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TRABAJO FIN DE GRADO

CHEMICAL CHARACTERIZATION OF SLUDGE FOR AGRICULTURAL PURPOSES

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ABSTRACT

RESUMEN

1. Abstract

Sludge.production is increasing worldwide, and one of the main uses of sludge is the use on agricultural land as fertilizer, if they fulfil the legal requirements that limits the use of sludge in agriculture according to its heavy metal content. This study evaluates the main chemical parameters. (Phophorus fraction, Nitrogen, Carbon, CN ratio, pH, Electrical Conductivity, Aluminium, Arsenic, Calcium, Cadmium, Chromium, Copper, Iron, Potassium, Magnesium, Manganese, Sodium, Nickel, Lead, Sulphur, Silicon and Zinc) that allows to know its possible use in agriculture and its dosage. This study is done using sewage sludge samples from 5 different places in Finland and two different manure samples from cow farms in Finland, taking 6 samples per each place and analysing the previously mentioned parameters following the official analysis methods. After that it was carried out an statistical analysis of the data, and using this data a dosage is made according to the legal requirements and the agronomic properties (macronutrient content, NPK).

According to the obtained results all sludge samples fulfils the legal requirements to be used in agriculture established in European, Spanish and Finnish legislation . The result show significant differences between chemical characterizations of both products. Regarding sewage sludge samples, the highest differences between each samples are found in phosphorus fractions, that's varies from place to place, there are also differences in nitrogen content, electrical conductivity, pH, aluminium, calcium, chromium, magnesium, manganese, sodium, iron and sulphur content . In manure the differences between each sample are also found in phosphorus fractionation, pH, nitrogen content, CN ratio, copper, sodium, magnesium and potassium.

Copper content is the most limiting factor for agricultural application, due to the limitation established by legislation. Using the maximum amount of sludge that can be legally used according to its copper content, there is enough phosphorus to compensate phosphorus crop requirements, in the other hand there is nitrogen and potassium deficit. Manure is not affected by legislation but its high nickel content could have negative effects in the plant and the soil.

The recommended application rate (for a rotation of maize, oilseed rape, hemp and fallow) for those sludge are between 16.000 and 24.000 kg ha^{-1} of sludge (depending on the copper content and humidity of the sludge sample) every cycle of four years. There would be needed an extra application of mineral fertilizer one year after sludge application and two year after sludge application in the order of 200-250 kg ha^{-1} of nitrogen and 100 kg ha^{-1} of potassium.

2. Resumen

La producción de lodos está aumentando en todo el mundo, y uno de los principales usos que se les puede dar es la aplicación agrícola como fertilizante, siempre y cuando se ajusten a las limitaciones que legales sobre todo en cuanto a presencia de metales pesados. En este estudio se evalúan las principales características químicas (Fracciones de fósforo, Nitrógeno, Carbono, CN ratio, pH, Conductividad Eléctrica, Aluminio, Arsénico, Calcio, Cadmio, Cromo, Cobre, Hierro, Potasio, Magnesio, Manganeso, Sodio, Nickel, Plomo, Azufre, Silicio and Zinc) que permiten conocer su posible utilización en agricultura y la dosificación de estos materiales. Se trabaja con lodos de 5 depuradoras de Finlandia y estiércol procedente de dos granjas de vacuno también en Finlandia; se toman 6 muestras de cada material y se analizan los parámetros indicados anteriormente siguiendo métodos oficiales de análisis. Se realiza un análisis estadístico de los datos obtenidos y se ajusta la dosificación de los lodos teniendo en cuenta: en primer lugar la limitación legal por metales pesados y en segundo lugar el valor agronómico de dichos lodos según su aporte en macronutrientes (N, P y K).

Con los datos obtenidos en los análisis, ninguna muestra de lodos supera los valores legalmente establecidos para todos los metales pesados, tanto en la directiva comunitaria como en las regulaciones nacionales en Finlandia y España. Los resultados muestras diferencias significativas entre las características químicas de lodos y estiércol. Dentro de las muestras de lodo, se encontraron diferencias entre las muestras en las fracciones de fósforo, contenido en nitrógeno, conductividad eléctrica, pH, aluminio, calcio, cromo, magnesio, manganeso, sodio, hierro azufre. En los estiércoles se encontraron diferencias entre ambas muestras en las fracciones fósforo, pH, contenido en nitrógeno, CN ratio, cobre, sodio, magnesio y potasio.

El cobre ha sido el elemento que ha limitado la máxima cantidad de lodo que se puede aplicar legalmente en el suelo de acuerdo a la actual legislación vigente. Esta dosis casi cubre totalmente las necesidades de fósforo por los cultivos, pero no así las de nitrógeno y potasio. El estiércol no está incluido en esta legislación, pero su contenido en niquel podría tener efectos negativos en planta y suelo.

La dosis recomendada (para una rotación de maíz, colza, cáñamo y barbecho) para los lodos analizados son entre 16.000 y 24.000 kg ha^{-1} (dependiendo del contenido en cobre

y de la humedad de la muestra de lodo) cada ciclo de cuatro años. Sería necesario aplicar una fertilización mineral de entre 200-250 kg ha^{-1} de nitrógeno 100 kg ha^{-1} de potasio el primer y segundo año tras la aplicación del lodo.

INTRODUCTION

3. -Introduction

3.1. -Definition of sludge

Sewage sludge is the product of removing suspending solids during water treatment process and it contains all different residues that are produced during the different stages of the water treatment (Przewrocki et al., 2004; Fytili and Zabaniotou, 2008). It is often in liquid or semi-solid form (Fytili and Zabaniotou, 2008). Sludge can be divided into three different categories: sludge from urban wastewater treatment, sludge from industrial wastewater treatment and finally sludge from drinking water treatment (Przewrocki et al., 2004; Fytili and Zabaniotou, 2008).

3.2. -Different process to get sludge

Water treatment has three phases: In the first phase (primary treatment), most of the organic compounds are removed by a process of screening (Fytili and Zabaniotou, 2008). Chemical products can be used in this step, to get the flocculation of the sediments. After this process, there is an accumulation of waste in the tanks and the remained of the water continues for the next processes (Fytili and Zabaniotou, 2008). In the second phase (secondary treatment), the microorganisms are used to digest the remained organic compounds in the aerobic and the anaerobic conditions. The action of the micro-organisms results in the flocculation of the organic components which are then removed (Fytili and Zabaniotou, 2008). In the third phase, the physical method such as filtration is used to separate the solid inorganic part. Also, it is possible to apply some chemical treatment during this phase in order to cause the flocculation of the dissolved compounds and remove them. The main aim of this step is to reduce the quantity of some nutrients, for instance phosphorous and nitrogen (Przewrocki et al., 2004; Fytili and Zabaniotou, 2008).

In some cases, some extra treatments can be done on the sludge produced from the third phase. Such these treatments are physical (thermal treatment), chemical and biological treatments (Przewrocki et al. 2004; Fytili and Zabaniotou, 2008; Even-Ezra et al., 2011). These treatments are important to reduce the water content in the final product, increase stability of organic compounds, and reduce the pathogens content and the volume of the product (European commission, 2001c). The most common treatments are conditioning (by chemical agents or by thermal treatment), thickening, dewatering, stabilization, disinfection and thermal drying (Fytili and Zabaniotou, 2008). From these treatments, conditioning treatment is considered the most important one, and it can be done in different ways such as using chemical agents or thermal treatments (Fytili and Zabaniotou, 2008).

In addition, there are some other treatments that can be done on the sludge for better sludge quality. For example, the ozonation is the process where two electrodes provoke ozone formation, and that lead to the solubilization of some nutrient and to the hygienization of the sludge due to the antibacterial effect of ozonation (Sui et al., 2011). To avoid volatile organic compounds (VOC's) and methane that cause most of the off-odors, is possible to use ozonation (Burton and Turner, 2003).

3.3. -Sewage sludge characterization

The most important characterizations of sewage sludge which should be analyzed are N, P and heavy metals contents (Johannesson, 1999). Sewage sludge contains N, P, and some other macro and micro elements depending on the feedstock and the origin sources of the sludge as well as on the treatment. Sewage sludge contains from 24 to 47 g P kg^{-1} (40 % is available for plant), N content can varied from 32 to 96 g kg^{-1}, K can range from 2.6 to 10.8 g kg^{-1}, while C content can vary from 20 to 35 % (Johannesson, 1999). The pH can be varied also from 6.7 from 8.0 (Johannesson, 1999). The electrical conductivity is about 2700 dS m^{-1} in the aerobically digested sludge and about 6200 dS m^{-1} in the anaerobic digested sludge (Johannesson, 1999). It was reported also that N ranges from 10 to 70 g kg^{-1} (ADEME 1996), while P varies from 25 to 120g kg^{-1} (ADEME 1996), which 30 g kg^{-1} to 98 g kg^{-1} can be mineralized (Johannesson, 1999).

Table 1. Chemical characterization of sludge and manure. (1): (De Saavedra et al., 2000); (2): (Casado-Vela et al, 2007); (3): Goi et al. (2005); (4): (Fytili and Zabaniotou, 2008); (5): (Eriksson, 2001) found ;(M): (Pomares and Canet, 2001)

Sludge analysis	1	2	3	4	5	M
Humidity (%)	22	-	-	90.0	79	77
pH	8	6,5	-	-	-	8,17
E.C. (dS/m)	4,6	5,03	-	-	-	4,03
C/N ratio	-	12,7	-	-	-	13,9
N g kg^{-1}	30	2,48	-	30	-	18,4
P g kg^{-1}	27	5,62	-	100	27	17,3
K g kg^{-1}	300	7,89	-	10	4,4	31
Al g kg^{-1}	-	-	-	-	40	-
As mg kg^{-1}	-	-	-	10	4,7	-
Ca g kg^{-1}	76	38,5	-	-	28	37,4
Cd mg kg^{-1}	4	1,6	2,24	10	1,4	1
Cr mg kg^{-1}	482	16,6	24,56	500	33	24
Cu mg kg^{-1}	302	157	54,11	800	390	33
Fe mg kg^{-1}	1.670.000	5,65	-	17.000	49.000	4.100
Hg mg kg^{-1}	-	n.d.	0,33	6	1,1	-
Mg mg kg^{-1}	860	2,65	-	-	3.400	10.800
Mn mg kg^{-1}	-	117	44,64	260	310	172

Na mg kg^{-1}	-	2.300	-	-	3.500	5.800
Ni mg kg^{-1}	69	n.d.	18,22	80	20	20
Pb mg kg^{-1}	269	40,8	24,78	500	33	14
S g kg^{-1}	-	-	-	-	9	-
Si g kg^{-1}	-	-	-	-	45	-
Zn mg kg^{-1}	1541	470	244,88	1700	550	133

n.d: not detected

One of the most important characteristic in sludge is its high content in organic matter (90%) (European commission, 2000c). It is well know that organic matter has a beneficial effect on the soil in terms of increasing water capacity and cationic exchange capacity, decreasing erodability and improving physical characteristics (European commission, 2000c). Moreover, the nutrients are slower released from it than from the mineral fertilizers (Brännvall et al., 2014). pH from sewage sludge can vary between slightly basic and slightly acid (Pomares and Canet, 2001). Salinity can be high due to the concentration of salts, which is an important disadvantage for agricultural application. Salinity can vary from 1 to 9dS/m (Pomares and Canet, 2001). Some of the main sources of salinity are the addition of iron chloride, calcium chloride… (Pomares and Canet, 2001).

Manure has higher content of carbon in the form of cellulose and lignin, and it requires to be stabilized by processes of organic matter degradation, mineralization and humification make by the microbes likes bacteria or fungi. Cow manure only mineralized 20-30% of the nitrogen during the first year. In cow manure mineral phosphorus represents 80% of total phosphorus (Pomares and Canet, 2001). The addition of straw causes an increase in organic phosphorus content. Usually the organic matter that is included in manure improves the assimilation of phosphorus (Pomares and Canet, 2001). Potassium is present as salts that are part of the urine, so the effect in the soil is the same as the inorganic fertilizers (Pomares and Canet, 2001). The high content of calcium can react as liming increasing the pH of acidic soils (Pomares and Canet, 2001). Most of the heavy metal content in manure comes from the enriched diet used in high productivity farms and sanitary treatments (Pomares and Canet, 2001).

3.4. -Uses of sludge

The sewage sludge production has been increased gradually worldwide. The total production of sludge as dry matter in European Union in 1992 was 5.5 Mt, and in 2005 was about 9 Mt (Eshtiaghi et al., 2013). The production of the sludge is still increasing yearly (Figure 1) due to the fact that the legislation of European Union as well as of many other countries is making compulsory to have water treatment plants in agglomeration of more than 2000 people (91/271/EEC). Also, it is due to the increase of the European population (Eshtiaghi et al., 2013).

Sludge can be utilized in various ways (i.e. incineration, landfilling, land application as a fertilizer and as construction material). It can be also utilized in forestry proposes, however it is not common. In some countries, it is forbidden to use sewage sludge on cropland (European commission, 2000c; Przewrocki et al., 2004; Fytili and Zabaniotou, 2008). The use of sludge on cropland is increasing yearly (Lundin et al., 2004; Fytili and Zabaniotou, 2008). The sludge is used as a fertilizer on cropland because of the high nutrient content and organic matter in such sludge which can improve the physical and chemical properties of the soil (Przewrocki et al., 2004; Fytili and Zabaniotou, 2008). However, there are some disadvantages of applying sludge on cropland such as the high content of heavy metals and some pollutants which can be potential problem for the environment (Fytili and Zabaniotou, 2008). In addition, there is a concern about the presence of pathogens that can cause some diseases for the animals and humans (European Commission, 2000b; Przewrocki et al., 2004; Fytili and Zabaniotou, 2008).

Incineration is the process where the sludge is combusted for energy production. It is necessary at beginning to reduce the water content of the sludge to reduce the energy consumed (Fytili and Zabaniotou, 2008; Ludin et al., 2004; Przewrocki et al., 2004). Nevertheless, during the combustion process, there is a generation of greenhouse gases (GHG) such as NO_x and SO_x, in addition to some toxic compounds such as heavy metals and volatile organic compounds. However, such these materials can be reduced by the treatment of flue gas (Rulkens, 2007). Finally, the incineration of sludge is a noisy, dusty and odorous process which can cause some problems for the human where they live (European commission, 2000d; Ludin et al., 2004).

Landfilling is the process where the sludge is burial in a specific place for waste residues (Przewrocki et al., 2004; Fytili and Zabaniotou, 2008). If there is no good management for this process in the proper way, some problems with the leachates and gas emissions can occurs which most of them can result in greenhouse effect (European commission, 2000a). Landfilling can cause some problems as the incinerating (i.e. noise, dust and smell) (European commission, 2000d; Przewrocki et al., 2004; Fytili and Zabaniotou, 2008).

