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Exergy assessment of topsoil fertility

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ABSTRACT

Soil degradation, affecting around 38% of the world's cropland, threatens the global food supply. Due to the soil's complexity, the measure of soil degradation that involves the loss of soil fertility due to crop system management processes represents an unsolved problem. Exergy is a property with the potential to be used in soil fertility and/or degradation analysis. A methodology to determine the exergy value fenced in a fertile soil due to its inorganic and organic components is established in this study and will be applied to evaluate soil fertility, degradation, and quality. As a first step, the exergy of perfect topsoil with optimum characteristics called "OptSOIL" is determined. The "OptSOIL" is established by agronomic expertise and will allow establishing a general theoretical reference suitable to execute exergy assessments of soils and compare the degradation grade of any soil concerning the best possible. Consequently, we introduce a perfect fertile planetary crust made of "OptNUT" and "OptSOM" invariant and independent of the different local textures, but not independent of their water content and aeration. We call this imaginary crust -copiously fertile- Pristinia as opposed to Thanatia, a dead state referring to abiotic resources. Thus, any real agricultural soil will be an intermediate soil between Pristinia and Thanatia. This idea might serve to quantitatively diagnose an assessment of all the concepts by which soil is degraded. The methodology has been validated through laboratory agronomic tests for different soils, concluding that exergy is a rigorous indicator to measure topsoil fertility.

1. Introduction

Valero and Valero (2014), Valero et al. (2011a) developed a reference baseline to evaluate the planet's abiotic resources in previous studies. This reference baseline was called Thanatia and represented a degraded planet where all resources would have been extracted and dispersed throughout the Earth's crust. It is composed of a degraded atmosphere, hydrosphere, and upper continental crust. Particularly for the upper continental crust, it represents the starting point to assess the exergy of mineral capital on Earth because it provides the concentration of the around 300 most abundant elements found in the Earth's crust.

The degradation of the mineral capital is an important source of concern since the transition to low carbon technologies will require a considerable amount and variety of raw materials, some of which are scarce and with serious supply problems (Calvo et al., 2016; Valero et al., 2018).

Exergy is defined as a thermodynamic property that measures the quantity and quality of any resource and exergoecology is a discipline whose objective is to evaluate natural resources through the exergy property (Valero and Valero, 2014). Exergoecology has been widely developed in the evaluation of water resources, opening the branch called "physical hydronomics" and mineral resources with the branch "physical geonomics". This study, the aims to develop a new and innovative application of exergoecology for the exergy assessment of soil fertility. Like water and minerals, the soil is a valuable and limited natural resource. The irreversible degradation of this resource is a problem and a challenge for securing the world's food supply and the production of biomass and biofuels for the future. Maintaining the quality and fertility of soils is, therefore, a global priority.

The sustainability of the agroecosystems is also an important issue considering that the global population is expected to continue growing, reaching almost 11 to 13 billion in 2100 (United Nations, 2019).

Abbreviations: FAO, Food and Agricultural Organization; SOM, Soil organic matter; OM, Organic matter; SOC, Soil organic carbon; OC, Organic carbon; HHV, Higher heating value; OptSOIL, Optimum topsoil established; OptTEXT, Optimum topsoil texture; OptNUT, Optimum topsoil nutrients content; OptSOM, Optimum topsoil organic matter content.

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Consequently, food demand will continue to grow and is expected to be satisfied, for example, by increasing about 49 percent in the agricultural production required by 2050 (Food and Agriculture Organization of the United Nations, 2019). Crop production yield has been raised, employing intensive agriculture based on high inputs of inorganic fertilizers and pesticides, resulting in severe environmental impacts, erosion, and soil quality loss. The agricultural sector causes approximately 25 percent of the global greenhouse gasses (Food and Agriculture Organization of the United Nations, 2019). Besides, degradation caused in soils threatens around 40 percent of the land area. In Europe, it is estimated that there are 12 million hectares affected by erosion, which currently generates losses of 1.250 million euros per year (Görlach et al., 2004). The continued degradation of soil fertility due to human actions threatens the sustainability on Earth that will turn into Thanatia.

As it has been done for the mineral capital, one can assess soil fertility through exergy. However, for an exergy evaluation of soil, the Thanatia model is not enough since it does not consider the specific attributes that make a given soil fertile. Therefore, it is necessary to establish an adequate methodology that serves as a starting point to evaluate soil fertility.

FAO defines soil fertility as "the capacity of the soil to support the growth of plants on a sustained basis yielding quantities of expected products that are close to the known potential" (Gachene and Kimaru, 2003). Soil Science Society of America defines soil quality as "the capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity" (Karlen et al., 1997). Soil quality can be considered for agricultural and natural ecosystems where the main objectives are to maintain environmental quality and biodiversity conservation. The decline in soil quality caused by its improper use or poor management, usually for agricultural, industrial or urban purposes is defined as soil degradation.

This study focuses on agricultural soils. Agricultural soils are complex systems formed by physical, chemical, and biological properties interacting with each other. Due to this complexity, a unified approach does not exist to evaluate soil fertility or soil quality despite the high number of studies performed (Arshad and Martin, 2002).

The incapacity of using a single indicator in the characterization and evaluation of a soil is one of the main and most important disadvantages that can be found in the study of the soil system (Bongiorno et al., 2019; Bünemann et al., 2018; Dexter, 2004; Johannes et al., 2019). Due to the complexity of soil and a large number of factors and parameters that interact in the system, studies have been found in the literature that focuses on determining a "minimum data set" (MDS) of soil characteristics with the most significant effect on quality (Garrigues et al., 2012; Reynolds et al., 2009, 2008; Thoumazeau et al., 2019; Xu et al., 2017).

Then, this study use exergy as a unifying tool to assess soil fertility and degradation to lay the foundations of the fourth dimension of Thanatia: soils and its fertility assessment.

2. Definition of an optimum soil

In any exergy evaluation, it is necessary first to define a reference state. Usually, a reference state is contemplated a dead figure, the most degraded state with the minimum exergy (Valero et al., 2011). In soil, our initial endeavor has been to determine the minimum attributes above which the system is inefficient, and a plant's growth is not possible (Valero et al., 2019). Nevertheless, the implementation of an optimum level is more appropriate in the case of fertile soils study. In this way, to assess the degradation and deterioration suffered by soil, Szargut's reference environment and the baseline defines as Thanatia will be applied to define an optimum state called "OptSOIL". Instead of considering the degraded worst case as a reference, we adopt a new strategy, proposing an optimum soil that allows us to analyze all real soils as deviations from the optimum towards Thanatia.

The establishment of the "OptSOIL" will provide an ideal top-level by quantifying the exergy content of the optimal fertile soil selected according to the chemical, concentration, and comminution exergy from the dispersed state Thanatia.

