Bottom algae. The model explicitly simulates attached bottom algae using either zero-order or first-order growth kinetics.
- Luxury uptake. Variable stoichiometry of nitrogen and phosphorus in bottom algae and phytoplankton.
- Light extinction. Light extinction is calculated as a function of algae, detritus and inorganic solids.
- pH. Both alkalinity and total inorganic carbon are simulated. These are used to determine pH.
- Pathogen indicator. A generic pathogen indicator is simulated (e.g. fecal coliform or Enterococci). Pathogen indicator removal is determined as a function of temperature, light, and settling.

- Sediment-water interactions. Sediment-water fluxes of dissolved oxygen and nutrients are simulated internally rather than being prescribed. Oxygen (SOD) and nutrient fluxes are simulated as a function of settling particulate organic matter, diagenesis reactions within the sediments, and the concentrations of soluble forms in the overlying waters.
- Sediment heat flux. Sediment-water heat flux and sediment temperature is simulated using a Fick's law formulation to account for conduction between the water and sediment and hyporheic flow and heat exchange.
- Hyporheic respiration. Exchange of water between the surface water column and the hyporheic zone, and simulation of sediment pore water quality, including optional simulation of growth and respiration of heterotrophic bacteria biofilm in the hyporheic zone.
- Total dissolved gas. Dissolved nitrogen and argon gases are included in addition to oxygen and carbon dioxide for the calculation of total dissolved gas. Optional calculation of the super-saturation of dissolved gases in spillways of large dams is also included.

E.2.2. Segmentation and hydraulics

The model presently simulates the main stream of a river as depicted Figure E.1. Tributaries are not modelled explicitly, but can be represented as point sources. Each reach is characterized by identical hydraulic characteristics along itself (for instance, slope or base with). Reaches are numbered in ascendant order, starting from the headwater of the main stream. Inputs and outputs flows, diffuse or in a point, can be set at any point in each reach.

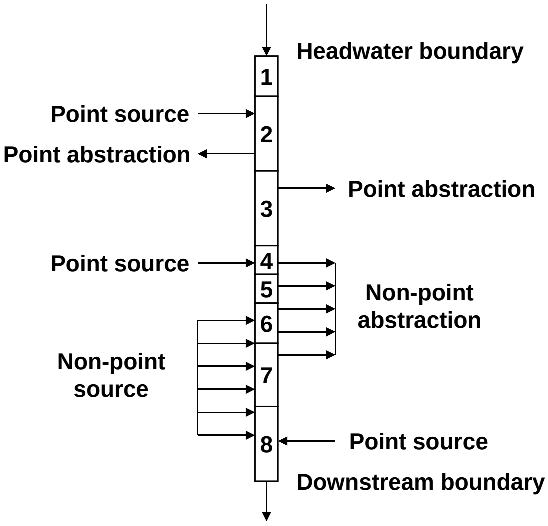
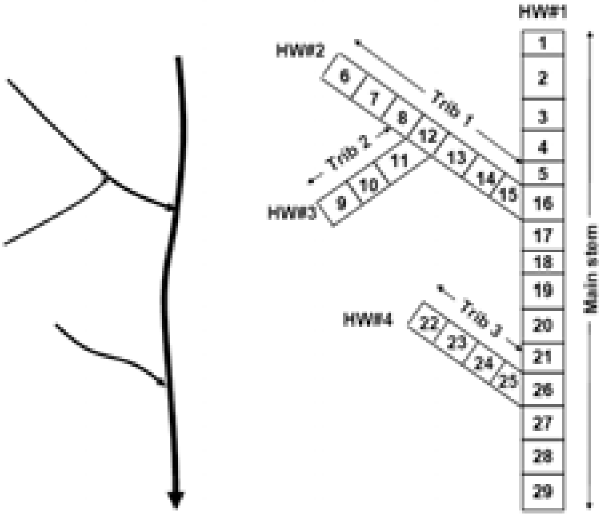


Figure E.1. QUAL2K segmentation scheme.

For Networks with tributaries (Figure E.2), reaches are upward numbered, starting with the reach 1 in the main stream headwater. When the incorporation to the tributary happens, the numeration continues from the tributary headwater. Both headwaters and tributaries are consecutively numbered, following a structure similar to that used for the reaches. Moreover, the main stretches of the system are designed as “segments”. Within the software, it is possible to graphically represent the calculation results for each of those segments. That is, the model generates independent graphs for the main stream and each of its tributaries. Paying attention to the correct topologic description of the hydrologic network that wants to be modelled is very important. The correct numeration, following the explained criteria, is the base for the program to carry out the corresponding simulation.



(a) A river with tributaries (b) Q2K reach representation

Figure E.2. QUAL2K scheme for a river with tributaries

Each defined reach can be sub-divided in a set of elements, equally separated, by only indicting the desired number of elements, as indicated in Figure E.3.

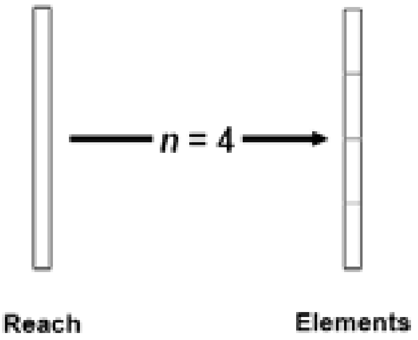


Figure E.3. Each reach can be divided in elements

As a summary, the nomenclature to be used in the Qual 2K topology is as follows:

- Reach: each part of the river with similar hydraulic features. It is the unit of data introduction in the model.
- Element: Each of the parts in which a reach can be divided. It is the unit of data output in the model.
- Segment: Set of reaches representing a branch of the network. They consist on the main headwater and each of its tributaries.
- Headwater: Upper limit of each of the segments in the model. Each headwater constitutes a boundary condition in the model.

E.2.3. Flow balance

A steady-state flow balance is implemented for each model reach (Eq. E.1):

Eq. E.1. $$Q_i = Q_{i-1} + Q_{in,i} - Q_{ab,i}$$

where Q_i = outflow from reach i into the downstream reach i + 1 [m^3/d], Q_{i-1} = inflow from the upstream reach i – 1 [m^3/d], $Q_{in,i}$ is the total inflow into the reach from point and nonpoint sources [m^3/d], and $Q_{ab,i}$ is the total outflow from the reach due to point and nonpoint abstractions [m^3/d].

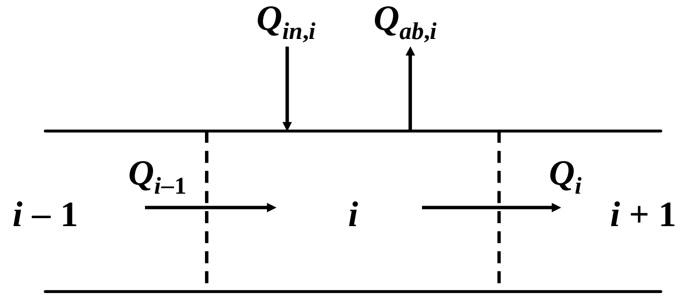


Figure E.4. Reach flow balance.

The total inflow from sources is computed as Eq. E.2 indicates:

Eq. E.2. $$Q_{in,i} = \sum_{j=1}^{psi} Q_{ps,i,j} + \sum_{j=1}^{npsi} Q_{nps,i,j}$$

where $Q_{ps,i,j}$ is the jth point source inflow to reach i (m^3/d), psi = the total number of point sources to reach i, $Q_{nps,i,j}$ is the jth non-point source inflow to reach i (m^3/d), and $npsi$ = the total number of non-point source inflows to reach i.

The total outflow from abstractions is computed as shown in Eq. E.3:

Eq. E.3. $$Q_{ab,i} = \sum_{j=1}^{pai} Q_{pa,i,j} + \sum_{j=1}^{npai} Q_{npa,i,j}$$

where $Q_{pa,i,j}$ is the jth point abstraction outflow from reach i [m^3/d], pai = the total number of point abstractions from reach i, $Q_{npa,i,j}$ is the jth non-point abstraction outflow from reach i [m^3/d], and $npai$ = the total number of non-point abstraction flows from reach i.

The non-point sources and abstractions are modelled as line sources. As in Figure E.5, the non-point source or abstraction is demarcated by its starting and ending kilometre points. Its flow is distributed to or from each reach in a length-weighted fashion.

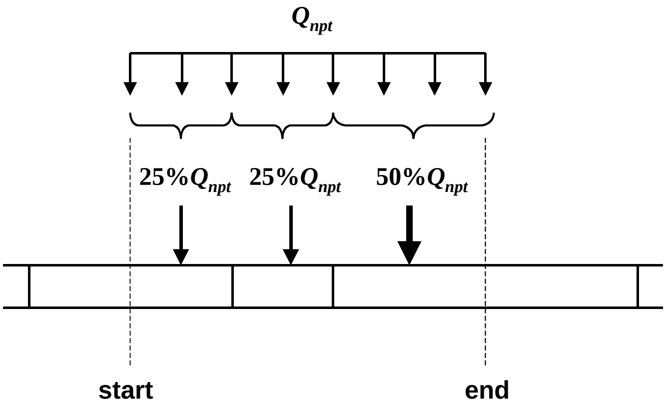


Figure E.5. The manner in which non-point source flow is distributed to a reach.

E.2.4. Hydraulic characteristics

Once the outflow for each reach is computed, the depth and velocity are calculated in one of three ways: weirs, rating curves, and Manning equations. The program decides among these options in the following manner:

- If a weir height is entered, the weir option is implemented.
- If the weir height is zero and a roughness coefficient is entered (*n*), the Manning equation option is implemented.
- If neither of the previous conditions are met, Q2K uses rating curves.

In this work, the roughness coefficient is entered, so the manning equation option is implemented.

E.2.4.1. Manning Equation

Each reach is idealized as a trapezoidal channel (Eq. E.4). Under conditions of steady flow, the Manning equation can be used to express the relationship between flow and depth as

Eq. E.4.
$$Q = \frac{S_0^{1/2}}{n} \frac{A_c^{5/3}}{P^{2/3}}$$

where Q = flow [m^3/s], S_0 = bottom slope [m/m], n = the Manning roughness coefficient, A_c = the cross-sectional area [m^2], and P = the wetted perimeter [m].

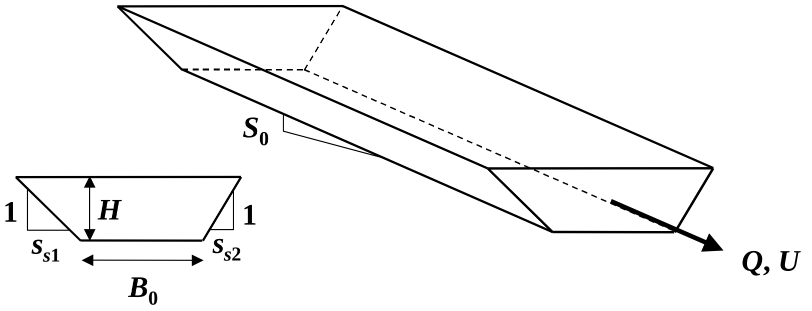


Figure E.6. Trapezoidal channel.

The cross-sectional area of a trapezoidal channel is computed as indicated in Eq. E.5:

Eq. E.5. $$A_c = \left[B_0 + 0.5(s_{s1} + s_{s2})H\right]H$$

where B_0 = bottom width (m), s_{s1} and s_{s2} = the two side slopes as shown in Figure E.6 (m/m), and H = reach depth (m).

The wetted perimeter is computed as

Eq. E.6. $$P = B_0 + H\sqrt{s_{s1}^2 + 1} + H\sqrt{s_{s2}^2 + 1}$$

After substituting Eq. E.4, Eq. E.5 and Eq. E.6, it can be solved iteratively for depth (Chapra and Canale 2002):

Eq. E.7. $$H_k = \frac{(Qn)^{3/5}\left(B_0 + H_{k-1}\sqrt{s_{s1}^2 + 1} + H_{k-1}\sqrt{s_{s2}^2 + 1}\right)^{2/5}}{S^{3/10}\left[B_0 + 0.5(s_{s1} + s_{s2})H_{k-1}\right]}$$

where $k = 1, 2, \ldots, n$, where n = the number of iterations. An initial guess of $H_0 = 0$ is employed. The method is terminated when the estimated error falls below a specified value of 0.001%. The estimated error is calculated as

Eq. E.8. $$\varepsilon_a = \left|\frac{H_{k+1} - H_k}{H_{k+1}}\right| \times 100\%$$

The cross-sectional area can be determined with Eq. E.15 and the velocity can then be determined from the continuity equation (Eq. E.9).

Eq. E.9. $$U = \frac{Q}{A_c}$$

The average reach width, B [m], can be computed as shown in Eq. E.10.

Eq. E.10.
$$B = \frac{A_c}{H}$$

Suggested values for the Manning coefficient are listed in Table E.2.

MATERIAL	n
Man-made channels	
Concrete	0.012
Gravel bottom with sides:	
Concrete	0.020
mortared stone	0.023
Riprap	0.033
Natural stream channels	
Clean, straight	0.025-0.04
Clean, winding and some weeds	0.03-0.05
Weeds and pools, winding	0.05
Mountain streams with boulders	0.04-0.10
Heavy brush, timber	0.05-0.20

Table E.2. The Manning roughness coefficient for various open channel surfaces (from Chow et al. 1988).

Manning's *n* typically varies with flow and depth (Gordon et al. 1992). As the depth decreases at low flow, the relative roughness increases. Typical published values of Manning's *n*, which range from about 0.015 for smooth channels to about 0.15 for rough natural channels, are representative of conditions when the flow is at the bankfull capacity (Rosgen, 1996). Critical conditions of depth for evaluating water quality are generally much less than bankfull depth, and the relative roughness may be much higher

E.2.5. Travel time

The residence time of each reach is computed as

Eq. E.11.
$$\tau_k = \frac{V_k}{Q_k}$$

where

τ_k = the residence time of the k^{th} reach [d],

V_k = the volume of the k^{th} reach [m^3] $= A_{c,k}\Delta x_k$, and Δx_k = the length of the k^{th} reach [m].

These times are then accumulated to determine the travel time from the headwater to the downstream end of reach i, Eq. E.12. $$t_{t,i} = \sum_{k=1}^{i} \tau_k$$

Where $t_{t,I}$ = the travel time [d].

E.2.6. Longitudinal dispersion

Two options are used to determine the longitudinal dispersion for a boundary between two reaches. First, the user can simply enter estimated values on the *Reach Worksheet*. If the user does not enter values, a formula is employed to internally compute dispersion based on the channel's hydraulics (Fischer et al. 1979),

Eq. E.13. $$E_{p,i} = 0.011\frac{U_i^2 B_i^2}{H_i U_i^*}$$

Where:
$E_{p,i}$ = the longitudinal dispersion between reaches *i* and *i* + 1 [m²/s],
U_i = velocity [m/s],
B_i = width [m],
H_i= mean depth [m], and
U_i^*= shear velocity [m/s], which is related to more fundamental characteristics by

Eq. E.14. $$U_i^* = \sqrt{gH_iS_i}$$

Where:
G= acceleration due to gravity [= 9.81 m/s²] and
S= channel slope [dimensionless].

After computing or prescribing $E_{p,i}$, the numerical dispersion is computed as

Eq. E.15. $$E_{n,i} = \frac{U_i \Delta x_i}{2}$$

The model dispersion E_i (i.e., the value used in the model calculations) is then computed as follows:

If $E_{n,i} \le E_{p,i}$, the model dispersion, E_i is set to $E_{p,i} - E_{n,i}$.
If $E_{n,i} > E_{p,i}$, the model dispersion is set to zero.

For the latter case, the resulting dispersion will be greater than the physical dispersion. Thus, dispersive mixing will be higher than reality. It should be noted that for most steady-state rivers, the impact of this overestimation on concentration gradients will be negligible. If the discrepancy is significant, the only alternative is to make reach lengths smaller so that the numerical dispersion becomes smaller than the physical dispersion.

E.2.7. Temperature model

As in Eq. E.16, the heat balance takes into account heat transfers from adjacent reaches, loads, abstractions, the atmosphere, and the sediments. A heat balance can be written for reach *i* as

$$\frac{dT_i}{dt} = \frac{Q_{i-1}}{V_i}T_{i-1} - \frac{Q_i}{V_i}T_i - \frac{Q_{ab,i}}{V_i}T_i + \frac{E'_{i-1}}{V_i}\left(T_{i-1} - T_i\right) + \frac{E'_i}{V_i}\left(T_{i+1} - T_i\right) +$$

Eq. E.16.
$$+\frac{W_{h,i}}{\rho_w C_{pw} V_i}\left(\frac{\mathrm{m}^3}{10^6\ \mathrm{cm}^3}\right) + \frac{J_{h,i}}{\rho_w C_{pw} H_i}\left(\frac{\mathrm{m}}{100\,\mathrm{cm}}\right) + \frac{J_{s,i}}{\rho_w C_{pw} H_i}\left(\frac{\mathrm{m}}{100\,\mathrm{cm}}\right)$$

where T_i = temperature in reach *i* [ºC], *t* = time [d], E'_i = the bulk dispersion coefficient between reaches *i* and *i* + 1 [m^3/d], $W_{h,i}$ = the net heat load from point and non-point sources into reach *i* [cal/d], ρ_w = the density of water [g/cm^3], C_{pw} = the specific heat of water [cal/(g ºC)], $J_{h,i}$ = the air-water heat flux [cal/(cm^2 d)], and $J_{s,i}$ = the sediment-water heat flux [cal/(cm^2 d)].

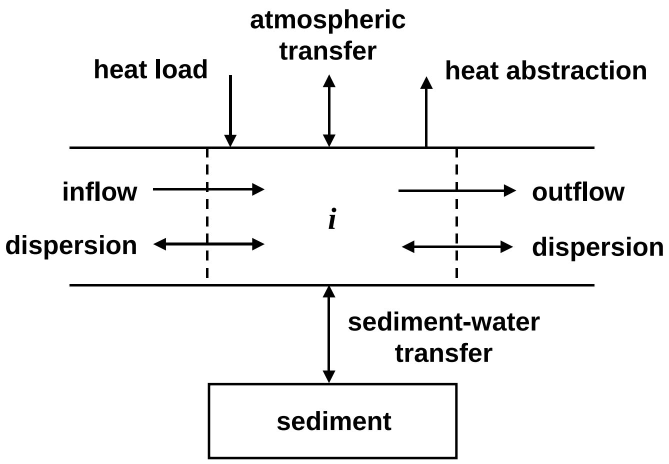


Figure E.7. Heat balance.

The bulk dispersion coefficient is computed as

Eq. E.17.
$$E'_i = \frac{E_i A_{c,i}}{\left(\Delta x_i + \Delta x_{i+1}\right)/2}$$

Note that two types of boundary condition are used at the river's downstream terminus: (1) a zero dispersion condition (natural boundary condition) and (2) a prescribed downstream boundary condition (Dirichlet boundary condition). The choice between these options is made on the Headwater Worksheet.

The net heat load from sources is computed as

Eq. E.18.
$$W_{h,i} = \rho C_p \left[\sum_{j=1}^{psi} Q_{ps,i,j} T_{psi,j} + \sum_{j=1}^{npsi} Q_{nps,i,j} T_{npsi,j} \right]$$

where $T_{ps,i,j}$ is the *j*th point source temperature for reach *i* [°C], and $T_{nps,i,j}$ is the *j*th non-point source temperature for reach *i* [°C].

E.2.8. Surface heat flux

As depicted in Figure E.8, surface heat exchange is modeled as a combination of five processes:

Eq. E.19.
$$J_h = I(0) + J_{an} - J_{br} - J_c - J_e \qquad (1)$$

where $I(0)$ = net solar shortwave radiation at the water surface, J_{an} = net atmospheric longwave radiation, J_{br} = longwave back radiation from the water, J_c = conduction, and J_e = evaporation. All fluxes are expressed as cal/cm^2/d.

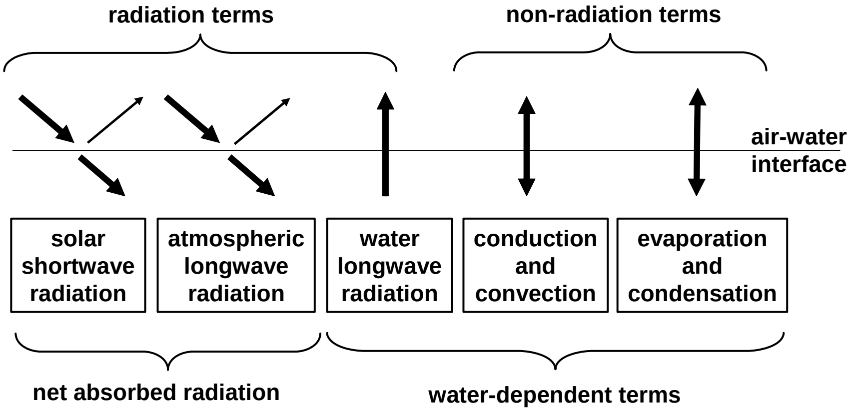


Figure E.8. The components of surface heat exchange

E.2.9. Constituent model

E.2.9.1. Constituents and general mass balance

A general mass balance for a constituent concentration (ci) in the water column of a reach (excluding hyporheic exchange) is written as (Fig. 1):

Eq. E.20.

$$\frac{d_{ci}}{d_t}=\frac{Q_{i-1}}{V_i}c_{i-1}-\frac{Q_i}{V_i}c_i-\frac{Q_{ab,i}}{V_i}ci+\frac{E'_{i-1}}{V_i}\left(c_{i-1}-c_i\right)+\frac{E'_i}{V_i}\left(c_{i+1}-c_i\right)+\frac{W_i}{V_i}+S_i$$

Where:

Q_i = flow [m^3/d, ab=abstraction],
V_i = volume(m^3),
E'_i = the bulk dispersion coefficient between reaches
W_i = the external loading of the constituent to reach i [g/d or mg/d],
S_i = sources and sinks of the constituent due to reactions and mass transfer mechanisms [g/m^3/d or mg/m^3/d].

For bottom algae in the water column the transport and loading terms are omitted from the mass balance differential equations (mg/l).

State variables in QUAL2Kw

Variable	**Units**
Temperature	ºC
Conductivity	μmhos
Inorganic suspended solids	mg D/l
Dissolved oxygen	mg O_2/l
Slowly reacting CBOD	mg O_2/l
Fast reacting CBOD	mg O_2/l
Organic nitrogen	μg N/l
Ammonia nitrogen	μg N/l
Nitrate nitrogen	μg N/l
Organic phosphorus	μg P/l
Inorganic phosphorus	mg P/l
Phytoplankton	mg A/l
Detritus	mg D/l
Pathogen	Cfu/100 ml
Alkalinity	mg $CaCO_3$/l
Total inorganic carbon	mole/l
Bottom algae biomass	g D/m^2
Bottom algae nitrogen	mg N/m^2
Bottom algae phosphorus	mg P/m^2

Table E.3. Model state variables

Exchange of mass between the surface water and the hyporheic sediment zone is represented by the bulk hyporheic exchange flow in reach i [$E'_{hyp,i}$ in m3/day] and the difference in concentration in the surface water (ci) and in the hyporheic sediment zone (c2,i).

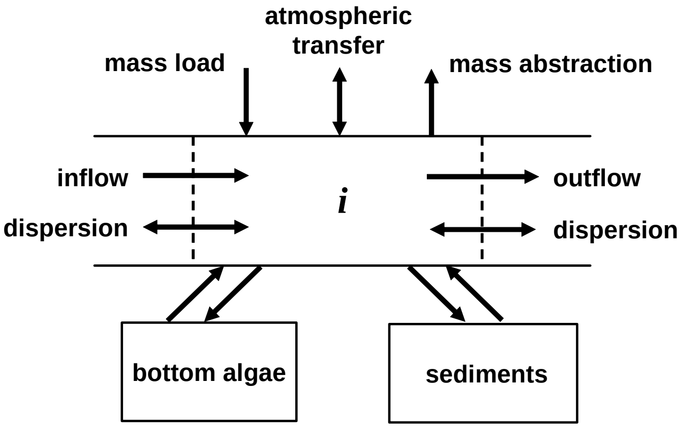


Figure E.9. Mass balance

For all but the heterotrophic bacteria biofilm, the general mass balance for a constituent concentration in the hyporheic sediment zone of a reach ($c_{2,i}$) is written as

$$\text{Eq. E.21.} \qquad \frac{dc_{2,i}}{dt} = S_{2,i} + \frac{E'_{hyp,i}}{V_{2,i}}\left(c_i - c_{2,i}\right)$$

where $S_{2,i}$ = sources and sinks of the constituent in the hyporheic zone due to reactions, $V_{2,i} = \phi_{s,i} A_{st,i} H_{2,i} / 100$ = volume of pore water in the hyporheic sediment zone [m^3], $\phi_{s,i}$ is the porosity of the hyporheic sediment zone [dimension less number between 0 and 1], $A_{st,i}$ = the surface area of the reach [m^2], and $H_{2,i}$ = the thickness of the hyporheic zone [cm]. Porosity is defined as the fraction of the total volume of sediment that is in the liquid phase and is interconnected (Chapra, 1997).

The external load is computed as

$$\text{Eq. E.22.} \qquad W_i = \sum_{j=1}^{psi} Q_{ps,i,j} c_{psi,j} + \sum_{j=1}^{npsi} Q_{nps,i,j} c_{npsi,j} \;)$$

Where:

$c_{ps,i,j}$ is the j^{th} point source concentration for reach i [mg/L or μg/L], and
$c_{nps,i,j}$ is the j^{th} non-point source concentration for reach i [mg/L or μg/L].

Settled inorganic suspended solids, phytoplankton, and detritus are assumed to be deposited from the water column layer to the sediment diagenesis zone and do not enter the hyporheic pore water. The rationale for this assumption is that hyporheic exchange typically does not occur in depositional areas of fine sediment. The sediment diagenesis sub-model accounts for anaerobic metabolism of settled material in the sediment. The hyporheic sub-model accounts for aerobic metabolism of heterotrophic bacteria in the hyporheic zone.

E.2.10. Reaction fundamentals and constituents reactions

An important amount of equations are used to represent de major chemical reactions that take place in the model. They are classified as biochemical reactions and stoichiometry of organic matter (reaction fundamentals) and conservative substance, phytoplankton, detritus, slowly reacting CBOD, fast reacting CBOD, organic nitrogen, ammonia nitrogen, unionized ammonia, nitrate nitrogen, organic phosphorus, inorganic phosphorus, inorganic suspended solids, dissolved oxygen, pathogen, generic constituents, ph and total inorganic carbon. Detailed information about all of them can be found in Pelletier and Chapra (2005).

E.2.11. The genetic algorithm for the calibration of QUAL2Kw

The advantages of global optimization algorithms for calibration of water quality models have been noted by many authors (e.g. Zou and Lung, 2004; Mulligan and Brown, 1998). Several alternative tools are available for automatic calibration of models (e.g. UCODE by Poeter and Hill, 1998, or PEST by Scientific Software Group). However, the present model is not compatible with the requirements of tools such as UCODE and PEST, and a customized function optimization algorithm was required.

A flowchart of the PIKAIA GA used in QUAL2Kw is shown in Figure E.10. The GA maximizes the goodness of-fit of the model results compared with measured data. The GA carries out its maximization task on a user-selected number of model runs to define a population. The population size remains constant through out the evolutionary process. Rather than evolving the population until some preset tolerance criterion is satisfied, the GA carries the evolution for ward over a user specified number of generations.

Charbonneau and Knapp (1995) provide a tutorial for GA concepts and comprehensive documentation of the PIKAIA GA. The PIKAIA GA is adaptable for use in a wide variety of modeling applications. The original Fortran 77 code for PIKAIA was translated to Excel VBA for use in QUAL2Kw.

The VBA code accounts for only a small fraction of the computational time when the GA is run. Most of the computational time is spent by the compiled Fortran program that is driven by the GA to perform the numerical integration of the water quality model each time the fitness function is evaluated.

The user may select any combination of kinetic rate parameters to include in the optimization. The user also specifies the minimum and maximum values for any kinetic rate parameters that are being optimized.

The GA maximizes the function f(x) in a bounded n-dimensional space, for

Eq. E.23. $$x = (x_1, x_2, ..., x_n) \quad x_k \in [0.0, 1.0]$$

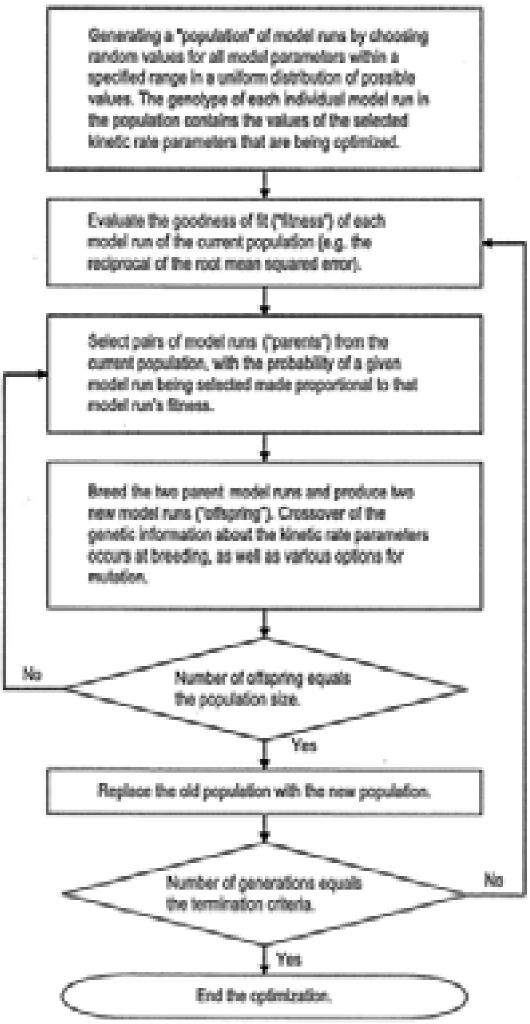


Figure E.10. Flowchart for the genetic algorithm.

where n is the number of parameters that are being optimized. The parameters (x) are bounded in the range of 0.0 to 1.0 in the GA. The kinetic rate parameters for the model are scaled from the values of x according to a linear interpolation between the specified minimum and maximum value of each kinetic rate parameter that is being optimized.

The Excel framework provides flexibility to construct any fitness function with any combination and weighting of water quality constituents to control the calibration results. At the beginning of an evolutionary run, the initial values for x for each individual model run in the population are selected from a uniform random distribution between 0 and 1. Most of the individual model runs in the initial population have very poor fitness values. However, some individuals have better fitness than others, and the natural selection process during the evolution favors those individuals.

E.2.12. Model parameter worksheets

The computer code used to implement the calculations for QUAL2K is written in Visual Basic for Applications (VBA). A Fortran executable is also available as an option. Excel serves as the user interface.

Color is used to signify whether information is to be input by the user or output by the program:

- Pale Blue designates variable and parameter values that are to be entered by the user (14 sheets)
- Pale Yellow designates data that the user enters. This data are then displayed on graphs generated by Q2K (6 sheets)
- Pale Green designates output values generated by Q2K (9 sheets)
- Dark solid colors are used for labels and should not be changed.