Is also possible to use it as construction material, mixing the sludge with clay and then heat them up to 1.500ºC (Lin et al., 2012; Cuisdó and Cremaades, 2012). The resulting product is a clay brick that can be used in construction (Lin et al., 2012; Cusidó and Cremaades, 2012). There is also some concern about the possible health issues that the use of sludge as brick material can cause, due to the content of heavy metals (Cusidó and Cremaades, 2012). Some heavy metals such cadmium, chromium, arsenic, lead mercury and nickel are known to cause health problems when there is exposition to those materials, and that exposition can be cause by the gas emission and the leachates from those products, but the literature shows that the heavy metals emission by those processes are almost nothing (Cusidó and Cremaades, 2012). There are others concerns about the use of sludge as brick material, due to the possible loss of mechanical properties such as flexural strength resistance and compressive strength resistance, although the literature shows that there is a decrease in compressive strength resistance, they also show an increase in flexural strength resistance, in lightness and un thermal and acoustic isolation using bricks with 5-25% of sludge comparing to conventional clay bricks (Lin et al., 2012).

3.5. -Phosphorous in the soil and in sludge

Phosphorous is one of the main elements in sludge, with a high level of 15% DM (Fytili and Zabaniotou, 2008), but this level of phosphorous can be high for agricultural application causing problems for instance eutrophication (Millier and Hooda, 2010). Environmental problems such eutrophication is caused due to the run-off of the available phosphorous. Other forms such as dissolved organic phosphorous and soluble reactive phosphorous can also be leached and contaminate ground-water (Miller and Hooda, 2010). Some of the un-available phosphorous that cannot be used by the plants and microorganisms in the current form can be converted into available phosphorous by the action of phosphatase, and enzyme that releases ortho-phosphate from the organic form (Xie et al., 2011). The high concentration of seaweed decreases the amount of light that enter in the water and they decrease the oxygen concentration in the water (Sostres, 2001). There is also off odors caused by the breakdown of the seaweeds and presence of harmful microbes that can cause diseases (Sostres, 2001).

Phosphorous can precipitated in flooding environments such as in rice fields (Abolfazli et al., 2012). pH soil is considered the main factor that can determine the precipitation of the phosphorous. Ions such Ca, Al and Fe can act with phosphorous to form precipitated phosphorous compounds (Abolfazli et al., 2012). In alkaline soils, Ca precipitate is the dominant form. Fe and Al forms are insoluble under anaerobic conditions and are mainly form under acid conditions. Extractable Olsen phosphorous increases when the rate of fertilizer is increased (Wang et al., 2010). Application of organic fertilizers based on nitrogen needed for each species can lead to phosphorous accumulation in the soil due to the lower nitrogen: phosphorous ratio of the organic fertilizer (Kashem et al., 2010).

There is a high level of the lost phosphorous due to increase of washing powders use and due to the change in nutrition and life style (industrialization process). Detergents are the main phosphorous source in municipal wastewater, since it contains high level of sodium tripolyphosphate (Rybicki, 1997). Some countries such as Switzerland have prevented the use of the detergents as a result of the eutrophication problems. Phosphorous can be removed by chemical process through the precipitation or by biological process (Rybicki, 1997). In the chemical process, it is common to use aluminum salts or iron salts. However, sludge with biological treatment is usually more unstable and more odorous (Rybicki, 1997).

There has been an excessive application of phosphorus in the fields. The estimated average of phosphorus that is added per year in excess is 19kg/ha (Breeuwsma et al., 1995). A big part of that problem is cause by the excessive use of phosphate fertilizers, but is also caused by the excessive manure application. Manure usually has N:P ratio much lower than which is needed by the plant, and as a result there is phosphorus accumulation (Sostres, 2001).

Small part of organic phosphorous can be biologically active. Primary phosphorus minerals are slowly dissolves providing phosphate ion to the solution (Carpenter, 2005). A part of these ions will be precipitated as secondary phosphorous minerals and this is unavailable forms (Smil, 2000). Biomass phosphorous is the most active form and can be taken up by predators or saprophytes and incorporated to new consumers biomass (Smil, 2000). Mineralization of organic phosphorous occurs due to the action of an enzyme called phosphatase that can be produced by the microorganism or by the plants (Richardson 2001). Phosphorous mineralization is mainly mediated by bacteria such as *Bacillus* and *Pseudomonas spp.,* fungi such as *Penuicillium and Aspergillus spp.* and protozoa such as *Tetrahymena pyriformis* (Barsdate, R. et al., 1974; Richardson 2001).

Eutrophication is the process was the excessive grow of algae caused by the excessive nutrient content in the water, causing anoxia problems (Carpenter, 2005). Problems caused by eutrophication include purifying water cost to make the water available for humans, losses in wild life, problems of bad odors and reduction in fish population (Carpenter, 2005; Smil, 2000). One of the major causes of eutrophication is the high phosphorous content in the water that can be due to factories discharges to the rivers, run off from agricultural lands, sewages, construction sites and urban areas (Smil, 2000). For this reason, some countries have developed some regulations in factories and municipal discharges to the rivers. Agricultural land is one of the most important sources of phosphorous due to the excessive fertilization that leads to phosphorous accumulation in the soil, and can be then washed and remove from the soil by leaching or by run-off and finally accumulate in the lakes causing eutrophication (Carpenter, 2005).

Phosphorus enters in the soil as inputs in inorganic form when fertilizer, sludge or crop residues are incorporated to the soil (Smil, 2000) Organic phosphorus cannot directly be uptake by the plant roots. The microorganisms such as bacteria and protozoa can use this organic phosphorus. After it is used by these microorganisms, organic phosphorous can become an available form in the soil solution. Also, some part of the soluble phosphorous can precipitate with other elements such as calcium, iron or aluminum making it less available for the plant. But, such fractions of mineral forms can become solubilized again, making long-term phosphorus storage (Smil, 2000).

Phosphorus end in the water by desorption, by dissolution or by removal, then there is the transport which is made by runoff or by deep rising (Sostres, 2001). Water of the rainfall is responsible of the that process, but the effect is minimized by the sorption of the soil (Sostres, 2001). When the water flux is made by the macropores, the phosphorus lost can be high (Sostres, 2001). High losses can be caused by having bad drainage or due to an excessive organic fertilization (Simard et al., 2000).

Regarding the flux of phosphorus particles, is mostly caused by superficial erosion or soil erosion in drainage channels (Sostres, 2001). During this process there is a selection of phosphorus where the smallest particles are selected, and those particles are the ones that has higher sorption capacity and higher phosphorus content (Haygarth and Jarvis, 1999). In manure there is a higher rinsing of phosphorus due to the higher amount of organic phosphorus whose diester phosphate groups can be barely adsorbed by the soil surface (Sostres, 2001).

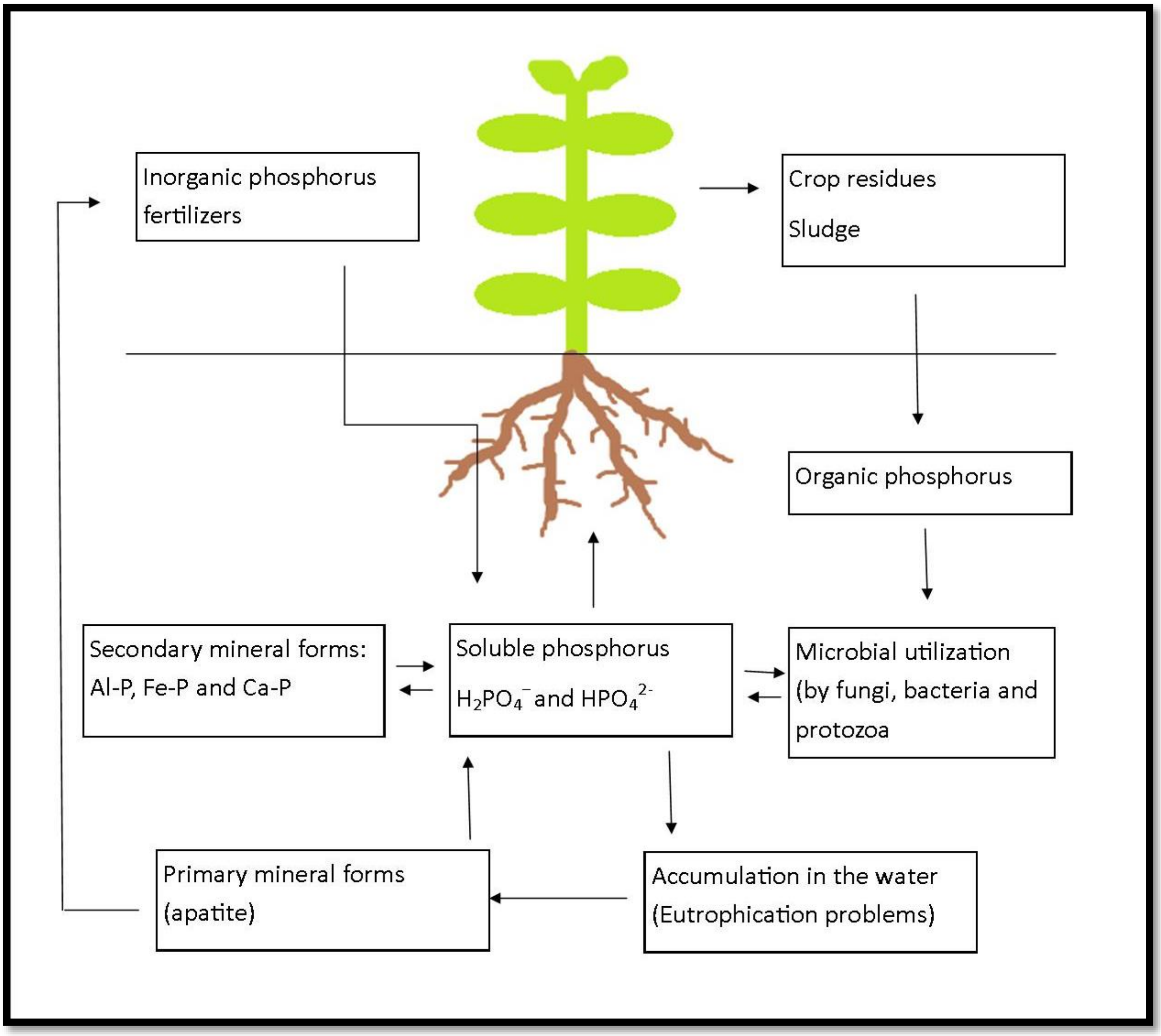

Figure 1. Phosphorus cycle

Regarding phosphorus fractionation in sludge, there are some studies were they tried to find out how phosphorus fractionation was influenced by the sludge treatment.

Choi et al. (2009) carried out a study in order to differentiate between the different phosphorus fractions that are present in sludge (biologically bound phosphorus and physiochemical bound phosphorus). They also differentiate in the physiochemical bound phosphorus between soluble phosphorus and adsorbed phosphorus. Moreover the adsorbed phosphorus was divided into the soluble reactive phosphorus and soluble non-reactive phosphorus. The experiment included different treatments (sludge with iron precipitation or sludge without iron precipitation). The results showed that iron precipitation decreased the biologically bound phosphorus, but it has not affected the soluble fraction. In addition, the phosphorus bound to Al and Fe was quite high comparing to sludge without iron precipitation.

Huang et al. (2012) conducted an experiment where they use sewage sludge treated with different chemicals (Fresh dewatered anaerobically digested sludge, stabilized with ferrous sulfate, stabilized with calcium oxide and stabilized with aluminum sulfate) to study the different phytoabailability of phosphorus in the different treatments. The fertilizer was highest in phytoavailability, followed by the aluminum sulfate and the dewatered and fresh sludge, while calcium oxide has less and ferrous sulfate.

Criquet et al. (2007) studied the effect of sewage sludge application (aerobically and aerobically digested sludge). The sludge application resulted in an increase in the phosphorus content, phosphatase activity and microbial activity, but also the phosphatase activity was decreased over with the time.

Xie et al. (2011) studied phosphatase activity and phosphorus fraction in sewage sludge. The results shows that the main fraction in sludge was the inorganic phosphorus and non-apatite inorganic phosphorus were the highest fractions. Phosphatase activity was high, and that can be one of the causes why inorganic phosphorus was the main fraction.

3.6. -Heavy metal concentration in sludge, and its effects in the soil.

Probably the main strain of research in sludge issues is its heavy metal content, there is a lot of literature where they measure the different concentration of heavy metals in the sludge, and in some studies they also measured heavy metal content in the soil or in plants that have grown in soil fertilized using sludge.

Goi et al. (2005) studied the heavy metals levels that are present in different sludges. Ten different samples from ten different wastewater plants were used for about 11 elemental analyses (Cd, Cr, Cu, Hg, Ni, Pb, Zn, Ba, Co, Mo and Mn). The results illustrated that these sludges contain lower heavy metal levels than the limits values that are established by the European Union.

Nyamangara and Mzezewa (1999) studied the effect of sludge application on the long term (19 years) on Zn, Cu, Ni and Pb accumulation in the soil. The content of Zn, Pb, and Cu was highest in the upper layers of the soil. The results showed also that lowest content of the heavy metals in the lowest layers indicates that water contamination was very low comparing to run-off.

Alonso et al carried out an experiment in 2005 where they measured the concentration of various elements (Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Ti and Zn) in anaerobic treated sludge. In small wastewater plants, anaerobic treatment is the most common. To make the digestion they used a mixture of 10 mL of nitric (HNO3), hydrochloric (HCl) and hydrofluoric acid (HF), in the ratio 5:4:1 to digest in the microwave 0,5g of sample. They also distinguished between exchangeable fraction, oxidizable fraction, reducible fraction and residual fraction. They couldn't measure mercury content due to its lower fraction that was lower than the detection level of the ICP machine. Most of the elements had low percentage of exchangeable form, only cobalt (17%), manganese (35%), nickel (11%) and zinc (12%) had relatively high percentage of exchangeable form. Zinc and manganese again showed the highest rate of reducible form. Despite the already mentioned elements, all elements show a high percentage of oxidizable form, ranging from 20 to 40% and even higher the case of molybdenum (53%) and cobalt (61%). Finally the residual fraction was also high in most of the elements and represents fractions that are bound to the mineral matter of the sludge. These results explained why cobalt, manganese, nickel and zinc are the most common elements analyzed in the literature and why their presence can cause toxicity problems in lower concentrations than in other elements.