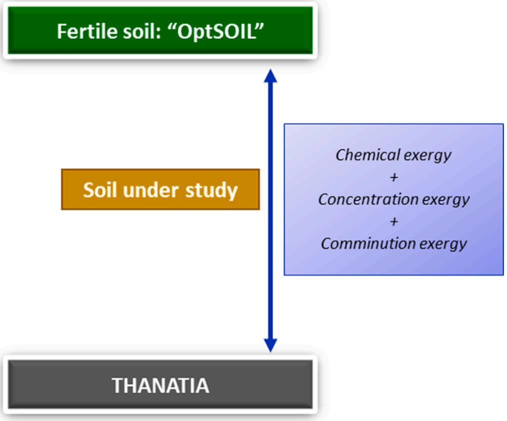

Fig. 1. Representation of the references selected in the methodology: "OptSOIL" as optimum vs. Thanatia as a dead state.

Although "OptSOIL" will be established using agronomic values, our objective is far from providing agronomic recommendations. Furthermore, agricultural soil preferences depend not only on intrinsic characteristics but also on other factors such as crop selection or climate conditions. On the planet, there are numerous fertile soils following their location and climate. Thus, optimum soil does not exist from an agronomical point of view. That said, the purpose of the definition of "OptSOIL" is to establish a general theoretical line that will allow an exergy evaluation of soil degradation (Fig. 1).

The main components that define fertile soil and a methodology to calculate its exergy are identified and developed in this study. Furthermore, we select these components' levels to establish the "OptSOIL" needed as a reference state.

3. Assessment of the inorganic part of the soil

A great variety of interactions between the different parameters and properties take place in the soil. Soil parameters are categorized into physical, chemical, and biological properties.

The texture is one of the soil parameters included in the physical properties. Texture plays an important role in the soil as it defines soil porosity. The texture also influences other physical properties such as soil aeration, plant available water, compaction, bulk density, structure. In addition to physical properties, texture also impacts chemical properties. Different textural composition influences the processes of nutrient retention, soil permeability and breakdown of organic matter. In addition, aeration and water holding capacity influence the microorganisms' biological interactions in the soil processes.

The interactions of texture on soil properties cause the texture to be indirectly responsible for the biogeochemical processes of the soil system. Therefore, as a representative for physical properties, texture has been selected as a key to be considered to quantify soil exergy.

On the other hand, as a representation of chemical properties, nutrients have been chosen. Nutrients play a very significant role in the soil because their concentration and composition influence the biogeochemical cycles of the soil and the development and growth of the plant. Therefore, they are essential in healthy soils (Valero et al., 2020).

3.1. *Texture*

The texture is defined by the three primary particles' size distribution: sand, silt, and clay. Each of these primary groups has a distinct particle size. According to the US Department of Agriculture (USDA) classification, sand is formed by particles smaller and larger than 2 mm and 0.05 mm, respectively. Silt particles are smaller than 0.05 mm and larger than 0.002 mm. Clay is constituted by particles smaller than 0.002 mm. The texture of each soil is determined by the ratio of the elemental particles in the soil.

The various properties influenced by texture can be shown, for example, in sandy soils. These are loose and gritty systems, which have few and large pores. Therefore, these soils are often well-aerated and permeable, and thus they cannot provide the plants with high amounts of water and nutrients stored. On the contrary, clay soils are sturdy systems with many pores but smaller pore sizes. As a result, this kind of soil is more condensed, less permeable, and can be a major reservoir of water and nutrients (Kirkham, 2014; Weil and Brady, 2017; White, 2006).

Although there is no optimal soil texture suitable for any crop and weather, loam texture can be selected. Loam texture, situated around in the middle of the USDA-NRCS (1999) texture triangle, is thought to have optimum characteristics among sandy, silty, and clay soils (FAO). Generally, loam soils blend the three elemental soil particles with equal quantities of silt and sand and smaller clay particles. The clay fraction influences soil properties more significantly and more robustly, such as cation exchange capacity and water retention. Thus, the required proportion of clay is lower compared to the silt and sand fractions.

$$Relative\ Abundance_{mineral}\ (mass\%) = \frac{Earth's\ crust\ mineral\ abundance\ (mass\ \%)}{\sum Mineral\ Abundance\ of\ the\ group} \cdot 100, \tag{1}$$

In loam soils, water retention capacity and nutrients reservoir are more beneficial than in sandy soils, while their aeration, drainage, and management characteristics are more advantageous than in clay soils (Hillel, 2008). Moreover, loams are potently fertile soils and can be suitable for various crop types such as cereals, potatoes, oilseed rape, and sugar beet, among others (Finch et al., 2014). Based on (Jaja, 2016), one of the best loam's textures is around 40, 40, and 20% of sand, silt, and clay, correspondingly. Therefore, these values composed what we denoted "OptTEXT", are chosen as characteristics of the texture in our "OptSOIL".

3.1.1. *Mineral composition of the texture*

To establish the mineral composition of the different textural fractions, the mineral composition proposed in (Weil and Brady, 2017) was adopted, as shown in Table 1.

Table 1 indicates four major mineral categories in soil: quartz, primary silicate minerals, secondary silicate minerals, and other secondary minerals. Sand and silt particles are mainly composed of quartz. In clay particles, they have predominantly secondary silicate minerals and a minor quartz fraction. The components contained in each category of minerals have been established by extensive and completely bibliographic analysis.

Silica minerals are composed of quartz, which has a course packing of the crystal structure, and significant activation energy is required to modify the bonds. Resulting in very stable quartz and, hence, an inactive and non-soluble mineral (Huang and Wang, 2005).

Primary silicate minerals combine feldspars, amphiboles, micas, olivines, and pyroxenes, among other things. Feldspars are reservoirs of potassium and calcium macronutrients. Micas are the leading supplier of potassium in soils. In the case of olivines, minerals provide the concentration of the nutrient magnesium and iron. Pyroxenes, amphiboles, and olivines are crucial in keeping soil carbon from mineralization and losses to the atmosphere (Hillel, 2008; Huang and Wang, 2005; Schulze and Lafayette, 2005; Sparks, 2003; Weil and Brady, 2017).

Secondary silicate minerals are aluminosilicates, identified as phyllosilicates (Hillel, 2008; Schulze and Lafayette, 2005; Sparks, 2003; Weil and Brady, 2017; White, 2006).

Other secondary minerals are typically metallic oxides, carbonates, and sulfates. This mineral group is present in soils but generally at minor concentrations. Despite their minor concentration, oxides are significant in chemical procedures. For instance, manganese oxides offer a resource of manganese vital for plants and can adsorb heavy metals (Schulze and Lafayette, 2005; Sparks, 2003; Weil and Brady, 2017).

We have accepted that each mineral's relative abundance in each category is related to the abundance of the minerals in the Earth's crust, as defined in (Valero and Valero, 2014), based on a model established in (Valero, 2008). Hence, the following equation is employed (Eq. (1)).