The most representative sheets for our work are going to be explained here.

E.2.12.1. Qual 2K input worksheets

The QUAL2K worksheet (Table E.4) is used to enter general information regarding a particular model application.

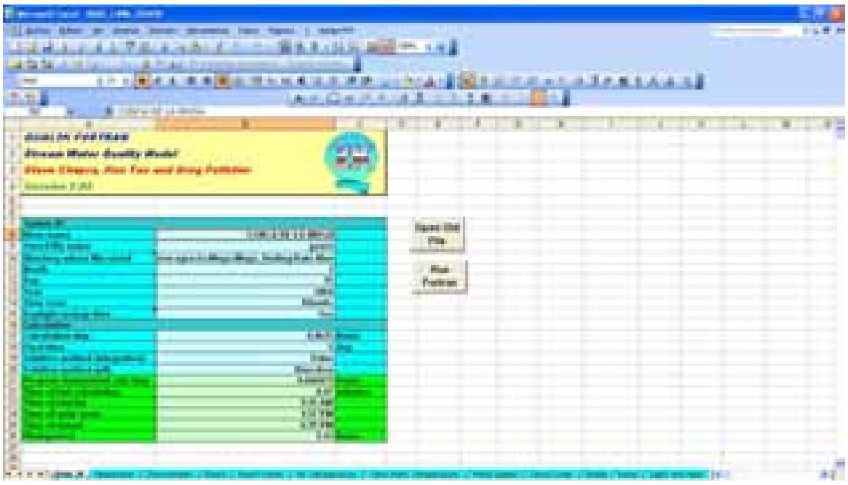


Table E.4. The QUAL2K Worksheet.

River name. Name of the river or stream being modeled. After the program is run, this name along with the date, is displayed on all worksheets and charts.
Saved File name. This is the name of the data file generated when Q2K is run.
Directory where file saved. This specifies the complete path to the directory where the file is saved.
Month. The simulation month. This is entered in numerical format (e.g., January = 1, February = 2, etc.).
Day. The simulation day.
Year. The simulation year
Time zone. A pull-down menu (Table E.5) allows to select the proper time zone.

Time zone Mountain

Daylight savings time

Calculation:

Calculation step

Final time

Solution method (integration)

Solution method (pH)

Table E.5. The pull down menu for setting the time zone.

Daylight savings time. A pull down menu allows you to specify whether daylight savings time is in effect (Yes or No).

Calculation step. This is the time step used for the calculation. It must be selected from the pull down list.

Number of days. This defines the duration of the calculation. It must be an integer that is greater than or equal to 2 days. This constraint is imposed because the model is run in a time variable mode until it reaches a steady state. Therefore, the first day of simulation is by definition overwhelmingly dominated by its initial conditions. If the user enters a value less than 2 days, the program automatically sets the final time to 2 days. The final time should be at least twice the river's travel time. For streams with short travel times where bottom algae are simulated, it must usually be longer.

Solution method (integration). A pull down menu allows you to choose between three numerical methods for solving the differential equations for the state variables. These are (1) Euler's method, (2) the fourth-order Runge-Kutta (RK4) method, and (3) an adaptive time step method.

Solution method (pH). A pull down menu allows you to choose between two numerical methods for solving for pH using root location. These are (1) Newton-Raphson (the default) and (2) bisection. Detailed descriptions of these methods can be found in Chapra and Canale (2002). Newton-Raphson is suggested as the default because it is faster. However, there are some cases where it can go unstable. If this occurs, the bisection, although slower, may be preferable.

Simulate hyporheic exchange and pore water quality. Three options are available for simulation of hyporheic exchange and water quality.

- 'No': to bypass calculation of mass transfer between the water column and the hyporheic pore water, and water quality kinetics in the hyporheic zone.

- 'Level 1': to simulate mass transfer between the water column and the hyporheic pore water, with water quality kinetics in the hyporheic zone as an enhanced zero-order or first-order oxidation rate of fast-reacting DOC with limitation from fast-reacting DOC and dissolved oxygen.

- 'Level 2': to simulate mass transfer between the water column and the hyporheic pore water, with water quality kinetics with attached heterotrophic bacteria as a state variable in the hyporheic sediment zone with growth limitation from fast-reacting DOC, nitrate, ammonia, soluble reactive P, and dissolved oxygen.

Mass transfer between the water column and hyporheic pore water only occurs if there are positive values entered in column AL of the 'Reach' sheet for the hyporheic exchange flow. Kinetic model options and parameters are specified on the 'Rates' sheet.

Display dynamic diel output. Two options are available for displaying the dynamic output results:

- 'Yes': to display the dynamic diel results in output sheets and charts.
- 'No': to bypass writing of the dynamic diel results. This option will result in faster writing of the output files and charts and will save the users time if they are doing many runs and don't need to look at the dynamic output. The longitudinal results and charts are not affected by this choice.

E.2.12.2. Headwater worksheet

This worksheet (Table E.6) is used to enter flow and concentration for the system's boundaries.

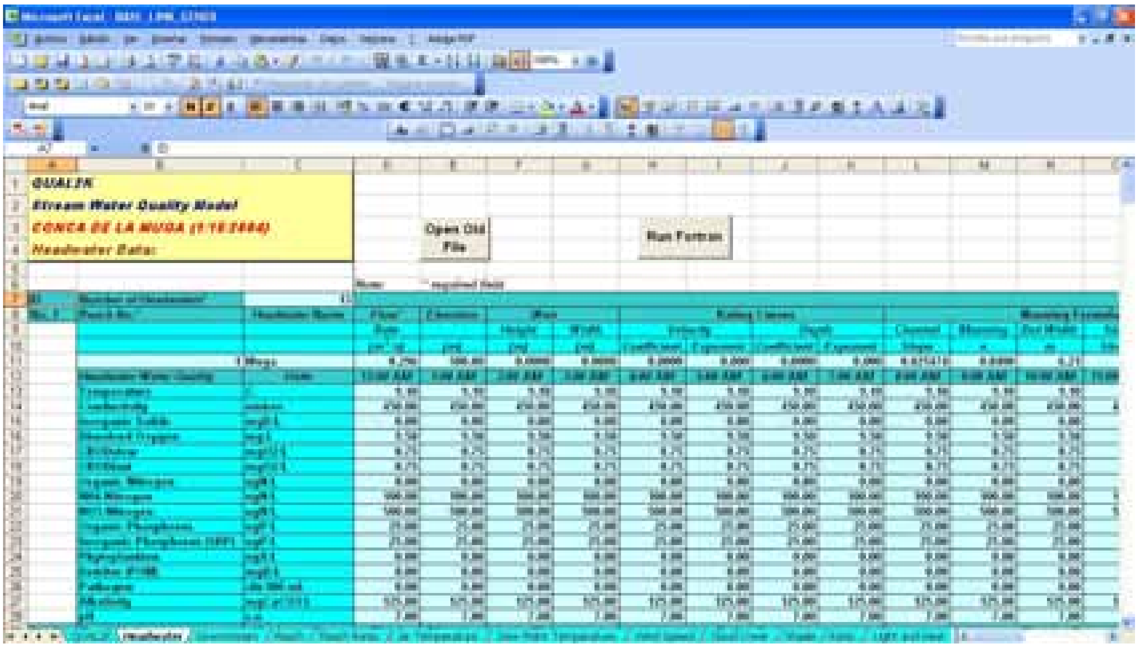


Table E.6. The Headwater Worksheet used to enter the headwater and downstream (optional) boundary conditions

Flow. The headwater's flow rate in m^3/s.

Prescribed Downstream Boundary. If the downstream boundary has an effect on the simulation, this option is set to yes. If this is done, the downstream boundary concentrations should be entered in cells D27:Z42.

Headwater Water Quality. This block of cells is used to enter the temperature and water quality boundary conditions at the river's headwater. For cases where the data varies in a diel fashion, Q2K allows you to enter values on an hourly basis. If the values are constant over the daily cycle, just enter the mean value in column D (that is, for

12:00 AM) and leave the other cells (columns E through Z) blank. Q2K will automatically apply the 12:00 AM value to the other times of day.

Downstream Boundary Water Quality. If the downstream boundary has an effect on the simulation, this block of cells is used to enter the temperature and water quality conditions at the river's downstream boundary headwater. As was the case with the headwater, if the values are constant over the daily cycle, just enter the mean value in column D (that is, for 12:00 AM) and leave the other cells to the right blank (columns E through Z). Q2K will automatically apply the 12:00 AM value to the other times of day.

E.2.12.3. Reach worksheet

This worksheet is used to enter information related to the river's headwater (Reach Number 0) and its reaches (Table E.7).

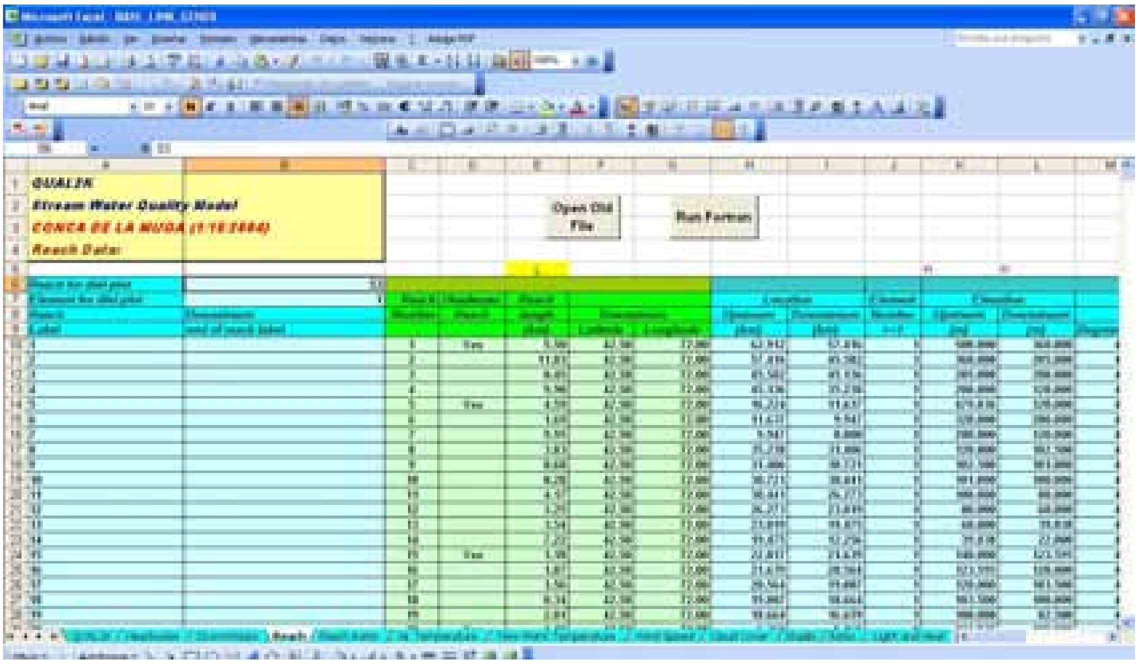


Table E.7. The first part of the Reach Worksheet used to specify reach labels, distances and elevations.

Reach for diel plot. Cell B6 is used to enter the number of the reach for which diel plots will be generated. If a negative, zero or a value greater than the number of reaches is entered, the program automatically sets the value to the last downstream reach. Note that there is also a button to the right of cell B6 that allows the user to display a different reach on the diel plots if the model has been run with the option of displaying dynamic diel results.

Reach Label (optional). Q2K allows you to enter identification labels for each reach. Figure E.11 provides an example to illustrate the naming scheme. The first two reaches of a river are shown. Because it includes the Jefferson City WWTP discharge, we might choose to enter the reach label "Jefferson City WWTP" for the first reach. Similarly we might label the second reach as "Sampling Station 27."

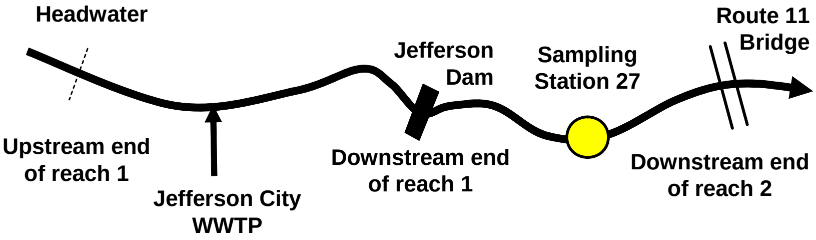


Figure E.11. The first two reaches of a river system.

Downstream end of reach label (optional). Q2K allows you to enter identification labels for the boundaries between reaches. These labels are then displayed on other worksheets to identify the reaches. As shown in Table E.8, the downstream end of the first reach in Figure E.11 could be labelled as "Jefferson Dam". Similarly, the downstream end of the second reach could be labelled as "Route 11 Bridge".

Reach Label	Downstream end of reach label	Number
	Headwater	0
Jefferson City WWTP	Jefferson Dam	1
Sampling Station 27	Route 11 Bridge	2

Table E.8. An example of the labels that could be entered for the reaches.

Reach numbers (output). The model automatically numbers the reaches in ascending order.

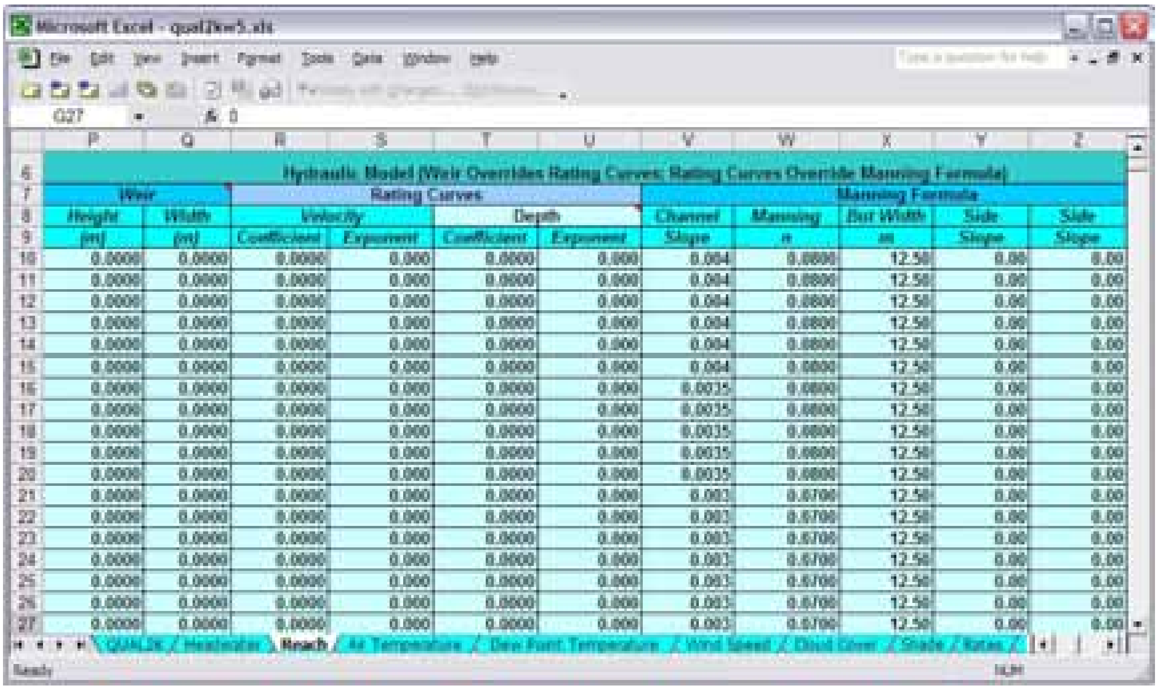
Reach length (output). The model automatically computes and displays the length of each reach.

Downstream Latitude and Longitude (output). The model automatically computes and displays the latitude and longitude of the downstream ends of each reach in decimal degrees.

Downstream location. The user must enter the river kilometer for the downstream end of each reach. Note that the reach distances can be in descending or ascending order.

Upstream and downstream elevation. The user must enter the elevation in meters above sea level for both the upstream and downstream ends of the reach. Note that this information is used for two primary purposes. First, it is used to detect an elevation drop due to a waterfall at the end of a reach. Second, it is used to correct oxygen saturation for elevation effects. **Note that it is not used to determine channel slope.** Channel slope is entered independently in column W.

Downstream Latitude and Longitude. The user must enter the latitude and longitude of the downstream end of each reach in degrees, minutes, and seconds. Alternatively, they can be entered in decimal degrees, in which case, the minutes and seconds entries would be left blank or zero.



	P	Q	R	S	T	U	V	W	X	Y	Z
6	Hydraulic Model (Weir Overrides Rating Curves; Rating Curves Override Manning Formula)										
7	Weir		Rating Curves				Manning Formula				
8	Height	Width	Velocity		Depth		Channel	Manning	Bot Width	Side	Side
9	(m)	(m)	Coefficient	Exponent	Coefficient	Exponent	Slope	n	m	Slope	Slope
10	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.004	0.0800	12.50	0.00	0.00
11	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.004	0.0800	12.50	0.00	0.00
12	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.004	0.0800	12.50	0.00	0.00
13	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.004	0.0800	12.50	0.00	0.00
14	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.004	0.0800	12.50	0.00	0.00
15	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.004	0.0800	12.50	0.00	0.00
16	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.0035	0.0800	12.50	0.00	0.00
17	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.0035	0.0800	12.50	0.00	0.00
18	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.0035	0.0800	12.50	0.00	0.00
19	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.0035	0.0800	12.50	0.00	0.00
20	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.0035	0.0800	12.50	0.00	0.00
21	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.003	0.0700	12.50	0.00	0.00
22	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.003	0.0700	12.50	0.00	0.00
23	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.003	0.0700	12.50	0.00	0.00
24	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.003	0.0700	12.50	0.00	0.00
25	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.003	0.0700	12.50	0.00	0.00
26	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.003	0.0700	12.50	0.00	0.00
27	0.0000	0.0000	0.0000	0.000	0.0000	0.000	0.003	0.0700	12.50	0.00	0.00

Table E.9. The part of the Reach Worksheet used to specify the system's hydraulics.

Hydraulic Model. Q2K allows two options for computing velocity and depth based on flow: (1) rating curves or (2) the Manning formula. It is important to pick one of the options and leave the other blank or zero. If the model detects a blank or zero value for the Manning *n*, it will implement the rating curves. Otherwise, the Manning formula will be solved.

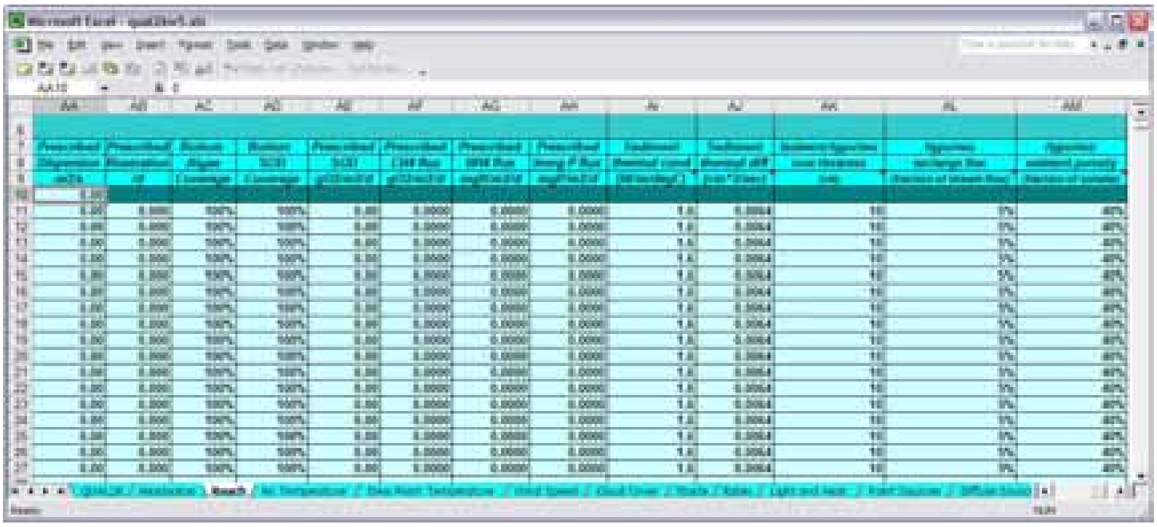


Table E.10. The last part of the Reach Worksheet.

E.2.12.4. Point sources worksheet

This worksheet is used to enter information related the system's point sources

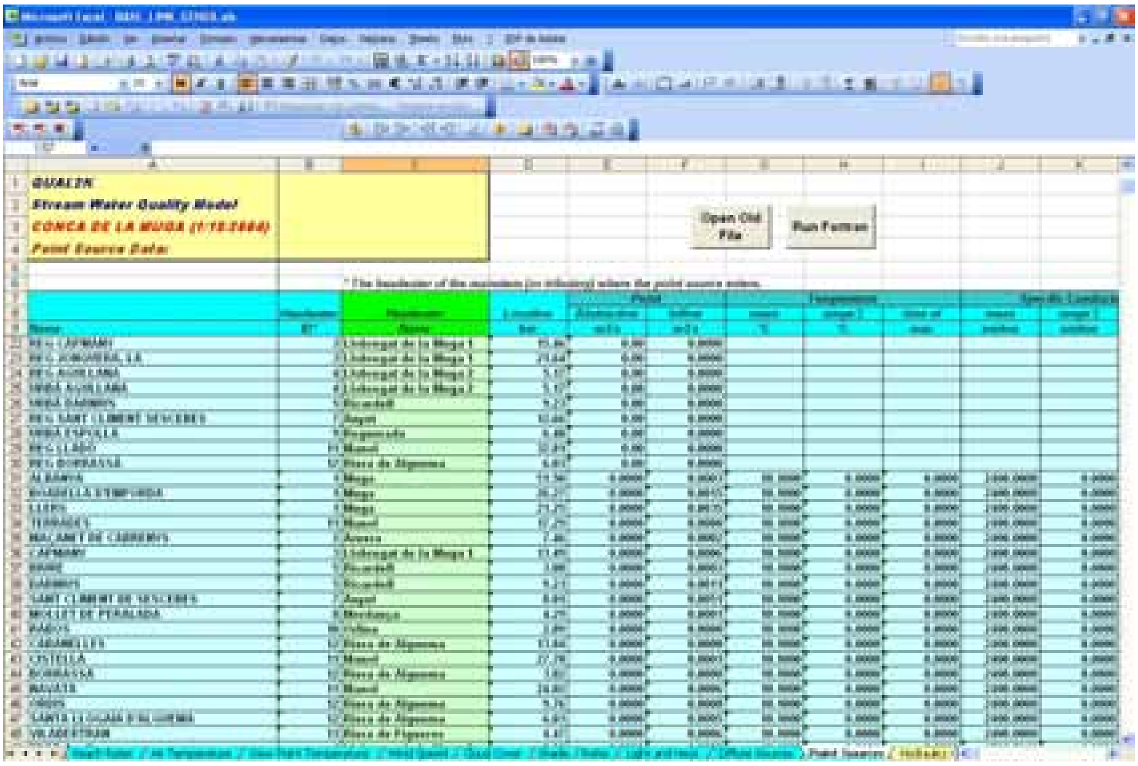


Table E.11. The Point Sources Worksheet.

Name. User-specified label to identify the particular point source inflow or abstraction.
Location. The kilometer where the point source or abstraction enters or leaves the river.
Source Inflows and Outflows. A source can either be an inflow (loading or tributary) or an outflow (abstraction). Note that it can not be both. If there is an abstraction flow (i.e., a positive value in column C), the remaining information in columns D through AZ will be ignored.
Point abstraction. For an abstraction, a positive value for flow (m^3/s) must be entered. If this is done, the values in columns D through AZ should be left blank.
Point inflow. For an input, a value for flow (m^3/s) must be entered in column D. Column C should be a zero or a blank.
Constituents. The temperature and the water quality concentrations of the inflow are entered in columns E through AZ.

QUAL2K allows the temperature and concentrations of each point source to be entered as a sinusoid that varies over the diel cycle. Figure E.12 shows an example for the temperature of the Boulder CO WWTP.

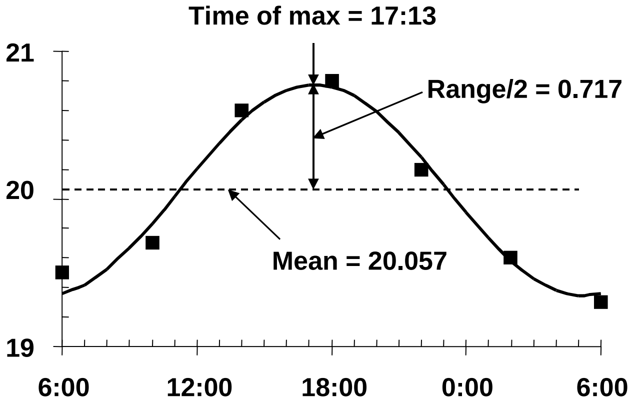


Figure E.12. Temperature for the Boulder, CO wastewater treatment plant effluent on Sept. 21-22, 1987 along with a sinusoidal fit to the data.

E.2.12.5. Diffuse sources worksheet

This worksheet is used to enter information related the system's diffuse (i.e., non-point) sources and abstractions.

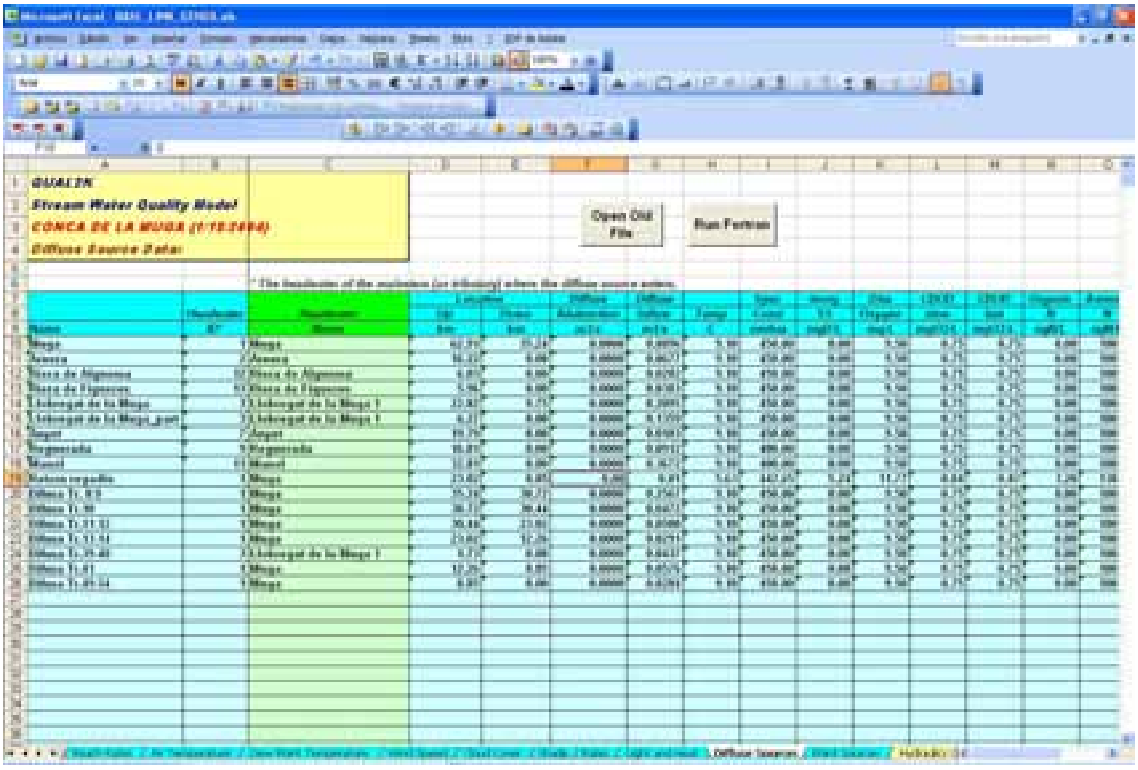


Table E.12. The Diffuse Sources Worksheet.

Name. User-specified label to identify the particular diffuse inflow or abstraction.

Location. The upstream and downstream kilometers over which the diffuse source or abstraction enters or leaves the river.

Source inflows and outflows. A distributed source can either be an inflow (loading or tributary) or an outflow (abstraction). Note that it can not be both. If there is an abstraction flow (i.e., a positive value in column D), the remaining information in columns E through U will be ignored. If a particular segment location actually has diffuse inflow and outflow, then these can both be entered on separate rows.

Diffuse abstraction. For an abstraction, a positive[1] value for flow (m^3/s) must be entered in column D. If this is done, the values in columns E through U should be left blank.

Diffuse inflow. For an input, a value for flow (m^3/s) must be entered in column E. Column D should be a zero or a blank.

Constituents. The temperature and the water quality concentrations of the diffuse inflow are entered in columns F through U.

E.2.13. Qual 2K output worksheets

These are a series of worksheets that present tables of numerical output generated by Q2K. This information is displayed on plots along with measured data. These are identified by pale green tabs.

E.2.13.1. Hydraulics summary worksheet

This worksheet summarizes the hydraulic parameters for each model reach.

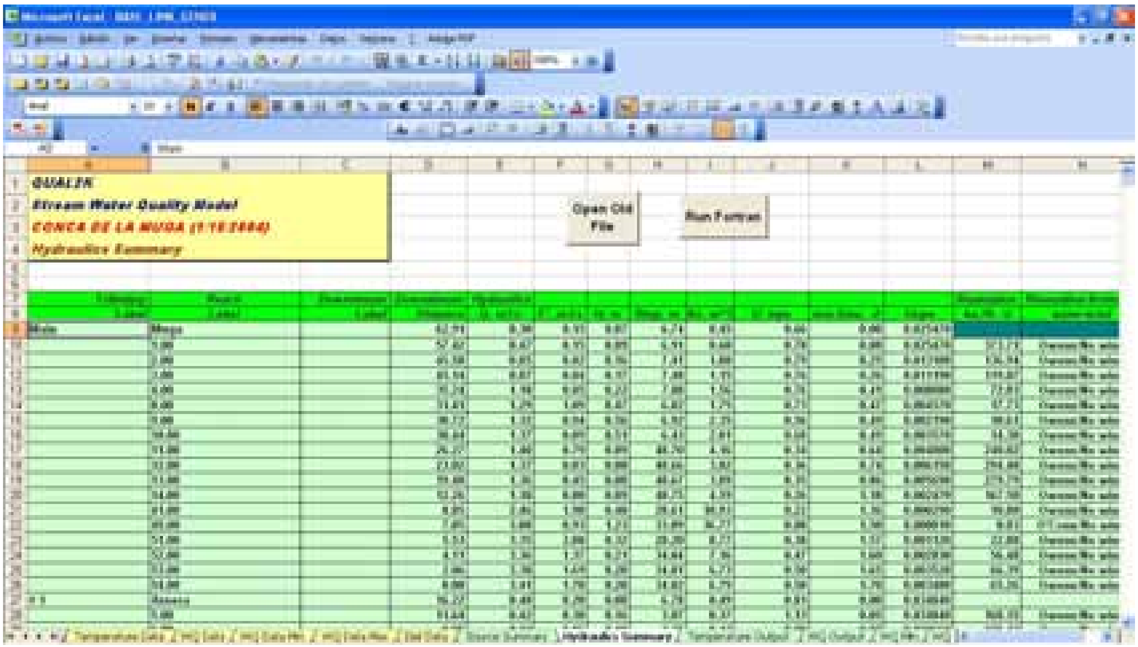


Table E.13. The Hydraulics Summary Worksheet.