Doelsch et al made a research in 2006 where they evaluate the impact of sewage sludge in the tropical soils of the island of Reunion in the Indian Ocean. This island has a volcanic origin, and soils with volcanic origin have naturally higher content of heavy metals than other type of soils. Due to that they cannot legally apply sewage sludge in most of the soils. In the research they compare control fields fertilized by NPK and sewage sludge. They found out that Zinc had the highest mobility; nickel mobility was also high and much bigger than copper and cadmium. But there weren't significant changes in the soil concentration of heavy metal after two year of sewage sludge application, but sewage sludge application increased the mobility of heavy metals.

Ahlberg et al in 2006 studied the leachates and size of the particles that were leaching from a soil amended with sewage sludge at different times. They used a lysimeter to obtain the samples. The studied elements were Na, Ca, Mg, Mn, Sr, Zn, K, Li, Ni, Cd, Co, Rb, Ag, Cr, Ba, Cu, Ga, Al, Pb and Fe. They found out that the relative amounts of metals leached after one year, expressed as percent of total environmentally available content per kg DS of sludge, have the order: Na > Ca =Mg > Mn > Sr > Zn > K > Li = Ni > Cd > Co > Rb >Ag > Cr > Ba = Cu > Ga > Al = Pb = Fe. They also distinguished two groups of heavy metals, those that has a higher rate of leaching just after the application and then decreases, but there is another group (Zn, Cd, Mn, Ni, Sr, Ca, Al and Li) that have a cycling rate, being higher in colder months. They show that most of the elements leachated in particles smaller than 10 kDa, but other elements such as Fe, Al and Cr had important reduction in leachates rates (20-70%) when a filter of 0,45µm was used.

Mattana et al in 2014 investigated the effect of three different types of sludge application (aerobic digested, aerobic digested + composted and aerobic digested + thermal threated) in the soil bacterial community. ATP activity was significantly higher in aerobic digested + composted sludge and aerobic digested + thermal threated sludge, which means that the microbial activity was higher in those sludge types. Sludge application enhanced in all cases enzymatic activity, but this increase was significantly higher in aerobic digested + thermal threated sludge. Community fingerprinting analysis showed that there were genetic differences between bacterial communities of each sludge type. The authors link the higher bacterial activity and the higher concentrations of nutrients and heavy metals in aerobic digested + thermal threated sludge to the particle size reduction that enhance bacterial activity and as a result, enhance the availability of different elements.

Cornu et al in 2001 carried out an experiment to estimate the potential consequences that sewage sludge can cause in ferralsols in Brazil. Ferrolitic soils are quite acid with pH lower than 5, with low content in nutrients and organic matter, those characteristics made them more vulnerable to sewage sludge applications. They analyzed the sludge, soil, drainage water and runoff water using 24 ton of sludge per hectare. Runoff had slightly higher concentrations of Cl, Ca, Cu, Ni and Pb when it was flowing in soils amended with sewage sludge. Drainage water increased its elements exports when they flow across soil amended with sewage sludge. Despite this increase of element transport when there is sludge application, the total average of element exported is still small. Soil characteristics didn't change after sludge application, due to the nutrient export by the crop, and the existing high concentration of heavy metals which in comparison with the added by sewage sludge wasn't significantly higher.

3.7. -Effect of sludge on the plant and the soil

High content of heavy metals can be more dangerous under acid conditions due to the increase of the plant uptake of elements such as Zn, Cu, Cd and Ni, which can cause toxicity to the plants (Bhargava et al., 2012; Guala et al., 2010a). The high content of heavy metals in the plant can lead to chlorosis, physiological disorders, decrease in growth rate and it causes a decrease in nitrogen fixation in the leguminous species (Guala et al., 2010b). There are some plant species which are able to take up the heavy metals (phytoremediation) from the soil and store them in their harvestable parts. The biomass of these species can be used for bioenergy purposes (Seleiman et al., 2013a, 2013b).European Union has established some limits values for heavy metals and some organic compounds due to the possible negative effects of sludge application on the cropland. The legislation also established the period of the time (usually 1 year) which is necessary to wait until the possible harvest to use the productivity of the crops for human consumption (86/278/EEC). Some European States have established more strict legislation which has lower values for the heavy metals and some microorganisms (Schickler and Caspi, 1999; Przewrocki et al., 2004). Heavy metals that have been accumulated by plants can be transfer to animals during feeding process, and then can accumulate in the meat or in the milk which means it can cause problems for the human and animals (Guala et al., 2010a). Generally, different types of sludge can have different effects in the physical and chemical as well as biological properties of the soil. For instance composted sludge has stronger effect on physical characteristics of the soil due to its higher organic matter content (European commission 2000c).

Zinc, copper, nickel and cadmium have the highest mobility in the soil so they can be easily absorbed by the crops, in contrast lead and chromium are strongly kept in the clay and as a result the plant cannot uptake them as easily as zinc, nickel copper or cadmium (Bhargava et al., 2012; Guala et al., 2010a; Pomares and Canet, 2001). There is antagonism between cadmium and zinc that can modify the cadmium tolerance of the crop (Pomares and Canet, 2001).

Low solubility lead to high solubility of heavy metals (Pomares and Canet, 2001). Cationic exchange capacity should be also taken in account, because soils with high cationic exchange capacity like soils with high clay content or high organic matter content can contain higher concentrations of heavy metals without causing problems in the crops due to the fact that they are kept in those compounds (Pomares and Canet, 2001).

Most of the heavy metals accumulation is located in leaf, stem and roots; in contrast the seeds show lower heavy metals accumulation (Bhargava et al., 2012; Guala et al., 2010a; Pomares and Canet, 2001). That fact is the main reason why plants such as maize, rapeseed, sunflower… have low phytotoxicity risk and others such as lettuce, peas… have higher phytotoxicity risk Bhargava et al., 2012; Pomares and Canet, 2001).

The European Union has regulated the amount of heavy metals that can be applied on the soil per year, the maximum concentration of heavy metals that sludge can have to be allow for being used for agriculture proposes and the maximum concentration of heavy metals that the soil can have to allow the fertilization by sludge (86/278/EEC).

Table 2. Limit values for heavy metals (Annexes IA, IB and IC of Directive 86/278/EEC).

Element	Limits values in soil (mg kg^{-1})	Limit values in sludge for use in agriculture (mg kg^{-1})	Limit values of heavy metals which may be added annually to agricultural land based on a 10 year average (kg ha^{-1} y^{-1})
Cadmium	1-3	20-40	0.15
Chromium	-	-	-
Copper	50-140	1000-1750	12.00
Mercury	1-1.5	16-25	0.10
Nickel	30-75	300-400	3.00
Lead	50-300	750-1200	15.00
Zinc	150-300	2500-4000	30.00

Every country has incorporated that directive to their own law, in the cases named before, Spain and Finland, there are substantial differences between both countries, if we compare the limit concentration that appears in their respective laws:

Table 3. Limit concentration for heavy metals content in soil for sludge application, content in sludge and total amount of heavy metals loaded in the soil. (Minesterio de Agricultura, Pesca y Alimentación, 1310/1990).

Element	Limit value mg kg^{-1} of soil		Limit value mg kg^{-1} of sludge		Limit value (kg/ha/year)
	Soil with pH<7	Soil with pH >7	Soil with pH<7	Soil with pH >7	
Cd	1	3,0	20	40	0,15
Cu	50	210,0	1.000	1750	12,00
Ni	30	112,0	300	400	3,00
Pb	50	300,0	750	1.200	15,00
Zn	150	450,0	2.500	4.000	30,00
Hg	1	1,5	16	25	0,10
Cr	100	150,0	1.000	1.500	3,00

Table 4. Limit concentration for heavy metals content in soil for sludge application, content in sludge and total amount of heavy metals loaded in the soil. (Ministry of Agriculture and Forestry, 282/1994).

	Limit in sludge and sludge mixtures mg kg^{-1} DM	Limit in sludge as raw material in mixtures mg kg^{-1} DM	Limit concentration in soil mg kg^{-1} DM	Limit heavy metal load in soil g ha^{-1} $year^{-1}$
Cd	1,5	3,0	0,5	1,5
Cr	300	300	200	300
Cu	600	600	100	600
Hg	2,0	2,0	0,2	1,0
Ni	100	100	60	100
Pb	100	150	60	100
Zn	1500	1500	150	1500

We can observe that in Spain there is a different regulation for different pH, in Finland there is no differentiation due to the absence of basic soils. Other difference is the differentiation in Finnish law of sludge that will be directly apply on the field, and sludge that will be mixed with other products to then be further apply, in the Spanish legislation it doesn't appear. But the main difference between both legislations is the limit values for heavy metal content. In Spain the limit values are practically the same as in the European directive, but the Finnish legislation is more restrictive putting values much smaller than in the European directive.

Long term use of organic fertilizers such as sludge can lead to an excess in P and its consequent leachate and water contamination (Motavalli and Miles, 2002a). The use of sludge leads to high increase in organic forms of phosphorous rather than inorganic phosphorous comparing to manufactured fertilizer, but plants doesn´t show a higher uptake of inorganic or organic phosphorous forms (Motavalli and Miles, 2002a).

Organic residues have been use as a fertilization source for a long time in human history (Johannesson, 1999; Motavalli and Miles, 2002a, 2002b). However, the uncontrolled use of such materials can cause some environmental problems such as diseases and soil deterioration. Other problems that can be cause by the excessive of sludge application on agricultural land is P accumulation, particular when sludge is applied based on the available N to each species. The high level of phosphorous accumulation in the soil will be leached with the groundwater (Kashem et al., 2003; Motavalli and Miles, 2002).

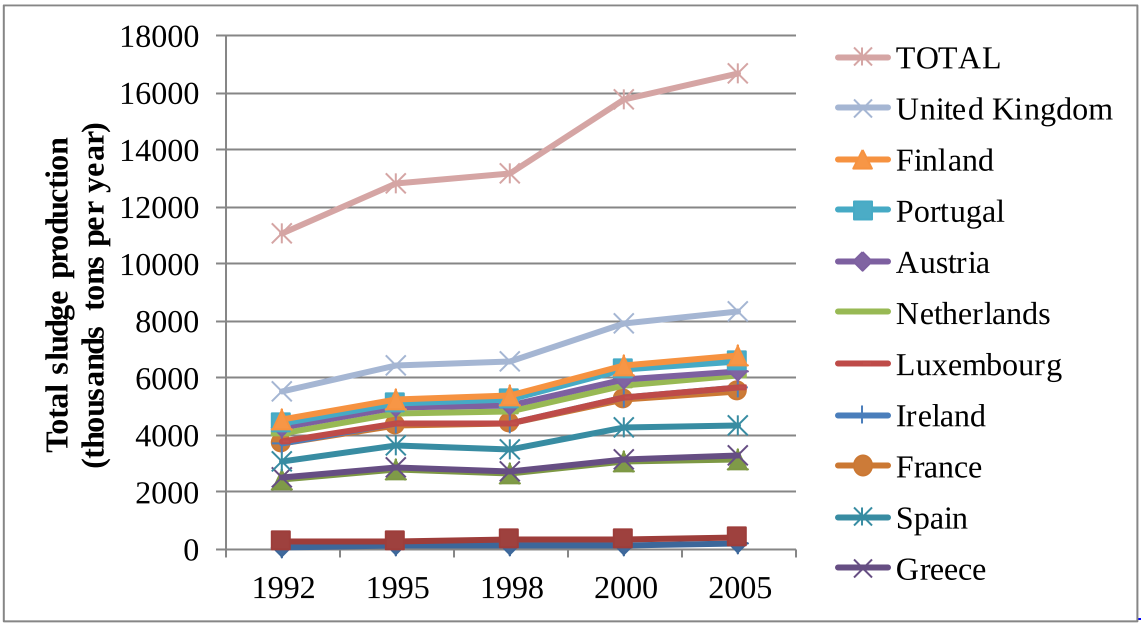

Figure 2. The total production of sludge in European countries (Langenkamp et al., 2006).

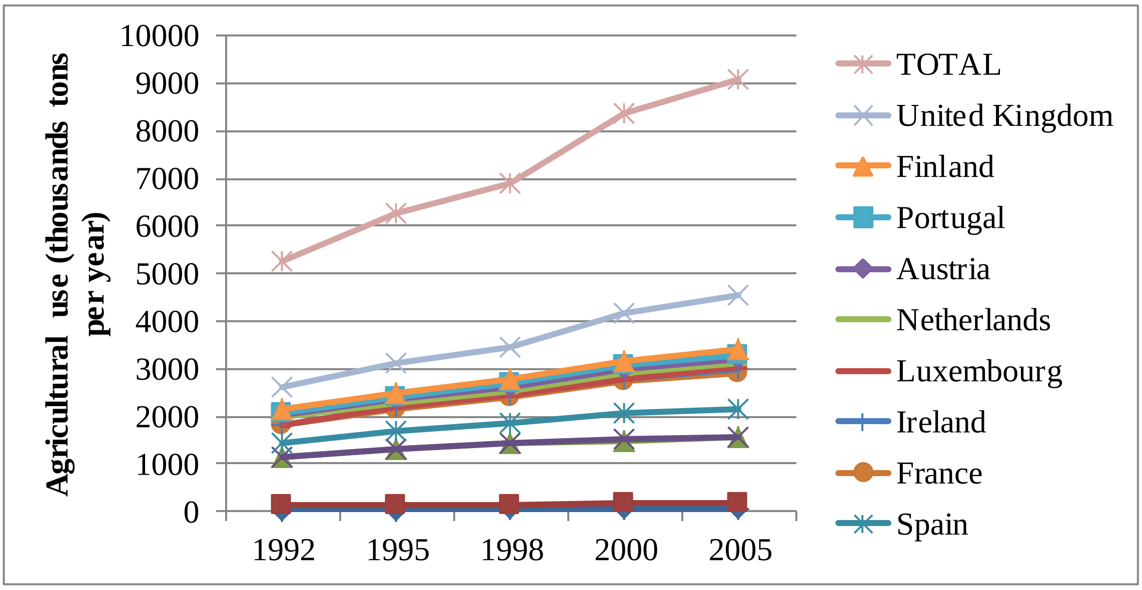

Figure 3. Agricultural use of sludge in different European countries. (Langenkamp et al., 2006).

According to the European Union legislation, there are restrictions for the use of sewage sludge on agricultural land (European commission, 2000a). In most of the European states, sludge must be treated before being used as fertilizer. In some other states, it is allowed to use the untreated sludge but under some strict conditions (European commission, 2000a). There is also restriction for the sludge application on grasslands, where some vegetables, berries and medicinal plants are growing (European commission, 2000b). The level of the sludge applications can be around 5-10 t ha^{-1} (Keeney et al., 1975). There is also more legislation that affects to sewage sludge application in agricultural land, every country has their own legislation that adapts the Eurpean directive to their own requirements, varying from country to country, and also inside a country there can be regional legislation that affects sludge uses in agriculture (European commission, 2000b).