3.1.2. *Texture chemical exergy*

The relative abundance established was applied to determine the chemical exergy, jointly with the exergy values of the minerals in the Earth's crust (Valero and Valero, 2014).

$$Ex_{am,ch}\,(J/kg) = \frac{\left[\frac{Ex_{ch,mineral}(kJ/mol)}{Molecular\,Weight(g/mol)}\right] \cdot Relative Abundance_{mineral}(mass\%) \cdot 10^6}{100}, \tag{2}$$

As shown in the equation below, the chemical exergy is calculated for the case of hematite. It has a chemical exergy value of 3.30 kJ/kg with the data of the abundance in the Earth's crust and the relative abundance in primary silicate minerals.

Table 2
Chemical exergy of the most relevant soil minerals composition.

	Exergy (kJ/kg)
Quartz	13.65
Primary silicate minerals	93.80
Secondary silicate minerals	138.54
Other secondary minerals	386.86

Table 1
Calculations of the soil particle composition (in percentage) were obtained through the information and graphics of Weil and Brady (2017).

	Quartz (%)	Primary Silicate Minerals (%)	Secondary Silicate Minerals (%)	Other Secondary Silicate Minerals (%)
Sand Particles	77	17.8	0	5.2
Silt Particles	59	14.2	7	19.8
Clay Particles	16.8	0.9	62.5	19.8

$$Ex_{ab,ch,\ Hematite}\ (kJ/kg) = \frac{\left[\frac{17.23\ kJ/mol}{159.68g/mol}\right]\cdot 3.05\ mass\%\cdot 1000}{100} \cong 3.30kJ/kg$$

We have proceeded in this way for each mineral of each category. A complete inventory of the chemical exergy and abundance in mass percentage of all the minerals studied can be seen in supplementary documents (Tables C.1, C.2., C.3., C.4.)

After obtaining the contribution of every mineral of the respective categories, the chemical exergy was obtained with Szargut's reference environment (Szargut, 1989), per unit of mass values of quartz, primary silicate, secondary silicate, and other secondary minerals is determined. It could be appreciated that the secondary silicate minerals have the greatest specific chemical exergy and quartz has the most negligible specific chemical exergy value (Table 2).

Based on the data calculated in Table 2 and the quantity of every category of minerals in sand, silt, and clay divisions (Table 1), every textural fractions' specific chemical exergy is estimated (Table 3).

Every particle size has a specific chemical exergy value. The data indicates the substantial impact and dominance of clay in the soil texture's specific chemical exergy. This is so because the clay fraction has the three mineral groups with the most significant exergy values. On the contrary, sand and silt fractions have quartz, a great and most stabilized mineral, hence the most negligible chemical exergy value.

Successively, by studying the values of the three particle sizes that establish soil texture (Table 3) and Eq. (3), one can determine the soil texture's chemical exergy.

$$Ex_{ch,texture}\ (kJ/kg) = \frac{Sand(\%)\cdot Ex_{ch,sand}}{100} + \frac{Silt(\%)\cdot Ex_{ch,silt}}{100} + \frac{Clay(\%)\cdot Ex_{ch,clay}}{100} \tag{3}$$

In the case of the "OptTEXT" chemical exergy will have a value of 95.26kJkg^{-1}.

$$Ex_{ch,texture}(kJ/kg) = \left[\frac{40\%\cdot 47.32kJ/kg}{100}\right]_{sand} + \left[\frac{40\%\cdot 107.67kJ/kg}{100}\right]_{silt} + \left[\frac{20\%\cdot 166.33kJ/kg}{100}\right]_{clay} \cong [18.93]_{sand} + [43.07]_{silt} + [33.26]_{clay} \cong 95.26\ kJ/kg$$

3.1.3. Texture concentration exergy

As well as the chemical exergy, a substance has concentration exergy because of its specific structure. A substance that is higher in concentration than in the reference state can do work, and thus it has concentration exergy. The concentration exergy related to texture is determined by applying the relative abundance.

The minimum theoretical work needed to concentrate a substance from an ideal mixture of two components is given by the concentration exergy, which derives from the expression of the entropy of mixing (Eq. (4)). Thus, the concentration exergy (Eq. (5)) of each one of the minerals that form the soil is estimated as the variation among the mineral concentration in the "OptSOIL" state, and the average concentration in the Earth's crust derived from the abundance in mass percentage in Thanatia established in Valero et al. (2011,2013,2014,2011b).

$$\sigma = -R\sum_{i=1}^{2} x_i \ln x_i \tag{4}$$

σ is the minimum entropy generation of mixing, x_i is the concentration of a mineral or substance, R is the universal gas constant (8.314·10^{-3}kJmol^{-1}K^{-1}).

$$Ex_{c,mineral}(kJ/mol) = -RT_0\left[\ln x_i + \frac{(1-x_i)}{x_i}\cdot \ln(1-x_i)\right], \tag{5}$$

R is the universal gas constant (8.314·10^{-3}kJmol^{-1}K^{-1}), T_0 is the standard ambient temperature (298.15 K), x_i is the concentration of a mineral or substance.

Each mineral or substance has specific concentration exergy. The variation among the concentration of the mineral in the Earth's crust with the average mass concentration of x_c (g.g^{-1}) and the concentration of the mineral in the "OptTEXT" selected, with a mass concentration of x_m (g.g^{-1}), is the concentration exergy per unit of mol of the mineral. This variation indicates the lowest exergy required to constitute and concentrate the mineral from the Earth's average crust to the "OptTEXT" or the reverse (Valero et al., 2013; Valero and Valero, 2014).

$$\Delta Ex_c = Ex_c(x_i = x_c) - Ex_c(x_i = x_m), \tag{6}$$

Table 4 indicates x_m the involvement of every category of soil minerals for the "OptTEXT" designated as a reference state. Based on these data, the estimate of the value of x_m for each mineral involved in every mineral category is feasible.

Consequently, the concentration exergy per unit of mol, and hence per unit of mass, is estimated for all the soil minerals (quartz, primary silicate minerals, secondary silicate minerals, and other secondary minerals) (Valero et al., 2020). In the "OptTEXT", the total concentration exergy value is calculated as 492.1 kJkg^{-1}.

3.1.4. Texture comminution exergy

Considering the method reported in (Valero and Valero, 2014, 2012), the specific comminution exergy for the texture elements has been determined. As an example, the comminution exergy per unit of mass of clay partition in hematite is 0.245 kJkg^{-1}, which is a minor amount compared to the concentration exergy per unit of mass 23.0 kJkg^{-1}. Because of the small influence of the comminution exergy, only chemical and concentration exergy will be studied to calculate the total texture exergy. This agrees with what Valero et al. (Valero and Valero, 2014, 2012) demonstrated, affirming that the comminution exergy is irrelevant related to chemical and concentration exergy values.