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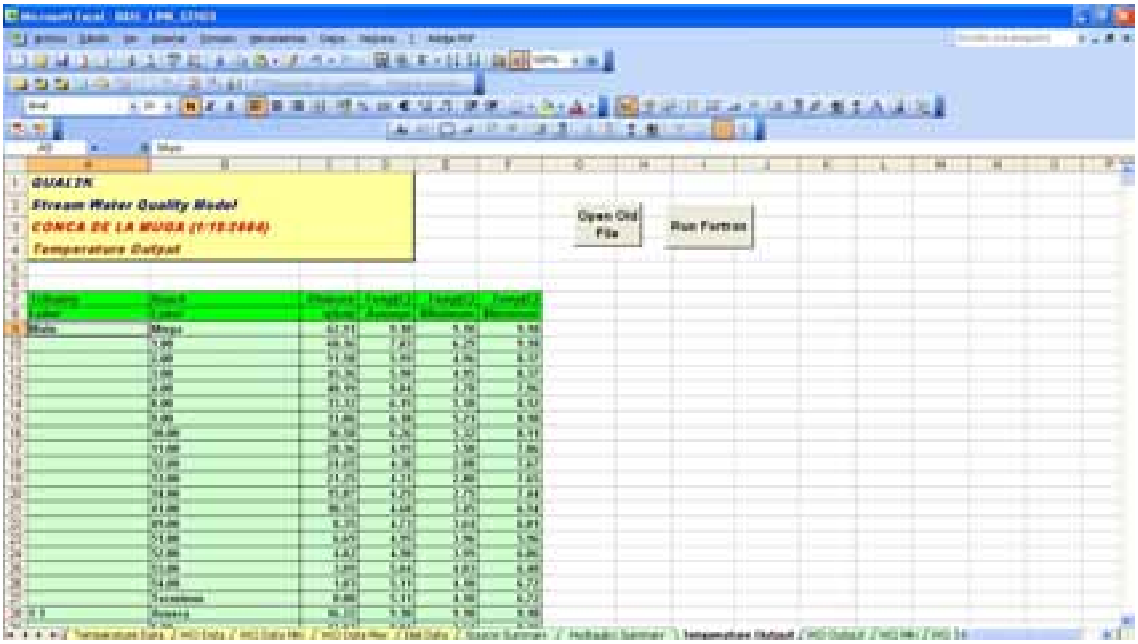
[1] Some software treats an abstraction as a negative inflow. In Q2K, the flow is entered as a positive number and the software internally calculates it as a loss from the reach.

E.2.13.2. Temperature output worksheet

This worksheet summarizes the temperature output for each model reach.



QUAL2K

Stream Water Quality Model

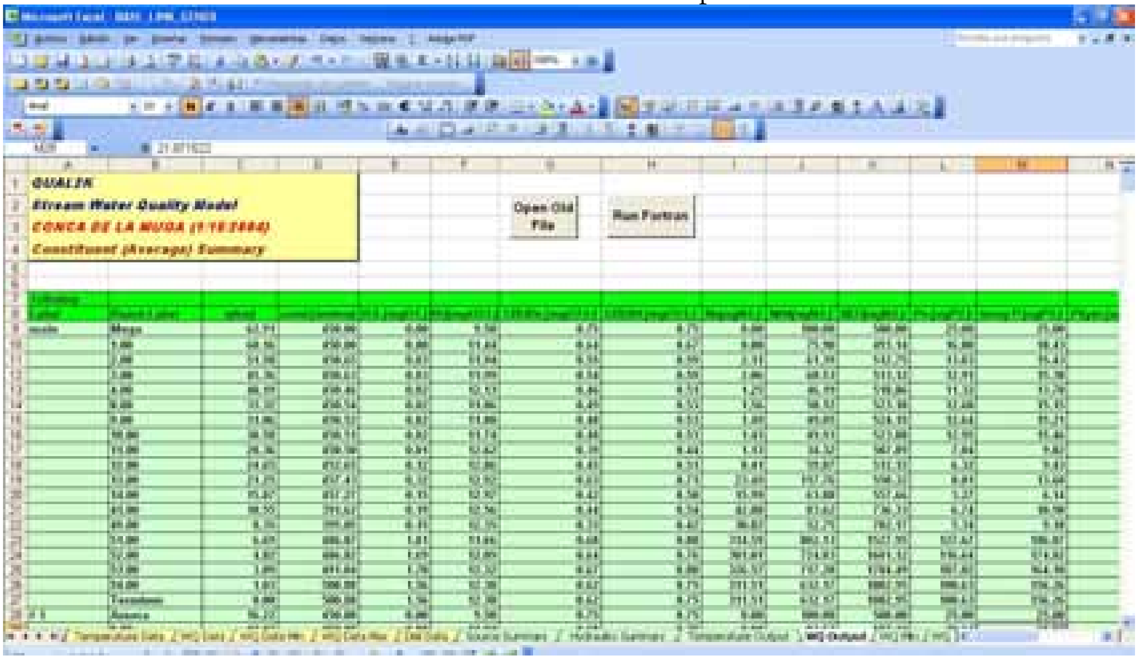
CONCA DE LA MUGA

Temperature Output

Table E.14. The Temperature Output Worksheet.

E.2.13.3. Water quality output worksheet

This worksheet summarizes the mean concentration output for each model reach



QUAL2K

Stream Water Quality Model

CONCA DE LA MUGA

Constituent (Average) Summary

Table E.15. The first part of the Water Quality Output Worksheet

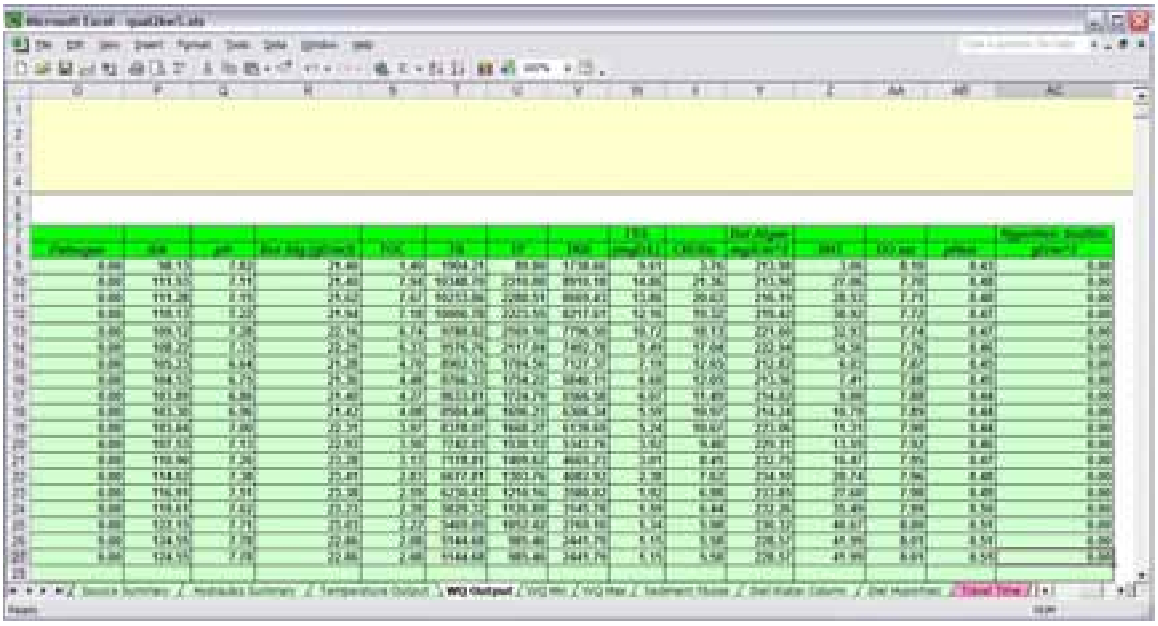


Figure E.1. The last part of the Water Quality Output Worksheet

E.2.14. Model Validation

The values obtained from the programme have to be contrasted with the real measurements, where available, to check the accuracy of the simulation. Next figures show, respectively, the location of the sampling station in the Muga basin (one of the case studies presented in Chapter 6), and the comparison of results between the real and the simulated situation. The simulated values fit quite well with the real figures.

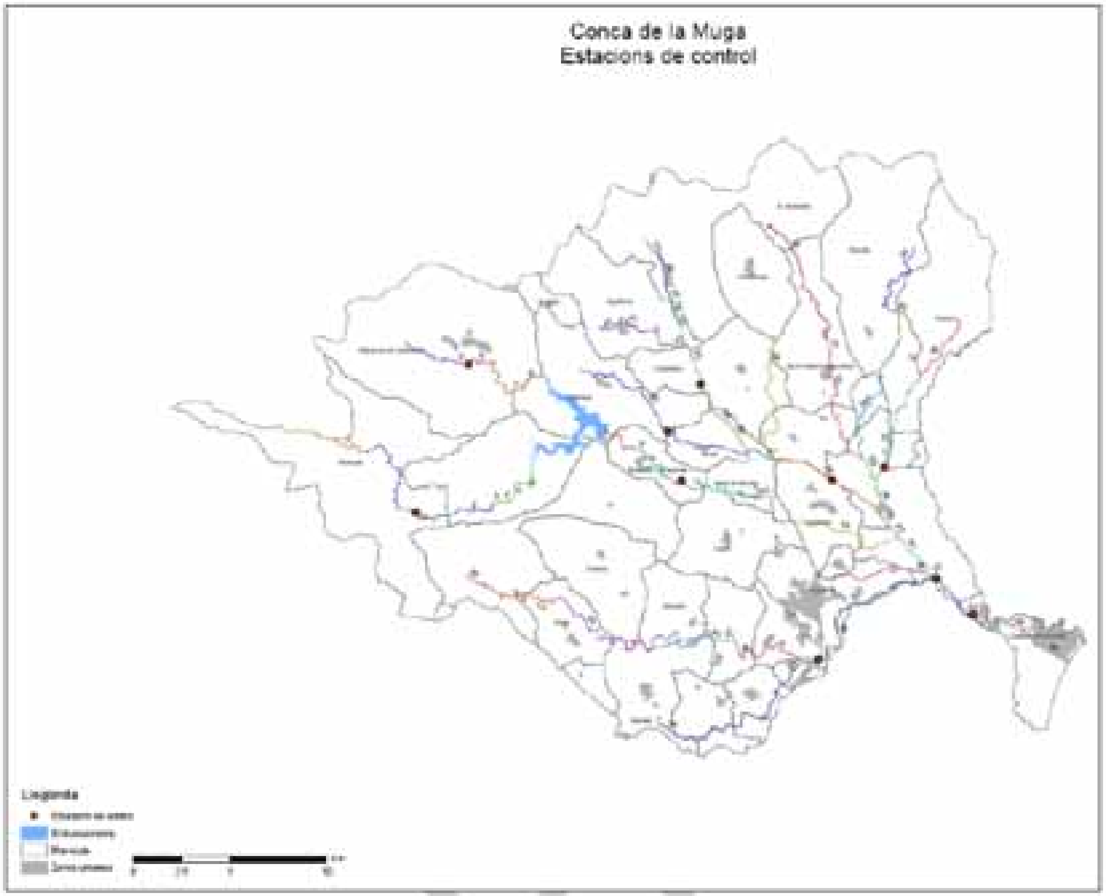


Figure E.13. Location of the sampling stations in the Muga watershed.

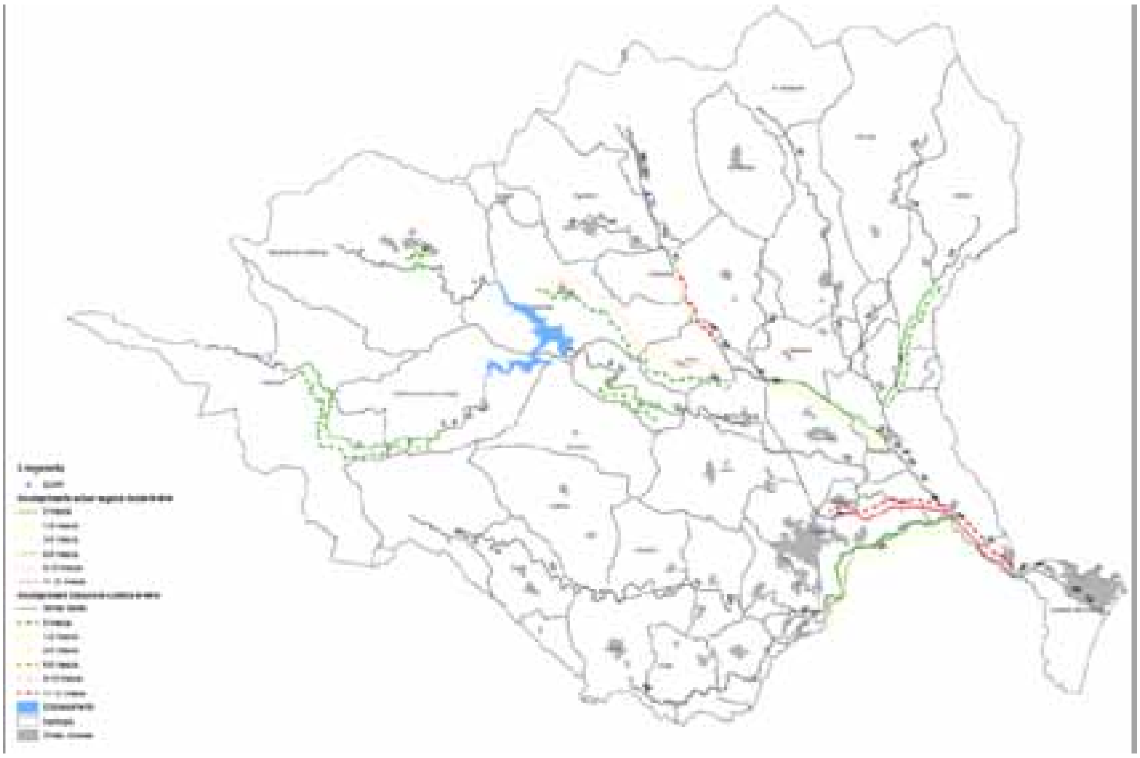


Figure E.14. Comparison between the real and simulated values.

Annex F

Technical data

Two well-differentiated parts comprise this Annex. On the one hand, the sludge treatment processes are briefly explained in the first section, as complementary information to the sludge section in Chapter 5. On the other hand, the main features and the process diagrams of the twelve WTP considered in the analysis to define k^* for the quality-restoring technologies are given. They were collected from the CCB reports.

F.1. Sludge treatment

In order to protect the environment from urban and certain industrial sectors waste water discharge, collection, treatment and mixture, the Council Directive 91/271/EEC was adopted on 21 May 1994. Articles 12 and 14 studies the reuse of treated waste water and the obtained WWTP sludge management, respectively.

Main features of this European legislation are schematized in Figure 6.1

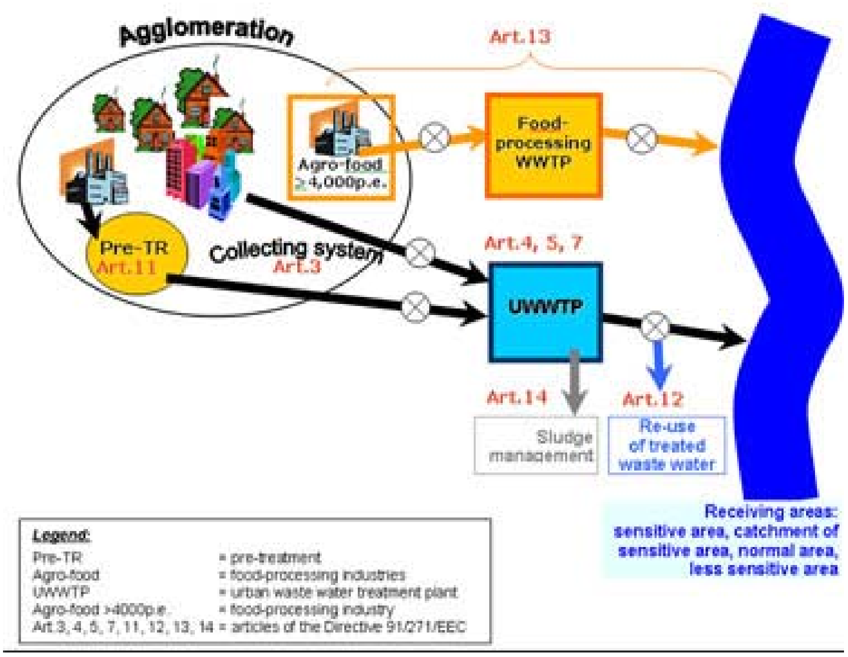


Figure 6.1. Scheme in with main features concerning to Council Directive 91/271/EEC are collected. (Source: Water Information System for Europe, 2008)

Council Directive principles are Planning, Regulation, Monitoring, Information and reporting. Specifically, the Directive requires:

- The Collection and treatment of waste water in all agglomerations of >2000 population equivalents
- Secondary treatment of all discharges from agglomerations of > 2000 p.e., and more advanced treatment for agglomerations >10 000 population equivalents in designated sensitive areas and their catchments;
- A pre-authorisation of all discharges of urban wastewater, of discharges from the food-processing industry and of industrial discharges into urban wastewater collection systems
- Monitoring of the performance of treatment plants and receiving waters
- Controls of sewage sludge disposal and re-use, and treated waste water re-use whenever it is appropriate.

Sludge generation, if possible, must be, firstly, minimized. When the techniques have been optimized, the generated sludge can be valorizated. If valorization is not possible because of the presence of toxic or metallic substances, sludge is treated as solid waste in a dumping waste site.

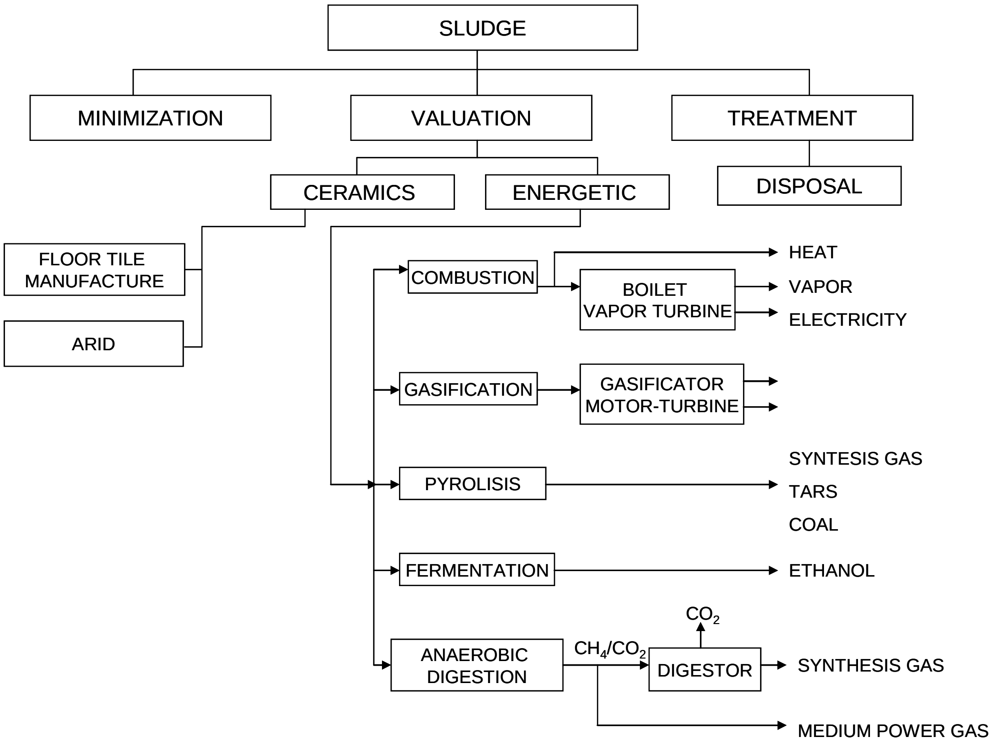


Figure F.1. Sludge final use (source: adapted from Elias, 2006)

Nowadays, the final obtained sludge reuse treatments are focussed mainly on agriculture (directly applied in crops, or with a previous composting of dewatered or anaerobically treated sludge) and thermal process obtaining energy (combustion, gasification, incineration). In some cases, sludge can be reused in some industries as a commodity. Finally, if these processes are not possible because of the presence of toxic or metallic substances, sludge is treated as solid waste in a dumping waste site.

Most of these sludge treatments, which are going to be briefly explained, start with a conditioning step of separation of water and sludge, to reduce the volume and mass of the sludge (diminishing manipulation problems and transport cost). Depending on the source, sludge has water contents from 93 % to 99.5 %. Main ways to dewatering the sludge are chemical processes (using inorganic precipitant chemicals -lime, iron salts, aluminium salts- or organic chemicals -polyelectrolytes or polymeric substances), mechanical processes (addition of ashes or coal), and physical processes (thermal dewatering process).

F.1.1. The sludge agricultural use

The basic conditions for sludge agricultural use are the quantity of pollutants contained in the sludge (avoiding the transmission of these contaminants along the ecosystem), and the adequacy of the soil. Although dry sludge disposal at a landfill was commonly used for a long time, it is decreasing because of new European Guidelines. Because of it, sludge treatment is very important (aerobic or anaerobic) previously to use it in landscape or crops.

F.1.1.1 Sludge aerobic stabilization

Consist on the reduction of organic matter by the metabolism of the MO and higher organism, based in further aeration of the sludge without or with only minimal nutrition.

Wastewater ponds
This treatment is effective in treating organic matter, nitrogen, phosphorus, and additionally for, decreasing the concentrations of heavy metals, organic chemicals, and pathogens. Compared to other methods, usually need less operation and maintenance.

Can be classified in sedimentation ponds, stabilization ponds (non aerated oxidation ponds, without artificial aeration), artificial aerated wastewater ponds, and wastewater ponds with intermediary situated trickling filters. Main advantages of this technology are low technology costs, long-term sludge management, and the simultaneously stabilization of the settled sludge. However, there are some disadvantages: high specific space required, small controllability, and that treatment performance is affected by seasonal changes

Composting
Aerobic biological process in which by means of, proper aeration, moisture and temperature conditions, residues with organic matter content are transformed by microorganisms, in a stable and sanitized product which can be used as fertilizer or as substratum (*compost).* The C/N initial ratio, pH and nutrients presence are another ver important aspects to obtain a good product.

Main advantages of this process are the reduction of odours emission (up to 80%), the disease-causing and parasite eggs reduction -organic matter is sanitized- (temperatures higher than 70º C are required for complete remove), small quantities of microorganisms are produced, a gas with high methane content is generated, and fertilising efficiency is improved, retaining the maximum nutritional components (N,K,P). Wastes volume and weight are reduced.

Main disadvantages are the high costs, possible fires and explosions, and soil contamination (if contaminants presence is not taken into account).

This kind of treatment is used in some of the studied WWTP examples, as a way to use sludge in agriculture, but without obtaining energy.

F.1.1.2 Anaerobic digestion

Anaerobic digestion is the organic matter microbial decomposition (*INFLUENT*) in a without oxygen atmosphere. The organic matter is transformed in a gas with an important heating value content (*BIOGAS*) and in other materials which conserve all the mineral elements and the difficult degradation components (*SLUDGES or WASTE*). The digested matter (*WASTE*) can be separated in fibre and in a liquid solution. The first one can be transformed into a soil conditioner (*COMPOST*) and the latter is a high nutrient content compound which can replace inorganic fertilizers (*FERTILIZER*).

Since anaerobic digestion is the main way to obtain energy from sludge used by the studied WWTP examples (although others techniques as composting and agricultural sludge reuse are used in some of theses plants, but not to obtain energy –see annex C-), the process is schematized in Figure F.2

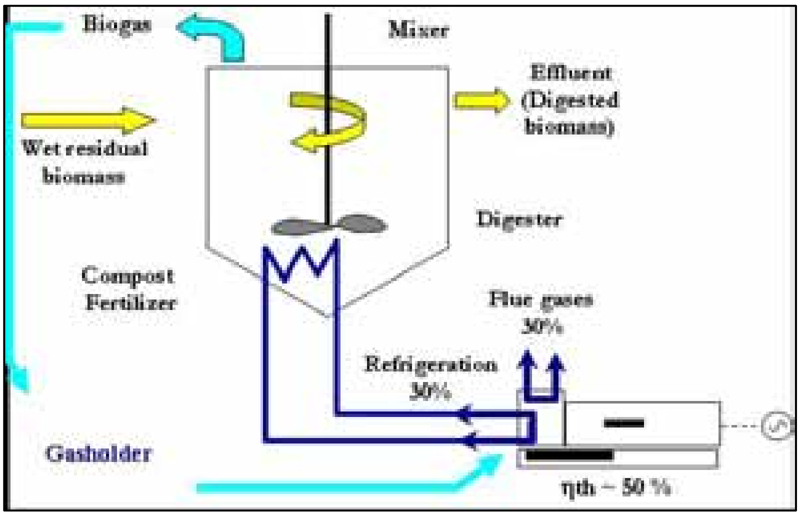


Figure F.2. Anaerobic digestion process scheme. (Source: Sebastián, 2009)

Anaerobic process does not require energy (biogas energy is recovered by the anaerobic degradation). Some disadvantages are the bad smell, biologically unstability and the strong affection by temperature.

F.1.2. Sludge thermal processes

Incineration, gasification and pyrolisis are techniques to obtain energy at high temperatures and/or pressures.

Incineration and gasification are thermo-chemical process, in which OM of dry sludge reacts with an oxidant substance (air, oxygen, or steam water). Combined cycles are commonly used obtaining electricity. Main problems are the previous dewatering of the sludge, and separating particles, eliminating moisture, and cooling, complementary systems.

On the other hand, pyrolisis it is a way to obtain energy applying elevated temperatures and/or pressures, destroying the OM. Although advances in this field have improved in last years, research must rises. Because of the high percentage of carbon in the obtained pyrolized waste which difficults its use in agriculture, this process is not the best alternative to treat sludge.

F.1.3. Use in industy

In some cases, sludge can be reused in some industries as a commodity, taking into account economic aspects (e.g transport), and profitability.

F.1.4. Disposal

Finally, as mentioned previously, if other processes are not possible because of the presence of toxic or metallic substances, sludge is treated as solid waste in a dumping site, using a controlled treatment of toxic and hazardous waste, if necessary, by mean of chemical, physical or biological treatments, to collect, detoxify and diminish its volume.

There are many different ways to obtain energy, taking into account the sludge possible treatments. Dry sludge can be combusted/ gasified / pirolyzed in a fluidized bed (previously reduced its humidity/moisture in a press filter -70 % moisture-) with a final dehydration. Combustion gases pass through a Ranquine cycle + steam turbine (combustion process) or pass though a gas turbine + Joule Cycle (gasifying process) to obtain electricity.

On the other hand, the sludge, with approximately 4% OM, can be introduced in an anaerobic reactor, obtaining biogas (with an average composition of 75% CH_4 and 25 % CO_2, approximately), which can be combusted to obtain to obtain electricity. The sludge is finally filtrated and used as fertilizer (or waste).

Finally, other option is an aerobic sludge digestion. However, although it is not a way to obtain energy, produced sludge is commonly composted to be used in agriculture.

In most of the case studies, it can be considered the treatment of dry sludge, existing output sludge exergy (kJ/kg treated water). Nevertheless, since Blanes and Palamós plants process generates biogas anaerobically, they have to be studied in a different way.

According to the Aragonian Environment Department (2005) anaerobically treatment obtained energy supposes between 0,13 y 0,16 kWh per m^3 of treated water, an important percentage of the total energy required in a WWTP (between 0.20 and 0.35 kWh/m^3).

F.2. Technical data of some WTP in Catalonia.

Real data from some running WTPs in Catalonia were used in Chapter 5 in order to define the k^* value of the quality-restoring technologies. In particular, the considered plants are detailed below (CCB, 2008).