As examples of two different legislation for sludge application in the soil we can study the Spanish and the Finnish legislation, those cases are quite different to each other due to the differences in climate, population and politics. In Spain the use of sludge in agriculture is regulated by Royal Decree 1310/1990, and every regional government has adapted the national legislation in their own laws, but in Finland a country with less population and more centralized there is only national legislation mainly regulated by Decree 282/1994. The content is mainly the same, because both are adaptation from the

European directive 86/278/EEC, nut there are important differences in requirements like the number of analysis that must be done per year, in Spain the analysis is done every 6 months, excepting places with less than 5.000 habitants where there is needed just one analysis per year (Minesterio de Agricultura, Pesca y Alimentación, 1310/1990). In Finland, the law requires more analysis per year depending on the size of the population, and also concrete the number of analysis needed during the first year:

Table 5. Number of sludge analysis in Finland according to Decree 282/1994.

Population	Frecuency of analysis per year	
	First year	Later years
>100.000	≥12	≥4
40.000-100.000	≥6	≥3
5.000-40.000	≥4	≥2
200-5.000	≥1	≥1
<200	≥1	At least once every two years

There are a lot of studies where they have assessed the agronomic value of sludge for agricultural application. Some of them study the yield changes in different crops after sludge application, others measured heavy metal concentration in the plant after being fertilized by sludge and there some that investigate germination rate or plant growth at different sludge concentrations.

Hossain et al. (2010) conducted an experiment to assess the agronomic properties of sludge treated with pyrolysis (biochar). The study included the effect of four different treatments (control soil, soil treated with biochar, soil treated with biochar and fertilizer, and soil treated with fertilizer), on the growth of cherry tomato (*Lycopersicon esculentum* L.). The results showed that biochar application resulted in an increase of 64% in the yield. This could attribute to the enhancing nutrient availability and improving soil properties.

Brännvall et al. (2014) carried out an experiment to investigate the effect of some treatments (plain soil, fertilized soil with $CaPO_4$, fertilized soil with $CaKP_2O_7$, soil treated with biowaste, soil treated with biofuel, and soil treated with incinerated sludge) on growth of grass species (commercial mixure). The results showed that there was no correlation between plant growth and nutrient availability. Although, the highest nutrient content was in soil treated with biosolids, but the high salinity of this material resulted in a decrease in the growth of the grass.

Abolfazli et al. (2012) carried out an experiment to find out what are the effects of chemical phosphorus fertilization and organic fertilization in submerged soil. The study included 5 treatments (phosphorus fertilizer triple superphosphate, phosphorus fertilizer diamonnium phosphate, and cow dung manure and sewage sludge) to investigate the effect of these treatments on rice growth and production in acid soil and calcareous soil). The phosphorus fractions (available phosphorus, aluminum fraction, iron phosphorus and calcium phosphorus) were analyzed in the soil before and after the treatments. The results showed that organic fertilizers such as manure or sludge resulted in an increase in the available phosphorus. In addition, phosphorus bounded with Ca was the highest in calcareous soils, while the phosphorus bounded with aluminum and iron were the predominant forms.

Singh and Agrawal (2007) investigated the effect of sewage sludge application as fertilizer for *Beta vulgaris* L. plants. The Cd contents in the soil where above the permissible level in India legislation, pH decreases and conductivity increases in the soil treated with sludge. Also Cd, Ni and Zn content in the plant were above the limit values that have been established by India government for this crop. The high content of such heavy metals resulted in a reduction in root length, leaf area, photosynthetic rate and chlorophyll content and an increase in lipid peroxidation activity and protein level.

Seleiman et al. (2012) conducted an experiment to find out how sewage sludge application affects the quality and productivity of bioenergy crops. Different quantities of sludge were added to pots where maize and oilseed rapes were sown. The sludge application resulted in an increase in the leaf area and biomass accumulation, but it also increased the heavy metals content in plant biomass without adverse effect on plant growth.

Hernández et al. (1990) investigated the effect of sludge and poultry manure application on the crop yield of maize and the availability of heavy metals in the soil. The results showed that sludge increased the yield and the N content, whereas K content in plant was lower than in plants fertilized with poultry manure.

Casado-Vela et al studied in 2007 in Alicante (Spain) the effect of increasing composted sludge application in the growth of sweet pepper (*Capsicum annuum*). They measured the nutrient, heavy metal content, pH and salinity in the water used for irrigation, in the composted sludge and in the soil. In most of the experiments they don´t measured the average content of heavy metals in water, but it can be an important source of those elements. They also made the experiment in two different places, in the open field and in the greenhouse.

The four different treatments that they used were T1 = 0 kg m^{-2}; T2 = 3 kg m^{-2}; T3 = 6 kg m^{-2} and T4 = 9 kg m^{-2}. They found out that there were an increase in conductivity as sludge was increasing, and there were also an increase of conductivity with the passage of time after sludge application due to the increasing solubilisation of its compounds. In addition there were differences between conductivity in open field and greenhouse, in the open field the conductivity was higher due to the higher temperature changes that enhance solubilization. Usually is consider that a conductivity increase higher than 3000 µS/cm lead to yield decreases, but even in the highest application rate (9 kg m-2) the conductivity only reached an increase of 1200 µS/cm. There weren't changes in pH. Organic matter content was higher in the higher application rates, but in the greenhouse the increase was lower due to the higher mineralization rate caused by the higher temperature. As it was expected, there was a significant increase of phosphorus with the increasing application rate, but with the high pH (upper than 7) and high temperature there can be a precipitation of phosphorus into calcium phosphates. In addition, there were also an increase in soil concentration of Kjendahl nitrogen, sodium, potassium, calcium, iron, manganese, copper, zinc and boron, but there was a decrease in the concentrations after 200 days of growing due to the absorption by the plants. The highest yield and biggest fruits were found in the greenhouse using 9 kg m-2, but the negative effect that the continiuos applicatoin of that product can cause, allow to the authors to advice using a smaller application rate of 6 kg m-2.

De Saavedra et al studied in Spain in 2000 where they sow maize using three different treatments of basal dressing, mineral fertilizer, 8.000 kg ha-1 of sludge compost (Mixture I) and 12.000 kg ha-1 (Mixture II). In all of them top dressing was 350 k ha-1 of urea. Yield was 10% higher in mixture I than in mineral fertilization, and if we compare with mixture II, yield was 20% higher. There weren't changes in the pH of the soil and there was an small increase in the electrical conductivity in all of the treatments. After sludge application there is an increase in the concentration of heavy metals, but it was still below the established limit by the Spanish and European legislation.

A study made by Vasseur et al in Quebec (Canada) in 2000, tried to find out the effect of countiuos sewage sludge application in the biodiversity, yield, weeds and chemical characteristics of the soil. The studied soil was well drained loam, clasify by the FAO as Podzols. The used sludge was biologically treated during 21 days in places with similar farming practices and crops, same area, growing hay for animal feeding and plowing after harvest. The total amount of sludge appied varied from 1,3 to 9,4 Mg DM ha-1. The dry matter content was really low, ranging from 2,5% to 13,2% so as to be applied by sprayers. There was also a different treatment using composted sludge that was applied with higher dry matter content (44,7%), and had much higher pH, 12,3 comparing to the 6,2-6,9 of sewage sludge. Results showed that diversity index varied from place to place, due to the differences in the grown species by farmers and the edafic differences, but there were also significant differences in two places were the not treated fields showed higher diversity index than the treated field. Usally weeds have higher tolerances to high concentration of heavy metals, so they could adapt better to the sludge application, but in that study there were no significant differences between not treated fields and sludge treated fields. Regarding soil composition there were no significant differences in their chemical characteristics in sludge treated soils and not treated soils.

De Imperial et al investigated in 2002 in Spain the differences in the emergence of six crops using composted sludge, not composted sludge and control under greenhouse conditions. They used Tomato (*Lycopersicon esculentum* Mill.), spinach (*Spinacia oleracea* L.), lentil (*Lens esculenta* Moench), maize (*Zea mays* L.), wheat (*Triticum aestivum* L.), and ryegrass (*Lolium perenne* L.) for the experiment. Application ranges were 0 ton ha-1, 40 ton ha-1 and 80 ton ha-1. They measured the amount of emerged plants, stem length and root length. The results shows that there were significantly higher values of all of the measure characteristics with 40 ton ha-1 of composted sludge in all plants excepting Lens esculenta, where the highest values were found using 40 ton ha-1 of fresh sewage sludge. The difference was attributed by the authors to the higher sentitive of Lens esculenta to salinity increases, and fresh sewage sludge has lower salinity than composted sludge.

In India is quite difficult to find fresh water to be further used in irrigation, that's why is usual to use sewage effluents as a water source for irrigation. Rattan et al studied in 2005 the effect that this practice can have on the soil. They made a chemical analysis of sludge used in irrigation, ground water, soil and plants (Oryza sativa L., Triticum aestivum L., Shorgum vulgare Pers., Zea mays L., Avena sativa L., Brassica napus L., Brassica campestris L., Spinacea oleracea L., Cucumis sativus L., Raphanus sativus L. and Trifolium alexandrium L. They found out that the sewage sludge used in irrigation just had slightly higher concentration of heavy metals than groundwater, and even the same in cases like Pb and Cd. Regarding nutrients like P, K and S, the concentration were various folds higher in sewage sludge than in groundwater. All the sludge samples were below the limit established by the Indian irrigation recommendations made by the Ministry of Agriculture. Only conductivity exceeded the recommendations by 1 dS m-1. As a result of sewage sludge application they measured an increase in heavy metal concentration in the soil irrigated using sewage sludge. Heavy metal content in plants varied between species, in the case of Oryza sativa there were high accumulation of Zn and Cu. In Triticum aestivum the increase was higher in Zn, Cu, Fe, Mn and Ni. Shorgum vulgare accumulates higher amounts of Fe, Cu and Ni. Avena sativa and Raphanus sativus only showed increases in Mn concenctration. Spinacea oleracea has higher amounts of Zn, Cu and Ni. In the rest of the plants the results didn't have enough significance to allow conclusions about them. Despite the increase in heavy metals concentration any of them had enough concentration to cause phytotoxcity effects.

Ramirez et al tried to find out in 2008 the toxic effects of digested sludge, composted sludge, thermally dried sludge and pig slurry in three different plants (Brassica rapa, Lolium perenne and trifolium pratense). To do that, they made a seedling test using the reduction in emergence rate as a measure of toxicity. The results showed that composted sludge inhibit less germination than fresh sludge or thermally dried sludge. To reach the total inhibition they needed 20 g kg-1 in pig slurry, 50 g kg-1 in not composted sludge, 151 g kg-1 in thermal treated sludge and 300 g kg-1 in composted sludge. This study shows a clear negative correlation between sludge stability and toxicity. The authors suggested that phytotoxicity was mediated by the release of ammonium, phenols, and organic acids during waste degradation.

Seleiman et al carried out and experiment in 2014 in Finland where they measured the concentration of different elements in maize, oilseed rape and hemp fertilized with high dose of sewage sludge and low dose of sewage sludge. They obtained the different extraction made by those plants.

Table 6. Heavy metal extraction by maize, oilseed rape and hemp at different dose of sludge.

Specie	As mg kg^{-1}	Cd mg kg^{-1}	Cr mg kg^{-1}	Cu mg kg^{-1}	Ni mg kg^{-1}	Zn mg kg^{-1}
High dose						
Maize	1,72	0,06	10,55	5,6	0,98	85,5
Oilseed rape	0,05	0,05	0,12	2,5	0,22	19,5
Fiber hemp	0,07	0,05	0,28	6,7	1,68	38,0
Low dose						
Maize	1,55	0,05	10,43	5,9	0,97	79,3
Oilseed rape	0,05	0,06	0,13	2,4	0,22	13,5
Fiber hemp	0,07	0,05	0,14	6,0	1,22	31,3

Specie	Cl g kg^{-1}	K g kg^{-1}	S g kg^{-1}	Si g kg^{-1}	C g kg^{-1}	N g kg^{-1}
High dose						
Maize	1,9	3,1	1,23	1,36	426	15,0
Oilseed rape	2,1	3,4	4,87	0,24	422	5,5
Fiber hemp	2,2	7,0	2,99	5,60	408	13,8
Low dose						
Maize	1,6	3,3	1,29	1,13	427	15,0
Oilseed rape	2,0	2,8	4,46	0,27	423	5,0
Fiber hemp	2,2	8,0	1,81	4,77	424	10,9

RESEARCH OBJECTIVES

4. Research objectives

The overall objective is to quantify the nutrients and heavy metals from sewage sludge and calculate the dose of these products can be applied to crops.

The specific objectives are considered:

Perform a chemical analysis of sludge from water treatment plants as well as sludge from cow farms.

Compare the chemical properties of both products and analyze if the studied sludge can be legally used for agriculture proposes according to three different legislations: European Directive (91/271/EEC), Spanish legislation (Minesterio de Agricultura, Pesca y Alimentación, 1310/1990) and Finnish legislation (Ministry of Agriculture and Forestry, 282/1994).

Make the dosage of sludge and manure for fertilization, firstly based on the legal limitation of heavy metal concentration and total amount of heavy metals applied to the soil per year. Then it will be based on the main nutrient extractions (nitrogen, phosphorus and potassium) and it will be evaluated the effect in the nutrient balance for a three year period. Finally it will be discuss which the best legally possible fertilization plan is for a three year period using maize, oilseed rape and hemp (all for biomass production) as crop rotation.

MATERIAL AND METHODS

5. -Material and methods

Seven different products of sewage sludge were collected from different places, Finland (Viikki (urban distrit of Helsinki, 100.000.000 m^3 of waste water per year, 608.000 habitants), Forssa (17.700 habitants), Vaasa (57.200 habitants), Jyvaskyla (132.000 habitants), Kauvula (87,300 habitants), Maanika (cow farm), Kalmari (cow farm)). Only sludge collected from Kalmari and Maaninka was from dairy cows, which was in a liquid form before it was centrifuged to obtain the solid part for the analysis. No any treatments have been done on sludge collected from dairy cows. The biological treatments was used in the sludge production obtained from Forssa, while chemical treatments were used during the production process of sludge collected from Viikki (Helsinki), Jyvaskyla, Vaasa, Kauvula. All samples were randomly taken from the trailer that was used to transport and then homogenized. The samples were collected by university workers the 22th of November of 2013.

Figure 4. Region where the samples were obtained.