3.2. Nutrients

Nutrients are usually categorized into two groups: the macronutrients, which are needed in elevated concentrations, and the

Table 3
Chemical exergy of sand, silt, and clay as the three parts of soil texture, adapted from (Valero et al., 2020).

	Exergy (kJ/kg)
Sand	47.32
Silt	107.67
Clay	166.33

Table 4
Impact of each category of minerals in the "OptTEXT". The contribution is established on the quantity of sand, silt, and clay in the reference state.

	"OptText" X_m (g.g^{-1})
SiO_2	0.5776
All Primary silicate mineral	0.1298
All Other secondary minerals	0.1396
All Secondary silicate minerals	0.1530

Table 5
Optimal concentration of "OptNUT", chosen from bibliography and the mass fraction for nutrients in the "OptSOIL" state (x_m).

	Form uptake by plants	OptNUT (kg/ha)	Refs.	$x_m(gg^{-1})$
Nitrogen	NH_4^+/NO_3^-	8,400	Feiza et al. (2011), Mukherjee and Lal (2014)	1.27E-03
Phosphorus	$HPO_4^{2-}/H_2PO_4^-$	70.0	FAO. et al. (2006); Horneck et al., (2011)	2.50E-04
Sulfur	SO_4^{2-}	40.0	FAO. et al. (2006); Horneck et al., (2011)	2.50E-05
Magnesium	Mg^{2+}	840.0	Horneck et al., (2011)	4.00E-03
Calcium	Ca^{2+}	11,206	FAO. et al. (2006); Hazelton and Murphy (2017)	3.00E-04
Potassium	K^+	700.0	FAO. et al. (2006)	2.30E-05
Iron	Fe^{2+}/Fe^{3+}	7.0	FAO. et al. (2006)	2.00E-06
Manganese	Mn^{2+}	14.0	FAO. et al. (2006)	2.50E-06
Copper	Cu^+/Cu^{2+}	5.6	Fageria (2001); FAO. et al. (2006); Horneck et al., (2011)	5.00E-06
Zinc	Zn^{2+}	4.2	Fageria (2009); FAO. et al. (2006); Horneck et al., (2011)	1.50E-06
Nickel	Ni^{2+}	1.1	Siqueira Freitas et al. (2018)	1.43E-05
Molybdenum	MoO_4^{2-}	0.6	FAO. et al. (2006)	3.93E-07
Boron	$B(OH)_3$	2.8	Ahmad et al. (2012); Horneck et al., (2011)	2.14E-07
Chlorine	Cl^-	56.0	Fageria (2009); Horneck et al. (2011)	1.00E-06
Sodium	Na^+	64.3	FAO. et al. (2006)	2.00E-05
Silicon	$Si(OH)_4$	294.0	Liang et al. (2015)	1.05E-04
Cobalt	Co^{2+}/Co^{3+}	4.2	Mengel and Kirkby (2001)	1.50E-06
Selenium	SeO^{2-}/SeO_3^{2-}	0.3	Dhillon and Dhillon (2003)	1.07E-07
Aluminum	Al^{3+}	3,831	Asher (1991; U.S. Environmental Protection Agency, 2003)	1.37E-03

micronutrients required in lower concentrations but not less significant, all of them are presented in Table 5. Additionally, sodium, silicon, cobalt, selenium, and aluminum are recognized beneficial elements that promote growth but are only necessary for specific species or in particular circumstances (Marschner, 2011; Valero et al., 2019).

Nutrients in agricultural soils undergo immediate alterations from outside forces but with an intermediary timescale of alteration due to inside procedures and exchanges. These variations might happen over days to months (Wiesmeier et al., 2018), forming helpful knowledge for the development of soil quality or degradation.

This work's aim is far removed from assessing all the procedures and components implicated in acquiring every nutrient or, as previously discussed, from providing suggestions appropriate for harvest management. Following this, the most favorable values for determining the "OptSOIL" from several resources are chosen, in most situations applying average values between the different references quoted (Table 5).

The exergy of the nutrient is calculated by studying a combination of substances whose quantitative formula is presented in Table 5. What we could name "OptNUT", the deficiency or overload of one of its elements produces injury to the plant. Thus, it should be the concentration of every of its elements that is the significant property that can be assessed with the concentration exergy, regardless of the detail of which chemical compounds are components of a provided soil.

3.2.1. *Nutrients concentration exergy*

The optimal concentration level of the various nutrients (OptNUT) has been defined based on the literature review. The chosen values and the cations or anions are taken into consideration for every nutrient are presented in Table 5.

The concentration exergy will be calculated based on the concentration of the nutrients chosen (Table 5). A nutrient that is more concentrated than in the reference environment has the potential to do work and hence it has concentration exergy. Then, the variation among the concentration of the nutrient in a reference state with an average mass concentration of x_c (gg^{-1}) and the "OptNUT" selected, with a mass concentration of x_m (gg^{-1}), is the specific concentration exergy of the nutrient (Eqs. (7), (6)). This variation indicates the minor exergy required to produce and concentrate the nutrient to the "OptSOIL" or the reverse (Valero et al., 2013; Valero and Valero, 2014).

$$Ex_{ec,nutrient}(kJ/mol) = -RT_0\left[\ln x_i + \frac{(1-x_i)}{x_i}\cdot \ln(1-x_i)\right] \tag{7}$$

Table 6
Concentration exergy of the diverse soil nutrients in the "OptSOIL".

	Form uptake by plants	C_{opt} (kg/ha)	Concentration x_m (gg^{-1})	C_{SEA} (g/kg)	Concentration $x_{c,sea}$ (gg^{-1})	Concentration exergy (kJ/mol)	Concentration exergy (kJ/kg)
Nitrogen Inorganic	NH_4^+/NO_3^-	3,542	1.27E-03	3.00E-05	3.00E-08	26.40	426
Phosphorus	$HPO_4^{2-}/H_2PO_4^-$	70	2.50E-05	1.90E-04	1.90E-07	12.10	127
Sulfur	SO_4^{2-}	700	2.50E-04	3.99E-01	3.99E-04	−1.16	−29.6
Magnesium	Mg^{2+}	11.206	4.00E-03	4.15E-01	4.15E-04	5.62	140
Calcium	Ca^{2+}	840	3.00E-04	1.28	1.28E-03	−3.60	−148
Potassium	K^+	64.3	2.30E-05	1.08E+01	1.08E-02	−15.26	−664
Iron	Fe^{2+}/Fe^{3+}	5.6	2.00E-06	1.20E-07	1.20E-10	24.10	379
Manganese	Mn^{2+}	7	2.50E-06	4.00E-08	4.00E-11	27.37	490
Copper	Cu^+/Cu^{2+}	14	5.00E-06	1.00E-08	1.00E-11	32.53	592
Zinc	Zn^{2+}	4.2	1.50E-06	3.90E-07	3.90E-10	20.46	313
Nickel	Ni^{2+}	40	1.43E-05	2.71	2.71E-03	−13.01	−135
Molybdenum	MoO_4^{2-}	1.1	3.93E-07	4.80E-04	4.80E-07	−0.50	−8.46
Boron	$B(OH)_3$	0.6	2.14E-07	1.10E-05	1.10E-08	7.36	46.0
Chlorine	Cl^-	2.8	1.00E-06	4.40E-03	4.40E-06	−3.67	−59.4
Sodium	Na^+	56	2.00E-05	1.94E+01	1.94E-02	−17.07	−481
Silicon	$Si(OH)_4$	294	1.05E-04	1.01E-02	1.01E-05	5.80	60.3
Cobalt	Co^{2+}/Co^{3+}	4.2	1.50E-06	2.00E-09	2.00E-12	33.53	569
Selenium	SeO^{2-}/SeO_3^{2-}	0.3	1.07E-07	1.70E-07	1.70E-10	15.98	134
Aluminum	Al^{3+}	3,831	1.37E-03	1.00E-09	1.00E-12	52.15	1,930