F.2.1. WTP Begur

WWTP Name: Begur
Location: Begur
Design flow : 2,190 m^3/d
Treatment : Active Mud (N,P elimination) Secondary and reuse
Sludge reuse: Agriculture
Treated water reuse: ground infiltration

Used area: 0.4 Ha
Equivalent population: 7,300

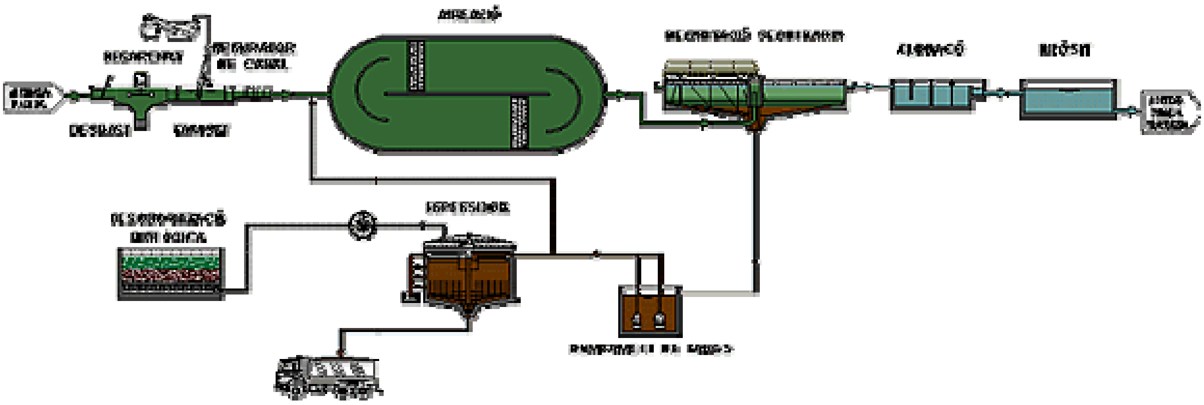


Figure F.3. Process diagram in the WTP Begur (CCB, 2008)

F.2.2. WTP Blanes

WWTP Name: Blanes
Location: Blanes
Design flow : 23,500 m^3/d
Treatment : Active Mud (N,P elimination) Secondary and reuse
Sludge reuse: Agriculture
Treated water reuse: Agriculture, Sea, aquifers recharge
Used area: 3.5 Ha
Equivalent population: 109,985

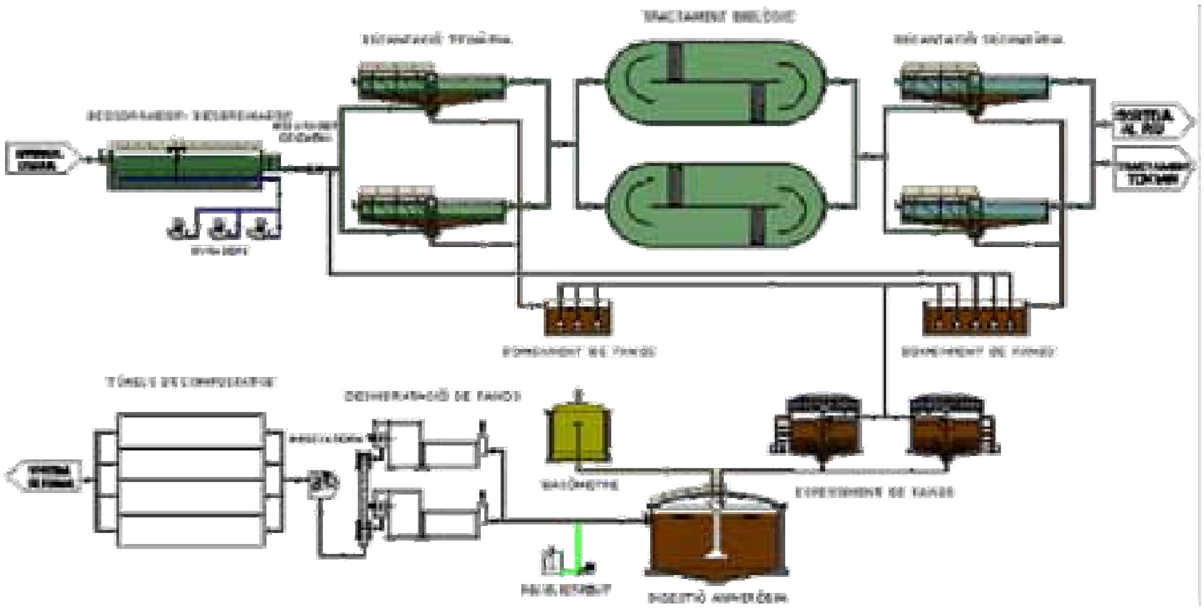


Figure F.4. Process diagram in the WTP Blanes (CCB, 2008)

F.2.3. WTP Cadequés

WWTP Name: Cadaqués
Location: Cadaqués
Design flow : 4,000 m^3/d
Treatment : Active Mud (N,P elimination) Tertiary. Reuse
Sludge reuse: Agriculture
Treated water reuse: Sea and municipal uses
Used area: 0.38 ha
Equivalent population: 20,000

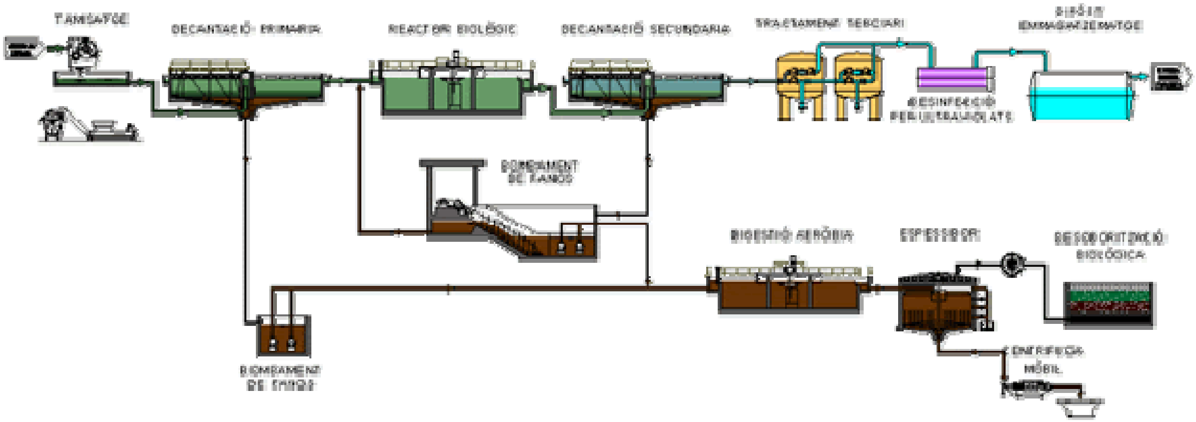


Figure F.5. Process diagram in the WTP Cadequés (CCB, 2008)

F.2.4. WTP Castell d'Aro

WWTP Name: Castell d`Aro
Location: Platja d'Aro, Sant Feliu i Santa Cristina
Design flow :35,000 m^3/d
Treatment : Active Mud (N,P elimination) Secondary
Sludge reuse: Agriculture
Treated water reuse: Sea and irrigation
Used area: 3.5 Ha
Equivalent population: 175,000

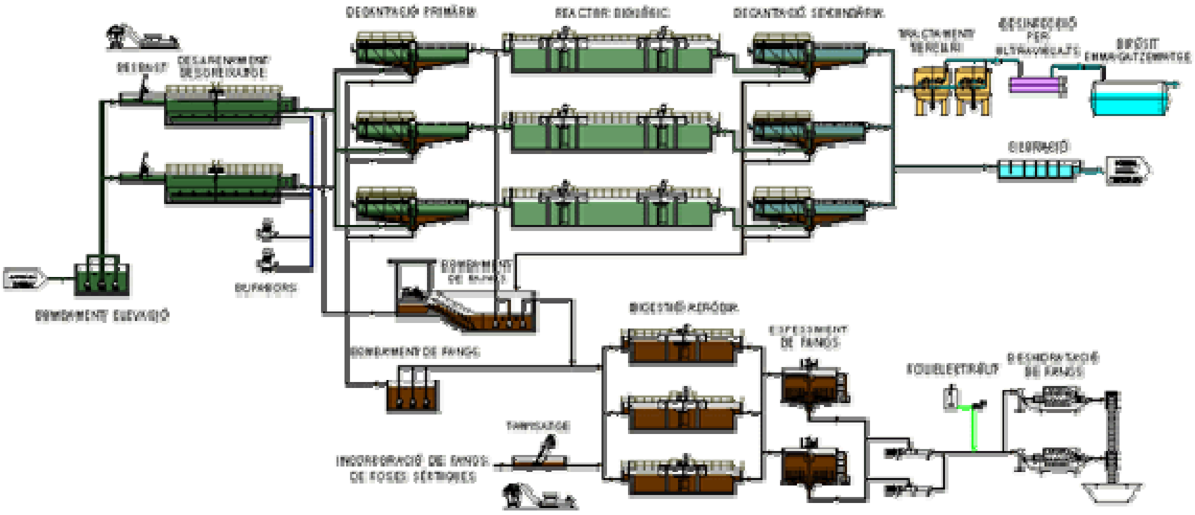


Figure F.6. Process diagram in the WTP Castell d'Aro (CCB, 2008)

F.2.5. WTP Colera

WWTP Name: Colera
Location: Colera
Design flow :1,300 m^3/d
Treatment : Active Mud (N,P elimination) Tertiary
Sludge reuse: Agriculture
Treated water reuse: Sea
Used area: 0.2 Ha
Equivalent population: 7,400

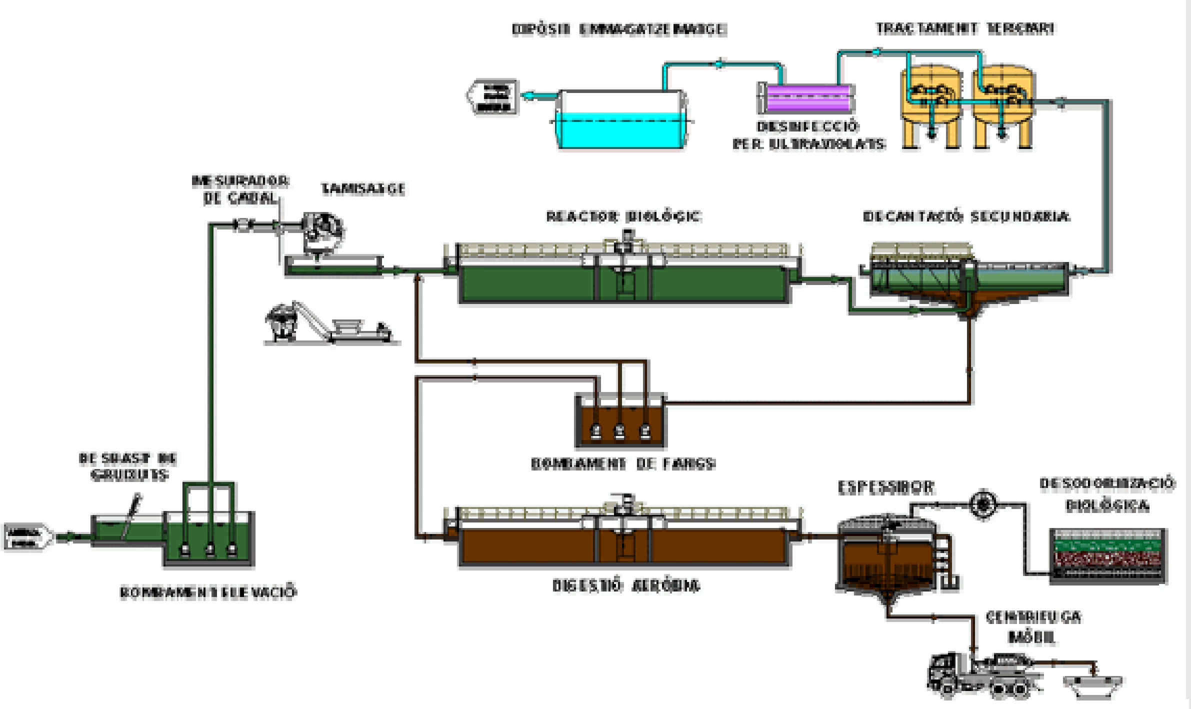


Figure F.7. Process diagram in the WTP Colera (CCB, 2008)

F.2.6. WTP El Port de la Selva

WWTP Name: El Port de la Selva
Location: El Port de la Selva
Design flow :2,625 m^3/d
Treatment : Active Mud (N,P elimination) Tertiary
Sludge reuse: Agriculture
Treated water reuse: Sea
Used area: 0.3725 Ha
Equivalent population: 10,500

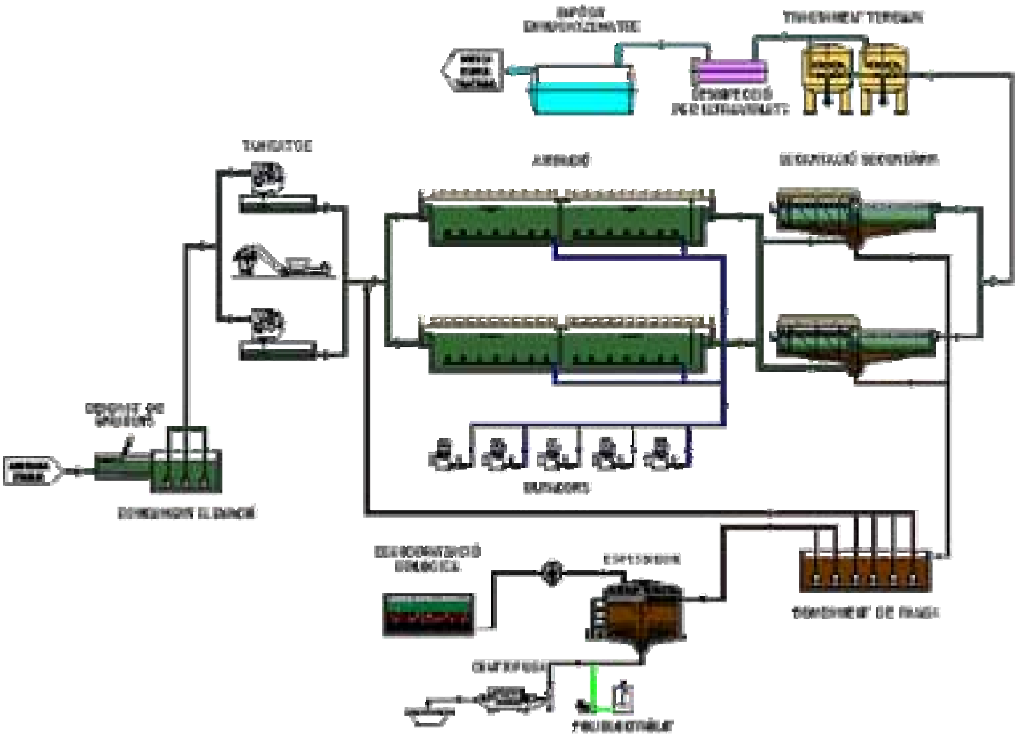


Figure F.8. Process diagram in the WTP El Port de la Selva (CCB, 2008)

F.2.7. WTP Empuriabrava

WWTP Name: Empuriabrava
Location: Muga river, Parc Natural Aiguamollls Empordà i Up Pitch & Put Castelló Empúries
Design flow: 16,750 m^3/d
Treatment : Natural aireation, waste stabilization ponds. Tertiary treatment
Sludge reuse: Agriculture
Treated water reuse: Muga river, Parc Natural Aiguamollls Empordà i Up Pitch & Put Castelló Empúries
Used area: 49.5 ha
Equivalent population: 35,000

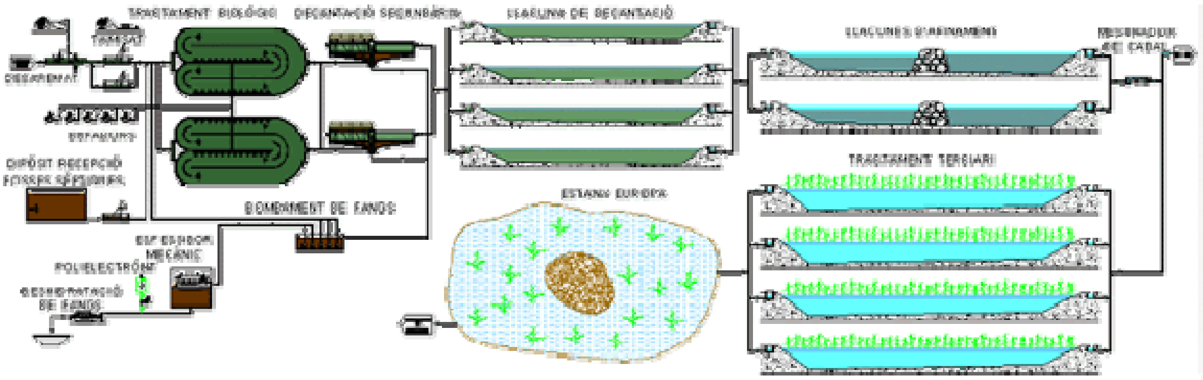


Figure F.9. Process diagram in the WTP Empuriabrava (CCB, 2008)

F.2.8. WTP L'Escala

WWTP Name: L´Escala
Location: L'Escala, Albons i Bellcaire d'Empordà
Design flow :16750 m3/d
Treatment : Active Mud (N,P elimination) Secondary and reuse
Sludge reuse: Agriculture, compost
Treated water reuse: Sea
Used area: 3.2 ha
Equivalent population: 70000
(Diagram not available)

F.2.9. WTP Lançà

WWTP Name: Llançà
Location: Llançà
Design flow :9625 m3/d
Treatment : Active Mud (N,P elimination) Secondary and reuse
Sludge reuse: Agriculture
Treated water reuse: Sea
Used area: 22,400 ha
Equivalent population: 38,500

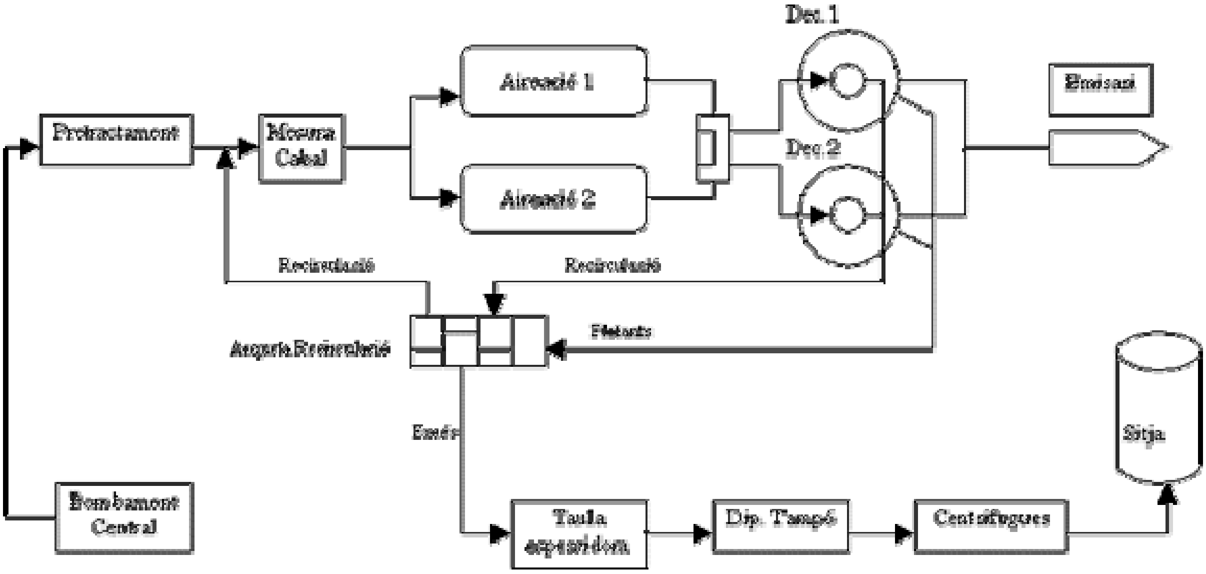


Figure F.10. Process diagram in the WTP Lançà (CCB, 2008)

F.2.10. WTP Lloret de mar

WWTP Name: Lloret de mar
Location: Lloret de mar
Design flow :20,000 m^3/d
Treatment : Active Mud , Phisico-Chemical treatment, Secondary and reuse
Sludge reuse: Agriculture, Compost
Treated water reuse: Sea and Gulf l'Angel
Used area: 2.5 Ha
Equivalent population: 185,000

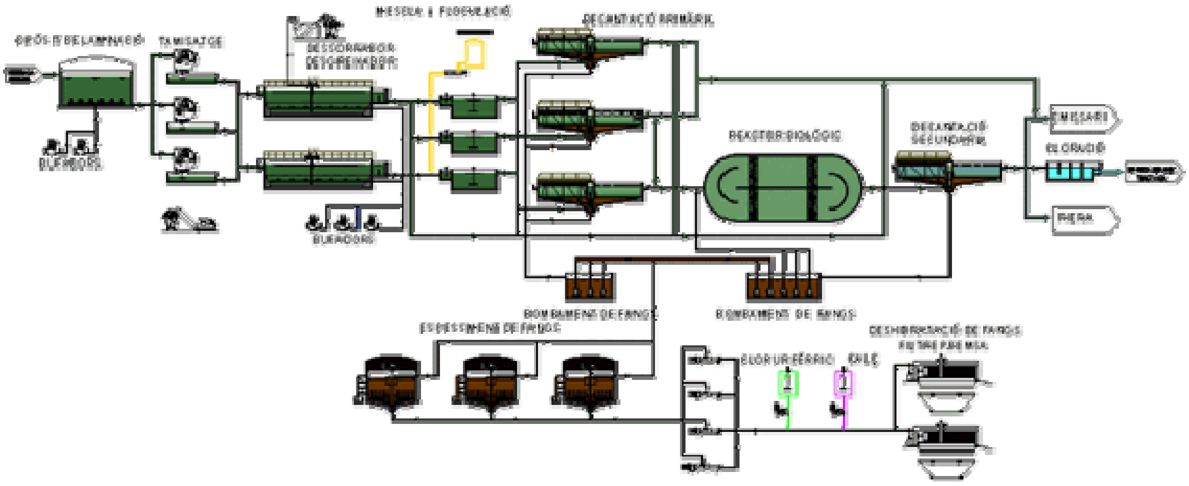


Figure F.11. Process diagram in the WTP Lloret de Mar (CCB, 2008)

F.2.11. WTP Palamós

WWTP Name: Palamós
Location: Palamós, Palafrugell Calonge, Montrás i Vall-Llobregat
Design flow :33,000 m^3/d
Treatment : Active Mud (N, P elimination), Secondary and reuse
Sludge reuse: Agriculture
Treated water reuse: Sea and municipal uses
Used area: 3.3 ha
Equivalent population: 165,450

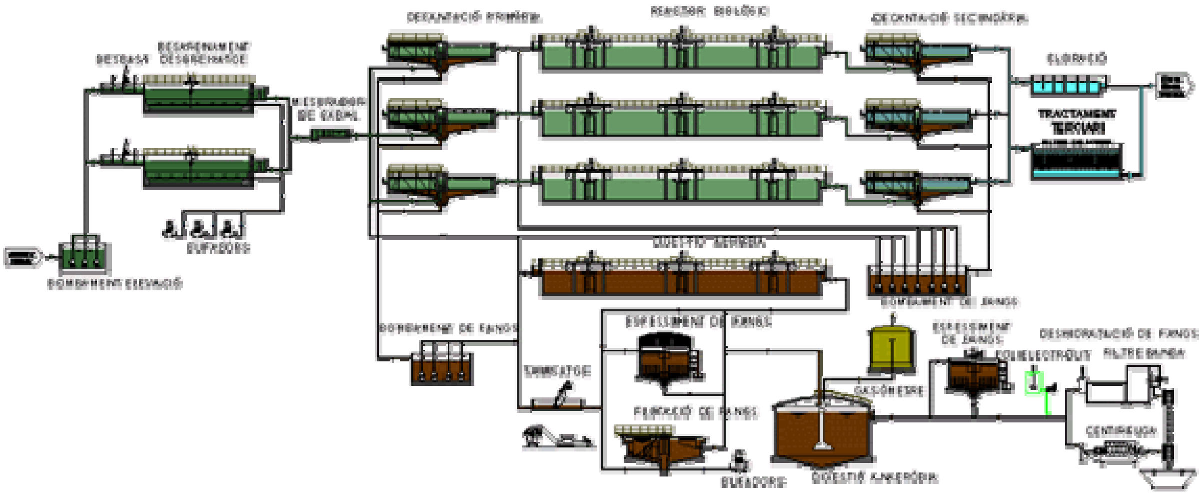


Figure F.12. Process diagram in the WTP Palamós (CCB, 2008)

F.2.12. WTP Pals

WWTP Name: Pals
Location: Pals, Regencos i Sa Riera
Design flow :6,750 m^3/d
Treatment : Active Mud , Phisico-Chemical treatment, Secondary and reuse
Sludge reuse: Agriculture
Treated water reuse: Riera and Gulf Serres de Pals
Used area: 0.14 Ha
Equivalent population: 27,000

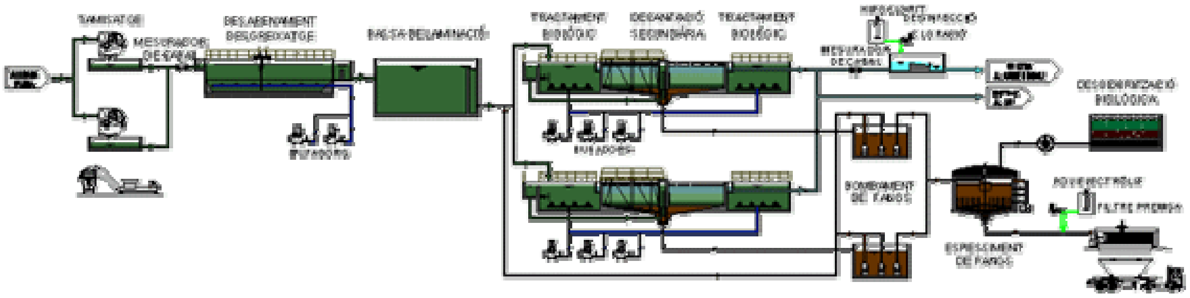


Figure F.13. Process diagram in the WTP Pals (CCB, 2008)

Annex G

Cálculo de los costes exergéticos del agua: Hidronomía Física

Siguiendo los requerimientos para la obtención del doctorado europeo, en lo que sigue se presenta un resumen en castellano del trabajo realizado.

G.1. Síntesis

Las propuestas de Georgescu-Roegen sobre la relación entre la Economía y la Termodinámica, junto con el enfoque Eco-integrador establecido por Naredo después de analizar las definiciones económicas sobre los costes del agua que figuran en la Directiva Marco del Agua (DMA), constituyen los antecedentes del trabajo presentado en esta tesis.

Entendiendo que las leyes físicas están llamadas a ser el objetivo y las herramientas universales para evaluar los costes del agua, la Hidronomía Física (PH) se ha desarrollado como herramienta de contabilidad para la aplicación de la DMA. La PH se define como la aplicación específica de la Termodinámica para caracterizar físicamente la degradación y la restitución de las masas de agua.

La Segunda Ley de la Termodinámica, a través del cálculo de las pérdidas de exergía, es la herramienta básica de trabajo de este estudio. El objetivo final de la PH es utilizar los costes físicos calculados, como guía para asignar los costes ambientales y del recurso propuestos por la DMA.

En este documento, se explican el marco general y los principios básicos de contabilidad de la PH. En primer lugar, a partir de las medidas de cantidad y la calidad del agua en el río (que dan el valor de exergía a las masas de agua). A continuación, se obtienen los perfiles de exergía del río en distintos estados de las masas de agua (los definidos por la DMA). Después, el coste ambiental del agua se obtiene (en unidades de energía) como la exergía necesaria para cubrir la diferencia entre el estado actual del río y el estado objetivo definido por la legislación vigente para cumplir con los requisitos europeos. Para ello, debe introducirse en el análisis la eficiencia termodinámica de las tecnologías de tratamiento de agua.

Para ilustrar la aplicación de la metodología, el ejemplo de la cuenca del río Muga, situado en las cuencas internas de Cataluña, se resume al final de este anexo. Los resultados muestran que se obtienen resultados similares a las mediciones convencionales de los planes para cumplir los objetivos de la DMA. Sin embargo, la PH presenta una ventaja importante: los costes pueden ser asignados de acuerdo a la degradación (coste exergético) provocado por los diferentes usuarios del agua.

G.2. Introducción

El desarrollo humano y su sostenibilidad dependen del agua de manera incondicional. El agua como recurso es esencial para todas las actividades diarias humanas y puede ser considerado en la actualidad como un recurso incluso más valioso que el petróleo.

Las filosofías de orientación de la gestión del abastecimiento de agua han cambiado durante el siglo XX. Hasta la segunda mitad de 1900, la gestión del agua se regía por el objetivo de trasladar el agua a donde más se necesitaba, especialmente para el riego de las tierras agrícolas. Ríos, lagos y otras masas de agua también se utilizaron para llevarse los desechos de los usos municipales e industriales, porque se creía que los contaminantes se dispersarían en los volúmenes de agua de gran tamaño.

Sin embargo, en las últimas tres décadas, el enfoque de la gestión del agua ha pasado a restringir los suministros municipales, agrícolas e industriales, centránose en la calidad del agua y la protección de los ecosistemas acuáticos. Un cambio de paradigmas está por lo tanto teniendo lugar. Las preocupaciones ambientales, así como la preservación del ecosistema, subyacen en la legislación actual para la gestión del agua. Ello conduce inexorablemente a la búsqueda de una integración objetiva y útil entre los servicios naturales y mediambientales, dentro del sistema económico.

En un sentido amplio, puede decirse que existen dos enfoques diferentes para abordar a la economía de los recursos naturales. El primero, el enfoque tradicional, utiliza un conjunto de modelos y técnicas enraizadas dentro de la corriente neoclásica estándar de pensamiento económico, para aplicar conceptos económicos al medio ambiente. La teoría neoclásica de precios pone de relieve la función esencial del precio de mercado en alcanzar el equilibrio entre la oferta y la demanda y se basa en los conceptos de utilidad y productividad marginal (Harris, 2006). La introducción de medio ambiente en Economía de esa manera se conoce como Economía Ambiental. El segundo enfoque, designado como Economía Ecológica, toma una perspectiva diferente. En lugar de aplicar conceptos económicos para el medio ambiente, la economía ecológica busca situar la actividad económica en el contexto de los sistemas físicos y biológicos que sostienen la vida, incluyendo todas las actividades humanas. Esto último implica, en cierto modo, una vuelta al concepto de la "Madre Tierra" del mundo, defendida por los fisiócratas.

La Economía Ecológica se distingue de la Economía Ambiental por su interés en operar una economía dentro de los límites ecológicos de los recursos naturales de la Tierra y por su conexión con las disciplinas de las ciencias naturales.

La energeticistas fueron pioneros de la Economía Ecológica a principios de siglo XX. Vieron claro que el sistema monetario no es la manera adecuada de valorar el medio ambiente y desarrollaron su teoría del valor basada en la unidad de la caloría, defendiendo que cualquier artículo puede traducirse en que esa unidad de energía. Estas corrientes mantuvieron los conocimientos en un paradigma mecanicista, pero abrieron la puerta a una nueva forma de análisis.

La contabilidad de energía y los balances son las herramientas más poderosas utilizadas por Economía Ecológica. El balance de energía se puede utilizar para rastrear la energía a través de un sistema, y es una herramienta muy útil para determinar el uso de los recursos y los impactos ambientales, utilizando las leyes de la termodinámica para determinar cuánta energía se necesita en cada punto de un sistema, y en qué forma esa energía es un coste en diversas cuestiones ambientales (Cleveland and Ruth, 1997). El sistema de contabilidad de la energía sigue la pista de la energía que entra y la que sale.

Un paso más en la valoración ambiental dentro de la economía consiste en incluir aspectos de calidad y degradación en el análisis. Desde una perspectiva física, significa incluir la segunda ley de la termodinámica (Ley de la Entropía). Es decir, tomar la exergía como herramienta de trabajo: energía no útil frente a trabajo realizado, y las transformaciones dentro del sistema.

Georgescu-Roegen (1971) conexionó dos concepciones lejanas de los recursos naturales, proporcionando un enlace para unir el mecanicismo de la economía tradicional, donde la percepción imperativa era que cualquier proceso puede ser reversible (y la consiguiente idea de que cualquier activo es reemplazable), y la economía ecológica, donde la entropía se yergue como la herramienta de valoración más adecuada.

En las últimas décadas, la utilización de exergía se ha diseminado fuera de la Física y de la Ingeniería a los campos de la Ecología Industrial, Economía Ecológica y la Ecología de Sistemas. En consecuencia, además de la aplicación convencional de evaluación de la eficiencia de los sistemas de utilización de la energía y detección cuantitativa de las causas de la imperfección termodinámica, la exergía atrae cada vez más interés en la contabilidad de los recursos ambientales, evaluación de impacto ambiental, evaluación del coste ecológico y los modelos ecológicos.

En cuanto a la evaluación de exergía del agua, Zaleta et al. (1998) presentaron un análisis simplificado de la exergía perdida a lo largo de un curso fluvial. Una evaluación global de los recursos hídricos fue presentada por Martínez et al. (2009) en trabajos anteriores, aprovechando el paralelismo entre la pérdida de exergía y el agotamiento de los recursos. Algunos estudios más específicos usando la exergía como herramienta principal son las de Hellstörm (1997, 2003), que estima y compara el consumo de exergía de recursos físicos en algunas plantas de tratamiento de aguas residuales y de alcantarillado.

Además, Chen and Ji (2007) desarrollaron una evaluación objetiva y unificada de la calidad del agua basado en la exergía química: la exergía química específica relativa con referencia a un espectro de sustancias asociadas con la norma especifica de calidad del agua se propone para la evaluación de la calidad del agua, con implicaciones más prácticas, resultando en cuantificadores objetivos unificados para la capacidad de transporte y déficit de recursos hídricos.