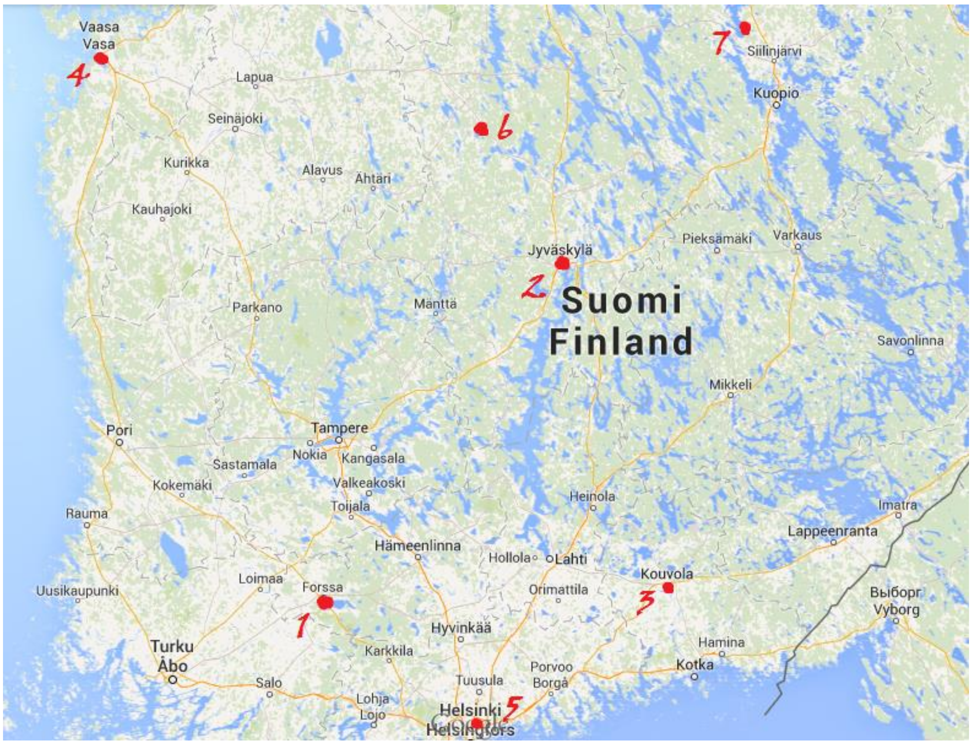

Figure 5. Sample locations. 1: Forssa; 2: Jyväskylä; 3: Kouvola; 4: Vaasa; 5: Viikki (Helsinki); 6: Kalmari; 7: Maanika.

Soil samples were taken from a field in Viikki (Helsinki, Finland), Coordinates 60.224301,25.024950, owned by the Department of Agricultural Sciences, Helsinki University the 24th of March of 2014. Four samples were collected from 4 different random places of the field. The sample was taken from the first 50cm and then homogenized.

Figure 6. Field location.

Figure 7.. Extraction of manure asmple from Kalmari.

5.1. -Measurements

All analysis (dry matter, pH, EC, C:N ratio, N, C, P fractions, Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Si and Zn) from different sludge products and soil were conducted at the Department of Agricultural Sciences, Helsinki University.

Sludge, manure and soil samples were then kept in a cold room at -20ºC.

5.1.1. -Dry matter (%)

To measure the dry matter content, the fresh sludge samples and soil samples (about 20 g) were weighted and dried in the oven (GWB WTC binder, GW BERG & CO, Finland) on 60 ˚C for 3 days. Then the samples were inserted in the desiccator for 30 min. Then the samples were weighted to measure the dry matter.

Calculations where made using the equation: $DM = \left(1 - \frac{FW - DW}{FW}\right).100$

Where DM is dry matter, FW is fresh weight and DW is dry weight.

In addition, manure samples needed to be centrifuged due to its high humidity, to remove easily its high water content. They were put in the centrifuge (Kendra, Multifuge IS-R D-37520 Osterode, Germany) for three minutes at 2.600 r.p.m. and then decanted to remove the water.

Figure 8.. Dried sludge samples.

5.1.2. -pH and electrical conductivity (EC)

pH and EC was measured in the seven different products of sludge and soil using the pH meter (model T70, GWB Mettle Toledo, Switzerland). First, sludge samples were dried at 105 ˚C and then grinded using the mortar. About 20 mL of the grinded samples were weighted and then taken into a cups and 50 mL of distilled water was added. The meter was calibrated before measuring the EC using the distilled water. Also, the machine was calibrated before measuring pH using buffer pH 4 and 7 (Oy FF-chemicals Ab, Finland). The cups were rinsed three times with distilled water between each two samples in order to avoid contamination.

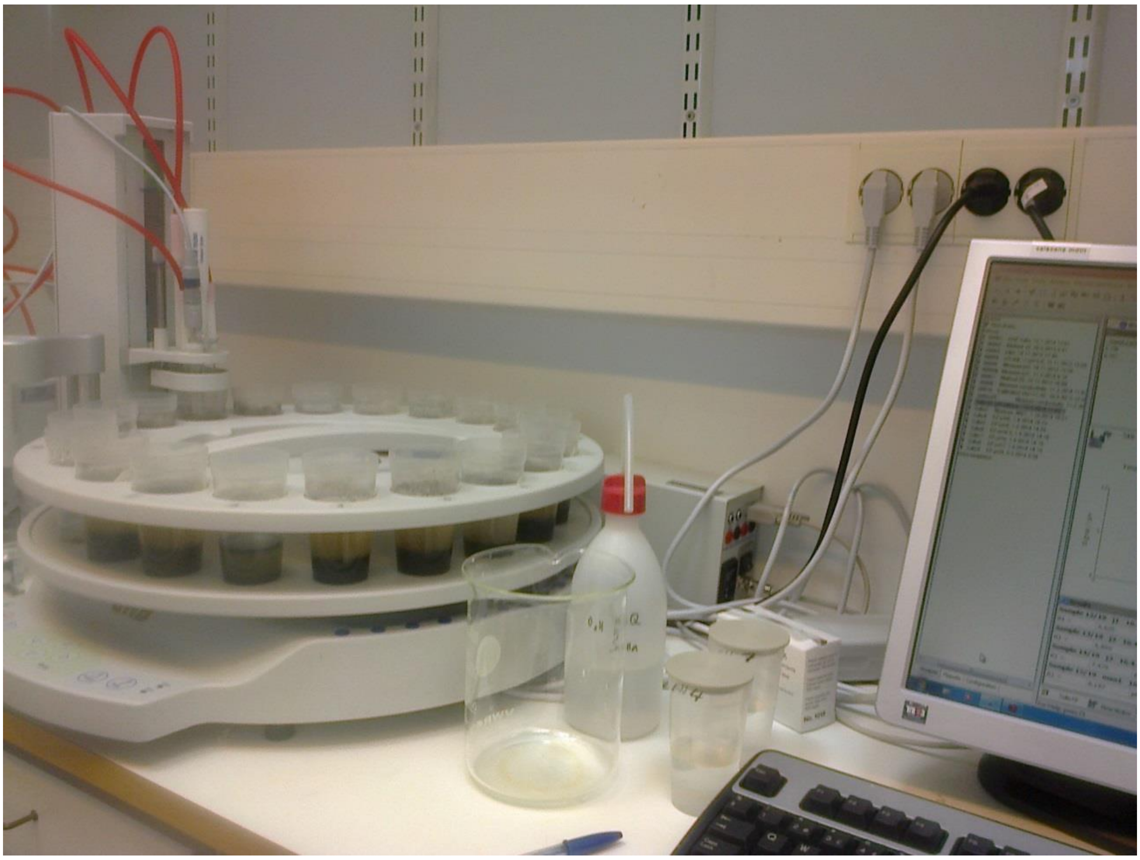

Figure 9. pH and EC meter.

5.1.3. -Phosphorous fractions

About 1 g from each sample was taken for analyzing four phosphorous fractions: NH_4Cl extraction (extracted form of soluble phosphorous and calcium), NH_4F extraction (aluminum oxides and hydroxides bounding phosphorous), NaOH extraction (iron oxide bound phosphorous) and H_2SO_4 extraction (primary calcium phosphate). In the first extraction of P, about 1g of the dried samples were inserted in plastic tubes (50 mL), then 50 mL of 1M NH_4Cl was added to the sample and shaked for about 30 min using shaker (Roto-shake genie, Scientific industries.INC, USA). Then, the samples were centrifuged using Multifuge IS-R (D-37520 Osterode, Germany). The samples were then filtered using Whatman paper (Filter paper circles ashless/ Blue ribbon, 589/3, GE Healthcare Life Sciences, Germany) into plastic bottles. The filtered samples were then analysed using the spectrophotometer at 660 nm (Ordior, Model UV-1800 240V IVDD, SHIMADZU INC., USA). In the second extraction, the tubes with the sediment were used and 50 mL of 0.5 M NH_4F was added for each sample. The samples were then shaked for 1h. Then the samples were centrifuged and filtered. The samples were then taken for the measurements using the spectrophotometer at 660 nm. Third extraction was made by washing the sediment with NaCl solution, then centrifuged and the liquid part was removed. After that 50 mL of 0.1 M NaOH was added to the sediment and shaked for 30 min. The samples were left on the table in room temperature overnight. Then, the samples were again shaked for 30 min and then were centrifuged and were filtered. Then 20 mL of filtered solution was taken to a beaker and 5 mL of 0.5 M H_2SO_4 was added and finally this solution was filtered. Then, the measurement was made using the spectrophotometer at 660 nm.The fourth extraction was made by adding 50 mL of 0.25 M H_2SO_4 to the sediment and was shaked for 1 h. Then it was centrifuged and filtered. The measurement was made using the spectrophotometer at 660 nm.

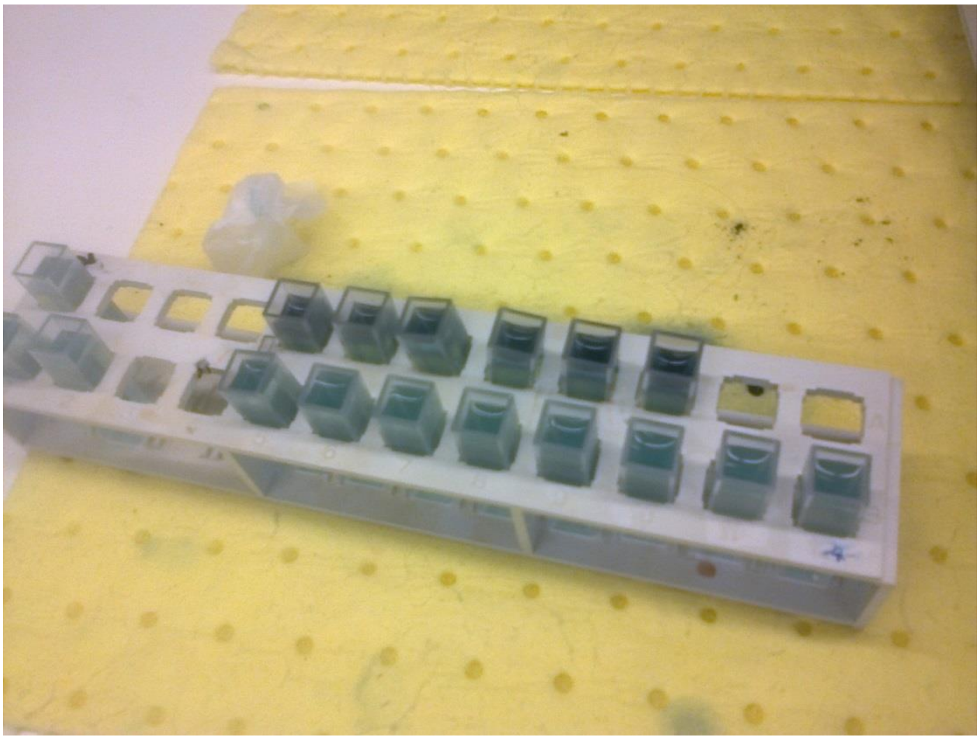

Figure 10. Phosphorus fractionated samples ready to be measured by spectrometry.

Figure 11. Spectophotometer.

5.1.4. -Elemental analysis using ICP-OES

To make the ICP analysis, two different methods were used. In the first method: 9 mL of HCl and 3 mL of HNO_3 (67-69%, VWR International BVBA, Geldenaaksebaan, Leuven, Belgium) were added to digest samples. In the second method: 3 mL of HCl and 9 mL of HNO_3 were added to digest sludge samples [300 mg either that have been dried in oven, room temperature or Freeze-drying (Cool Safe 100-9 PRO XS superior freeze-dryer, GWB, Finland)]. The sludge sample or soil were inserted in PTFE Teflon tubes (CEM, Matthews, North Carolina, USA) with the acids mentioned above, and then the PTFE were inserted in the microwave (MARSXpress, MARS 240/50, CEM, Matthews, NC, USA) for digestion. The microwave digestion program used for heavy metals digestion was 250 W for 6 min, then 400 W for another 6 min and 650 W for 6 min. Then microwave energy was decreased to 250 W and maintained for 6 min and finally 5 min of ventilation at 0 W was applied. After the extraction, the vessels were allowed to cool at room temperature before they were opened.

After the digestion, the samples were filtered and diluted with distillated water up to 50 mL. Then they were kept in the storage room overnight in cold room at -5 ºC. Finally the measure was made by Inductively Coupled Plasma-Optical Emission Spectrometry (iCAP 6200, Thermo Fisher Scientific, Cambridge, UK). To make the measured it was necessary to make three different standard solutions to be able to make the calibration of different concentrations. The standard solutions are summarized in the following table:

Table 7. Standard solution I for ICP analysis.

	S1	S2	S3	S4	S5
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
Al	2	12,5	25	50	100
Ca	2	25	50	100	200
Fe	2	25	50	100	200
K	2	5	10	50	100
Mg	2	5	10	50	100
Zn	2	5	10	50	100
Na	2	5	10		
As	2	5	10		
Hg	2	5	10		

Table 8. Standard solution II for ICP analysis.

	S6	S7	S8	S9	S10
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
As	0,01	0,05	0,1	0,5	1
Hg	0,01	0,05	0,1	0,5	1
Al	0,01	0,05	0,1	0,5	1
B	0,01	0,05	0,1	0,5	1
Ca	0,01	0,05	0,1	0,5	1
Cd	0,01	0,05	0,1	0,5	1
Cr	0,01	0,05	0,1	0,5	1
Cu	0,01	0,05	0,1	0,5	1
Fe	0,01	0,05	0,1	0,5	1
K	0,01	0,05	0,1	0,5	1
Mg	0,01	0,05	0,1	0,5	1
Mn	0,01	0,05	0,1	0,5	1
Na	0,01	0,05	0,1	0,5	1
Ni	0,01	0,05	0,1	0,5	1
Pb	0,01	0,05	0,1	0,5	1
Zn	0,01	0,05	0,1	0,5	1
P				0,5	1

Table 9. Standard solution III for ICP analysis.