The optimum concentration selected has been applied to determine the amount of each nutrient's mass fractions (x_m) in the "OptSOIL". These mass fractions are applied to analyze the specific concentration exergy (Table 5).

We have chosen the concentration exergy of the Earth's crust as a reference state for the texture. However, plants' nutrients are anions and cations in solution and not minerals as it occurs in the texture. Thus, the hydrosphere is selected as a reference state for nutrients. The hydrosphere contains oceans, seas, rivers, rain, ice, and even atmospheric water vapor. The hydrosphere's major factor is oceans that include more than 97% of all Earth's water. In this investigation, the composition of minor elements in seawater, also found in Thanatia and reported in (Quinby-Hunt and Turehian, 1983), will be applied to calculate the mass fraction in the reference state (x_c).

The reference state concentration (seawater) is lower than in the "OptNUT" in certain elements. Therefore, the value of specific concentration exergy is positive. In contrast, if the concentration is higher in the reference state (seawater) than in the "OptNUT" state, the nutrient's specific concentration exergy value is negative.

The total concentration exergy per unit of mass estimated for the nutrients gives a value of 3684.1 $kJkg^{-1}$ (Table 6). As it is indicated, it is considerable support to the total soil exergy in the "OptSOIL".

For a laborious and meticulous exergy assessment of a provided soil, it would be ideal for taking into account all nutrients. Nevertheless, in reality, the evaluation of all 19 nutrients is generally unrealistic. Therefore, we involve only the most significant and simply established nutrients in the calculations: nitrogen, phosphorus, potassium, calcium, magnesium, copper, sodium, iron, manganese, and zinc (Valero et al., 2020). The specific concentration exergy estimated for the chosen nutrients resulted in 1626.3 $kJkg^{-1}$.

4. Assessment of the soil organic matter

Soil organic matter (SOM) is a primary and essential component because it influences all factors of a fertile soil: physical, chemical, and biological properties are linked to the organic matter (OM) fraction (Bünemann et al., 2018; Lal, 2016; Liebig and Doran, 1999; Parisi et al., 2005) (Fig. 2).

In the case of physical properties, SOM influences the structural stability of the soil. Soil aggregates are made up of organic binding agents like polysaccharides and humic acids associated with polyvalent metal cations. Then, SOM interacts with the soil's physical fraction, contributing to the structure, bulk density, and porosity (Amézketa, 1999; Dexter et al., 2008; Hillel, 2004; Pieri, 1992; Schjønning et al., 2012; Tisdall and Oades, 1982; Weil and Brady, 2017; White, 2006). Moreover, SOM improves the water retention in the soil due to the hydrophilic nature and the influence on the structure (Bauer and Black, 1992; Haynes and Naidu, 1998; Huntington, 2003; Minasny and McBratney, 2018; Olness and Archer, 2005). However, the influence and specific relationships remain unclear.

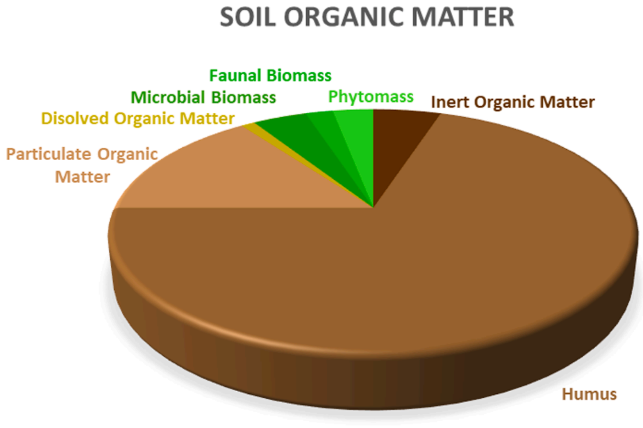

Fig. 2. Representation of all organic materials found in soils and its estimated contribution in SOM.

The content of SOM also influences the chemical properties such as cation exchange capacity, pH, and cation complexes. A fraction of the cation exchange capacity is pH-dependent (Allison, 1973); in other words, soil possesses cation exchange sites activated with increased pH. These cation exchange sites are the carboxyl and hydroxyl functional groups, among others, that form OM (Allison, 1973). In particular, humus represents between 50% and 90% of the cation adsorption capacity on its surface (Weil and Brady, 2017). OM can also behave as a chelating agent. Some of the enclosed cations would be available as reservoirs for the plant (Weil and Brady, 2017; White, 2006).

SOM also influences the soil's biological properties because it is a source of energy and nutrients for soil biota. Differents fractions with different chemical compositions conforming SOM act as a nutrient reservoir for various microorganisms or fauna (Haynes, 2005; Hazelton and Murphy, 2017; Weil and Brady, 2017; White, 2006).

Regarding SOM exergy value, Jørgensen, in previous articles and investigations, had already determined an average exergy value for detritus, 18.7 kJg^{-1}. This value corresponds to an average of green grass's energy values, standing dead vegetation, litter, roots, and green herbs (Jørgensen, 2002, 2001; Jørgensen et al., 2004). Jørgensen considered the approximation that detritus represent the total SOM, equalizing their exergy value.

SOM is a resource with a complex and heterogeneous composition. It is commonly accepted that SOM is composed of rapid turnover carbon, defined as labile organic carbon, and protected or slow turnover carbon, defined as hummus (Adhya et al., 2017; Campbell, 2008; Gregory and Nortcliff, 2013; Haynes, 2005; Lal, 2017; Murphy, 2014; Weil and Brady, 2017). Detritus constitutes a part of the labile organic matter fraction, not the total of SOM. Consequently, the approximation suggested by Jørgensen in which the detritus exergy value is considered similar to the total exergy of SOM is going to be revised. Firstly, according to the updated knowledge of the composition of SOM, an average composition will be selected. Then, an experimental model will be used to calculate its exergy content.