G.2.1. Directiva Europea Marco del Agua

Diferentes referencias de gestión de la Unión Europea de agua y programas de acción ambiental culminaron con la publicación de la CE Directiva Marco del Agua, que entró en vigor en 2000 (EU-WFD, 2000). Este texto legal establece un nuevo enfoque integrado para la protección, mejora y uso sostenible de los ríos, lagos, estuarios, aguas costeras y aguas subterráneas de Europa.

Reconocer que la naturaleza es el usuario más importante de los recursos hídricos proporciona una visión diferente del uso del agua. Se han introducido dos cambios principales respecto de la forma en que el agua tiene que ser gestionada a través de la Comunidad Europea: objetivos ecológicos más amplios y la definición de unidades hidrológicas para aplicar los Programas de gestión de cuenca.

En términos generales, la DMA propone un marco para la protección de todas las aguas, incluidas las aguas superficiales continentales, aguas de transición y de agua de mar, así como de las aguas subterráneas. En concreto, los objetivos de lograr un buen estado del agua implican un conjunto de medidas en todos los ámbitos relacionados con el medio acuático, de los aspectos naturales (hidrología, ecología, geodinámica...) a su naturaleza económica y social. En este sentido, la DMA define los métodos, procedimientos y parámetros indicadores necesarios para caracterizar la condición del agua y las estrategias e instrumentos necesarios para proteger esta condición y para regenerarla, si es necesario. El concepto clave de esta directiva comunitaria es la integración transversal de los factores y agentes implicados en la gestión del agua y en la protección de sus valores.

En cuanto al coste del agua, la nueva Directiva introduce el principio de recuperación total (con algunas excepciones justificadas) y la internalización de los costes ambientales y de recursos (recuperación total de costes, FCR). Surgen de los servicios asociados con el uso del agua y del mantenimiento sostenible de los ecosistemas. También indica que el coste del uso sostenible del agua y de la zona del río debe ser asumido por el beneficiario o el operador de la actividad que genera el coste, es decir, sigue el principio de "quien contamina paga".

G.2.2. Definición de costes en la DMA.

La legislación europea dice explícitamente en su artículo 9 que *los Estados miembros deberán tener en cuenta el principio de recuperación de los costes de los servicios de agua, incluyendo los costes ambientales y del recurso, teniendo en cuenta el análisis económico ... y en particular de conformidad con el principio de quien contamina paga* .

En consecuencia, las políticas de tarificación del agua deberían reajustarse en 2010 siguiendo las directrices del Principio de recuperación total (FCR) establecido en la Directiva. El concepto FCR contiene diversos términos que, según la guía del grupo WATECO (ECO1, 2003 y ECO2, 2004) son los siguientes:

- *Gastos Financieros (FC)* -o costes de servicio- que incluyen el coste de la prestación y administración de los servicios de agua, como el abastecimiento, saneamiento, transporte y almacenamiento, que en la actualidad se reflejan a los usuarios en una cantidad menor o mayor. Se incluyen todos los costes de operación y mantenimiento y los gastos de capital (pago de capital principal e intereses), y el retorno en equidad en su caso, es decir, los costes de amortización de capital, los costes de financiación, los costes de mantenimiento y funcionamiento, los gastos administrativos y otros costes directos que podrían ser incluidos.

- *Coste Ambiental (EC)* respecto a la alteración de los aspectos físicos y biológicos de las masas de agua debido a actividades humanas. Representa el coste de los daños que imponen los usos del agua en el medio ambiente y los ecosistemas y los que utilizan el medio ambiente (por ejemplo, una reducción en la calidad ecológica de los ecosistemas acuáticos o la salinización y degradación de los suelos productivos). En consecuencia, el coste ambiental también incluye "externalidades económicas", como la pérdida de empleo en el sector servicios en las zonas rurales debido a los impactos de carácter social, por la degradación de los recursos hídricos.

- *Coste de recursos (RC)* como el coste de oportunidades perdidas que sufren otros usos debido al agotamiento de los recursos más allá de su tasa natural de recarga o recuperación, derivados de un uso ineficiente o alternativo (por ejemplo, vinculado a la sobre-extracción de metro las aguas). Aunque esta fue la concepción inicial, sucesivas interpretaciones de la Directiva han integrado la RC en el EC.

El primer término puede ser fácilmente calculado a partir de la contabilidad de la economía clásica. Sin embargo, los términos segundo y tercero son obviamente más difíciles de evaluar, al menos con las herramientas de análisis actual de las políticas existentes de gestión de agua.

Además, como las medidas para restaurar la calidad y cantidad de las aguas se introducen gradualmente, éstas deberían ser consideradas como gastos financieros siguiendo el concepto FCR, y por lo tanto podría aparecer doble contabilidad si esta circunstancia no es tenida en cuenta.

Esta idea ha sido ya puesta de relieve por muchos autores. Naredo (2007) presentó algunos gráficos interesantes mostrando esta idea, que se han utilizado para contextualizar este trabajo.

G.3. Interpretación de los costes de la DMA desde el enfoque eco-integrator

Según Naredo, la hipótesis subyacente proviene de la economía tradicional e indica que los costes mencionados son uni-dimensionales (sólo se expresan en unidades monetarias), no se superponen (formando conjuntos disjuntos) y que son aditivos (tienen que sumarse para obtener el coste total que se asignará a los usuarios).

Después de un análisis detallado de las restricciones incluidas en las definiciones de costes de la DMA por la interpretación económica tradicional, este autor propone una nueva metodología dirigida a abrir los razonamientos cerrados (y por lo general unidimiensionales). De esta manera, el enfoque podría estar abierto a ampliarse con tratamientos multidimensionales y transdisciplinarios, más adecuados para la gestión de la sociedad industrial actual.

La propuesta no trata de eliminar o marginar los enfoques tradicionales monetarios e hidráulicos, pero los reubica en el marco más amplio de los nuevos enfoques. Por ejemplo, el estudio y la buena información de los costes ambientales de la masa de agua no están llamados a excluir los estudios dedicados a conocer la disposición a pagar por su calidad ambiental. Simplemente, se derivan a nuevos ejercicios de participación social informada, que sirvan para llegar a un consenso sobre los estándares de calidad con pleno conocimiento de la razón por la que se originan los costes y sus repercusiones en el pago.

La metodología de cálculo para el coste del agua afirma su carácter multidimensional, lo que no niega, sino refuerza, los enfoques monetarios, ofreciendo nuevos puntos de apoyo. Asimismo considera que los costes del servicio, ambientales y del recurso no son conjuntos disjuntos (y por lo tanto ni aditivos), sino que se superponen: la gestión del agua debe precisamente ser capaz de jugar con las intersecciones y solapamientos a fin de diseñar instrumentos económicos razonables.

Estas ideas se resumen en el llamado planteamiento Ecointegrator, cuyo principal interés es la orientación de los costes del agua para conseguir que el coste del servicio de agua refleje fielmente los costes ambientales y del recursos, atendiendo a los principios de buena gestión del agua y paso de los esquemas clásicos a un análisis completo y plural.

La base de lo que podría llamarse nuevo concepto de gestión del agua también ha sido estudiado y desarrollado por varios autores, como Arrojo (2004), Llamas (2003) y Naredo y Gascó (1994), entre otros. En estos trabajos, el agua es valorada no sólo como una necesidad para uso humano, sino también por su función ecológica, geodinámica, social e incluso estética; es reconocida y considerada como un patrimonio que debe ser protegido y preservado.

G.4. Propuesta metodológica: Hidronomía Física

El texto de la Directiva establece unas directrices generales, pero su aplicación está todavía muy abierta a la interpretación por los gestores del agua.

El objetivo final de la Directiva es proporcionar a cada cuenca fluvial un plan hidrológico, incluyendo todos los elementos de gestión de los recursos hídricos necesarios para alcanzar los objetivos indicados. La planificación hidrológica es un medio para mejorar y prestar apoyo a la gestión adecuada, facilitando la toma de decisiones. Debe entenderse como un proceso sistemático en la descripción y el control de las masas de agua, integrando diversos usos y sensibilidades con respecto a los recursos, así como iterativo, en el sentido de que debe ser flexible para incorporar nuevos criterios y adaptarse a las circunstancias cambiantes.

Partiendo de estas ideas, se presenta en este trabajo, una metodología adicional y completa que ayude en la aplicación de la DMA. La Hidronomía Física es la aplicación específica de la Termodinámica para caracterizar físicamente la degradación y la restauración de las masas de agua. Es decir, la aplicación física de la DMA europea. El objetivo final de la PH es utilizar los costes físicos calculados como una guía para asignar los costes ambientales y del recurso.

En primer lugar, la DMA ha sido cuidadosamente estudiada e interpretada desde una perspectiva termodinámica. Los diferentes costes del agua definidos en la Directiva han sido traducidos a conceptos de exergía y se estableció una hipótesis del estudio. Los diversos estados del agua propuestos por la Directiva han sido definidos en términos de exergía por medio de la caracterización de su cantidad y calidad.

El paralelismo existente entre las características cambiantes del agua a lo largo del río y la degradación de la cuenca del río provocada por los usos del agua proporciona la clave fundamental para postular que la degradación del agua calculada a partir de estas dos perspectivas deberían coincidir teóricamente. En consecuencia, el principio de que quien contamina paga, intensamente promulgado por la DMA, puede aplicarse para asignar los costes del agua, identificar la contaminación de usuarios del agua a la degradación de la calidad, y también para el consumo de agua (degradación en cantidad).

G.4.1. Exergía de una masa de agua

La analogía entre la disponibilidad de un recurso natural y su exergía nos ayuda a relacionar cada parámetro de recurso con sus componentes de exergía. Estos parámetros son físicos y químicos. En la evaluación de los recursos hídricos, la altitud, temperatura y composición química darán la información más importante (Valero et al, 2008).

La exergía de una masa de agua se define por su flujo de masa y seis mediciones de parámetros que caracterizan las condiciones físicas del agua: temperatura, presión, composición, concentración, velocidad y altitud (Zaleta et al., 1998). El método de la exergía asocia cada parámetro con su componente de exergía: térmica, mecánica, química, cinética y potencial. Por lo tanto, y partiendo de estos componentes, es posible evaluar una masa de agua y cualquier recurso hídrico caracterizado por sus componentes exergéticos en términos cuantitativos (flujo, Q) y cualitativos (exergía específica, b) (Wall, 1986). El modelo asume la aproximación a un líquido incompresible (Valero et al, 2008).

Eq. G.1.
$$\underbrace{b_{H_2O}\,(kJ\ /\ kg)}_{Total\ .exergy} = \underbrace{c_{p,H_20}\left[T_a - T_0 - T_0\ln\left(\frac{T_a}{T_0}\right)\right]}_{Thermal\ .Ex} + \underbrace{v_{H_2O}\left(p_a - p_0\right)}_{Mechanical\ .Ex} +$$
$$\underbrace{\Delta G_f + \sum_e n_e b_{chne}}_{Chemical\ .Ex} - \underbrace{R_0 \sum xi\ln\frac{a_i}{a_0}}_{Concentrat\ ion.Ex} + \underbrace{\frac{1}{2}\left(C_a^2 - C_0^2\right)}_{Kinetic\ .Ex} + \underbrace{g\left(z_a - z_0\right)}_{Potential\ .Ex}$$

Cada componente debe ser calculada de forma separada. La suma de todos los componentes expresa la exergía del recurso de agua determinado y se puede entender como la energía mínima necesaria para restablecer el recurso a partir de su ambiente de referencia (RE). Cada componente de la Eq. G.1 será explicado en detalle en las siguientes secciones.

Un RE adecuado se define como aquel en el que su nivel, presión, temperatura y composición, tiene exergía mínima (todos los parámetros contemplados en el RE se denotan con el índice $_0$). El RE propuesto por Szargut (Szargut et al., 2005) puede tomarse como el más conveniente para evaluar la exergía en el ciclo del agua. Sin embargo, como se explica en la siguiente sección, algunas consideraciones adicionales deben observarse en cuanto a la presencia (o no) de la materia orgánica en ese RE.

G.4.1.1. Componente de exergía térmica

La exergía térmica depende del calor específico de la solución acuosa $C_{p,\ H2O}$, lo que podría asimilarse a la correspondiente del agua pura (para aguas de ríos y lagos), y su temperatura absoluta T_a (K).

Eq. G.2.
$$b_{thermal} = c_{p,H_2O}\left[T_a - T_0 - T_0\ln\left(\frac{T_a}{T_0}\right)\right]$$

Este termino no es representativo generalmente, ya que esta fuente de calor tiene una baja calidad con respecto a la RE (lo que significa un valor de exergía baja). Sin embargo, puede tener un valor representativo en algunas situaciones concretas, como los sistemas de refrigeración o los usos recreativos del agua tales como las fuentes de aguas termales en una cuenca hidrográfica.

G.4.1.2. Componente mecánica de exergía

El término de exergía mecánica se calcula a partir del volumen específico de la disolución *v*, que se determina sin gran error si se considera el agua pura (Perry and Green, 1984), aproximadamente tiene un valor de 0,001 m^3/kg, y considerando también la diferencia de presión con el ambiente de referencia RE $(p_a$-$p_0)$.

Eq. G.3. $$b_{mechanical} = v_{H_2O}\left(p_a - p_0\right)$$

Esta componente podría ser representativa si las estaciones de bombeo y la presión de los sistemas de tuberías enterradas fuesen analizados en el estudio, así como agua recogida en los embalses, ya que aumentaría la capacidad de ese flujo de agua para producir energía. Cuando se estudia un río o cualquier masa de agua, puede asignarse un valor a esta componente, si la altura de flujo se conoce en cada punto, superficie o tramo de río.

G.4.1.3. Componente de exergía potencial

El término de exergía potencial se calcula teniendo en cuenta la altura z_a (m) donde se toma la medida. El parámetro g representa la fuerza gravitatoria de la Tierra (9,81 m/s^2) y z_0, la altura del nivel de referencia ($z_0 = 0$ al nivel del mar).

Eq. G.4. $$b_{potential} = g\left(z_a - z_0\right)$$

Aunque este término es muy importante en la fuente del río de una cuenca, se debe considerar con especial atención el caso de los embalses con instalaciones de generación de energía hidroeléctrica: esta exergía potencial se convertirá sucesivamente en energía cinética, mecánica y eléctrica en la central.

No importa el nivel de desagregación, este componente potencial estará presente en cualquier análisis de agua relacionado con la energía.

G.4.1.4. Componente de exergía cinética

La exergía cinética se calcula tomando la velocidad absoluta C_a (en m/s) en el lugar de muestreo.

Eq. G.5. $$b_{kinetic} = \frac{1}{2}\left(C_a^2 - C_0^2\right)$$

A menos que la estación de medida se encuentre en rápidos o en el corazón de una cascada, este término no debería ser un componente muy importante en ningún caso. El RE se considera estático, por lo que C_0 es cero por definición.

G.4.1.5. Componente de exergía química

La exergía química intrínseca de cualquier elemento se encuentra fácilmente en cualquier tabla de exergía química (Szargut et al, 2005):

Eq. G.6. $$b_{chn} = \Delta G_f + \sum_e n_e b_{chne}$$

donde ΔG_f es la energía de formación de Gibbs, *n* es la cantidad de kmol del elemento *e* y b_{chne} es la exergía química estándar del elemento. Esta componente da idea de la energía necesaria para formar una molécula desde las sustancias existentes en el RE. Si la molécula forma parte del RE, su componente de exergía de formación es igual a cero (puesto que ya existe en ese RE).

G.4.1.6. Componente de concentración de exergía

Además de la exergía química de formación, la concentración de la sustancia en la masa de agua tiene que ser comparada con su concentración en el estado de referencia. Este término es el término más complejo de calcular porque hay tres diferentes contribuciones que han de tenerse en cuenta: la concentración de agua pura y las contribuciones correspondientes a las sustancias inorgánicas y orgánicas disueltas.

Eq. G.7. $$b_c = R\, T_0 \sum x_i \ln \frac{a_i}{a_0}$$

Donde x_i es la fracción molar y a_i es el coeficiente de actividad de la sustancia *i* en el agua. Las actividades son más utilizadas que las concentraciones molares, ya que estamos tratando con disoluciones.

G.4.1.7. Ambiente de referencia para los análisis de las masas de agua

La elección de un ambiente de referencia determinado afecta al valor de exergía final de una masa de agua en cualquier caso. El mar es la referencia natural para las masas de agua que participan en el ciclo hidrológico: el río pierde su capacidad para producir trabajo cuando se diluye en un reservorio tan enorme. El agua del río alcanza el equilibrio termodinámico con el agua de mar a unos pocos kilómetros de la costa.

La potencia que mueve todas las contribuciones exergía es el sol, ya que el ciclo hidrológico con la evaporación, precipitación y escorrentía renueva el perfil exergético de río. Por lo tanto, tiene sentido pensar en el agua del océano como el RE más adecuado para el agua siguiendo el ciclo hidrológico.

El RE elegido finalmente es un estado de agua de mar sin materia orgánica, nitrógeno ni fósforo. Este es el RE más adecuado para el análisis y también es coherente con que el agua de mar es una parte muy importante del ciclo hidrológico (véase el estudio completo en Martínez y Uche, 2009). La composición de la referencia usada en este estudio es la composición media del Mar Mediterráneo, ya que los casos de estudio considerados se encuentran en la costa oriental española.

G.4.2. Perfil exergético de un río

La exergía total se obtiene multiplicando la exergía específica por el flujo de agua. Va variación de exergía permite la obtención del perfil a lo largo del río, lo que representa una herramienta útil para lograr el objetivo propuesto. Cada uno de los estados definidos queda determinado por su perfil exergético.

El perfil de exergía de un río a lo largo de su curso tiene una curva característica, que es bastante similar para todos ellos. Este hecho se puede explicar analizando los perfiles típicos de la exergía específica y del flujo de agua en un río.

El perfil de exergía ideal y simplificado específico de un río se ilustra en la Figure G.1. En el nacimiento río, el agua se encuentra a la mayor altitud y en el estado más puro, por lo que su exergía física y química son las más altas en ese punto. A medida que fluye hacia la desembocadura, la masa de agua va perdiendo altura y pureza y por lo tanto disminuye su exergía específica hasta alcanzar el punto de exergía mínima (máxima degradación), que es el mar (ambiente de referencia). Por otra parte, el flujo de agua generalmente sigue exactamente el camino opuesto: mínimo en la fuente y el máximo en la desembocadura a causa de las contribuciones recibidas. Ambos efectos juntos dan un patrón de exergía total ideal de la curva de campana dada en la parte derecha de la Figure G.1.

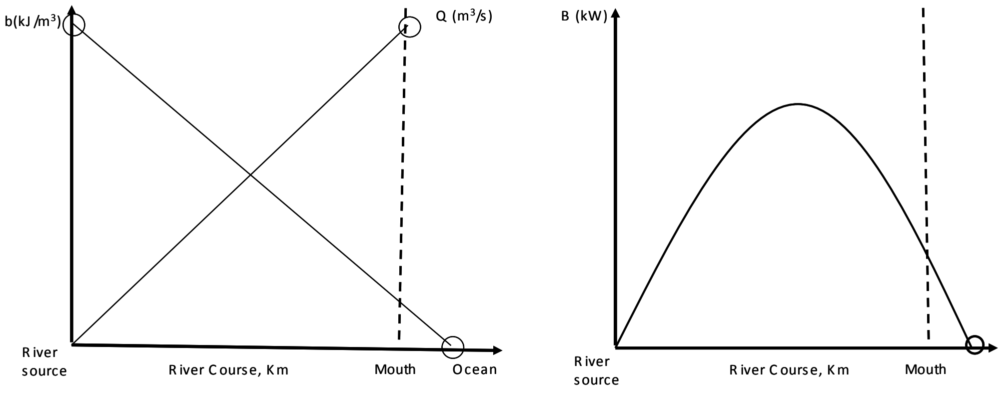


Figure G.1. Perfiles típicos de Exergía específica (b), flujo de agua (Q) exergía total ($B = b \cdot Q$) de un río ideal.

Este patrón ideal (para un río normal sin captaciones o contribuyentes especiales) se modifica en los ríos reales, ya que ni la exergía específica ni el caudal siguen una línea recta perfecta. La existencia de ríos afluentes, filtraciones a los acuíferos, captación para los diversos usos de consumo, la evaporación solar, fugas, etc crean desviaciones positivas o negativas en la calidad y cantidad de agua de los ríos. La exergía química también puede aumentarse aguas abajo, debido a la adición de sustancias químicas espurias y materia orgánica. Según nuestra definición, la exergía máxima correspondería a agua pura, destilada. Sin embargo, puesto que la materia orgánica, nitrógeno y fósforo añaden exergía positiva, una muestra de agua con un alto contenido orgánico tiene también una mayor exergía. El punto clave es analizar por separado las componentes de exergía química. Además, una importante pérdida de exergía se produce mediante la mezcla de los ríos y aguas marinas en la desembocadura del río, pero sucede a cierta distancia de la costa, después de haber sido parcialmente invertido en las aguas de transición. Allí, el desequilibrio químico es un generador básico de vida (playas, bancos de pesca...).

El perfil de un río es aleatorio debido a su carácter torrencial y los usos de temporada. Por lo tanto, en términos prácticos, el perfil de exergía de un río determinado se describe mejor por mes o incluso diariamente, si existen datos disponibles (Martínez et al., 2008).

G.4.3. Caracterización de los estados de las masas de agua e implementación práctica

Siguiendo las directrices de la DMA, cada unidad de gobierno de cuencas aplica la legislación y la prepara la caracterización de los diferentes estados de río. Desde la publicación del DMA en 2000, se han presentado diversos informes de alcance muy diferente.

En este trabajo, después de revisar cuidadosamente las demandas de la DMA, tanto en la definición de los estados y costes, se han definido varios estados objetivo (OS) para las masas de agua:

- *Estado de Explotación (ES)*: Es un estado hipotético con la degradación más elevada, que representa las masas de agua sin plantas de depuración de aguas residuales existentes. Las cifras para describir este estado se obtienen mediante la simulación de la situación real, pero eliminando las plantas de tratamiento de aguas existentes en la cuenca del río considerado.

- *Estado Presente (PS):* Es el estado actual de la masa de agua. Este estado se obtiene de la medición directa en las estaciones de toma de muestras y puestos de control existentes. Con mayor o menor precisión, están presentes en todas las cuencas, aunque normalmente sólo unos pocos datos reales están disponibles a lo largo del río. Así, se necesita generalmente un software de simulación del río para la caracterización su completa caracterización. De esta forma, se dispone al menos de un dato de cantidad y otro de calidad en cada uno de los tramos del río en los que se segmenta el cauce.

- *Estado Natural (NS).* Hay un estado natural de cada masa de agua, que se caracteriza como si no se viera afectada por las actividades económicas humanas. Este estado natural se determina por medio de modelos de restauración del flujo (de las precipitaciones, la evapotranspiración potencial -ETP-, y datos de consumo). Los puntos de referencia que están situados generalmente en las cabeceras del río (sin influencia antrópica).

- *Estado Futuro (FS).* Se entiende como el futuro estado de las masas de agua en 2015. Este estado es simulado a partir de la situación actual y la adición de todas las presiones futuras esperadas en la zona. Esas presiones son generalmente proporcionadas por organismos oficiales competentes, donde los estudios se realizan para los estados de futuro previstos.

- *Estado Objetivo (OS).* La DMA establece varios estados objetivo de las masas de agua en 2015 de acuerdo con el tipo de río o masa de agua que está siendo considerado. La caracterización de la cuenca del río, así como los valores objetivos de calidad para cada tramo del río fueron definidos en el documento de Impress para cada cuenca hidrográfica. Este documento es obligatorio e incluye la categorización y definición de las masas de agua y el riesgo de incumplimiento de los objetivos de la DMA. También responde a los artículos 5, 6 y 7 de la DMA

G.4.4. Definición de los costes de la DMA en términos de exergía

El coste exergético del agua (en unidades de energía) es el coste considerado en esta tesis en primer lugar y se define como la diferencia de exergía entre dos estados energéticos diferentes del río. La Hidronomía Física tiene por objeto utilizar los costes físicos calculados como una guía para asignar los costes ambientales propuestos por la DMA.

Siguiendo la DMA y las directrices del grupo WATECO, junto con la segunda ley de la Termodinámica termodinámico, los diferentes costes del agua se definen dentro de la metodología de Hidronomía Física, tratando de satisfacer las exigencias europeas.

- *Coste del Servicio (SC) o Coste Financiero (FC)*: es el coste asociado a las medidas ya existentes que permiten a las masas de agua encontrarse en el PS en lugar de estar en el ES.

- *Coste Ambiental (EC)*: da cuenta de la diferencia entre el estado futuro del río (FS) y el estado objetivo fijado por la Directiva (OS).

- *Coste Remanente del recurso (RRC)*: es el coste restante, que evalúa las medidas necesarias para alcanzar el NS a partir del OS.

Por último, el *Coste Integral del Recurso (IRC)* es la suma de los tres costes mencionados, y se asocia a las medidas necesarias para alcanzar el NS, a partir de la ES. En la Figure G.2 se muestran estas definiciones.

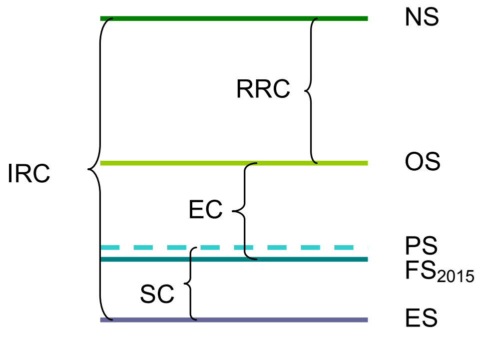


Figure G.2. Estados del río y costes requeridos por la DMA.

El IRC definido de esta manera va, de hecho, más allá del principio de la completa recuperación de costes marcados por la DMA: la Directiva marca el OS como estado final. Sin embargo, cuando el RRC está incluido, con el NS como objetivo final, el proyecto es más ambicioso y el ciclo integral del agua puede ser considerado realmente. Luego, todos los aspectos necesarios (servicios, medio ambiente y los recursos) para la PH se incluyen en el cálculo de coste propuesto.

Una vez establecidos los estados, la diferencia de exergía puede ser calculada como la diferencia entre dos perfiles del río y ΔB se entiende, en sentido general, como el coste exergético (en unidades de energía), provocado por las actividades humanas. La Eq. G.8 y la Eq. G.9 sintetizan las definiciones anteriores:

Eq. G.8.

$$
\begin{aligned}
RRC &= \Delta B_{NS-OS} = B_{NS} - B_{OS} \\
EC &= \Delta B_{OS-FS} = B_{OS} - B_{FS} \\
SC &= \Delta B_{FS-ES} = B_{FS} - B_{ES}
\end{aligned}
$$

Eq. G.9.

$$IRC = SC + EC + RRC = \Delta B_{NS-ES} = B_{NS} - B_{ES}$$

Como los actuales y futuros del río para el año 2015 son dos estados similares, se definen por separado para seguir definiciones DMA. Sin embargo, cuando los cálculos se llevan a cabo, puede observarse que su diferencia es mínima y el solapamiento es insignificante.

.

G.4.5. Componentes de cantidad y calidad en el coste exergético

Además de la consideración anterior, es importante resaltar que la diferencia de exergía entre a los estados río puede dividirse en sus términos cuantitativos (t) y cualitativos (l) los términos, como se muestra en la Eq. G.10.

Eq. G.10.

$$
\begin{aligned}
\Delta B &= \dot{m}_o \cdot b_o - \dot{m}_r \cdot b_r = (\dot{m}_r + \Delta \dot{m}) \cdot (b_r + \Delta b) - \dot{m}_r \cdot b_r = \\
&= \dot{m}_r \cdot \Delta b + \Delta \dot{m} \cdot b_o = \Delta B_l + \Delta B_t
\end{aligned}
$$

Donde m es el flujo y B es la exergía específica. El subíndice *0* representa el estado objetivo y *r* el estado real. También pueden ser considerados como el estado inicial y final, ya que este razonamiento va a ser aplicado repetidas veces y el estado inicial y final van a cambiar. Debe advertirse que la Eq. G.10 se calcula de forma separada para los diferentes componentes de exergía del agua presentados en la sección G.4.1.

El cambio en una masa de agua se debe al consumo de masa, y también al deterioro de su calidad. Ambas contribuciones deben estar presentes para describir con precisión la degradación del agua. Una razón importante para la separación del ΔB en dos partes es la naturaleza diferente de cada uno de ellos. En un paso siguiente, este salto de exergía tiene que ser restaurado por medio de la mejor tecnología disponible. Los procedimientos de restauración de cantidad y calidad son diferentes y, por supuesto, tienen costes diferentes.

El desarrollo metodológico presentado cumple con el espíritu de la DMA. El punto 34 de su preámbulo establece que *a efectos de la protección del medio ambiente es necesario una mayor integración de los aspectos cualitativos y cuantitativos* tanto de las aguas superficiales como subterráneas, teniendo en cuenta las condiciones de escorrentía natural del agua dentro del ciclo hidrológico. Como indica la Eq. G.10, la cantidad y calidad de los componentes se pueden dividir en caso necesario.

G.4.6. Coste exergético

En la explicación metodológica anterior, el coste de exergía ha sido considerado desde una perspectiva estrictamente reversible desde el punto de vista termodinámico: la diferencia de exergía entre diferentes estados de río se han calculado y, de acuerdo con las definiciones dadas para SC, CE y CRR, se da el IRC de la cuenca en términos de exergía.

Sin embargo, el rendimiento real de las técnicas de restauración tiene que ser tenido en cuenta cuando el coste exergético real tiene que ser calculado. De esta forma, como los procesos de depuración que transforman un caudal sucio en un curso de agua limpia no son reversibles, el consumo adicional de exergía del proceso (debido a la inevitable irreversibilidad de los procesos reales) tiene que ser tenida en cuenta.

El proceso tecnológico considerado para tratar (una Planta de Tratamiento de Aguas Residuales) o generar agua (desalación, más de bombeo hasta el punto del río requerido) tiene que ser claramente definido a fin de calcular su coste exergético. Los límites del sistema deben establecerse como primer paso. Entonces, cualquier flujo de entrada y salida se identifican y traducen a unidades de exergía.

La base teórica para estas definiciones se basa en la definición de coste exergético de un flujo de masa o energía como la cantidad de exergía requerida (fuel) para producir una unidad de exergía de la corriente de salida (producto). Si B_i representa la exergía de la corriente *i y* B^*_i es su coste exergético, el coste exergético unitario medio se expresa como indica la Eq. G.11:

Eq. G.11. $$k_i^* = \frac{B_i^*}{B_i}$$

De esta forma, considerando la información proporcionada por el coste exergético unitario, k^*, el coste real del proceso considerado puede calcularse a partir del coste mínimo teórico. Posteriormente, se traducirá en unidades económicas incluyendo en el análisis el precio de la energía considerada.

G.4.7. Relación entre el IRC y la degradación debida a los usos del agua

El IRC (SC + EC + RRC) representa la distancia existente entre el estado natural del río y el estado que el río se presentaría si no se realizara ningún tratamiento de agua después de su uso. Por tanto, representa una degradación global a lo largo del curso del río.