	S11	S12	S13	S14	S15
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
P	2	25	50	100	200
Si	0,1	1	10	25	50
S	0,1	1	10	25	50

Using these standard solutions the machine was able to measure the following range of concentrations:

Table 10. Limit precision ranges.

	Al	As	Mn	Cd	Cr	Cu	Pb	Ni
mg kg^{-1}	1000-6500	1-5	60-220	0,4	10-30	90-270	5-20	5-20
	Zn	Hg	K	Ca	Mg	P	S	Si
mg kg^{-1}	130-470	0,5	2100	38000	3300	10 000-26000	100-1800	9500-36000

All reagents were of analytical-reagent grade. The water used in the dilution was deionized and it was purified using Millipore (Bedford, MA, USA) Milli-Q system. Aqueous stock solutions of Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, S, Si, Mg, K and Na were prepared by dilution of the respective standard 1000 mg L^{-1} solutions (Merck, Germany). All standard and reagent solutions were stored in polyethylene bottles.

Figure 12. Sludge prepared for microwave digestion.

Figure 13. ICP analysis machine.

5.1.5. -Nitrogen and carbon content and ratio

Nitrogen and carbon content was analyzed using Dumas combustion method (Etheridge et al., 1998). In this method, dried samples (500 mg) from oven and air drying were milled using a mortar and then put into Vario MAX CN (Elemental Analyze system GmbH, Hanau, Germany).

5.1.6. -Statistical analysis

All of the physico-chemical analyses were repeated four times for phosphorus fraction, dry matter, nitrogen content, carbon content, CN ratio, salinity and pH, and for ICP the analysis was repeated six times using independent samples from each sub-plot corresponding to sludge from Viikki, Forssa, Vaasa, Jyvaskyla and Kauvula, cattle manure from Mannika, Kalmari, and soil from a field in Viikki. ANOVA statistical analyses of data at 95% significance were carried out. Significant statistical differences, as F-values, among means are shown as different letter (a, b, c, d, e). The values of means were compared with each other through Duncan's multiple range test. Data manipulation was performed with Microsoft Excel and PASW statistics v. 18. (IBM Inc., Chicago, IL, USA).

5.2. -Evaluation of sludge of agricultural use

5.2.1. -Legal requirements

To evaluate if it is legally possible to use the analyzed sludge samples, there will be done three analyses:

1- Soil characteristics will be compared with the limit values established in the European Directive, in the Spanish legislation and in the Finnish legislation.
2- Sludge characteristics will be compared with the limit values established in the European Directive, in the Spanish legislation and in the Finnish legislation.

3- Maximum amount of sludge that can be used for the studied soil will be calculated according to the European Directive, the Spanish legislation and the Finnish legislation. For that propose there will be used the following equation:

$$Max.amount\ (kg\ ha^{-1}) = \frac{Maximum\ legal\ load\ (kg\ ha^{-1})}{10^{-6} * Sludge\ concentration\ (mg\ kg^{-1})}$$

5.2.2. -Fertilization dosage

All calculation will be done for a three year period, using a rotation with maize, oilseed rape and hemp. The expected yield data will be obtained by from the study done by Seleiman et al in 2013. To calculate the dosage of the sludge, nutrients extractions of maize, oilseed rape and hemp made by Seleiman et al in 2014 will be used.

For micronutrients (As, Cd, Cr, Cu, Ni and Zn) the following equation will be used.

$$Crop\ Nutrient\ extraction(kg\ ha^{-1}) = \frac{Nutrient\ concentration\ (mg\ kg^{-1})}{10^{6}} * Yield\ (kg\ ha^{-1})$$

For macronutrients (C, N, P, K, S and Si) there will be used:

$$Crop\ Nutrient\ extraction(kg\ ha^{-1}) = \frac{Nutrient\ concentration\ (g\ kg^{-1})}{10^{3}} * Yield\ (kg\ ha^{-1})$$

The total amount of nutrient extracted by the successive crops will be calculated as the sum of each crop extraction, represented in the following equation:

$$Total\ crop\ extraction\ (kg\ ha^{-1}) = \sum_{i=3}^{n} Crop\ extraction_i\ (kg\ ha^{-1})$$

Then, to calculate the dosage there will be used three hypothesis:

1- Using Nitrogen extraction:

$$Dosage\ (kg\ ha^{-1}) = \frac{Nitrogen\ extraction\ (kg\ ha^{-1})}{10^{-3} * Sludge\ Nitrogen\ concentration\ (g\ kg^{-1})}$$

2- Using Phosphorus extraction:

$$Dosage\ (kg\ ha^{-1}) = \frac{Phosphorus\ extraction\ (kg\ ha^{-1})}{10^{-3} * Sludge\ Phosphorus\ concentration\ (g\ kg^{-1})}$$

3- Using Potassium extraction:

$$Dosage\ (kg\ ha^{-1}) = \frac{Potassium\ extraction\ (kg\ ha^{-1})}{10^{-3} * Sludge\ Potassium\ concentration\ (g\ kg^{-1})}$$

5.2.3. -Final nutrient balance

Finally there will be calculated the resulting nutrient balance in the soil. To do that first there will be calculated the amount of nutrient that is incorporated by the dosage (previously calculated for N, P and K dosages).

$$Nutrient\ incoroporation\ (kg\ ha^{-1}) = \frac{Sludge\ nutrient\ concentration\ (mg\ kg^{-1})}{10^{6}} * Dosage\ (kg\ ha^{-1})$$

Then there will be calculated nutrient extraction by the crop using:

$$Crop\ extraction\ (kg\ ha^{-1}) = Crop\ nutrient\ concentration\ (mg\ kg^{-1}) * Yield\ (kg\ ha^{-1})$$

Total extraction will be calculated by:

$$Total\ crop\ extraction\ (kg\ ha^{-1}) = \sum_{i=3}^{n} Crop\ extraction_i\ (kg\ ha^{-1})$$

Balance will be obtained by:

$$Balance\,(kg\ ha^{-1}) = Total\ crop\ extraction\,(kg\ ha^{-1}) - Nutrient\ incorporation\,(kg\ ha^{-1})$$

6. -Results

6.1. -Chemical characterization of the soil

The soil was slightly acidity with a pH of 6.05. There were no salinity problems because the conductivity was low (0.17 ds m^{-2}). P fractions in the soil showed how most of the P was presented in the secondary phosphorus minerals (Al-P, Fe-P and Ca-P), and the highest precipitated P was with the aluminum (0.66 g kg^{-1}). The lowest fraction of P was the soluble form. The soluble form was account for about 5%, while the P bounded with Al was accounted for 44% of the total P.

Table 11. Chemical and physical characterization of the soil

	Soil	Standard desviation
Dry matter %	98.06	0,05
Moisture %	1.94	0,05
pH	6.05	0,10
EC ds m^{-1}	0.17	0,01
N g kg^{-1}	1.99	0,08
C g kg^{-1}	25.43	1,89
C:N ratio	12.81	1,32
Soluble P g kg^{-1}	0.08	0,00
Al-P g kg^{-1}	0.66	0,02
Fe-P g kg^{-1}	0.41	0,03
Ca-P g kg^{-1}	0.34	0,01
Total P g kg^{-1}	1.48	0,04

Table 12. ICP analysis of the soil:

	Mean	Standard deviation
Al mg kg^{-1}	1.473,27	16,77
As mg kg^{-1}	1,71	0,11
Ca mg kg^{-1}	9.606,75	3.790,30
Cd mg kg^{-1}	0,11	0,01
Cr mg kg^{-1}	7,56	0,16
Cu mg kg^{-1}	7,87	0,12
K mg kg^{-1}	10.505,68	20,81
Fe mg kg^{-1}	150,13	1,78
Mg mg kg^{-1}	109,16	1,25
Mn mg kg^{-1}	7,63	0,36
Na mg kg^{-1}	17,49	0,58
Ni mg kg^{-1}	3,18	0,17
P mg kg^{-1}	16.375,90	158,28
Pb mg kg^{-1}	8,30	0,62
S mg kg^{-1}	7,77	0,31
Si mg kg^{-1}	384,61	6,06
Zn mg kg^{-1}	31,87	2,42

6.2. -Chemical characterization of sludge and manure.

Table 13. Dry matter content in sewage sludge (S) and manure (M).

Sludges	N	Mean	Std. Deviation
Forssa (S)	3	27,98[b]	0,61
JKL (S)	3	29,80[a]	0,46
Kouvula (S)	3	29,38[ab]	0,18
Vaasa (S)	3	29,50[a]	0,30
Viikki (S)	3	30,29[a]	0,62
Kalmari (M)	3	10,71[d]	0,14
Maanika (M)	3	12,48[c]	0,90

Different letters indicates differences with a significance of 95%.

As we can see in the results, moisture was quite higher in dairy cattle sludge comparing to sewage sludge from water treatment plants (Table 13). Between manure samples there were significant differences, being Kalmari the sample with lowest dry matter content.

Table 14. Total phosphorus content in sewage sludge (S) and manure (M).

Sludges	N	Mean g kg^{-1}	Std. Deviation g kg^{-1}
Forssa (S)	3	22,34^{ab}	2,24
JKL (S)	3	20,26^{bc}	4,37
Kouvula (S)	3	22,36^{ab}	2,97
Vaasa (S)	3	21,00^{bc}	0,61
Viikki (S)	3	30,08^{a}	4,48
Kalmari (M)	3	18,98^{bc}	0,75
Maanika (M)	3	13,54^{c}	2,10

Different letters indicates differences with a significance of 95%.

There was highest concentration of phosphorus in sludge; in the case of Vikki and Forssa they showed significant highest values than the others samples (Table 14). Manure had the lowest concentration, but manure from Kalmari didn't have much significant differences with sludge samples as Maanika (Table 14).

Table 15. Aluminum bound phosphorus fraction in sewage sludge (S) and manure (M)..

Sludges	N	Mean g kg^{-1}	Std. Deviation g kg^{-1}
Forssa (S)	3	$0,88^{c}$	0,15
JKL (S)	3	$1,33^{c}$	0,52
Kouvula (S)	3	$0,49^{c}$	0,09
Vaasa (S)	3	$3,58^{b}$	0,60
Viikki (S)	3	$0,50^{c}$	0,03
Kalmari (M)	3	$6,75^{a}$	0,95
Maanika (M)	3	$3,37^{b}$	0,34

Different letters indicates differences with a significance of 95%.

Aluminum bound phosphorus fraction has higher values in dairy cow manure, but there was one sewage sludge sample Vaasa that had significantly higher values than the others (Table 15). Is remarkable that sludge from Vaasa had significantly similar values than manure from Maanika (Table 15). The highest value was found in manure from Kalmari (Table 15).

Table 16. Calcium bound phosphorus fraction in sewage sludge (S) and manure (M).

Sludges	N	Mean g kg^{-1}	Std. Deviation g kg^{-1}
Forssa (S)	3	5,12[ab]	0,74
JKL (S)	3	7,77[a]	3,06
Kouvula (S)	3	6,50[a]	1,34
Vaasa (S)	3	6,76[a]	0,39
Viikki (S)	3	8,35[a]	3,44
Kalmari (M)	3	1,17[b]	0,17
Maanika (M)	3	3,56[ab]	1,36

Different letters indicates differences with a significance of 95%.

Calcium bound phosphorus fraction has lower differences between each sample, but again dairy cow manure had lower values than sewage sludge samples (Table 16).

Table 17. Iron bound phosphorus fraction in sewage sludge (S) and manure (M).

Sludges	N	Mean g kg^{-1}	Std. Deviation g kg^{-1}
Forssa (S)	3	$16{,}25^{b}$	1,67
JKL (S)	3	$11{,}12^{c}$	1,15
Kouvula (S)	3	$15{,}34^{b}$	1,76
Vaasa (S)	3	$10{,}62^{c}$	1,38
Viikki (S)	3	$21{,}17^{a}$	1,11
Kalmari (M)	3	$5{,}91^{d}$	1,03
Maanika (M)	3	$1{,}92^{e}$	0,12

Different letters indicates differences with a significance of 95%.

Fe-P is much higher in sewage sludge samples, was remarkable that Viikki has practically all of the phosphorus in this fraction and has significant differences with the others; the rest of sewage sludge samples also had high values (Table 17).

Table 18. Soluble phosphorus fraction in sewage sludge (S) and manure (M).

Sludges	N	Mean g kg^{-1}	Std. Deviation g kg^{-1}
Forssa (S)	3	$0,08^{b}$	0,01
JKL (S)	3	$0,04^{b}$	0,02
Kouvula (S)	3	$0,03^{b}$	0,01
Vaasa (S)	3	$0,04^{b}$	0,01
Viikki (S)	3	$0,05^{b}$	0,02
Kalmari (M)	3	$5,15^{a}$	0,49
Maanika (M)	3	$4,70^{a}$	0,42

Different letters indicates differences with a significance of 95%.

Soluble fraction was significantly lower in sludge than in manure (Table 18). Indeed soluble fraction was almost insignificant.

Table 19. Nitrogen content in sewage sludge (S) and manure (M).

Sludges	N	Mean g kg^{-1}	Std. Deviation g kg^{-1}
Forssa (S)	4	26,54^{c}	2,14
JKL (S)	4	35,41^{a}	1,09
Kouvula (S)	4	27,62^{bc}	0,77
Vaasa (S)	4	30,10^{b}	0,63
Viikki (S)	4	29,52^{b}	1,10
Kalmari (M)	4	30,14^{b}	0,84
Maanika (M)	4	22,68^{d}	0,96

Different letters indicates differences with a significance of 95%.

Jyvaskyla showed significant higher amount of nitrogen than the others samples (Table 19). Despite the fact that manure from Maanika has the lowest nitrogen content, there is no significant differences between nitrogen content in sludge and manure (Table 19).

Table 20. Carbon content in sewage sludge (S) and manure (M).

Sludge	N	Mean g kg^{-1}	Std. Deviation g kg^{-1}
Forssa (S)	4	267,54[b]	32,20
JKL (S)	4	251,67[b]	9,31
Kouvula (S)	4	258,46[b]	4,23
Vaasa (S)	4	270,62[b]	10,24
Viikki (S)	4	245,07[b]	13,54
Kalmari (M)	4	376,29[a]	29,64
Maanika (M)	4	380,81[a]	25,76

Different letters indicates differences with a significance of 95%.

Carbon content was significant higher in manure than in sludge (Table 20).

Table 21. CN ratio in sewage sludge (S) and manure (M).