4.1. *Composition of SOM*

Nowadays, due to the significant development and progress of new analytical techniques, such as electron-microscopic, analytical pyrolisis, IR, 13 c-NMR, X-ray spectroscopic, it has been possible to study the composition of OM in greater detail (Jansen et al., 1996; Schulten and Schnitzer, 1997,1995).

In this way, a molecular representation of SOM, which contained 3% of water, was firstly proposed by Schulten and Schnitzer (1997) and subsequently improved by the same authors (Schulten and Leinweber, 2000), also considering the molecule of total humic substance (Schulten and Schnitzer, 1995). The molecule representing SOM contains one trapped trisaccharide, one hexapeptide, and 12 water molecules, one of which is protonated. Then, the elemental formula of this complex is $C_{349}H_{401}N_{26}O_{173}S$, with a molecular weight of 7760.16 $gmol^{-1}$. The hexapeptide is AspGlyArgGluAlaLys with an elemental composition of $C_{26}H_{46}O_{10}N_{10}$. It is chosen because it is formed by the amino acids usually found in soils. The trisaccharide, selected as an example of a sugar molecule, is cellotriose. Cellotriose is considered as a cellulose subunit presented in SOM and has the elemental composition of $C_{18}H_{32}O_{16}$ (Table 7).

Authors like Weil and Brady (2017) or White (2006) exposed the ranges in which the elemental chemical composition of humus may be found. These ranges are in agreement with the chemical formula for humic substances proposed by Schulten and Leinweber. However, other authors disagree with the Schulten and Leinweber model of SOM because it can not explain some of the analytical data obtained (Mao et al., 2000; Piccolo, 2002). This is due to the heterogeneity of the OM, the soil variety, and environmental conditions. Despite that, the molecule proposed by Schulten and Leinweber (2000) has been selected as a representation of the composition of SOM in any given soil to calculate a representing value for exergy of SOM.

4.2. Organic matter exergy value

Like texture, OM is a substance that can do work, and hence it has an exergy value (Jørgensen et al., 2004). In this way, OM's exergy will be calculated through its higher heating value (HHV). The free energy of OM is assumed to be the same as its HHV. Like biomass and municipal solid waste, the HHV of OM reveals the energy it possesses inside. In a combustion process, it is released and converted into heat energy when all the water formed by combustion is in liquid form (Erol et al., 2010).

Several empirical models and linear regressions in the literature estimate the HHV of biomass and municipal solid wastes (Alves et al., 2018; Amen et al., 2020; Bagheri et al., 2019; Erol et al., 2010; Friedl et al., 2005; Kathiravale et al., 2003; Khuriati et al., 2017, 2015; Komilis et al., 2012; Liu et al., 1996; Nzihou et al., 2014; Sheng and Azevedo, 2005; Yin, 2011). The regressions have been developed from the elemental composition (ultimate components), physical composition, and the ash, moisture content, etc., of solid waste (proximate analysis) (Alves et al., 2018; Amen et al., 2020; Bagheri et al., 2019; Erol et al., 2010; Friedl et al., 2005; Kathiravale et al., 2003; Khuriati et al., 2017, 2015; Komilis et al., 2012; Liu et al., 1996; Nzihou et al., 2014; Sheng and Azevedo, 2005; Yin, 2011). Municipal solid wastes and biomass are compounds with a similar chemical composition to OM. Then, the HHV of OM will be estimated with the empirical models as a function of the elemental composition.

The more common models based on ultimate analysis have been studied due to the great amplitude of equations, models, and studies on the higher heating value determination (Corbitt, 1989; Kathiravale et al., 2003; Komilis et al., 2012; Tchobanoglous et al., 1993). Among these equations and models, the most widely and reported in the bibliography are those of Dulong. The Dulong model is suitable for biomass, while the Modified Dulong model is suitable for biomass and municipal solid waste. All the models and linear regressions used to estimate the HHV are empirical and always include an experimental error. Likewise, the models developed and improved in recent years have been compared to Dulong's equation, and the difference was insignificant (Kathiravale et al., 2003). In this way, modified Dulong's model is selected due to its greater versatility concerning the material's composition and origin.

Then, the HHV of the SOM is calculated using the total chemical formula previously selected (Table 8).

Hence, we propose that the exergy of SOM is 19,406.12kJkg^{-1}. This value seems slightly higher than that offered by Jørgensen (18,700 kJ/kg), confirming that his approximation is accurate and reliable.

4.3. Organic matter optimal content "OptSOM"

An optimal level or range of SOM concentration ("OptSOM")in the agricultural system is essential for studying soil quality. For years, an optimal or ideal value for the content of SOM has been investigated.

Table 7
Estimations of the chemical composition and molecular weight of the molecules chosen. Source: Schulten et al. (1996); Schulten and Leinweber (2000); (Schulten and Schnitzer, 1997, 1995).

	Chemical formula	Molecular weight (g/mol)
Total humic substance	$\mathbf{C_{305}H_{299}O_{134}N_{16}S}$	6364.65
Hexapeptide (AspGlyArgGluAlaLys)	$\mathbf{C_{26}H_{46}O_{10}N_{10}}$	658.70
Trisaccharide (cellotriose)	$\mathbf{C_{18}H_{32}O_{16}}$	504.43
Soil organic matter (with 3% of water)	$\mathbf{C_{349}H_{401}N_{26}O_{173}S}$	7760.2

Table 8
HHV calculated of total organic matter in the soil.

		Higher Heating Value (kJ/kg)
Total organic matter	$\mathbf{C_{349}H_{401}N_{26}O_{173}S}$	19,406.12

However, as seen in the previous sections, OM influences and modifies many soil parameters; this is why it has not been possible to establish any standard range (Loveland and Webb, 2003). Consequently, the optimal levels will depend on the soil properties considered in the different studies.

In crop production, a decrease of SOM produces an insufficient nutrient reservoir (84,85). If the organic carbon (OC) content is less than 2% in soil physical properties, the soil structure is vulnerable to decline (Greenland et al., 1975). After all, Spink et al. (2010) concluded that a concentration of soil organic carbon (SOC) of 2% should be considered as a" precautionary threshold." Above this value, no action is required. Nevertheless, below 2% of SOC, soils may have a poor structural condition, and more specific studies should be carried out to determine their agronomic conditions. The 2% threshold in OC has been subsequently used in other studies (Feiza et al., 2011; Haynes, 2005; Mukherjee and Lal, 2014; Olaya-Abril et al., 2017).