Centrando el análisis en los usos del agua, la degradación provocada por los usos del agua puede ser definida como muestra la Eq. G.12.

Eq. G.12. $$\Delta B_{uses} = \sum_i \Delta B_i = \sum_i B_{i,cat} - \sum_i B_{i,ret}$$

Donde *i* es el número de usos, y teniendo en cuenta que en algunos casos, como por ejemplo las transferencias de agua entre cuencas, sólo la captación (*cat*) o el retorno (*ret*) se tienen en cuenta.

El ΔB se ha definido de esta manera (*cat-ret*) porque se asume que la calidad en el flujo de retorno será inferior a la calidad en la captación ($\Delta b = b_{cat} - b_{ret} > 0$). El mismo argumento se aplica para el componente de calidad ya que una pequeña cantidad del agua suministrada se consume y luego no vuelve a la cuenca ($\Delta Q=Q_{cat}-Q_{ret}>0$).

Luego, Eq. G.12 puede ser escrito y calculado por sus componentes (cantidad y calidad), y después la contribución de cada uso para la degradación de la calidad del agua (o la pérdida de agua, degradación de la calidad-) se puede usar para dividir el coste del agua entre los usuarios.

$$\Delta B_{uses}=\sum_{i}(\Delta Q\cdot b_{cat}+Q_{ret}\cdot\Delta b)_i+\sum_{j}(\Delta Q\cdot b_{cat}+Q_{ret}\cdot\Delta b)_j+\sum_{z}(\Delta Q\cdot b_{cat}+Q_{ret}\cdot\Delta b)_z$$

Donde *i* representa el número de usos de agua doméstica, *j* el número de usos industriales y *z* el número de usos agrícolas. En líneas generales, la asignación de costes para la cantidad y la calidad de los componentes será diferente: los usos que suelen dañar la calidad del agua no necesariamente reducen la cantidad disponible de agua.

Para resumir la metodología explicada, un diagrama conceptual se presenta en la Figure G.3. A partir del perfil del río en sus diferentes estados y de las diferentes definiciones de costes de exergía, se calcula el mínimo de energía (ΔB) entre los estados definidos. En segundo lugar, se traduce en los requisitos de exergía real comparando los consumos teóricos de la energía con los reales consumidos por las tecnologías de tratamiento de agua aplicados. El precio de la energía ayuda después, para obtener los costes económicos de tales medidas de corrección para pasar del estado inicial al estado objetivo del río.

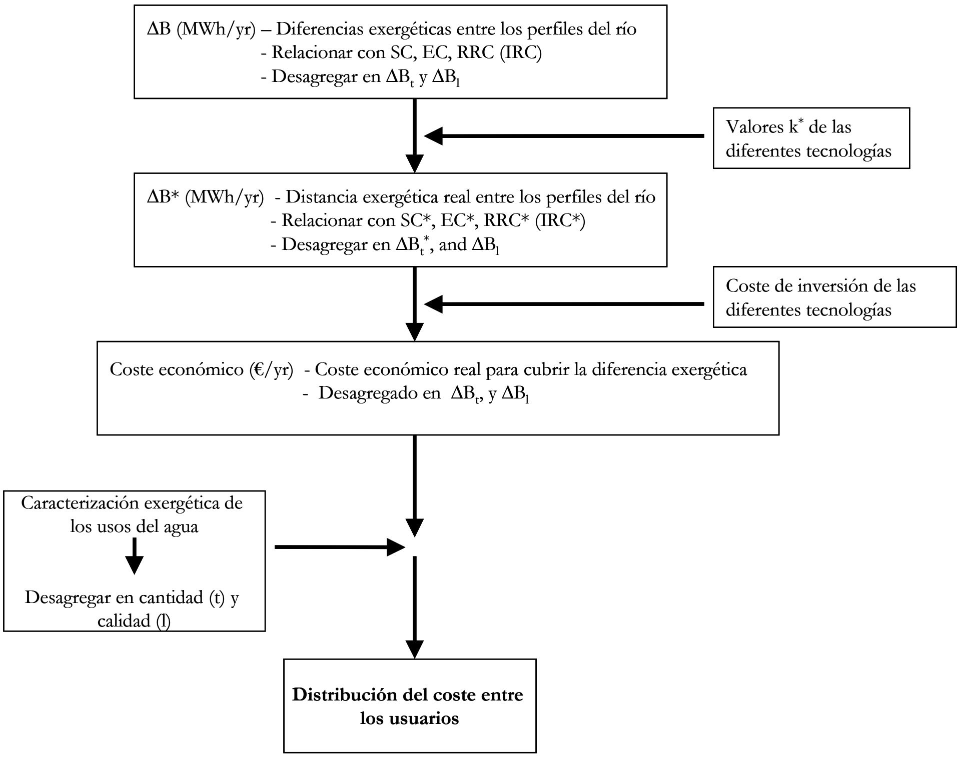


Figure G.3. Pasos básicos de la aplicación de la Hidronomía Física

Desde una perspectiva diferente, se sabe que la degradación sufrida por el río es provocada por los usuarios del agua. La cantidad y características de calidad de esos usos sirven para caracterizar los usos exergéticamente, y se introducen en la metodología para asignar los costes calculados previamente entre los diferentes sectores.

La metodología descrita se ha aplicado a dos cuencas ubicadas en las Cuencas Internas de Cataluña (cuenca de La Muga y cuenca del Foix). En este resumen, a modo de ejemplo, se ha incluido el primero de los estudios.

G.5. Case study: Muga Basin

La Cuenca de la Muga (Figure G.4) está situada en la región l'Alt Empordà, al noreste de Cataluña. Tiene una superficie de 758 km^2 (2.3% de Cataluña), con una pluviosidad media de 612 hm^3 (807 mm), y una contribución media annual al régimen natural cercana a los 150 hm^3. En el area de esta cuenca se encuentran unos 34 núcleos urbanos, con una población de 65,756 habitantes.

La mayor parte de los recursos disponibles en la cuenca de la Muga proceden del embalse de Boadella y de los acuíferos del rico subsuelo *altoampurdanés.*. La oferta se ha ampliado por medio de captaciones en el cauce del río principal y de sus afluentes, y con la reutilización de las aguas residuales tratadas en la planta de Empúriabrava. Las captaciones de agua superficial en este área son habituales, aunque no siempre se hacen de forma regulada. El caudal anual fluctúa de forma importante a lo largo del año (de media, entre 1.9 y 11.9 m^3/s), como cabe esperar debido al régimen de lluvias característico en los ríos mediterráneos y, todavía más, debido a la regulación del caudal que se ejerce en el embalse de Boadella.

La demanda urbana y agrícola para regadío son las más importantes en la cuenca de la Muga. En la modelización de la cuenca, once captaciones de regadío, seis plantas de tratamiento de aguas residuales, y siete vertidos no conectados, además del citado embalse y de una gran industria, se han contabilizado.

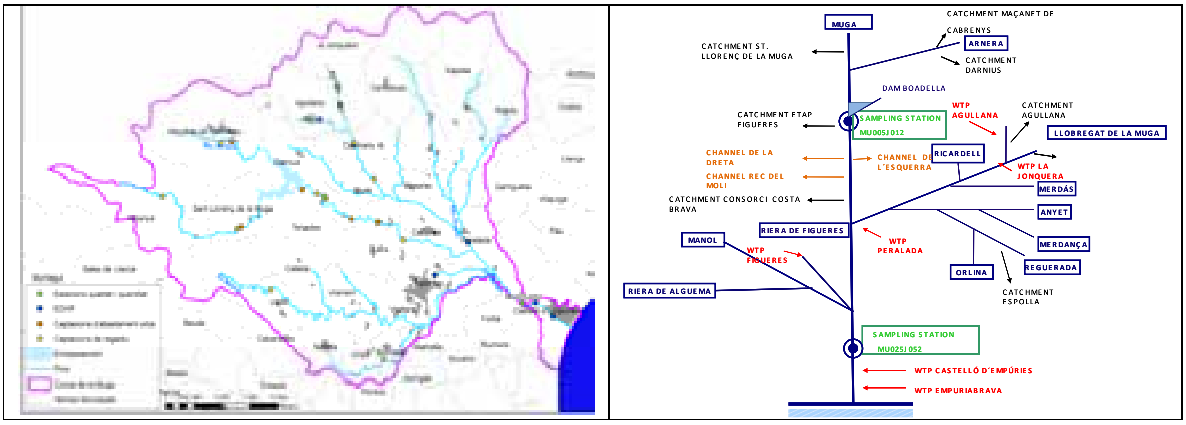


Figure G.4. General map of the Muga Basin (a) and structure of the pressures included in the simulation model (b).

Los resultados indican que la degradación en la componente química inorgánica, al igual que en la orgánica, se deben principalmente a la contribución del uso doméstico (77%

and 99% respectivamente). Sin embargo, la componente de degradación en cantidad tiene su origen principal en la demanda para regadío (97% en la materia inorgánica y 95% en la orgánica).

El coste integral del recurso en la cuenca de la Muga asciende, por ejmplo, a 10,269 MWh/año para la componente potencial y 5,343 MWh/yr para la componente química que da cuenta de la salinidad. El coste real de restaurar esa agua a su estado natural sería de 71,163 y 28,639 MWh/yr, respectivamente, para las componentes citadas.

Estos valores se obtienen tras introducir en el análisis la eficiencia de las tecnologías propuestas para restituir la cantidad y calidad del agua hasta el estado final deseado, esto es, el estado objetivo definido por la DMA. Finalmente, tras incluir también en el cómputo los costes de inversión correspondientes a las plantas de tratamiento, el coste económico de alcanzar los objetivos de la DMA en la cuenca de la Muga en 2015 es 9.5 millones de euros al año. Atendiendo al principio de asignación del coste de acuerdo a la degradación producida, la distribución del coste ambiental es: 60.5% para el sector urbano, 2.5% para la industria, y 37% para el sector agrícola.

G.6. Resumen y conclusiones

En este anexo, se ha presentado el contenido de esta tesis lo más resumidamente posible. A partir del texto de la DMA y la perspectiva de la sostenibilidad del enfoque ecointegrator, junto con las leyes básicas de la termodinámica, se han dado definido las bases de la Hidronomía Física.

Los resultados obtenidos, en términos globales, son comparables con los resultados de los análisis económicos convencionales, por lo que ambas formas de cálculo pueden interactuar para ser validadas. Sin embargo, la Hidronomía Física presenta unas características diferenciadoras que la hacen muy útil para calcular el coste ambiental exigido por la DMA: permite asignar costes a los diversos usuarios del agua, desagregando en el análisis la degradación del agua en cantidad y calidad.

Algunos otros aspectos incluidos en la DMA aún deben ser debidamente incluidos en la metodología de la HF, como son los efectos aguas abajo provocados por una nueva planta de tratamiento de agua incluida en una cuenca fluvial (efectividad del Plan de Medidas), o el tratamiento adecuado de la interfaz entre la superficie y las aguas subterráneas en algunas cuencas fluviales .

La necesidad de operar con los parámetros definidos por los requisitos legales (tipos de ríos, corrientes de mantenimiento, objetivos de calidad ...) supone en ocasiones algún inconveniente. En particular, la tramificación de los ríos en su caracterización por tipos, que es un parámetro ya definido en el documento IMPRESS.

REFERENCES

[1] Aertgeerts, R. and Angelakis, A, 2003. *Health Risks in Aquifer Recharge using Reclaimed Wastewater: State of the Art.* Report, SDE/WSH/03.08. World Health Organization.

[2] Aguilera Klink, F. and Arrojo, P., 2004. *El agua en España. Propuestas de futuro.* Ediciones del Oriente y del Mediterráneo. In Spanish.

[3] Ahrendts, J. 1977. *The exergy of chemically reacting systems.* Technical report, VDI. Forschungsheft 579, Düsseldorf, 1977. (In German).

[4] Albiac, J; Hanemann, M; Calatrava, J; Uche, J; Tapia, J., 2006. *The Rise and Fall of the Ebro Water Transfer.* Natural Resources Journal. Vol. 46. No. 3, pp. 727-757.

[5] Albiac, J; Uche Marcuello, J; Valero Capilla, A; Serra de Renovales, L; Meyer, A; Tapia Barcones, J, 2003. *The Economic Unsustainability of the Spanish National Hydrological Plan.* International Journal of Water Resources Development Vol. 19, No. 3 437-458.

[6] Alcamo, J.; Henrichs, T. and Rösch, T., 2000. *World Water in 2025: Global modeling and scenario analysis for the World Commission on Water for the 21st. Century.* Kassel World Water Series. Report nº 2. Center for Environmental Systems Research. University of Kassel.

[7] Allan, J.A. 1993. *Fortunately there are substitutes for water otherwise our hydro-political futures would be impossible.* In ODA Priorities for water resources allocation and managemen. ODA, London.

[8] Allan, J. A 1997. *Virtual Water: A long term solution for water short Middle Eastern Economies?* Paper presented at the British Association Festival of Science, Water and Development Session. TUE.51, 14.45. Roger Stevens Lecture Theatre, University of Leeds.

[9] Allan, J.A. 1999. *Water stress and global mitigation: Water, food and trade.* Arid Lands Newsletter . nº.45.

[10] Allan, J. A., 2003. *Virtual Water- the Water, Food, and Trade Nexus: Useful Concept or Misleading Metaphor?* Water International. Vol.28, nº1.

[11] Alpatjyev, A. M., 1969. *Water Cycles in Nature and their Transformations.* Leningrad. Hydrometeoizdat.

[12] Alpatjyev, A.M., 1983. *Development, Transformation and Environment protection.* Leningrad. Nauka´Punl.

[13] APHA, AWWA, WPCF. 1985. *Standard Methods for the Examination of Water and Wastewater.* APHA, Washington, 16th edition: 34 American Public Health Association.

[14] Arrojo, P., 2004. *El reto de la sostenibilidad en la nueva política de aguas en España*. Revista del Colegio Oficial de Físicos.No.15, pp.32-36. Colegio Oficial de Físicos. In Spanish.

[15] Arrojo, P., 2006. *Los retos éticos de la nueva cultura del agua*. Polis, Revista de la Universidad Bolivariana, nº 14. In Spanish.

[16] Arrojo, P. and Naredo, J.M., 1997. *La gestión del agua en España y California*. Bakeaz. Centro documentación estudios para la paz. In Spanish.

[17] Artyushkow, E.V., 1970. *Differentation with respect to the Earth matter density and the related phenomena*. New acad. Sci. USSR, Ser.Physics of the Earth. 5. Pp-25-37.

[18] Asano, T., 2006. *Water from (waste) water-the dependable water resource*. Doboku Kenkyujo Koenkai Koenshu.

[19] Ayres, R.U. and Ayres, L.W., 2002. *A Handbook of industrial ecology*. Edwar Elgar publishing.

[20] Ayres, R.U.; Ayres, L. W.; and Warr, B., 2003. *Exergy, power and work in the US economy, 1900-1998*. Energy.28. Pp.219-273.

[21] Ayuntamiento de Zaragoza, 2008. *Real Average Values for tap-water in Zaragoza* http://www.zaragoza.es/weboficial/. Ayuntamiento de Zaragoza

[22] Azqueta, D. and Sotelsek, D., 2007. *Valuing nature: From environmental impacts to natural capital*. Ecologial Economics.63, pp.22-30.Elsevier

[23] Bansil, P.C. 2004. *Water Management in India Commercial Block*. Mohan Garden. Concept Publishing Company

[24] Barney, G.O. 1980. *The global 2000 report to the President of the U.S. entering the 21st century*. US Department of State. Council on Environmental Quality. Pergamon press. New York.

[25] Bastianoni, S. Pulselli, F.M. and Rustici, M., 2006. *Exergy versus emergy flow in ecosystems: is there an order in maximizations?* Ecological indicators 6. Pp.58-62.

[26] Bastianoni, S. and Marchenttini, N., 1996. *Ethanol Production from Biomass: Analysis of Process Efficiency and Sustainability*. Biomass and Bioenergy. Vol. 11 nº5, pp.411-418.Pergamon

[27] Bayod, A. 2009. *Sistemas fotovoltaicos*. Prensas Universitarias. Universidad de Zaragoza. (In Spanish).

[28] Bayod, A.A. and Martínez, A., 2009. *Photovoltaic system for brackish water desalination by electrodialysis and electricity generation*. Desalination and Water Treatment. Vol. 7, pp. 142–151.

[29] Bejarano, M.D., 2009. *Informe de Coagret sobre Criterios sobre Implantación de caudales ambientales. Esquema de temas importantes. Plan hidrológico 2007*. Coagret.

[30] Bertalanffy, L., 1968. *General System Theory*. New York, NY. George Braziller (Ed)

[31] Bezdicek, D.F. and Kenedy, A.C., 1998. *Microorganisms in Action*. Black-well Scientific Publications.

[32] Blyutgen, I., 1972. *Geography of Climates*.Vol.1. Moskow Progress Publ.

[33] Boddy, C; 1995. *Cost, Price and Value*. Mendocino Coast Real Estate Magazine.

[34] Bonnieux, F. 2003. *Using the principles of environmental economics to manage water resources.* Houille blanche-revue internationale de l'eau.

[35] Borja, A, et al. 2006. *The European Water Framework Directive and the DPSIR, a methodological approach to assess the risk of failing to achieve good ecological status*. Estuarine, coastal and shelf science. Vol. 66, nº 1-2 pp. 84-96. Elsevier.

[36] Botero, E., 2000. *Valoracion exergética de recursos naturales, minerales, agua y combustibles fósiles.* Tesis doctoral. Departamento de Ingeniería Mecánica. Universidad de Zaragoza.

[37] British Antartic Survey, 2006. *Weather in the Antartic.* <http://www.antartica.ac.uk> British Antartic Survey.

[38] Brown, M. T., 2009. Personal communication. Unpublished data.

[39] Brown, M.T. and Bardi, E., 2001. *Handbook of Emergy Evaluation. Emergy of Ecosystems, Folio #3*. Center for Environmental Policy. Environmental Engineering Sciences. University of Florida.

[40] Brown, M. T.; Martínez, A. and Uche, J., 2008. *Emergy analysis applied to the estimation of the recovery of costs for water services under the European Water Directive Framework*. Proceedings of the 5th Biennial Emergy Research Conference: Theory, applications and methodologies, January 31-February 2, 2008, Gainesville -Florida-, USA.

[41] Brown, M.T. and Herendeen, R.A, 1996. *Embodied energy analysis and Emergy analysis: a comparative view*. Ecological Economics. Vol.19, pp.219-235. Elsevier.

[42] Brown, M.T. and Ulgiati, S. 2001. *Emergy Measures of Carrying Capacity to Evaluate Economic Investments*. Population and Environment: A Journay of Interdisciplinary Studies.Vol-22, pp.471-501.Human Sciences Press, Inc.

[43] Brown, M.T. and Ulgiati, S. 1999. *Emergy Evaluation of the Biosphere and Natural Capital.* Royal Swedish. Academic of Science services. AMBIO. Vol. 28 No. 6, pp.486-493. Allen Press.

[44] Brown, M.T. and Ulgiati, S. 2002. *Emergy evaluations and environmental loading of electricity production systems.* Journal of Cleaner Production, 10. Pp.321-334. Elsevier.

[45] Brown, M.T. and Ulgiati, S. 2004. *Emergy Analysis and Environmental Accounting.* Encyclopedia of Energy. Vol.2. Pp. 32-354. Elsevier.

[46] Brown, M.T. and Vivas, M.B., 2005. *A Landscape Development Intensity Index.* Proceeding of the 4th Biennial Emergy Conference. Vol.101 nº1-3, pp.289-309. Center for Environmental Policy. University of Florida.

[47] Buenfil, A.A. 2001a. *Emergy Evaluation of Water.* Doctoral Dissertation. University of Florida.

[48] Buenfil, A.A. 2001b. *Will Desalination Solve Global Freshwater Scarcity?*. Proceedings of the 2nd International workshop. Advances in Energy Studies. pp.159-168. SG Editoriali. Padova.

[49] Campbell, D.E. 1998. *Emergy analysis of human carrying capacity and regional sustainability: an example using the state of Maine*. Environmental Monitoring and Assessment. Vol.51. nº 1-2 pp. 531-569. Springer.

[50] Campbell, D.E., Meisch, M., Demoss, T. Pomponio, J., and Bradley, M.P. 2004. *Keeping the books for environmental systems: and emergy analysis of West Virginia*. Environmental Monitoring and Assessment. Vol.94, nº 1-3 pp. 217-230. Springer.

[51] Campolo, M., Andreussi, P., and Soldati, A. 2002. *Water quality control in the river Arno*, Technical note. Water Research, 36, pp. 2673–2680.

[52] Cánovas Cuenca, J. 1986. *Calidad agronómica de las aguas de riego*. Ministerio de Agricultura, Pesca y Alimentación. Extensión Agraria. (In Spanish).

[53] Cantó, J. 1999. *L'abastament d'aigua a la zona de Barcelona. Recursos d'aigua*. Pp. 190-201. Fundació AGBAR. (In Catalan).

[54] Castañón, O.; Mas-Pla, J.; Munné, A.; Prat, N.; Sauri, D.; Alcantara, V.; Roca, J.; Costeja, M.; and Font, N. 2007. *The Water framework Directive in Catalonia: concepts, challenges and expectations in water resource management*. Agéncia Catalana de l´Aigua. Generalitat de Catalunya, Departament de Medi Ambient i Habitatge.

[55] Castells, X.E; Cadavid, C. 2005. *Tratamiento y valorización energética de residuos*. Fundación Universitaria Iberoamericana. Ediciones Díaz de Santos. (In Spanish).

[56] Causape, J. Quilez, D. and Aragues, R. 2004. *Assessment of irrigation and environmental quality at the hydrological basin level I. Irrigation quality*. Agricultural water management, 70 pp. 195-209. Elsevier.

[57] CCB, 2008. *Sanejament Data* (waste-water treatment data) <http://www.ccbgi.org > Consorci de la Costa Brava.

[58] Cech, T.V. 2003. *Principles of Water Resources History: development, management, and Policy*. John Wiley & Sons, Inc.

[59] Chapagain, A.K. ,Hoekstra, A.Y. 2003. *Virtual water flows between nations in relation to trade in livestock and livestock products*. Value of Water Research. Report Series. No. 13. UNESCO-IHE. Institute for Water Education.

[60] Chen, G.Q. 2006. *Scarcity of exergy and ecological evaluation based on embodied exergy*. Nonlinear Science and Numerical Simulation 11, pp. 531-552. Elsevier.

[61] Chen, G.Q. and Ji, X. 2007. *Chemical exergy based evaluation of water quality*. Ecological Modelling. Pp. 259-268. Elsevier.

[62] Chen, G.Q, and Qi, Z.H. 2007. *Systems account of societal exergy utilization: China 2003*. Ecological modelling, 208 nº 2-4 pp. 102-118 Elsevier.

[63] Chou, F. and Lee, C.P. 2007. *Evaluation of Watershed Management Strategy Using Emergy Synthesis*. Journal of Ecotechnnology 1, pp. 49-63. WERC.

[64] Cleveland, C.J. 2006. *Biophysical economics*. Encyclopedia of Earth. Last Updated: November 18, 2008 (Available at: http://www.eoearth.org).

[65] Cleveland, C. and Ruth, M. 1997. *When, where, and by how much do biophysical limits constrain the economic process? A survey of Georgescu-Roegen's contribution to ecological economics*. Ecological Economics 22: 203-223.

[66] Cohen, M.J. and Brown, M.T. 2007. *A model examining hierarchical wetland networks for watershed storm water management*. Ecological Modelling 201, pp.179-193. Elsevier.

[67] Condie, K. 1989. *Origin of the Earth´s crust*. Palaeoclimatol. Global and planetary change section75, pp. 58-81.

[68] Constanza, R. 2003. *The Early History of Ecological Economics and the International Society for Ecological Economics (ISEE)*. Internet Encyclopedia of Ecological Economics. ISEE.

[69] Corning P.A. 2002 *Thermoeconomics: Beyond the second law*. Journal of Bioeconomics, 4 nº 1 (January) pp. 57-88. Springer Netherlands

[70] Costanza, R. 1989. *What is the ecological economics?* Ecological Economics 1 pp. 1-7. Elsevier.

[71] Costanza, R. 1980. *Embodied Energy and Economic Evaluation*. Science. Vol. 210, pp. 1219-1224. Elsevier.

[72] Costanza, R. 1981. *Energy economics and the environments: conflicting views of an essential relationship*. AAAS selected symposium. Boulder, CO. Westview Press, Nº 64. Daly HE, Umana AF.

[73] Costanza, R. 1998. *The Value of ecosystem Services*. Special Section: Forum on Valuation of Ecosystem Services. Ecological Economics, 25 (1) pp. 67-72. Elsevier.

[74] Couchoud, G.M. 2003. *Régimen de precipitación en España*. Spanish National Meteorological Institute. I.N.M. (In Spanish).

[75] Council for Agricultural Science and Technology, 1996. *Overview of the Hydrologic Cycle in Livestock Farming Systems. Integrated Animal Waste management*. Armes. Iowa.

[76] Cournot, AA. 1861. *Traite´ de l'enchaı^nement des ide´ es fondamentales dans les sciences et dans l'histoire*. Reedited by Vrin in ´Bibliothe que des textes philosophiques`. Vrin, 2002. (In French).

[77] CWA 2002. *Estudi d'actualització de l'avaluació dels recursos hídrics de les Conques Internes de Catalunya*. Catalan Water Agency. Department of the Environment, Government of Catalonia. (In Catalan).

[78] CWA 2004. *Recull de dades. Els recursos hidrics en regim natural a les conques internes de catalunya (1940-200)*. Agéncia Catalana de l´Aigua. Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. (In Catalan).

[79] CWA 2005a. Caracterización de masas de agua y análisis del riesgo de incumplimiento de los objetivos de la Directiva Marco del Agua (2000/60/CE) en las Cuencas internas de Cataluña. Documento de Síntesis. Agéncia Catalana de l´Aigua. Generalitat de Catalunya. Departament de Medi Ambient i Habitatge.

[80] CWA 2005b. Economic Analysis of the use of Water in the Internal Basins of Catalonia for the implementation of the Water Framework Directive (2000/60/EC). Agéncia Catalana de l´Aigua. Caps.5. Generalitat de Catalunya, Departament de Medi Ambient i Habitatge.

[81] CWA 2005c. Pla Sectorial de Cabals de manteniment de les conques internes de catalunya.Agéncia Catalana de l´Aigua.Generalitat de Catalunya, Departament de Medi Ambient i Habitatge.

[82] CWA 2006. Internal communications. Catalan Water Agency and CIRCE Foundation.

[83] CWA 2008a. *Catalan Water Agency website*. Generalitat de Catalunya. Available at: http://aca-web.gencat.cat/aca/appmanager/aca/aca/

[84] CWA 2008b. Análisi Económica per a la planificació hidrológica. Catalunya: L´experiéncia pilot a la Conca de la Muga.Agéncia Catalana de l´Aigua.Generalitat de Catalunya. Departament de Medi Ambient i Habitatge.

[85] CWA 2008c. *Internal Communications* within the Project "y asignación de costos ambientales del uso del agua en Cataluña…". Catalan Water Agency and CIRCE Foundation.

[86] Daifullah, A.M. and Shakour, A.A. 2003. *Chemical Composition of rainwater in Egypt*. AJEAM-RAGEE, 6 pp. 32-43.

[87] Daily, G.C. 1997. *Nature´s Services*. Societal Dependence on Natural Ecosystems. Island press. Washington.

[88] Daly, H.E. and Cobb, J.B. 1989. *For the Common Good: redirecting the Economy toward Community, Environment, and a sustainable Future*. Beacon Press, Boston

[89] Daly, H.E 1992. *Allocation, distribution and scale: towards an economics that is efficient, just and sustainable*. Environmental Department, World Bank, Washington D.C; U.S.A. Elsevier Science.

[90] Daly, H. and Farley, J., 2004. *Ecological Economics: Principles and Applications Washington*. Island Press.

[91] Derpgolts, V.F. 1971. *Water in the Universe*. Leningrad. Nedra´Publ.

[92] Diederichsen, D. 1999. *Referenzumgebungen zur Berechnung der chemischen Exergie*. Technical Report, Fortschr.-Ber. VDI Reihe 19, Düsseldorf, Germany. (In German).

[93] Dincer, I. 2000. *Thermodynamics, exergy and environmental impact*. Energy Sources, 22 (8) pp. 723-732. Taylor and Francis Ltd.

[94] Dincer, I. 2002. *Technical environmental and exergetic aspects of hydrogen energy systems*. Int. J: Hydrogen Energy, 27 (3) pp. 265-285. Elsevier.

[95] Dyson, M; Bergkamp, G. and Scanlon, J. 2003. *Flow: The essentials of Environmental Flows*. International Union for Conservation of Nature and Natural Resources. IUCN, Gland, Switzerland.

[96] Dodds, S, 1997. *Towards a 'science of sustainability': Improving the way ecological economics understands human well-being*. Ecological Economics, 23 (2) pp. 95-111. Elsevier.

[97] Dunlap, R.E. 1993. *From environmental to ecological problems*. Calhoum, C., et al. (Eds). Social Problems. McGraw-Hill, New York.

[98] Duvanin, A. I. 1981. *On the choice of strategy for using water resources*. News Moskow State Univ. Ser. 5, Geography, 2 pp. 30-33.

[99] ECO1. Working Group 2.6-WATECO, 2003 for the water Framework Directive (2000/60/EC). *Policy summary. Economics and the Environment- The implementation challenge of the Water framework Directive*. European Union.

[100] ECO2. Working Group 2B: Drafting Group ECO2, 2004. *Information Sheet on Assessment of the Recovery of Costs for Water Services for the 200 River Basin Characterisarion Report (Art 9)*. DG. European Union.

[101] EEA, 2005. *Sustainable use and management of natural resources*. EEA Report, No 9. European Environment Agency.

[102] EEA, 2006. *The European environment - State and outlook 2005 State of the environment report No 12005*. The European Environment Agency and The Office for Official Publications of the European Communities.

[103] Eichler, E.E. and Sankoff, D, 2003. *Structural dynamics of eukaryotic chromosome evolution*. Science, 301 (5634) pp. 793-797. American Association for the Advancement of Science.

[104] Elias, X. 2006. *Criterios de valorización y tratamiento de residuos industriales en el diseño de producto (Valorización Integral de Fangos de EDAR)*. Posgrado en Ingeniería Química. Universidad de Cantabria. (In Spanish).

[105] EIA 2008. Energy Information Administration. Official Energy Statistics for the U.S. Government. International Energy Annual. Available at: http://www.eia.doe.gov/

[106] EMWIS, 2008. International portal website. http://www.emwis.net/. *Euro-Mediterranean Information System on know-how in the Water sector.*

[107] ENVIS, 2008. *Sewage Treatment and Technology Environmental Information System*. ENVIS. India.

[108] EPA 1976. *National Interim Primary Drinking Water Regulations*. U.S. Environmental Protection Agency. EPA 570/9-73-003, Washington, D.C.