Suldges	N	Mean	Std. Deviation
Forssa (S)	4	10,06[c]	0,48
JKL (S)	4	7,11[e]	0,08
Kouvula (S)	4	9,36[cd]	0,13
Vaasa (S)	4	8,99[cd]	0,17
Viikki (S)	4	8,30[de]	0,18
Kalmari (M)	4	12,50[b]	1,18
Maanika (M)	4	16,80[a]	1,05

Different letters indicates differences with a significance of 95%.

Regarding CN ratio, we can see that Jyvaskyla had the significant lowest CN ratio (Table 21). Manure had significant differences with sludge, but they also showed significant differences between each other, being higher in Maanika (Table 21).

Table 22. Electrical Conductivity in sewage sludge (S) and manure (M).

Sludge	N	Mean dS m^{-1}	Std. Deviation dS m^{-1}
Forssa (S)	3	$5{,}42^{c}$	0,14
JKL (S)	3	$3{,}58^{d}$	0,03
Kouvula (S)	3	$5{,}02^{c}$	0,41
Vaasa (S)	3	$3{,}33^{de}$	0,10
Viikki (S)	3	$2{,}90^{e}$	0,30
Kalmari (M)	3	$7{,}51^{a}$	0,20
Maanika (M)	3	$6{,}84^{b}$	0,12

Different letters indicates differences with a significance of 95%.

The highest values of EC was found in sludge obtained from Kalmari, while the lowest values of EC were found in sludge obtained from Viikki and Forssa (Table 22). There were significant differences between sludge and manure, but also there were significant differences between each sample (Table 22).

Table 23. pH in sewage sludge (S) and manure (M).

Sludge	N	Mean	Std. Deviation
Forssa (S)	3	7,73[c]	0,01
JKL (S)	3	6,91[e]	0,01
Kouvula (S)	3	7,50[d]	0,02
Vaasa (S)	3	6,98[e]	0,01
Viikki (S)	3	7,48[d]	0,05
Kalmari (M)	3	8,62[a]	0,05
Maanika (M)	3	8,41[b]	0,01

Different letters indicates differences with a significance of 95%.

The pH was higher in the dairy cow manure obtained from Manninka and Kalmari than sludge obtained from other places (Table 23). Moreover there were significant differences between sludge and manure, being higher in manure (Table 23). Despite the variation in pH from sample to sample, all of them were neutral or slightly basic (Table 23).

Table 24. Aluminum content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	4.498,11^{cd}	30,62
JKL (S)	6	4.587,26^{b}	14,26
Kouvula (S)	6	4.527,45^{c}	29,03
Vaassa (S)	6	4.672,11^{a}	8,77
Viikki (S)	6	4.492,27^{d}	8,94
Kalmari (M)	6	898,15^{e}	15,02
Maanika (M)	6	902,15^{e}	1,20

Different letters indicates differences with a significance of 95%.

Aluminum content was significant lower in manure than in sludge, but there also were significant differences between each sludge sample (Table 24). In addition, aluminum content in manure is not precise due to its low content, below the precision limit of 1000 mg kg^{-1} (Table 10).

Table 25. Arsenic content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	4,73^{b}	0,50
JKL (S)	6	4,86^{b}	0,22
Kouvula (S)	6	4,96^{b}	0,18
Vaassa (S)	6	4,99^{b}	0,13
Viikki (S)	6	4,87^{b}	0,26
Kalmari (M)	6	6,30^{a}	0,32
Maanika (M)	6	6,50^{a}	0,22

Different letters indicates differences with a significance of 95%.

Arsenic content was significant higher in manure than in sludge (Table 15). Moreover manure concentrations weren´t very precise because they were over the precision limit of 5 mg kg^{-1} (Table 10).

Table 26. Calcium content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	38.559,64[a]	96,57
JKL (S)	6	38.362,00[b]	35,10
Kouvula (S)	6	38.372,96[b]	14,62
Vaassa (S)	6	38.537,84[a]	19,61
Viikki (S)	6	38.437,08[b]	47,84
Kalmari (M)	6	3.236,47[c]	42,16
Maanika (M)	6	3.268,41[c]	4,31

Different letters indicates differences with a significance of 95%.

Manure had significant lower content of calcium than sludge (Table 26), but calcium content in sludge samples wasn't precise due to its high concentration that was over the precision limit of 38.000 mg kg^{-1} (Table 10).

Table 27. Cadmium content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	0,40[a]	0,05
JKL (S)	6	0,43[a]	0,04
Kouvula (S)	6	0,46[a]	0,04
Vaassa (S)	6	0,40[a]	0,06
Viikki (S)	6	0,44[a]	0,05
Kalmari (M)	6	0,44[a]	0,03
Maanika (M)	6	0,46[a]	0,05

Different letters indicates differences with a significance of 95%.

There wasn´t significant differences between samples (Table 27). All values were over the precision limit of 0,40 mg kg^{-1}, but they were very near to it (Table 10).

Table 28. Chromium content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	$30,61^{c}$	0,35
JKL (S)	6	$31,65^{b}$	0,31
Kouvula (S)	6	$31,41^{b}$	0,20
Vaassa (S)	6	$30,46^{c}$	0,21
Viikki (S)	6	$31,59^{b}$	0,30
Kalmari (M)	6	$41,86^{a}$	0,23
Maanika (M)	6	$41,82^{a}$	0,25

Different letters indicates differences with a significance of 95%.

Manure had significant higher concentration of chromium than sludge (Table 28). But these results aren't precise due to its high content in chromium, upper the precision limit of 30 mg kg^{-1} (Table 10).

Table 29. Copper content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	271,22[a]	0,37
JKL (S)	6	271,05[a]	0,50
Kouvula (S)	6	271,63[a]	0,31
Vaassa (S)	6	271,52[a]	0,57
Viikki (S)	6	272,89[a]	0,90
Kalmari (M)	6	39,74[c]	3,90
Maanika (M)	6	48,16[b]	1,23

Different letters indicates differences with a significance of 95%.

Copper concentration was significant lower in manure than in sludge, but there were also significant differences between both manure samples, being lower in Maanika (Table 29). Is also remarkable that all the values were out of the precision range of 90-270 mg kg^{-1} (Table 10).

Table 30. Iron content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	17.569,03^{b}	131,96
JKL (S)	6	18.032,58^{a}	114,49
Kouvula (S)	6	17.958,19^{a}	43,40
Vaassa (S)	6	17.485,92^{b}	29,17
Viikki (S)	6	18.099,35^{a}	178,44
Kalmari (M)	6	541,40^{c}	0,77
Maanika (M)	6	541,04^{c}	0,24

Different letters indicates differences with a significance of 95%.

Sludge showed significant higher concentration of iron than manure (Table 30). There were also some significant differences between sludge samples, being lower in Forssa and Jyvaskyla (Table 30).

Table 31. Potassium content in sewage sludge (S) and manure (M).

		Mean	Std. Deviation
Sludges	N	mg kg^{-1}	mg kg^{-1}
Forssa (S)	6	2.089,70[c]	9,54
JKL (S)	6	2.059,49[c]	17,17
Kouvula (S)	6	2.085,18[c]	12,39
Vaassa (S)	6	2.074,03[c]	22,74
Viikki (S)	6	2.076,64[c]	15,06
Kalmari (M)	6	2.387,92[a]	38,14
Maanika (M)	6	2.245,70[b]	91,95

Different letters indicates differences with a significance of 95%.

Manure had higher potassium content than sludge (Table 31). Between both manure samples, Kalmari had significant higher potassium content (Table 31). In addition, potassium concentration in manure wasn`t precise due to its concentration were upper the precision limit of 2.100 mg kg^{-1} (Table 10).

Table 32. Magnesium content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	3.411,84^{bc}	7,99
JKL (S)	6	3.396,63^{c}	3,11
Kouvula (S)	6	3.415,35^{bc}	9,27
Vaassa (S)	6	3.421,71^{bc}	1,80
Viikki (S)	6	3.411,10^{bc}	5,20
Kalmari (M)	6	3.507,34^{a}	30,19
Maanika (M)	6	3.439,79^{bc}	35,55

Different letters indicates differences with a significance of 95%.

Magnesium content was significant higher in Kalmari, but there weren't significant differences between the rest of the samples (Table 32). All those values weren´t precice because they were upper the precision limit of 3300 mg kg^{-1}(Table 10).

Table 33. Manganese content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	247,07^{c}	0,66
JKL (S)	6	250,37^{b}	0,80
Kouvula (S)	6	248,12^{c}	1,14
Vaassa (S)	6	247,58^{c}	0,14
Viikki (S)	6	247,85^{c}	0,58
Kalmari (M)	6	276,26^{a}	0,75
Maanika (M)	6	275,43^{a}	1,00

Different letters indicates differences with a significance of 95%.

Manganese content was significant higher in manure, but there were also significant differences between sludge samples, being higher in Jyvaskyla than in other places (Table 33). All manganese concentrations were over the precision limit of 220 mg kg^{-1} (Table 10).

Table 34. Sodium content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	548,81^{a}	4,61
JKL (S)	6	534,22^{b}	4,38
Kouvula (S)	6	539,96^{ab}	4,12
Vaassa (S)	6	539,66^{b}	5,14
Viikki (S)	6	538,03^{b}	4,54
Kalmari (M)	6	445,34^{c}	4,59
Maanika (M)	6	401,23^{d}	6,58

Different letters indicates differences with a significance of 95%.

Sludge had significant higher concentration of sodium, but there were some significant differences between each sample, being higher in Forssa (Table 34). Manure also showed significant differences between each sample, being lower in Maanika (Table 34).

Table 35. Nickel content in sludge and manure.

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	20,58[b]	0,95
JKL (S)	6	25,84[b]	8,78
Kouvula (S)	6	20,10[b]	0,08
Vaassa (S)	6	33,55[b]	29,65
Viikki (S)	6	20,22[b]	0,03
Kalmari (M)	6	148,69[a]	1,09
Maanika (M)	6	147,73[a]	1,17

Different letters indicates differences with a significance of 95%.

Nickel content was significant higher in manure than in sludge (Table 35). There wasn`t significant differences inside each type of sample (Table 35). All those values were over the precision limit of 20 mg kg^{-1} (Table 10).

Table 36. Lead content in sludge and manure.

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	19,63[b]	1,03
JKL (S)	6	20,53[b]	0,65
Kouvula (S)	6	19,94[b]	0,41
Vaassa (S)	6	19,76[b]	0,78
Viikki (S)	6	20,58[b]	0,84
Kalmari (M)	6	26,00[a]	0,99
Maanika (M)	6	26,82[a]	0,83

Different letters indicates differences with a significance of 95%.

Lead concentration was significantly higher in manure than in manure (Table 36). Some of those results weren´t precise, because there were slightly above the precision limit of 20 mg kg^{-1} (Table 10).

Table 37. Sulfur content in sludge and manure.

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	82,73^{ab}	2,48
JKL (S)	6	81,59^{ab}	1,41
Kouvula (S)	6	80,55^{b}	1,65
Vaassa (S)	6	84,67^{a}	2,59
Viikki (S)	6	82,33^{ab}	1,83
Kalmari (M)	6	32,27^{c}	1,06
Maanika (M)	6	30,32^{c}	1,38

Different letters indicates differences with a significance of 95%.

Sulfur content was significantly higher in sludge than in manure, moreover there were some significant differences between sludge samples (Table 37). All samples were below the precision limit of 100 mg kg^{-1} (Table 10).

Table 38. Silicon content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	16.071,20[a]	49,03
JKL (S)	6	16.052,72[a]	39,15
Kouvula (S)	6	16.048,23[a]	36,58
Vaassa (S)	6	16.074,00[a]	21,28
Viikki (S)	6	16.077,25[a]	25,08
Kalmari (M)	6	3.041,79[b]	1.548,40
Maanika (M)	6	4.041,36[b]	1,96

Different letters indicates differences with a significance of 95%.

Manure had significantly lower content of silicon than sludge (Table 38). But is should be said that silicon content in manure was significantly below the precision limit of 9500 mg kg^{-1} (Table 10).

Table 39. Zinc content in sewage sludge (S) and manure (M).

Sludges	N	Mean mg kg^{-1}	Std. Deviation mg kg^{-1}
Forssa (S)	6	200,44[a]	22,72
JKL (S)	6	210,83[a]	15,63
Kouvula (S)	6	220,34[a]	18,50
Vaassa (S)	6	200,20[a]	28,89
Viikki (S)	6	210,21[a]	19,84
Kalmari (M)	6	29,57[b]	0,83
Maanika (M)	6	29,95[b]	2,37

Different letters indicates differences with a significance of 95%.

Zinc content was significantly higher in sludge than in manure (Table 39). But in the case of manure, the values didn`t have much precision because their concentration was below the precision limit (Table 10).

There wasn`t enough mercury in the samples to be appreciated by the equipment.

6.3. -Nutrient extraction by each crop

According to the results obtained by Seleiman et al in 2014, the extraction of the crops are:

Table 40. Nutrient extractions of different crops.

	Maize	Oilseed rape	Hemp
Yield (kg ha^{-1})	25.000	10.000	15.000
As (mg ha^{-1})	43.000	500	1.050
Cd (mg ha^{-1})	1.500	500	750
Cr (mg ha^{-1})	263.750	1.200	4.200
Cu (mg ha^{-1})	140.000	25.000	100.500
Ni (mg ha^{-1})	24.500	2.200	25.200
Zn (mg ha^{-1})	2.137.500	195.000	570.000
Cl (g ha^{-1})	47.500	21.000	33.000
K (g ha^{-1})	77.500	34.000	105.000
S (g ha^{-1})	30.750	48.700	44.850
Si (g ha^{-1})	34.000	2.400	84.000
C (g ha^{-1})	10.650.000	4.220.000	6.120.000
N (g ha^{-1})	375.000	55.000	207.000
P (g ha^{-1})	24.500	30.200	92.000

As we can see in this table, there are differences in the nutrient extraction of the different crops. In all the nutrients, excepting sulfur, maize extracts higher amount of nutrients. In contrast, oilseed rape extracts lower amounts of nutrients (Table 50).

6.4. -Legal requirements

6.4.1. -Soil characteristics.

According to the legislation, sludge can only be applied in soil where the concentrations of cadmium, chromium, copper, mercury, nickel, lead and zinc are below the legal limits. Comparing the results from ICP analysis with European legislation (86/278/EEC), Spanish legislation (Minesterio de Agricultura, Pesca y Alimentación, 1310/1990) and Finnish legislation (Ministry of Agriculture and Forestry, 282/1994), we can say that this soil can be fertilized using sludge.

Table 41. Legal limitation for heavy metal concentrations in the soil.