Hence, in the definition of "OptSOIL", as a reference soil for assessing soil fertility and degradation, an optimum value for OC of 2% will be selected. Although there are studies where lower OM values do not generate production changes (Johnston, 1991; Kemper and Koch, 1966; Körschens et al., 1998; Loveland and Webb, 2003), the established limit is optimal both in production (also related to nutrients) and in the soil structural aspect.

Commonly, since SOM is estimated to contain 58% of OC, the relation between organic matter and organic carbon is OM/OC $=$ 1,724kgkg^{-1}. In this research, the chemical formula employed for SOM enclosed 54% of OC. Thus, the ratio between organic matter and organic carbon is slightly different (Eq. (8)).

$$SOM\ (\%) = 1.851 \cdot SOC(\%) \tag{8}$$

The value is considered optimal SOC (2%), and Eq. (10) allows obtaining the "OptSOM". The "option" is 3.7%. This value will be the OM concentration in the "OptSOIL".

$$SOM(\%) = 1.851 \cdot 2\% = 3.7\% \tag{9}$$

Thus, to know the contribution of OM in the "OptSOIL", considering the "OptSOM" selected (3.7%) and the proportions of the topsoil chosen (depth: 0,2 m and bulk density: 1400 kg/m^3).

$$\begin{aligned} Ex_{Ch,OM} &= 19,406.12kJ/kg \cdot \frac{3.7}{100} \cdot 1400kg/m^3 \cdot 10,000m^2/ha \cdot 0,2m \\ &= 2.01 \cdot 10^9\ kJ/ha \end{aligned} \tag{10}$$

In conclusion, the "OptSOM" suggested in this paper contributes with a chemical exergy value of 2.01·10^9 kJha^{-1} or 48.0 toe·ha^{-1} (tonne of oil equivalent·hectare^{-1}) to the total exergy of the "OptSOIL".

5. Results and validation

In the previous sections, the methodology for calculating the exergy

Table 9
Exergy values of "OptSOIL".

	Exergy	kJ kg^{-1}	kJ ha^{-1}	toe ha^{-1}
Texture	Chemical Exergy	95.26	2.67E+08	6.3
	Concentration Exergy	492.10	1.38E+09	32.9
	Total exergy	587.36	1.64E+09	39.3
Nutrients	Concentration Exergy	1626.37	4.55E+09	108.7
SOM	Chemical Exergy	19,406.12	2.01E+09	48.0
TOTAL	**Exergy**	**21,619.85**	**8.21**E+09	**196.1**

values of the inorganic fraction of the soil, represented by texture and nutrients, and the organic fraction represented by SOM is detailed. Furthermore, the different components' defined values conforming to the reference state selected as "OptSOIL" are given. Thus, in this section, firstly, the exergy value of the "OptSOIL" is summarised and discussed. Then, it is compared with the exergy values obtained for three soils determined experimentally.

Table 9 shown the exergy values calculate for the previously defined "OptSOIL" (considering a density of 1400 kg m^{-3} and a depth of 20 cm).

The exergy value of the "OptSOIL" calculate with the developed methodology, as a sum of the contributions of "OptTEXT", "OptNUT" and "OptSOM" defined, shows an exergy value of 196.1toe·ha^{-1}. The total texture specific exergy estimated is 39.3 toe·ha^{-1}. As it is shown, the concentration exergy contribution is higher than the chemical. Nutrients are the ones that offer the most significant contribution, equivalent to 108.7 toe·ha^{-1}, which represents 55% of the total. The SOM fraction represents a 48.0 toe·ha^{-1} value, equivalent to 25% of the total.

We validated the developed exergy methodology through the sampling of three soils in a greenhouse pilot test. Samples of 2 to 3 kg were taken homogeneously in a zig-zag pattern at different points of the field and at a depth of 30 cm. Sampling was carried out with a shovel, digging a small V-shaped hole 20 to 30 cm deep. All samples were mixed and prepared for the laboratory by sieving to eliminate any remains of previous harvests. Soil analysis to determine texture, nutrients, and OM was performed.

The greenhouse pilot testing design integrated into each homogeneous block the three types of soil under study. A total of 10 homogeneous distributed pots were prepared for each soil. Experimental conditions were optimal, minimizing external influences and weather conditions, allowing the soil's impact as a whole to be evaluated. Lactuca sativa was planted, and the average weight of leaves and stems, and roots were determined.

Based on the laboratory soil analysis data, each soil was evaluated using the exergy methodology developed in this study. When a value is greater than the “OptSOIL” threshold, the excess is not considered. Values obtained are shown in Table 10.

6. Discussion

As explained in previous sections, soils are complex systems in which many different elements interact. Thus, the three components "OptTEXT", "OptNUT" and "OptSOM" are not independent. For example, the texture influences and affects the soil nutrients due to the interactions between the minerals that form the texture and nutrient ions' elemental particles. OM also interacts with nutrients through mineralization processes and with texture, as OM conforms soil aggregates. Consequently, the independent study of the different components is useful to assign an exergy value to the soil, but fertile soils from an agronomical point of view cannot be understood interpreting each part independently but as a whole.

Fig. 3 shows "OptSOIL" and compares the specific exergy values obtained for different soils under analysis. In all the cases, the "OptSOIL" shows higher values than the studied soils. Soil 1 results in total exergy of 170.8 toe·ha^{-1}. It is the closest one to the "OptSOIL" value (196.1 toe·ha^{-1}). Soil 2 and 3 show a slight difference in their total exergy value (130.35 and 120.16 toe·ha^{-1}, respectively) due mainly to SOM.

Soil 1 showed a better crop yield, with a higher dry matter in leaves, stems, and roots; this corresponds with the higher value in exergy obtained. In soil 3, the dry matter obtained is slightly higher than soil 2, despite the lower exergy value (Fig. 4). However, in these two cases, the values in both parameters, exergy, and yield, are so close that the differences cannot be considered significant. This confirms that the methodology to calculate the exergy value of fertile soils is consistent with agronomic performances. That said, much more data would be needed to establish a relation between the exergy of soil and its yield, including the use of different crops.

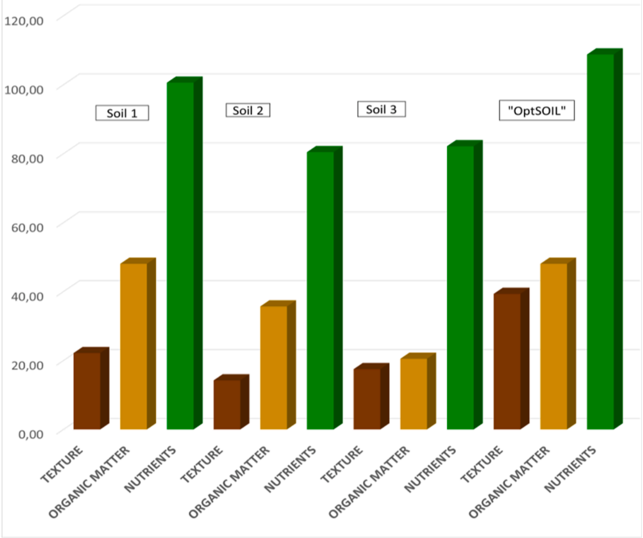

Fig. 3. Estimations of the exergy value in the three different soils selected for the pilot testing.