[109] EPA, 2001. *Superfund Basic Information*. http://www.epa.gov/superfund. U.S. Environmental Protection Agency.

[110] EPA 2004. *Guidelines for Water Reuse*. U.S. Environmental Protection Agency. U.S. Agency for International Development

[111] EPA-US 2006. *Turbidity and Total Solids*. Voluntary Estuary Monitoring Manual. 2nd edition. 15. Environmental Protection Agency. United States.

[112] EPA 2008. *Water Recycling and Reuse: The Environmental Benefits*. United States Environmental Protection Agency. Water Division Region IX-EPA 909-F-98-001.

[113] EPA 2009. *WASP7 general data*. EPA website <http://www.epa.gov>

[114] EPRI, 2002. *Water & Sustainability* (Volume 3): U.S. Water Consumption for Power Production. The Next Half Century. Technical Report. Electric power research institute.

[115] Escriu, J. 2007. *Estimación y asignación de costes de la DMA en Cataluña a la luz del enfoque eco-integrador. Métodos y criterios*. Seminari Costos i comptes de l¨aigua a Catalunya en relació amb la Directiva marc de l´aigua (DMA).Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona, 18-19 Junio 2007. (In Spanish).

[116] Escriu, J; Carriba, V; Guerra, E. 2007. *La calidad asociada a la cantidad. El análisis termoeconómico de dos aspectos indisociables del estado de una masa de agua*. 6º Congreso Ibérico sobre la planificación y gestión del agua. 4-7 Diciembre 2008. Vitoria. España. (In Spanish).

[117] ESCWA 2001a. *Energy options for water desalination in selected ESCWA member countries*. Economic and Social Commission for Western Asia. United Nations

[118] ESCWA 2001b. *Water desalination technologies in the ESCWA Member Countries*. Economic and Social Commission of Western Asia. United Nations.

[119] ES and EC 2003. *Guidance for Analysis of Pressure and Impacts in accordance with the Water framework Directive*. WFD Circa. European Commission.

[120] Estevan, A. 2007. *El Análisis Económico de la Directiva Marco del Agua a la luz de la Economía Ecológica Seminario sobre Cuentas y Costes del Agua en Cataluña*. Seminari Costos i comptes de l¨aigua a Catalunya en relació amb la Directiva marc de l´aigua (DMA).Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona, 18-19 Junio 2007. (In Spanish).

[121] Estevan, A. and Naredo, J.M. 2004. *Ideas y propuestas para una nueva política del agua en España*. Bakeaz. Centro de Documentacion y Estudios para la Paz.

[122] EU-WFD, 2000. *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, establishing a framework for Community action in the field of water policy (WFD)*. Official Journal of the European Communities. European Union.

[123] European Parliament, 1975. *Council Directive of 16 June 1975 concerning the quality required on surface water intended for the abstraction of drinking water in the Member States (75/440/EEC)*. Council of the European Communities.

[124] European Parliament 2008. *Directive 2008/105/CE of environmental water quality standards*. European Union.

[125] Faber, M., 2007. *How to be an Ecological Economics*. Discussion paper series nº 454. Department of Economics. University of Heidelberg.

[126] Faci, J.; Aragues,R.; Alberto, F.; Quilez, D.; Machin,J. and Arrue, J.L. 1985. *Water and salt Balance in an Irrigated Area of the Ebro River Basin (Spain)*. Irrigation Science, 6 nº 6 pp. 29-37. Springer.

[127] Falkenmark, M and Rockstrom, J. 2004. *Balancing Water for Humans and Nature: The New Approach in Ecohydrology*. Earthscan, UK.

[128] Farber, S; Costanza, R; Childers, DL; Erickson, J; Gross, K; Grove, M. 2006. *Linking*

ecology and economics for ecosystem management. Bioscience 56 (2) pp. 121-133.

[129] Fath, B.D; Patten, B.C; and Choi, J.S. 2001. *Complementarity of ecological goal functions.* J. Theor. Biol. 208. Elsevier.

[130] Finlayson, B.L. and McMahon, T.A. 1988. *Australia vs the world: a comparative analysis of streamflow characteristics.* Geomorphology of Australia. Academic Press. Sydney. Warner. R.F.

[131] Finnveden, G. and Ostlund, P. 1997. *Exergies of natural resources in life-cycle assessment and other applications.* Energy. Vol.22 nº 9, pp. 923-931. Pergamon.

[132] Foster,J.W. 1943. *Oxidation of Alcohols by Non-Sulfur Photosynthetic Bacteria.* Journal Bacteriol. Apr.47. (4). Pp. 355-372.

[133] Frachebourg, L. Krapivsky, P.L. and Ben-Naim, E. 1996. *Spatial organization in cyclic Lotka-Volterra systems.* Physical review. Vol.54. nº 6.

[134] Fritzmann, C.; Lowenberg, J.; Wintgens, T. and Melin, T. 2007. *State of the art of reverse osmosis desalination.* Desalination, 216 pp.1-76. Elsevier.

[135] Gabbrielli, E. 2008. *Nuevas fuente de agua: reutilización y desalación.* Water in the world. Semana Temática 10. Expo Zaragoza 2008.

[136] Gaggioli, R. and Petit, P. 1976. *Second law analysis for pinpointing the true inefficiencies in final conversion system.s* A.C.S. Division of Fuel Chemistry, 21 (2).

[137] Ganster. 2002. *The U.S. Mexican border environment: Economy and Environment for a sustainable Border Region: Now and in 2020.* San Diego, C.A. San Diego State University Press.

[138] García I Ruíz, C. 1997. *El abastecimiento de agua: un problema en las urbanizaciones de la cuenca del Foix.* Revista de geografía, ISSN 0048-7708, nº 30-31, pp. 53-68. (In Spanish).

[139] Gascó, G.; Saa, A.; Guerrero, F. and Gascó, A. 2005a. *Influence of salt concentration and topographicall position on water resource quality: The Spanish Case Study.* Water SA vol. 31 nº 2 pp. 199-208.

[140] Gascó, G.; Hermosilla, D.; Gascó, A. and Naredo, J.M. 2005b. *Application of a physical input-output table to evaluate the development and sustainability of continental water resources in Spain.* Environ Manage, 36 (1) pp. 59-72

[141] Gascó, G. 2004. *Influence of state support on water desalination in Spain.* Desalination, 165 pp. 111–122.

[142] Gascó, J. M., and Saa, A. 1992. *Economía y ambiente: características diferenciales del caso español.* Información comercial Española. Revista de Economía, 711 pp. 203–218 Secretaría de Estado de Comercio, Madrid.

[143] Gascó, J.M. 2007. *Las cuentas del agua en cantidad y calidad.* Seminari Costos i comptes de l¨aigua a Catalunya en relació amb la Directiva marc de l´aigua (DMA). Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona, 18-19 Junio 2007

[144] Gassman, P.W; Reyes, M.R; Green, C.H; Arnold, J.G 2007. *The Soil and Water Assisment Tool: Historical Development, Applications, and Future Research Directions.* Soil and Water Assesment Tool, invited Review Series. American Society of Agricultural and Biological

Engineers.

[145] Generalitat de Catalunya 2006. *MAH/2465/2006 de 13 de juliol, per la qual es fa públic l´Acord del Govern de 4 de juliol de 2006, pel qual s´aprova el Pla sectorial de cabals de mantenimient de les conques internes de Catalunya*. Diari Oficial de la Generalitat de catalunya. Num. 4685, Departament de Medi Ambient. (In Catalan).

[146] Georgescu-Roegen, N. 1966. *Analytical Economics*. Cambridge, MA. Harvard University Press.

[147] Georgescu-Roegen, N. 1971. *The Entropy Law and the Economic Process*. Harvard University Press, Cambridge.

[148] Chapagain, A.K. ,Hoekstra, A.Y. 2003. *Virtual water flows between nations in relation to trade in livestock and livestock products*. Value of Water Research Report Series. Nº 13. UNESCO-IHE. Institute for water Education.

[149] Giannantoni, C. 2000. *Toward a Mathematical Formulation of the Maximum Em-Power Principle*. In M.T. Brown (Ed). Emergy Synthesis: Theory and applications of the emergy methodology, Proceedings of the 1st Biennial Emergy Analysis Research Conference. Center for Environmental Policy. Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL.

[150] Giannantoni, C. 2002. *The Maximum em-power principle as the basis for Thermodynamics of Quality*. SGEditoriali Padova.

[151] Giannantoni, C. 2006. *Mathematics for generative processes: Living and non-living systems*. Journal of Computational and Applied Mathematics III, 189 pp.324-340. Elsevier.

[152] Gleick, P.H, 2008. *Water Conflict Chronology Pacific Institute for Studies in Development, Environment, and Security*. American University.

[153] Gleick, P, 2008. *The World's Water. 2008-2009*. The Biennial Report on Freshwater Resources. Island Press. Available at: http://www.islandpress.org.

[154] GEFN 2009. Global Environmental Flows Network. Available at: http://www.eflownet.org

[155] Gobierno de Aragón, 2005. *Catálogo Aragonés de Buenas prácticas Ambientales*. FED (Fundación Econ. y Desar-Ecology and Development Foundation). Gobierno de Aragón. (In Spanish).

[156] Gobierno de España, 1985. *Ley 29/1985, de 2 de Agosto de 1985, de Aguas*. Boletín Oficial del Estado (BOE) nº 189.

[157] Gobierno de España, 1998. *Real Decreto 1664/1998, de 24 de julio, por el que se aprueban los Planes Hidrológicos de cuenca*. Boletín Oficial del Espado (BOE), de 11 de Agosto, nº 191.

[158] Gobierno de España, 1999. *Ley 6/1999, de 12 de julio, de Ordenación, Gestión y Tributación del Agua*. Boletín Oficial del Estado (BOE).

[159] Gobierno de España, 2003. *Real Decreto Ley 3/2003, de 16 de Mayo, por el que se adoptan medidas urgentes para reparar los daños causados por la inundaciones producidas a finales de a finales del mes de Febrero y durante la primera quincena del mes de Mayo de 2003*. Boletín Oficial del

Estado (BOE) de 17 de Mayo.

[160] Gobierno de España, 2005. *Ley 11/2005, de 22 de junio, por la que se modifica la Ley 10/2001, de 5 de julio, del Plan Hidrológico Nacional*. Boletín Oficial del Estado (BOE), nº 149:29.

[161] Gong, M. and Wall, G. 2001. *On exergy and sustainable development, Part-2*. Exergy, an International Journal 4, pp-217-233. Elsevier.

[162] Government of Aragon 2001. *Arguments on the National Hydrological Plan of 2000*. Government of Aragon. CIVITAS, Madrid.

[163] Government of Aragon 2001. *Complaint of Breach of Community Law in Act 10/2001 of 5th July, concerning the National Hydrological Plan, presented by the Government of the Autonomous Community of Aragon, Spain*. Government of Aragón. Zaragoza. Spain

[164] Grave, N.A. 1968. *The frozen crust of the Earth*. Nature 1, pp. 46-53.

[165] GRIDA 2009. *World resources 2000-2001. People and Ecosystems*. World Resources Institute. UNEP.

[166] Griffin; Ronald C. 2006. *Water Resources Economics. The Analysis of Scarcity, Policies, and Proyects*. Massachusets Institute of Technology. MIT Press.

[167] GWI 2008. *Water Desalination Report*. Global Water Intelligence. GWI

[168] GWO and INBO 2009. *A Handbook for Integrated Water Resources Management in Basins Global Water*. Global Water Partnership and the International Network of Basin Organizations.

[169] GWP, 2004. *Catalyzing Change: A handbook for developing integrated water resources management (IWRM) and water efficiency strategies*. <http://portaunesco.org. >. UNESCO. Global Water Partnership and International Network of Basin Organizations. Sweden.

[170] Hall (Ed). 1995. *Maximum Power: The ideas and applications of H.T.Odum*. Univ. Press of Colorado, Niwot, Colorado.

[171] Hanbury W. T., Hodgkiess T. and Morris, R. 1993. *Desalination Technology 93*. An intensive Course Porthan Ltd, Easter Auchinloch. Lenzie, Glasgow, UK.

[172] Hanley, N; Kristrom, B; and Shogren, J. 2007. *Coherent Arbitrariness: On Value Uncertainty for Environmental Goods*. Land Economics 85(1) pp. 41-50.

[173] Harris, J.M 2006. *Environmental and Natural Resources Economics: a Contemporary Approach*. Tufts. University. USA.

[174] Hau, J.L., and Bakshi, B.R. 2004. *Promise and problems of emergy analysis*. Ecological Modelling, 178 pp. 215-225. Elsevier.

[175] Hellström, D. 1997. *An exergy analysis for a wastewater treatment plant- an estimation of the consumption of physical resources*. Water Environment Research Vol. 69, nº1. pp. 44-51.

[176] Hellström, D. 2003. *Exergy analysis of nutrient recovery processes*. Water Science and Technology Vol.48 nº1 pp. 27-36. IWA Publishing.

[177] Herendeen, R.A. 2004. *Energy analysis and Emergy analysis- a comparison.* Ecological Modelling 178 pp. 227-237. Elsevier.

[178] Hernández Muñoz, A. 2001. *Saneamiento y Alcantarillado.* Vertidos residuales. Colegio de Ingenieros de Caminos, Canales y Puertos.

[179] Higgins, J.B. 2003. *Emergy analysis of the Oak opening region.* Ecological Engineering, 21 (1) pp. 75-109

[180] Hoekstra, A.Y. 1998. *Perspectives on water: An integrated model-based exploration of the future.* International Books, Utrecht, the Netherlands.

[181] Hoekstra, A.Y. 2003. *Virtual water trade.* Proceeding of the International Expert Meeting on Virtual water trade. Value of Water Research report Series. Nº12. IHE. Delft. The Netherlands.

[182] Hoekstra, Y; Chapagain A.K. 2007. *Water footprints of nations: Water use by people as a function of their consumption pattern.* Water Resource Management 21 pp. 35–48.

[183] Hoekstra, A.Y, and Chapagain, A.K. 2009. *Glossary on Water Footprints and Virtual Water.* UNESCO IHE. Institute for Water Education.

[184] Horan, NJ. 1990. *Biological Wastewater treatment Systems- theory and operation.* Est Sussex, England. John Wiley and Sons.

[185] Honotoria, C.; Saa, A., Almorox, J; Cuadra, L.; Sánchez, A. and Gascó, J.M. 2003. The chemical composition of precipitation in Madrid. Water Air Soil Pollut., 146 pp. 36-54

[186] Hubacek, K. Van den Bergh, J. 2006. *Changing concept of land in economic theory: from single to multi- disciplinary approaches.* Ecological Economics, 56 pp. 5-27. Elsevier.

[187] Hunt, C.E. 2004. *Thirsty Planet: strategies for sustainable development.* Zed Books.

[188] ICOLD 2008. *Reservoirs Location.* http://www.icold-cigb.net/ International Commission on Large Dams

[189] IDAE 1998. *Documento técnico de la bomba de calor.* Instituto para la Diversificación y Ahorro de la Energía. Ministerio de Industria y Energía. Gobierno de España.

[190] IHA 2008. The contribution of hydropower. Factsheets. International Hydropower Association.

[191] Ikumi,S.; Luo C.D. and Wen, C.Y. 1982. *A method of estimating entropies of coals and coal liquids.* The Canadian Journal of Chemical Engineering, 60 (4) pp. 551-555. Canadian Society for Chemical Engineering.

[192] IADEN. 1998. *Proposta de Pla Integral de la Muga.* Castello d´Empuries. Institucio Altempor danesa per la defensa i l´Estudi de la Natura. (In Catalan).

[193] Interlandi, S.J.; Christopher, S.; Crockett, S. 2003. *Recent water quality trends in the Schuylkill River, Pennsylvania, USA: a preliminary assessment of the relative influences of climate, river discharge and suburban development.* Water Research 37 pp. 1737-1748. Elsevier.

[194] Isidoro, D. Causape, J. Quilez, D. and Aragues, R. 2002. *Calidad de las aguas de drenaje de la Comunidad de Regantes V del Canal de las Bardenas (Zaragoza).* Investigación agraria.

Producción y protección vegetales. Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA). Vol. 17 (3).

[195] Jørgensen, S.E. 2002. *Integration of Ecosystem Theories: A Pattern.* Academic Publishing Company, Dordrecht, The Netherlands. Vol. 4323 Ed Kluwer.

[196] Jørgensen, S.E. 1999. Integration of Ecosystem Theories: A Pattern. Ecological Modelling.117, Issue 1, pp.165-167. Elsevier.

[197] Jørgensen, S.E. 2001. Exergy of a isolated living system may increase. Proceedings of the 2º International workshop. Advances in Energy Studies. pp.573-578.SG. Editoriali Padova.

[198] Jørgensen, S.E. 2006. Eco - Exergy as Sustainability. WIT Press Southampton, Boston.

[199] Jørgensen, S.E. and Fath, B.D. 2001. *Toward a Consistent pattern of ecosystem theories.* Scientific World Journal. Vol. Abril 4 (1) pp. 71-5. The Scientific World, Ltd.

[200] Jørgensen, S.E. and Fath, B.D. 2004. *Modelling the selective adaptation of Darwin´s Finches.* Ecological Modelling 176, pp. 409-418. Elsevier.

[201] Jørgensen, S.E.; Marques, J. and Nielsen, S.N. 2002. *Structural changes in an estuary, described by models and using exergy as orientor.* Ecological Modelling 158, pp. 233-240. Elsevier.

[202] Jørgensen, S.E.; Nielsen, S.N. and Mejer, H. 1995. *Energy, environ, exergy and ecological modelling* . Ecological Modelling 77, pp. 99-109. Elsevier.

[203] Jørgesen, S.E.; Odum, H.T. and Brown, M.T. 2004. *Emergy and exergy stored in genetic information.* Ecological Modelling 178 Issues 1-2, pp.11-16. Elsevier.

[204] Jørgensen, S.E. ; Patten, B.C. and Straskraba, M. 2000. *Ecosystems emerging: 4. growth* Ecological Modelling 126 pp. 249-284. Elsevier.

[205] Kannel, P.R.; Lee, S. Kanel, S.; Lee, Y.S. and Ahn K.H. 2007. *Application of QUAL2Kw for watrer quality modeling and dissolved oxygen control in the river Bagmati.* Environ Monit Assess 125, pp. 201-217. Department of Industry. United States.

[206] Klare, M.T. 2001. *Resource Wars: The New Landscape of Global Conflict.* New York. Henry Holt and Company, LLC.

[207] Klein, G; Krebs, M; Hall, V; O'Brien, T. And Blevins, BB. 2005. *California´s Water- Energy Relationship.* California Energy Commission.

[208] Klige, R.K.; Danilov, I.D. and Konishchev, V.N. 1998. History of the Hydrosphere. Moskow: Scientific World.

[209] Klotz, I.M. and Rosenberg, R.M. 1977. *Termodinamica Química.* Teoría y métodos básicos. Editorial AC.

[210] Korzun, V.I. 1974. *World Water Balance and Water Resources of the Earth.* Leningrad: Hydrometeoizdat.

[211] Kotas, T.J. 1985. *The exergy method of thermal plant analysis.* Ed Essex.

[212] Kotwicki, V. 1991. *Water in the Universe.* Hydrol. Sci. J.36 (1)

[213] Kotlyakov, V.M. 1984. *Snow cover.* Glaciological Dictionary. pp. 416-418. Leningrad: Hydrometeoizdat.

[214] Kraev, E. 2002. *Stocks, flows and complementarity: formalizing a basic insight of Ecological Economics.* Ecological Economics 43, pp. 277-286.

[215] Kulp, J.L. 1951. *The origin of the hydrosphere.* Bull. Geol. Soc. Amer., 62 pp. 326-330

[216] Kundell, J. and Hussein, G.H.G. 2009. *Groundwater.* The encyclopedia of Earth. Available at: http://eoearth.org

[217] L´vovich, M.I. 1986. *Water and life.* Moskow. MyslPubl.

[218] Lagerberg C.; Brown M.T. 1999. *Improving agricultural sustainability: the case of Swedish greenhouse tomatoes.* Journal of Cleaner Production, 7 (6) pp. 421-434. Elsevier.

[219] Landreth, H; and Colander, D. 2002. *History of Economic Thought.* Boston. Boston: Houghton Mifflin Company.

[220] Landes, D.S, 1997. *Unbound Prometheus: Technological Change and Industrial Development in Western Europe from 1750 to the Present.* Cambridge University Press.

[221] Lane, C.R. and Brown, M.T. 2006. *Energy-based land use predictors of proximal factors and benthic diatom composition in Florida Freshwater Marshes.* Environmental Monitoring and Assesment 117, pp.433-450.

[222] Levine A, Asano T, 2004. *Recovering sustainable water from wastewater.* Environ Sci. Technol. 2001A. American Chemical Society.

[223] Linder, J; Costa, J; Stupak, B; Radanovich, J. and Napolitano, G. 2007. *Join the Bi-Partisan House water Caucus as an Original Member.* The Twelve Principles of Water Policy. House of Representatives, 29. Washington D.C.

[224] Llamas, R. 2003. *From hydro-schizophrenia to the farmers silent revolution. From the silent revolution to clamorous social conflicts.* Focus session 7. XI-IWRA World Water Congress. Madrid.

[225] Llamas, R.; Hernández-Mora, N. and Martínez-Cortina, L., 2000. *El uso sostenible de las aguas subterráneas.* Papeles del Proyecto Aguas subterráneas, Fundación Marcelino Botín, Santander, Serie A nº. 1, 54 p. (In Spanish).

[226] Lloyd, W. And Davenport, G. 1980. *Applying thermodynamics to Fossil Fuel.* Journal of Chemical Education. Vol.57 pp. 56-60.

[227] Lloyd, S. and Pagels, H. 1988. *Complexity as Thermodynamic Depth.* Annals of Physics.188. pp. 186-213.

[228] Los Alamos National Laboratory, 2001. *Air Nitrogen content.* Los Alamos. New Mexico.

[229] Malan, H.; Bath, A.; Day, J. and Joubert, A., 2003. *A simple flow-concentration modelling method for integrating water quality and water quantity in rivers.* Water SA. Vol.29. nº 3.

[230] Malecki, J.J. and Szortakiewicz, M. 2006. *The role of evapotranspiration in the formation of the chemical composition of shallow groundwater (the Polish Tatras).* Acta Geologica Polonica, Vol.56. nº.4. pp 485-492.

[231] Marcé, R., M. Comerma, J. C. García, J. Gomá & J. Armengol, 2000. *Limnology of Foix Reservoir (Barcelona, Spain)*. Limnetica. nº 19175-191. Asociación. Española de Limnología.. Madrid, España.

[232] Marcé, R; Comerma,M; García, J.C; Gomá, J; Armengol, J 2005. *The zooplanckton community in a small, hypertrophic mediterranean reservoir (Foix Reservoir, NE, Spain)*. Limnética, 275-294. Department d Ècologia. Universidad de Barcelona.

[233] Martínez-Gil, F.J. 1997. *La Nueva Cultura del Agua en España*. Ed. Bakeaz. (In Spanish).

[234] Martínez-Gil, F.J and Jiménez Torrecillas, N. 2003. *La Nueva Cultura del Agua: hacia un modelo sostenible de gestión hídrica*. Revista de cultura Aragonesa. ROLDE. (In Spanish)

[235] Martínez, A. and Uche, J., 2009. *Exergy of organic matter in a water flow*. Energy. Accepted 27 August 2009 (doi:10.1016/j.energy.2009.08.032).

[236] Martínez, A.; Uche, J.; Bayod, A. and Rubio, C. 2009. *Assessment of the world fresh water resources through energy requirements in desalination technologies*. Desalination and Water Treatment. Vol. 10.

[237] Martínez, A; Uche, J; Valero, A. and Valero, Al. *Environmental costs of a river watershed within the European water framework directive: Results from Physical Hydronomics*. Energy. Available online 9 July 2009.

[238] Martínez, A.; Uche, J.; Rubio, C. and Carrasquer, B., 2009 *Exergy cost of water supply and water treatment technologies*. Proceedings of the Conference and Exhibition on Desalination for the Environment organized by the European Desalination Society, 17-20 May 2009, Baden-Baden, Germany.

[239] Martínez, A.; Uche, J.; Rubio, C.; Carrasquer, B and Valero, A. 2009. *Exergy cost assesment for water-related technologies*. Proceedings of the 22nd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, August 31-September 3, 2009, Fox do Iguaçu, Brazil.

[240] Martínez, A.; Uche, J.; Valero, A. and Valero, Al., 2008. *Environmental costs of a river watershed within the Water Framework Directive results from Physical Hydronomics*. Proceedings of the 21st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, 24-27 June 2008, Krakow, Poland.

[241] Martinez-Alier, J. 1987. *Ecological Economics: Economics, environment and society*. Basil Blackwell, Oxford, 286 pp.

[242] Mazily, M; Ziubanu, M. 2009. *Binomial Inseparable Environmental Economics*. International Journal of Energy and Environment, 3 (1) pp. 19-28.

[243] McCutcheon, J.R.; McGinnis, R. L. and Elimelech, M. 2005. *A novel ammonia-carbon dioxide forward (direct osmosis desalination process)*. Desalination, 174 pp. 1-11. Elsevier.

[244] Metcalf and Eddy, Inc. 2003. *Wastewater Engineering Treatment and Reuse*. McGraw- Hill. Higher Education.

[245] Meybeck, M. and Helmer, R. 1989. *The quality of rivers; from pristine stage to global pollution*. Global Planet Change 1 pp. 283-309.

[246] Millero, F. 1996. *Chemical Oceanography*. 2^{nd} Edition. CRC Press.

[247] Ministerio de la Presidencia 2002. *Real Decreto 1074/2002, de 18 de octubre, por el que se regula el proceso de elaboración, circulación y comercio de aguas de bebida envasadas*. Boletín Oficial del Estado. Num.259, Gobierno de España.

[248] Ministerio de la Presidencia 2003. *Real Decreto 140/2003, de 7 de febrero, por el que establecen los criterios sanitarios de la calidad del agua de consumo humano*. Boletín Oficial del Estado.

[249] Ministerio de la presidencia 2007. *Real decreto 1620/2007 de 7 diciembre por el que se establece el régimen jurídico de la reutilización de las aguas depuradas*. Boletín Oficial del Estado. Gobierno de España.

[250] Ministerio de la Presidencia 2007. *Real Decreto 907/2007, de 6 de Julio, por el que se aprueba el Reglamento de la Planificación Hidrológica*. Boletín Oficial del Estado. num.162. Gobierno de España.

[251] Ministerio de Medioambiente 2001. *Real Decreto Legislativo 1/2001, de 20 de Julio, por el que se aprueba el texto refundido de la Ley de Aguas*. Gobierno de España.

[252] Ministerio de Medio Ambiente y Medio Rural y Marino 2008. *Orden ARM/2656/2008, de 10 de Septiembre, por la que se aprueba la Instrucción de Planificación Hidrológica*. Gobierno de España.

[253] Ministerio de Medio Ambiente 2009. *Actuaciones Públicas en Materia de Medio Ambiente*. BOE. Gobierno de España.

[254] Mishra, S.K. 2008. *Structural Changes in Economics During the Last Fifty Years*. Social Science Research Network. North-Eastern Hill University (NEHU).

[255] Molden, D., Murray-Rust, H., Sakthivadivel R. and Makin, I. 2003. *Water Productivity in Agriculture: Limits and Opportunities for Improvement. A water productivity framework for understanding and action*. Wallingford, UK, CABI.

[256] Monin, A.S. 1977. *The History of the Earth*. Leningrad. Nauka´Publ.

[257] Mora, C.H and De Oliveira, S. 2006. *Environmental exergy analysis of wastewater treatment plants*. Engenharia Termica (Thermal Engineering). Vol. 5 nº 2 pp. 24-29.

[258] MSU, 2008. The phosphorus cycle. Mississippi State University. Available at: http://msucares.com/crops/soils/images/phosphorus.gif&imgrefurl

[259] Munné, A. and Prat, N. 2000. *Delimitación de regiones ecológicas para el establecimiento de tipos de referencia y umbrales de calidad biológica: Propuesta de aplicación de la Nueva Directiva Marco del agua en la cuenca del Ebro*. II Congreso de la Fundación Nueva Cultura del Agua. Oporto, 2000.

[260] Munné, A. and Prat, N. 2002. *Regionalització del sistema fluvial a les Conques Internes de Catalunya. Aplicació de la Directiva Marc en Política d'Aigües de la Unió Europea*. Technical Catalan Water Agency documents 92. (In Catalan).

[261] Munné, A. and Prat, N. 2004. *Defining river types in a Mediterranean area. A methodology for the implementation of the EU Water Framework Directive*. Environmental Management 34 (5).

[262] Naredo Pérez, J.M. 1987. *La economía en Evolución.: Historia y perspectiva de las categorías*

básicas del pensamiento económico. Siglo XXI de España editores S.A.

[263] Naredo, J.M. 1997. *Environmental Economics in the European Union*. Universidad Carlos III de Madrid. Ed. Mundi.

[264] Naredo, J.M. 2007. *Costes y cuentas del agua. Propuestas desde el enfoque ecointegrador*. Seminari Costos i comptes de l¨aigua a Catalunya en relació amb la Directiva marc de l´aigua (DMA).Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona, 18-19 Junio 2007. (In Spanish).

[265] Naredo, J.M. and Gascó, J.M. 1994. *Spanish Water Accounts*. OECD. Environment Policy Committee (ENV/EPOC/SE/A(94)2. Paris.

[266] Naredo, J.M. and Valero, A. 1999. *Desarrollo económico y deterioro ecológico*. Fundación Argentaria. Visor.

[267] NBER 2007. *Environmental Economics*. National Bureau of Economics Research. Available at: http://nber.org

[268] Nell, E.J. 2009. *On the History of Economic Theory and the Emergence of Capitalism*. Atypon.

[269] Newhall, F. 1972. *Calculation of soil moisture regimes from the climate record*. Mimeo. Rev. 4. Soil Survey Investigation Report, USDA Soil Conservation Service, Washington, D.C.

[270] NLWRA. 2001. *Australian Water Resources Assessment 2000, Surface water and groundwater - availability and quality*. National Land and Water Resources Audit, Canberra. National Land and water resources Audit.

[271] Norgaard, R.B. and Bode, C., 1998. *Next, the value of God, and other reactions*. Ecological Economics.

[272] Odum, H.T. 1971. *Environment, Power and Society*. John Wiley & Sons Inc. New York.

[273] Odum, H.T. 1983. *Systems Ecology*. Willey, New York.

[274] Odum, H.T. 1988. *Self-Organization, Transformity, and Information*. Science, vol. 242 nº 4882 pp. 1132–1139.

[275] Odum, H.T. 1994. *Ecological and General Systems. An Introduction to Systems Ecology*. Systems Ecology. University Press of Colorado

[276] Odum, H.T. 1996. *Environmental Accounting: EMERGY and Environmental Decision Making*. John Wiley & Sons Inc. New York.

[277] Odum, H.T. 2000a. *Emergy evaluation of an OTEC electrical power system*. Energy 25 pp. 389-393. Pergamon.

[278] Odum, H.T. 2000b. *Handbook of Emergy Evaluation-Emergy of Global Processes*. Folio #1. Center for Environmental Policy Environmental Engineering Sciences. University of Florida.

[279] Odum, H.T. and Odum, E.C. 1976. *The Energy Basis for Man and Nature*. McGraw-Hill. New York.

[280] Odum, H.T. and Odum, E.C. 2000. *Modelling for All Scales: An Introduction to Systems and*

Simulation. Academic press, P.A.

[281] Odum, H.T., and Peterson, N. 1996. *Simulation and evaluation with energy systems blocks*. Ecological Modelling, 93 (1) pp.155-173. Elsevier.

[282] Odum, H.T.; Brown, M.T. and Ulgiati, S. 2000. *Ecosystems as Energetic Systems. Handbook of Ecosystems. Theories and Management.* In Jorgensen S.E, Müller F (eds). Lewis Publishers, London.

[283] Ostrom, E. 1990. *Governing the Commons*. Cambridge. Cambridge University Press.

[284] Palau, A. 2006. *Integrated environmental management of current reservoirs and regulated rivers. The ecology of the Iberian Inland Waters*. Asociación Española de Limnología, Madrid. ISSN: 0213-8409.

[285] Palau, A. 2009. *Aspectos clave sobre los caudales de mantenimiento en la Elaboración del Plan hidrológico del Ebro*. Departamento de Medio Ambiente y Ciencias del Suelo. Universitat de Lleida. Asociación Española de Limnología, Madrid. España.

[286] Paterson, W. S. B. 1994. *The physics of Glaciers*. 3rd Edition. Pergamon, Oxford.

[287] Pavlov, A.N. 1977. *Geological Water Cycle on the Earth*. Leningrad. Nedra´Publ.

[288] Pelletier, G. and Chapra, S. 2004. *QUAL2Kw theory and documentation (version5.1)*. Environmental Assessment Program Olympia, Washington 98504-7710. Washington State Department of Ecology.

[289] Pelletier, G. and Chapra, S. 2006. *QUAL2Kw user manual (version 5.1)*. Environmental Assessment Program. Olympia, Washington 98504-7710. Washington State Department of Ecology.

[290] Perry, R.H.; Green, D.W. 1997. *Perry's Chemical Engineers' Handbook*. Knovel. Mc-Graw-Hill.

[291] Pidwirny, M. 2008. *The Nitrogen Cycle*. Fundamental of physical geography (Physical Geography.net). Fundamentals eBOOK. University of British Columbia.

[292] Plana i Castellvi, J.A. 2004. *El consumo de agua en las cuencas internas de Cataluña*. Boletin de la A.G.E. nº 37 pp. 205-222.

[293] Plaza, F.I; Garralón, G. 2008. *Plataforma Experimental para la Valorización Energética de Fango de EDAR mediante gasificación*. I+D+i Deparment. Cadagua S.A.

[294] Plotnikov, N. I. 1976. *Underground Water: Our Wealth*. Moskow. Nedra´Publ.

[295] Prat, N and Munné, A. 2000. *Water use and quality and stream flow in a Mediterranean stream*. Water Research, 34 (15) pp. 3876-3881. Elsevier.

[296] Rajarsh, M. 2009. *Environmental Flow*. The Encyclopedia of Earth. Digital Universe, Powered by Trinity, Boston University. NCSE.

[297] Raluy, G.; Serra, L.; Uche, J. 2006. *Life cycle assessment of MSF, MED and RO desalination technologies*. Energy, Volume 31, Issue 13. Elsevier Ltd.

[298] Ranz, L. 1999. *Análisis de los costes exergéticos de la Riqueza Mineral Terrestre. Su aplicación para*

la gestión de la sostenibilidad. Tesis Doctoral. Departamento de Ingeniería Mecánica. Universidad de Zaragoza. (In Spanish).

[299] Rekacewicz, P. 2002. *Industrial and Domestic Consumption Compared with Evaporation from Reservoirs.* UNEP based on Shiklomanov. UNESCO.

[300] Rodrigues, J. Domingos, T. Conceiçao, P. and Belbute, J. 2005. *Constraints on dematerialisation and allocation of natural capital along a sustainable growth path.* Ecological Economics, 54 pp. 382-396. Elsevier.

[301] Rogers, P; Bhatia, R; Huber, A; Allan, T. 1998. *Water as a Social and Economic Good: How to Put the Principle into Practice.* Global Water Partnership. Technical Advisory Committee (TAC). Development Cooperation Agency. Stockholm. Sweden.

[302] Rosen, M.A. and Dincer, I. 2001. *Exergy as the confluence of energy, environment and sustainable development.* Exergy, an International Journal, 1 pp. 3-13. Elsevier.

[303] Rosen, M.A. and Dincer, I. 2003. *Exergy cost energy mass analysis of thermal systems and processe*s. Energy Conversion and Management, 44 pp. 1633-1651. Pergamon.

[304] Rosen, S. 1974. *Hedonic Prices and Implicit Markets: product Differentiation in Pure Competition.* The Journal of Political Economy, Vol.82. No.1. Pp. 34-55. The University of Chicago Press.

[305] R. Puselli, E. Simoncini, R. Ridolfi, and S. Bastianomi 2008. *Specific emergy of cement and concrete: an energy-based appraisal of building materials and their transport.* Ecological indicators, 8 647-656. Elsevier.

[306] Rubey, W.W. 1951. *Geologic history of seawater.* Bull. Geol. Soc. Amer., 62 pp. 111-114.

[307] Scheneider, E.D. and Sagan, D. 2005. *Into the cool: Energy flow, thermodynamics, and life.* Chicago: Univ. of Chicago Press.

[308] Shieh, J.H., Fan, L.T. 1982. *Estimation of energy (enthalpy) and energy (availability) contents in structurally complicated materials.* Energy Resour. 6, 1.

[309] Shiklomanov I.A. 1998. *World water resources a new appraisal and assessment for the 21srt century.* Designed and produced by RPL design, Milton Keynes, UK. Unesco

[310] Shiklomanov, I. A. 1997. *Assessment of Water Resources and Water Availability in the World.* Background Report for the Comprehensive Assessment of the Freshwater Resources of the World.Paris: WMO/SEI.

[311] Shiklomanov, I.A, and Rodda, J.C. 2004. *World Water Resources at the Beginning of the 21st Century.* International Hydrology series. Cambridge.

[312] Simeonov, V.; Stratis, J.A.; Samara C.; Zachariadis, G.; Voutsa, D.; Anthemidis, A.; Sofoniou, M. and Kouimtzis, T. 2003. *Assessment of the surface water quality in Northern Greece.* Water Research, 37 pp. 4119-4124. Elsevier.

[313] Smakhtin, V. 2009. *Environmental Flow Assessment for Aquatic Ecosystems: A database of Methodologies.* Eco-hydrological databases. Available at: http://dw.iwmi.org/ehdb/efm/efm.asp

[314] Soil Survey Staff 1998. *Keys to soil taxonomy.* United States Department of Agriculture,

Natural Resources Conservation Service, 8th edition. Washington, D.C., 327 pp.

[315] Spliegler, K.S. and El-Sayed, Y.M. 1994. *A desalination primer introductory book for students and newcomers to desalination*. Balaban Desalination Publications.

[316] Steffen, K.; Cullen, N. and Huff, R. 2005. *Climate variability and trend along the western slope of the Greenland ice sheet during 1991-2004*. Proceedings of the 85th American Meteorological Society Annual.

[317] Steinnes, D.N. 1992. *Measuring the economic value of water quality. The case of lakeshore land.* Ann Reg Sci. 26:171.

[318] Stepanov, V.N. 1983. *Oceanosphere*. Moskow. Mysl´Publ.

[319] Suomi, V. E. 1992. *Aqua and the planet, GEWEX and the role of TRMM: The global role of tropical rainfall.* Proceedings of the international symposium on aqua and planet. Pp.15-32. DEEPAK publishing; Hampton.

[320] Surampalli, R.Y. 2004. *Advances in Water and Wastewater Treatment.* ASCE Publications.

[321] Susani, L.; Pulselli, F.M.; Jorgensen, S. E. and Bastianoni, S. 2006. *Comparision between technological and ecological exergy*. Ecological Modelling, 193 pp.447-456. Elsevier.

[322] Sussman, M. 1979. *Choosing a reference environment-state for available-energy computations*. In 72nd Annual Meeting. American Institute of Chemical Engineers, San Francisco (USA).

[323] Sweeney, S.; Cohen, M.J.; King, D. and Brown, M.T. 2006. *Creation of a global emergy database for standardized national emergy synthesis*. In Bardi, E. (Ed.). Emergy Synthesis 4. Proceedings of the 4th Biennial Emergy Research Conference. Gainesville, FL.

[324] Szargut,J.; Morris, D.R; and Steward, F.R. 1988. *Exergy analysis of thermal, chemical and metallurgical processes*. New York: Hemisphere.

[325] Szargut, J.; Valero, A.; Stanek, W. and Valero-Delgado, A. 2005. *Towards an international legal reference environment.* Proceedings of ECOS. 2005. Pp.409-420. ECOS.

[326] Szargut, J.; Ziebik, A., and Stanek, W. 2002. *Depletion of the non-renewable natural exergy resources as a measure of the ecological cost.* Energy conversion & management, 43 pp. 1149-1163. Pergamon.

[327] Szargut, J.T. 2003. *Anthropogenic and natural exergy losses (exergy balance of the Earth´s surface and atmosphere)*. Energy, 28 pp.1047-1054. Elsevier.

[328] Szargut, J.T. 2004. *Optimization of the design parameters aiming at the minimization of the depletion of non-renewable energy*. Energy, 29 pp. 2161-2169. Elsevier.

[329] Szargut, J. *Exergy Application in Technology and Ecology*. Institute of Thermal Technology. Pp-205-217. Silesian University of Technology. Poland.

[330] Tai, S.; Matsushige, K. and Goda, T. 1986. *Chemical exergy of organic matter in wastewater.* International Journal Environmental Studies. Vol. 27 pp. 301-315. Science Publishers, Inc.

[331] Tharme, R.E. 2003. *A global perspective on environmental flow assessment: emerging trends in the development and application of environmental flow methodologies for rivers.* River Research and

Applications nº 191 (45).

[332] Tharme, R.E. and King, J.M. 1998. *Development of the Building Block Methodology for in stream flow assessments, and supporting research on the effects of different magnitude flows on riverine ecosystems.* Water Research Commission Report. No. 576/1/98. 452 pp.

[333] Tietenberg, T. 2006. *Environmental Natural Resources Economics*. Colby College. Canada. Pearson.

[334] Tilley, D.R. 2003. *Industrial ecology and ecological engineering: opportunities for symbiosis*. Ind. Ecol. 7 (2).

[335] Tilley, D.R. And Brown, M.T. 1998. *Wetland networks for storm water management in subtropical urban watersheds*. Ecological Engineering, 10 pp. 131-158. Elsevier.

[336] Tilley, D.R. and Swank, W.T. 2003. *Emergy-based environmental systems assessment of a multi-purpose temperate mixed-forest watershed of the southern Appalachian Mountains, USA*. Journal of Environnmental Management, 69 pp. 213-227. Elsevier.

[337] Tilley, D.R. 2006. *National metabolism and communications technology development in the United States: 1790 to 2000*. Environment and History. Vol. 12 nº2 pp.165-190.

[338] Tilman, D.; Cassman K.G.; Matson, P.A.; Naylor, R. and Polasky, S. 2002. *Agricultural sustainability and intensive production practices*. Nature, 418 pp. 671-677

[339] Tortajada, C. 2006. *Water Transfer from the Ebro River*. Antizapán, México. Third World Centre for Water Management.

[340] Uche-Marcuello, J. 2000. *Thermoeconomic Analysis and Simulation of a Combined Power and Desalination Plant*. Doctoral dissertation. Department of Mechanical Engineering. University of Zaragoza.

[341] Uche, J.; Valero, A. and Serra, L. 2006. *Potential paper of desalination. Water Crisis: Myth or Reality?* In Rogers, P. and Llamas, R. (Eds.), Harvard University, *USA*. Taylor & Francis.

[342] Ulgiati, S.; Odum, H.T. and Bastioni, S. 1994. *Emergy use, environmental loading and sustainability: an emergy analysis of Italy*. Ecological Modelling, 73 nº 3-4 pp. 215-268. Elsevier.

[343] UN-Agenda 21, 1992. *Agenda 21*. Agenda 21 website (full text). Available at: http://habitat.igc.org.

[344] UNEP 2008a. *GeoYearBook 2008*. Environment for development. United Nations Environmental Programme.

[345] UNEP 2008b. *Vital Water Graphics. An overview of the State of the World´s Fresh and Marine Waters*. UNEP-GRID Arendal. Available at: http://www.unep.org/dewa/vitalwater/index.html.

[346] UNEP, 2009. *Freshwater use by sector at the beginning of the 2000s*. UNEP-GRID Arendal. Available at: http://www.grida.no/publications.

[347] UNESCO, 2008. *UNESCO web-site*. www.unesco.org. United Nations Educational, social and scientific organization.

[348] UN-SEEA, 2003. *Integrated Environmental and Economic Accounting 2003 (SEEA 2003).*

United Nations Statistic Division. Available at: http://unstats.un.org

[349] UN-SEEAW, 2007. *Systems of Environmental Economic Accounting for Water*. United Nations Statistic Division.

[350] UN-SNA, 1993. *System of National Accounts*. United Nations Statistic Division. United Nations.

[351] UN-WWAP, 2006. *Water a shared responsibility*. World Water Assessment Programme. United Nations. Unesco.

[352] University of Victoria 2003. *8.0 Infiltration & Soil Moisture*. Geography. University of Victoria.

[353] Valero, A. 1998. *Thermoeconomics as a conceptual basis for energy ecological analysis*. Proceeding of the 1st International workshop Advances in Energy Studies. Pp. 415-444. SG Editoriali Padova.

[354] Valero, A.; Botero, E. and Serra, L. 2002. *The World´s renewable water resources and ice sheets*. Proceedings of the Conference on Sustainable Development of Energy, Water and Environmental Systems. Dubrovnik. Croatia. June 2-7/02. Unesco.

[355] Valero, A.; Lozano, M.A. and Muñoz, M. 1986. *A general theory of exergy saving, I, II and III. Computed Aided Engineering and Energy Systems: Second Law Analysis and Modelling*, AES. Vol 2-3 Vol. 2-3, ASME Book H0341C. New York.

[356] Valero Al.; Valero, A.; Martinez, A. and Mudd, G. 2006. *A Physical way to assess the decrease of mineral capital through exergy. The Australian case*. Proceedings of the 9th Biennial Conference of the International Society for Ecological Economics (ISEE). December 15-18, 2006, New Delhi, India.

[357] Valero, A; Uche, J; Valero, Al. and Martínez, A. 2007. *Fundamentos de la Hidronomía Física: Propuesta de metodología del enfoque termoeconómico para el cálculo de los costes ambientales de reposición del deterioro del agua asociado a los usos*. Seminari Costos i comptes de l¨aigua a Catalunya en relació amb la Directiva marc de l´aigua (DMA).Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona, 18-19 Junio 2007. (In Spanish).

[358] Valero, A; Uche, J; Valero, Al. and Martínez, A. 2007. *Physical Hydronomics: application of the exergy analysis to the assessment of environmental costs of water bodies. The case of the inland basins of Catalonia*. Energy. Available online 30 October 2008.

[359] Valero, A.; Uche, J.; Valero, Al.; Martínez, A. and Escriu, J. 2007. *Physical Hydronomics: application of the exergy analysis to the assessment of environmental costs of water bodies. The case of the Inland Basins of Catalonia*. Proceedings of the 20st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, 25-28 June, 2007, Padova, Italy.

[360] Valero, A.; Uche, J.; Valero, Al.; Martinez, A.; Naredo, J.M. and Escriu, J. 2006. *Fundamentals of Physical Hydronomics: a new approach to assess the environmental cost of the European Water Framework Directive*. Proceedings of the 9th Biennial Conference of the International Society for Ecological Economics (ISEE). December 15-18, 2006, New Delhi, India.

[361] Valero, A; Uche, J; Valero, Al; Martínez, A; Naredo, J. and Escriu, J. 2009. *The Fundamentals of Physical Hydronomics: a novel approach for physico-chemical water valuation*. In

"Water, Agriculture, and Sustainable Well-Being" Chapter 5, pp. 97-118. Oxford University Press.

[362] Vargas Gutiérrez, G.; Méndez Nonell, J; and López Ojeda, 2005. *Cementos odontológicos a base de Poli (ácido acrílico) y wollastonita*. Instituto de Bioingeniería. Universidad Miguel Hernández. Elche (Alicante). Sociedad Española de Cerámica y Vidrio.

[363] Velázquez, E. 2007. "Water Trade in Andalusia: an alternative way to management water demand". Ecological Economics, 63 (1) pp. 201-208.

[364] Ventura, M. ; Ribas, A. and Sauri, D. 2000. *Gestión del agua y conflictividad social en la Cuenca del Rio Mug*a. Geographicalia, 38 pp. 55-70. (In Spanish).

[365] Vinogradov, A.P. 1959. *Chemical Evolution of the Earth*. Moscow: Academy of Sciences of the USSR Publ.

[366] Vinogradov, A.P. 1973. *The cycle of matters*. Great Soviet Encyclopedia. Vol. 13 pp. 488-491. Moskow. Soviet Encyclopedia.

[367] Visco, G; Campanella, L. and Nobilli, V. 2005. *Organic carbons and TOC in waters: an overview of the international norm for its measurements*. Microchemical Journal. Department of Chemistry. Rome University "La Sapienza". Elsevier B.V.

[368] Vogel, W. 1994. *Glass Chemistry*. Berlín Springer. Berlín.

[369] Wall, G. 1986. *Exergy -A useful concept*. Physical Resource Theory Group. Chalmers Bibliot. Trick. University of Technology, Göteborg, Sweden 3,4 EOLSS Publisher.

[370] Wall, G. 2002. *Conditions and tools in the design of energy conversion and management systems of a sustainable society*. Energy Conversion & Managemen, 43 pp. 1235-1248. Pergamon.

[371] Wallace, J. 1996. *Hydrological processes*. Inst. Hydrol. Ann. Rep. 5 pp. 25-34.

[372] WEC 2007. *Survey of Energy Resources*. World Energy Council.

[373] White, D.E.; Hem, J. L. and Waring, G.A. 1963. *Data of Geochemistry. Chemical composition of sub-surface waters*. 6th Edition Bull. 440-F. U. S. Geological Survey.

[374] WHO 1996. *Hardness in Drinking Water. Background document for development of WHO Guidelines for Drinking-water Quality*. 2nd edition. World Health Organization.

[375] Williams, E.D.; Ayres, R.U. and Heller, M. 2002. *The 1.7 kilogram microchip: Energy and material use in the production of semiconductor devices*. Environmental Science and Technology 36 (24).

[376] WMO 2004. Soil Moisture- Details of Recommended Variables. World Meteorological Organization. Available at: www.wmo.ch/web/gcos/terre/variable/slmois.html

[377] World Bank 2003. *Environmental Flows: Concepts and Methods Water Resources and Environment.* Technical Note C.1. Davis, R. Hirji, R. Available at: http://www.ourwater.com.au

[378] World Data Center of Meteorology 2008. *Meteorological data Satellite and Information Service*. Asheville. NOAA

[379] WHO 2003. *Water Sanitation and Health (WSH)*. World Health Organization. Available at: www.who.int/water_sanitation_health/wastewater

[380] World Wide Fund for Nature 2004. *Analysis and socio-economic assessment of the Ebro transfers included in the Spanish National Hydrological Plan (SNHP)*. Spanish Parliament.

[381] WRI 2001. *Industrialization: Heavy Metals and Health*. World Resources Institute. Washington, DC.

[382] WWC. 1999. *Water GAP 2.0*. World Water Council.

[383] WWC 2009. World Water Council web page. Available at: http://www.worldwatercouncil.org/

[384] WWF-Adena, 2008. *Planeta Vivo*. World Water Fund for Nature.

[385] Yuri, G.K. 1959. *The initial atmospheres of planets*. Nature, 4 pp. 25-29.

[386] Zaleta-Aguilar, A.; Ranz, L. and Valero, A. 1998. *Towards a Unified measure of renewable resources availability: The exergy method applied to the water of a river*. Energy Conversion Management. Vol. 39 nº 16-18 pp. 1911-1917. Pergamon.

[387] Zalewski, M.; Janauer, G.A. and Jolankai, G. 1997. *Ecohydrology. A New Paradigm for the Sustainable Use of Aquatic Resources*. IHP-V. Technical Documents in Hydrology nº 7. UNESCO, Paris.

NOMENCLATURE

ABVC: Absortion Vapour Compression

ADVC: Adsortion Vapour Copression

aEmI: Areal Empower Intensity

A.G.E: Asociación de Geógrafos Españoles

ATLL: Ter-Llobregat Water Board

BD: Brine

bgl: background level

CAT: Tarragona Water Consortium

CCB: Costa Brava Consortium

COMP: Reference environment, without organic matter

CONC: Reference environment, with organic matter

CURI: Chemical use river index

CVC: Chemical Vapor Compression

CVR: Rainfall Variation Coefficient

CW: Cooling Water

CWA: Catalan Water Agency

DPP: Degrader Pays Principle

DASR: Desalination aquifer storage and recovery

D: Distilled water

DO: Dissolved Oxygen

EC: Environmental Cost (minimum)

EC^*: Environmental Cost

ED: Electro-Dialysis

ELA: Entodades Locales del Agua

esEC: Economic Service Cost

ecIRC: Economic Integral Replacement Cost

ecRRC: Economic Remainig Resource Cost

ecSC: Economic Service Cost

EEC: Economical Exploitable Capability

EF: Environmental Flow

EFA: Envrionmental Flow Assessment

EFMs: Environmental Flow Methodologies

EFR: Environmental Flow Regimen

EQS: Environmental Quality Standard

ES: Exploitation State

EV: Environmental Value

F: fuel

FC: Financial Cost

FCR: Full Cost Recovery Principle

F_RRI: Fuel-Residue River Index

FS: Future State

FV: Finantial Value

GAV: Gross Value Added

GDP: Gross Domestic Product

GEP: Good Ecological Potential

GES: Good Ecological Status

GIS: Geographic Information System

GTC: Gross Theorical Capability

HC: Hydrological Cicle

HP: Hydraulic Power

HS: High State

IBC: Inland Basins of Catalonia

ID: Reach identification number

IWRM : Integrated Water Resources Management

IRC: Integral replacement Cost (Minimum)

IRC*: Integral Replacement Cost

LDI: Lanscape Development Intensity Index

LDM: Land Digital Model

LU: Percentage of the total area of influence in a land use

MF: Maintenance Flow

MCL: Maximum Contaminant Level

MEE: Multi Effect Evaporation

MSF: Multistage Flash

N: Nitrogen

NF: Nano Filtration

NPP: Net Primary Productivity

NaF: Sodium fluoride

NS: Natural State

OP: Osmotic Power

OS: Objective State

P: Phosphor

Pr: product

PH: Physical Hydronomics

PURI: Potencial Use River Index

PV: Photovoltaic

pot: potential

PPP: Polluter Pays Principle

proc: process

prod: product

PS: Present State

PTC: Parabolic Though Collectors

QBM: Basic Maintenance Flows

QPV: Variable percentages flows

R: Reference State

RE: Reference Environment

RES: Renowable Energy Sources

RO: Reverse Osmosis

RRC: Remaining Resource Cost (Minimum)

RRC*: Remaining Resource Cost

RRI: Residue River Index

RS: Real State

RV: Resource Value

S: Waste Stabilization ponds and physico-chemical in the primary (waste-water treatment technology)

SC: Service Cost (minimum)

SC*: Service Cost

SE: Solar Energy

SEE: Single Effect Evaporation

SN: Secondary and Nitrogen and phosporous elimination (waste-water treatment technology)

SNR: Secondary plus N-P elimination and reuse (waste-water treatment technology)

SR: Secondary and Reuse (waste-water treatment technology)

SRP: Soluble Reactive Phosphoros

TDS: Total disolved Solids

TEC: Technical Exploitable Capability

ThO: Theoretical Oxygen Demand

TS: Total Solids

TSS: Total Suspended Solids

TVC: Thermal Vapor Compression

UF: Ultra Filtration

UV: Ultraviolet lights

WA: Water Act

WR: water resource

WQM: Water Quality Models

WTP: Water Treatment Plant

WWTF: Wastewater Treatment Facility

WWTP: Wastewater Treatment Plant

WWW: World Water Week

MATHEMATICAL VARIABLES

a: activity (mol/l)

a_i: number of nucleotides

aEmI: Areal Empower Intensity (sej/ha yr)

b: specific exergy (kJ/kg)

$\bar{b}$: specific exergy (kJ/mol)

B: exergy (kJ)

BOD: Biological Oxyden Demand (mg/l)

c: velocity (m/s)

C: Salts concentration (ppm)

CC: chemical compounds (kg$_{\text{chemical compounds}}$/kg$_{\text{treated water}}$)

COD: Chemical Oxigen Demand (mg/l)

COP: Coeficient of Performance

Cp: Specific Heat (kJ/kg K)

E^*: Exergy cost (kJ/kg)

EC^*: Environment Cost (J/yr)

EIMV: Emergy Intensity os Monetary Value (sej/euro)

Em: Emergy (EmJ)

En: Energy (J)

ERC: Exergy Replacement Cost

ex: specific biological exergy (kJ/kg)

Ex: biological exergy (kJ)

Ft: Fat flow (kg/m^3 treated water)

g: gravitational force (m/s^2)

GEmP: Gross Energy Product (sej/yr)

g_i: percentage of repeating genes (dimensionless)

h: altitude (m)

HV: heating value (kJ/kg)

I: ionic force

IRC^*: Integral Replacement Cost (J/yr)

IW: Imput Water flow (m^3/s)

IWSI: Irrigation Water Salinity Index

k^*: Unit Exergy Cost

m: molality (moles/kg)

$\dot{m}$: mass flow (kg/s)

M: molecular mass (g/mol)

MemV: Marginal Emergy Product (sej/m^3)

N: Mol number

p: probability

P: pressure (kJ/m^3)

Q: Flow (m^3/s)

$\bar{Q}$: Heat (kJ or kJ/m^3)

R_C: Recovery Ratio (dimensionless)

RRC^*: Remaining Resource Cost (J/yr)

Slg: Sludge flow (kg/m^3 treated water)

SC^*: Service Cost (J/yr)

seJ: solar emJoule

SERC: Specific Exergy Replacement Cost

Sn: Sand flow (kg/m3 treated water)

T: Temperature (K)

Tr: Quality emergy transformity factor (EmJ/J)

TDS: Total Dissolved Solids (mg/l)

TOC: Total Organic Carbon (mg/l)

TOD: Total Oxygen Demand (mg/l)

TW: Treated Water flow (m^3/s)

V: Volume (m3)

W: Electricity flow (kWh/m^3)

x: mass fraction (mol/kg)

$\bar{x}$: molar fraction (dimensionless)

GREEK VARIABLES

α: efficiency coeficient

β: genetical factor

Δ: Gap

ΔG_f: Formation Energy

η : efficiency

ϕ : efective diameter of the ion solution

γ: activity coefficient (dimensionless)

ν: specific volume (m^3/kg)

μ: electrical potential

Π: osmotic pressure (Pa)

ρ: density (kg/m^3)

θ_i: Carnot's factor

SUBSCRIPTS

BD: Brine

c: concentration

cat: catchment

CC: Chemical Compounds

ch: chemical

ch,ne: Chemical exergy of the n element

cool: cooling

CW: Cooling water

D: Distilled water

des: desalination

eco: ecological

exp: expected

f: formation

geop: geopotential

H_20: Water

HP: heating pump

i: substance i

inf: info

IM: inorganic matter

IW: input water

man: maintance

MF: Minimun Flow

NR: non-renewable

NS: Natural State

OM: Organic matter

OS: Objective State

OW: Output flow

phy: Physical

pot: potential

PS: Present State

r: real

ret: return

RS: Real State

S: salt

SS: suspended solids

ABREVIATIONS IN THE REFERENCES

AERE: Association of Environmental and Resource Economics

APHA: American Public Health Association

AWWA: American Water Works Association

CLC: Corine Land Cover

CAST: Council for agricultural Science and Technology

CEC: California Energy Commission

CGIAR: Consultative Group on International Agricultural Reseach

COAGRET: Coordinadora de Afectados por Grandes Embalses y Trasvases

CORINE: Coordination of information of the environment

CWA: Catalan Water Agengy

DEH: Australian Department of Environmental Heritage

DOGC :Official Gazette of the Catalan Goverment

EAERE: European Association of Environmental and Resource Economics

EC: European Community/European Commission

EEA: European Environment Agency

EIA: Energy Information Administration

EMIS: Euro-Mediterranean Information System

EPA: Environmental Protection Agency

ESCWA: Economic and Social Commission for Western Asia

ES: European States

EU: European Union

EPA-US or EPA: Environmental Protection Agency (United States)

FAO: Food and Agriculture Organization

FNCA: New Water Culture Foundation (Fundación Nueva Cultura del Agua)

GA: Gobierno de Aragón

GEFN: Global Environmental Flows Network (eFlowNet)

GEMS: Global Environmental Monitoring System

GC: Generalitat de Catalunya

GWP: Global Water Partnership

GWI: Global Water Inventory

IBRD: International Bank for reconstruction and development.

ICOLD: International Commission on Large Dams

IDA: International Development Asociation

IDAE: Instituto para la Diversificación y Ahorro Energético

IHE: Institute for Water Education.

IHP: International Hydrological Program

IMPRESS: Impacts and Pressures Report

INBO: International Network of Basin Organizations

ISAER: International Society for Research

ISEE: International Society of Ecological Economics

ITA: Aragonian Technological institute (Instituto Tecnológico de Aragón)

IWE: Institute for Water Education

IWMI: Integrated Water Mangement Institute

IWRM: Integrated Water Resource Management

MDG: Millennium Development Goals

MOPTMA: Ministry of Public Works, Transport and Environment

MSU: Missisipi State University

NBER: National Bureau of Economic Research

NIE: National Institute for Statistics

NLWRA: National Land and Water Resources Audit

OECD: Organization for Economic Cooperation and Development.

QUAL2K: Stream and water quality Model

SEEAW: System of Envinonmental – Economic Accounting for Water

SIWI: Stockholm International Water Institute

SNA: System of National Accounts

SNHP: Spanish National Hydrological Plan

SWAT: The Soil and Water Assissment Tool

SWH: Swedish Water House

UN: United Nations

UNCEEA: United Nations Committee of Experts on Environmental-Economic Accounting

UNEC: United Nations Statistical Commission

UNEP: United Nations Environment Program

UNESCO: United Nations Educational, Cientific and Cultural Organization

US EPA: United Nations Evaluation Protection Agency

USAID: United States Agency for International Development

WEAP: Water Evaluation and Planing System

WDM: Water Demand Management

WFD: Water Framework Directive

WHO: World Health Organization

WMO: World Meteorological Organization

WPCF: World Print and Comunication Forum

WRI: World Resource Institute

WWAP: World Water Assesment Program

WWC: World Water Council

WWDR: World Water Development Report

WWF: Worl Wide Fund for Nature

LIST OF FIGURES

LIST OF TABLES