7. Conclusions

Exergy is a useful tool to assess the complex problem of evaluating soil fertility or quality. Using Szargut and Thanatia as references, a methodology to calculate the exergy contained infertile soils due to their inorganic and organic components has been developed in this work. To do that, the establishment of an "optional" is proposed. The parameters considered to form a fertile soil are texture, "OptTEXT", nutrients, "OptNUT", and organic matter, "OptSOM". As a result of the methodology developed in the "OptSOIL", nutrients and SOM specific exergy are the predominant contributors. Therefore, as the main advantage, experimental validation has shown that the exergy values obtained agree with agronomic performance and showed the quality and quantity of energy contained in soil. However, exergy does not value and consider the interactions between these factors or the influences on the rest of the parameters and processes in the soil, and slight differences between soils in agronomic yield cannot be explained when exergy values are very close. Despite that, this methodology's development establishes the ground to assess the value of fertile soils using exergy as a unifying tool.

Soil texture is highly variable across the globe and is difficult to amend. The only thing that can be done, in practical terms, is to improve aeration and increase its water content according to its porosity. However, its energy value is relatively stable for different concentrations of silt, sand, and clay, and lower than that of nutrients and, in turn, lower

Table 10
Exergy values of the different soils studied and dry matter (leaves, stem, and roots) from the crop yield result from each soil.

Soils	Texture (MJ/kg)	Nutrients (MJ/kg)	Organic matter (MJ/kg)	TOTAL			Dry matter (g dm/kg soil)
				MJ/kg	MJ/ha	toe/ha	
Soil 1	331.27	1504.21	718.54	2554.02	7,151,252.97	170.80	3.25
Soil 2	212.82	1202.62	533.67	1949.12	5,457,526.63	130.35	1.63
Soil 3	261.61	1228.45	306.62	1796.68	5,030,698.44	120.16	1.71

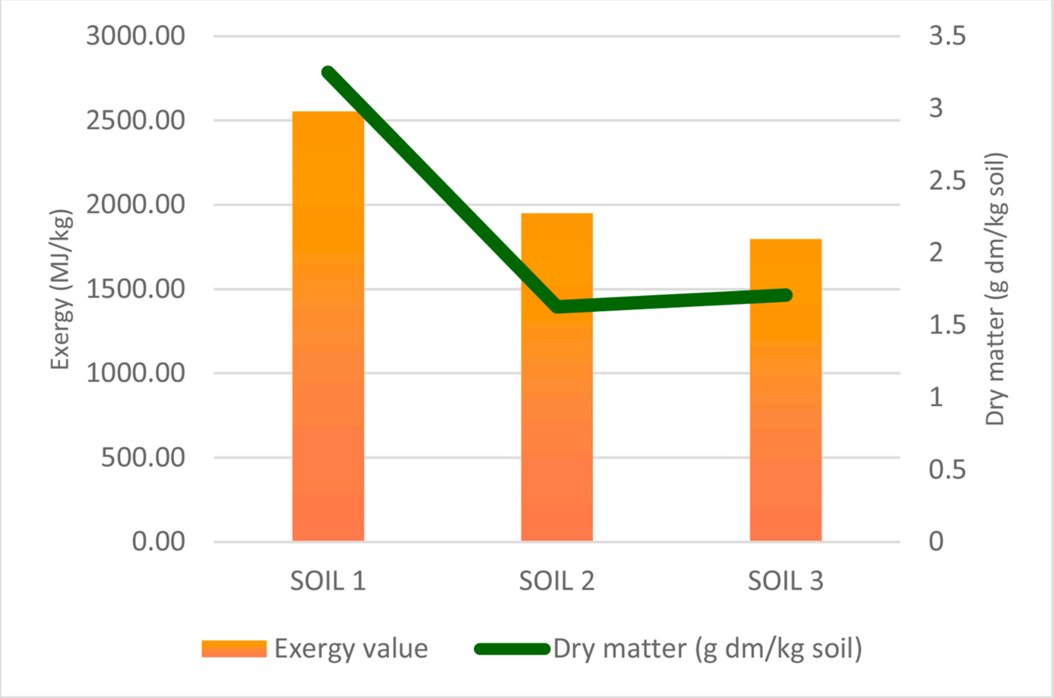

Fig. 4. Comparison between crop yield, which considers the total dry matter obtained (leaves, stem, and roots) versus the estimated exergy value for each soil's quality and work capacity for the parameters texture, nutrients, and OM.

than that of organic matter. However, the latter two can be modified at a lower cost. This means that one can select different "OptTEXT" without significant changes in their exergy value but take "OptNUT" and "OptSOM" as a universal basis to analyze the level of degradation of a real soil against the optimum.

Following these ideas, there is no universal optimum soil but soils with a great multiplicity of textures, nutrients, and organic matter. Soils are pretty edaphic-diverse. However, from the point of view of exergy, we have seen that all textures hardly differ from each other. What soil degradation depends on most is the lack of nutrients and organic matter to feed its microbiome. These soil components are essential for all living things. This idea can introduce an ideal fertile crust made of OptiNUT and OptiSOM invariant and independent of the different local textures, but not independent of their water content and aeration. Let us call this imaginary crust -copiously fertile- PRISTINIA ("Pristinia: from Latin pristine, former, early, original. Meaning 'unspoiled, untouched, pure'. (Pristinia: 2021)) as opposed to Thanatia, a dead state referring to abiotic resources. Thus, any real agricultural soil will be an intermediate soil between Pristinia and Thantia. Unfortunately, fertile soils take thousands of years to regenerate, and humans are accelerating their degradation to Thanatia.

The dialog between Pristinia and Thanatia will serve to quantitatively diagnose an assessment of all the concepts by which soil is degraded, using exergy (kWh) as the universal unit of measurement. From here, we will be able to apply thermo-economic theory to accurately assess the exergy replacement cost (kWh or €) of any soil degraded by multiple effects, both by excess or lack of nutrients.

We are also exploring the possibility of including the biotic part of the soil in the exergy methodology. Due to the numerous functions, soil microorganisms play a relevant role in soil fertility which is currently a priority focus of soil science research.

CRediT authorship contribution statement

Antonio Valero: Conceptualization, Methodology, Writing – review & editing, Supervision. **Bárbara Palacino:** Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing. **Sonia Ascaso:** Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing. **Alicia Valero:** Conceptualization, Methodology, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ecolmodel.2021.109802.

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