	European Union	Spain	Finland	Target soil	Legal
Cd mg kg^{-1}	1-3	1	0,5	0,11	Yes
Cr mg kg^{-1}	-	100	200	7,56	Yes
Cu mg kg^{-1}	50-140	50	100	7,87	Yes
Hg mg kg^{-1}	1-1.5	1	0,2	-	Yes
Ni mg kg^{-1}	30-75	30	60	3,18	Yes
Pb mg kg^{-1}	50-300	50	60	8,3	Yes
Zn mg kg^{-1}	150-300	150	150	31,87	Yes

6.4.2. Legal heavy metal concentration in sludge and manure.

To be able to be legally used in agriculture, sludge must fulfill heavy metals concentrations set by the European Union and the member country (Finland and Spain in this case).

Table 42. Legal limitation in heavy metal concentration in Forssa (S).

	European Union	Spain	Finland	Forssa	Legal
Cd mg kg^{-1}	20-40	20	1,5	0,4	Yes
Cr mg kg^{-1}	-	150	300	30,61	Yes
Cu mg kg^{-1}	1000-1750	1.000	600	271,22	Yes
Hg mg kg^{-1}	16-25	1,5	2	-	Yes
Ni mg kg^{-1}	300-400	112	100	20,58	Yes
Pb mg kg^{-1}	750-1200	300	100	19,63	Yes
Zn mg kg^{-1}	2500-4000	450	1500	200,44	Yes

Sewage sludge from Forssa can be legally used for agriculture proposes (Table 42).

Table 43. Legal limitation in heavy metal concentration in Jyväskylä (S).

	European Union	Spain	Finland	JKL	Legal
Cd mg kg^{-1}	20-40	20	1,5	0,43	Yes
Cr mg kg^{-1}	-	150	300	31,65	Yes
Cu mg kg^{-1}	1000-1750	1.000	600	271,22	Yes
Hg mg kg^{-1}	16-25	1,5	2	-	Yes
Ni mg kg^{-1}	300-400	112	100	25,84	Yes
Pb mg kg^{-1}	750-1200	300	100	20,53	Yes
Zn mg kg^{-1}	2500-4000	450	1500	210,83	Yes

Sewage sludge from Jyväskylä can be legally used for agriculture proposes (Table 43).

Table 44. Legal limitation in heavy metal concentration in Kouvula (S).

	European Union	Spain	Finland	Kouvula	Legal
Cd mg kg^{-1}	20-40	20	1,5	0,46	Yes
Cr mg kg^{-1}	-	150	300	31,41	Yes
Cu mg kg^{-1}	1000-1750	1.000	600	271,63	Yes
Hg mg kg^{-1}	16-25	1,5	2	-	Yes
Ni mg kg^{-1}	300-400	112	100	20,1	Yes
Pb mg kg^{-1}	750-1200	300	100	19,94	Yes
Zn mg kg^{-1}	2500-4000	450	1500	220,34	Yes

Sewage sludge from Kouvula can be legally used for agriculture proposes (Table 44).

Table 45. Legal limitation in heavy metal concentration in Vaasa (S).

	European Union	Spain	Finland	Vaassa	Legal
Cd mg kg^{-1}	20-40	20	1,5	0,4	Yes
Cr mg kg^{-1}	-	150	300	30,46	Yes
Cu mg kg^{-1}	1000-1750	1.000	600	271,52	Yes
Hg mg kg^{-1}	16-25	1,5	2	-	Yes
Ni mg kg^{-1}	300-400	112	100	33,55	Yes
Pb mg kg^{-1}	750-1200	300	100	19,76	Yes
Zn mg kg^{-1}	2500-4000	450	1500	200,2	Yes

Sewage sludge from Vaassa can be legally used for agriculture proposes (Table 45).

Table 46. Legal limitation in heavy metal concentration in Viikki (S).

	European Union	Spain	Finland	Viikki	Legal
Cd mg kg^{-1}	20-40	20	1,5	0,44	Yes
Cr mg kg^{-1}	-	150	300	31,59	Yes
Cu mg kg^{-1}	1000-1750	1.000	600	272,89	Yes
Hg mg kg^{-1}	16-25	1,5	2	-	Yes
Ni mg kg^{-1}	300-400	112	100	20,22	Yes
Pb mg kg^{-1}	750-1200	300	100	20,58	Yes
Zn mg kg^{-1}	2500-4000	450	1500	210,21	Yes

Sewage sludge from Viikki can be legally used for agriculture proposes (Table 46).

Manure is not regulated by that legislation but it will be just compared with the same legislation as sludge, to see if they would fulfill the legal requirements that sludge has to complete.

Table 47. Comparison with sludge legal limitation in heavy metal concentration. Manure from Kalmari.

	European Union	Spain	Finland	Kalmari	Legal
Cd mg kg^{-1}	20-40	20	1,5	0,44	Yes
Cr mg kg^{-1}	-	150	300	41,86	Yes
Cu mg kg^{-1}	1000-1750	1.000	600	39,74	Yes
Hg mg kg^{-1}	16-25	1,5	2	-	Yes
Ni mg kg^{-1}	300-400	112	100	148,69	No
Pb mg kg^{-1}	750-1200	300	100	26	Yes
Zn mg kg^{-1}	2500-4000	450	1500	29,57	Yes

If manure would has been included in sewage sludge legislation, this sample couldn't be used for agriculture proposes, due to its high nickel content (Table 47).

Table 48. Comparison with sludge legal limitation in heavy metal concentration. Manure from Maanika.

	European Union	Spain	Finland	Maanika	Legal
Cd mg kg^{-1}	20-40	20	1,5	0,46	Yes
Cr mg kg^{-1}	-	150	300	41,82	Yes
Cu mg kg^{-1}	1000-1750	1.000	600	48,16	Yes
Hg mg kg^{-1}	16-25	1,5	2	-	Yes
Ni mg kg^{-1}	300-400	112	100	147,73	No
Pb mg kg^{-1}	750-1200	300	100	26,82	Yes
Zn mg kg^{-1}	2500-4000	450	1500	29,95	Yes

If manure would has been included in sewage sludge legislation, this sample couldn't be used for agriculture proposes due to its high nickel content (Table 48).

6.4.3. -Maximum heavy metal load in the soil

There is a legal limit amount of heavy metals that can be incorporated per year. As we have seen earlier, this is regulated by the European directive and the laws of the countries.

Table 49. Maximum amount of sludge that can be applied on the soil according to its heavy metal content in Forssa (S).

	Accumulation kg ha^{-1} $year^{-1}$			Maximum amount of sludge kg ha^{-1} $year^{-1}$		
	European Union	Spain	Finland	European Union	Spain	Finland
Cd	0,15	0,15	0,0015	375.000,00	375.000,00	3.750,00
Cr	-	3	0,3	-	98.007,19	9.800,72
Cu	12	12	0,6	44.244,52	44.244,52	2.212,23
Hg	0,1	0,1	0,001	-	-	-
Ni	3	3	0,1	145.772,59	145.772,59	4.859,09
Pb	15	15	0,1	764.136,53	764.136,53	5.094,24
Zn	30	30	1,5	149.670,72	149.670,72	7.483,54

The most limiting element for agriculture application would be copper (Table 49). According to the European and Spanish legislation, the maximum amount of sludge that could be applied is 44.244,52 kg ha^{-1} $year^{-1}$ (Table 49). In Finland, with its more restrictive legislation, the maximum amount of sludge that can be legally used is 2.212,23 kg ha^{-1} $year^{-1}$(Table 49).

Table 50. Maximum amount of sludge that can be applied on the soil according to its heavy metal content in Jyvaskyla (S).

	Accumulation kg ha^{-1} $year^{-1}$			Maximum amount of sludge kg ha^{-1} $year^{-1}$		
	European Union	Spain	Finland	European Union	Spain	Finland
Cd	0,15	0,15	0,0015	348.837,21	348.837,21	3.488,37
Cr	-	3	0,3	-	94.786,73	9.478,67
Cu	12	12	0,6	44.244,52	44.244,52	2.212,23
Hg	0,1	0,1	0,001	-	-	-
Ni	3	3	0,1	116.099,07	116.099,07	3.869,97
Pb	15	15	0,1	730.638,09	730.638,09	4.870,92
Zn	30	30	1,5	142.294,74	142.294,74	7.114,74

The most limiting element for agriculture application would be copper (Table 50). According to the European and Spanish legislation, the maximum amount of sludge that could be applied is 44.244,52 kg ha^{-1} $year^{-1}$ (Table 50). In Finland, with its more restrictive legislation, the maximum amount of sludge that can be legally used is 2.212,23 kg ha^{-1} $year^{-1}$(Table 50).

Table 51. Maximum amount of sludge that can be applied on the soil according to its heavy metal content in Kouvula (S).

	Accumulation kg ha^{-1} $year^{-1}$			Maximum amount of sludge kg ha^{-1} $year^{-1}$		
	European Union	Spain	Finland	European Union	Spain	Finland
Cd	0,15	0,15	0,0015	326.086,96	326.086,96	3.260,87
Cr	-	3	0,3	-	95.510,98	9.551,10
Cu	12	12	0,6	44.177,74	44.177,74	2.208,89
Hg	0,1	0,1	0,001	-	-	-
Ni	3	3	0,1	149.253,73	149.253,73	4.975,12
Pb	15	15	0,1	752.256,77	752.256,77	5.015,05
Zn	30	30	1,5	136.153,22	136.153,22	6.807,66

The most limiting element for agriculture application would be copper (Table 51). According to the European and Spanish legislation, the maximum amount of sludge that could be applied is 44.177,74 kg ha^{-1} $year^{-1}$ (Table 51). In Finland, with its more restrictive legislation, the maximum amount of sludge that can be legally used is 2.208,89 kg ha^{-1} $year^{-1}$(Table 51).

Table 52. Maximum amount of sludge that can be applied on the soil according to its heavy metal content in Vaassa (S).

	Accumulation kg ha^{-1} $year^{-1}$			Maximum amount of sludge kg ha^{-1} $year^{-1}$		
	European Union	Spain	Finland	European Union	Spain	Finland
Cd	0,15	0,15	0,0015	375.000,00	375.000,00	3.750,00
Cr	-	3	0,3	-	98.489,82	9.848,98
Cu	12	12	0,6	44.195,64	44.195,64	2.209,78
Hg	0,1	0,1	0,001	-	-	-
Ni	3	3	0,1	89.418,78	89.418,78	2.980,63
Pb	15	15	0,1	759.109,31	759.109,31	5.060,73
Zn	30	30	1,5	149.850,15	149.850,15	7.492,51

The most limiting element for agriculture application would be copper (Table 52). According to the European and Spanish legislation, the maximum amount of sludge that could be applied is 44.195,64 kg ha^{-1} $year^{-1}$ (Table 52). In Finland, with its more restrictive legislation, the maximum amount of sludge that can be legally used is 2.209,78 kg ha^{-1} $year^{-1}$(Table 52).

Table 53. Maximum amount of sludge that can be applied on the soil according to its heavy metal content in Viikki (S).

	Accumulation kg ha^{-1} $year^{-1}$			Maximum amount of sludge kg ha^{-1} $year^{-1}$		
	European Union	Spain	Finland	European Union	Spain	Finland
Cd	0,15	0,15	0,0015	340.909,09	340.909,09	3.409,09
Cr	-	3	0,3	-	94.966,76	9.496,68
Cu	12	12	0,6	43.973,76	43.973,76	2.198,69
Hg	0,1	0,1	0,001	-	-	-
Ni	3	3	0,1	148.367,95	148.367,95	4.945,60
Pb	15	15	0,1	728.862,97	728.862,97	4.859,09
Zn	30	30	1,5	142.714,43	142.714,43	7.135,72

The most limiting element for agriculture application would be copper (Table 53). According to the European and Spanish legislation, the maximum amount of sludge that could be applied is 43.973,76 kg ha^{-1} $year^{-1}$ (Table 53). In Finland, with its more restrictive legislation, the maximum amount of sludge that can be legally used is 2.198,69 kg ha^{-1} $year^{-1}$(Table 53).

As it was done in the legal limit for heavy metals content, manure will be compared with the application limits established in the legislation to study the maximum amount of manure that could be applied in the soil if it would be included in sludge legislation.

Table 54. Maximum amount of sludge that can be applied on the soil according to its heavy metal content in Kalmari (M).

	Accumulation kg ha^{-1}			Maximum amount of sludge kg ha^{-1}		
	European Union	Spain	Finland	European Union	Spain	Finland
Cd	0,15	0,15	0,0015	340.909,09	340.909,09	3.409,09
Cr	-	3	0,3	-	71.667,46	7.166,75
Cu	12	12	0,6	301.962,76	301.962,76	15.098,14
Hg	0,1	0,1	0,001	-	-	-
Ni	3	3	0,1	20.176,21	20.176,21	672,54
Pb	15	15	0,1	576.923,08	576.923,08	3.846,15
Zn	30	30	1,5	1.014.541,77	1.014.541,77	50.727,09

In contrast with sludge, the higher limitation is in nickel content (Table 54). According to the European and Spanish legislation, the maximum amount of manure that could be applied is 20.176,21 kg ha^{-1} $year^{-1}$ (Table 54). In Finland, with its more restrictive legislation, the maximum amount of manure that can be legally used is 672,54 kg ha^{-1} $year^{-1}$(Table 54).

Table 55. Maximum amount of sludge that can be applied on the soil according to its heavy metal content in Maanika (M).

	Accumulation kg ha^{-1}			Maximum amount of sludge kg ha^{-1}		
	European Union	Spain	Finland	European Union	Spain	Finland
Cd	0,15	0,15	0,0015	326.086,96	326.086,96	3.260,87
Cr	-	3	0,3	-	71.736,01	7.173,60
Cu	12	12	0,6	249.169,44	249.169,44	12.458,47
Hg	0,1	0,1	0,001	-	-	-
Ni	3	3	0,1	20.307,32	20.307,32	676,91
Pb	15	15	0,1	559.284,12	559.284,12	3.728,56
Zn	30	30	1,5	1.001.669,45	1.001.669,45	50.083,47

In contrast with sludge, the higher limitation is in nickel content (Table 55). According to the European and Spanish legislation, the maximum amount of manure that could be applied is 20.307,32 kg ha^{-1} $year^{-1}$ (Table 55). In Finland, with its more restrictive legislation, the maximum amount of manure that can be legally used is 676,91 kg ha^{-1} $year^{-1}$(Table 55).

6.5. -Fertilization dosage

6.5.1. -Fertilization dosage according to Nitrogen extractions

Using Nitrogen extraction to make fertilization dosage, the dosages are:

Table 56. Nitrogen extractions of Maize, oilseed rape and hemp.

	Maize	Oilseed	Hemp	Total
N (g ha^{-1})	375.000	55.000	207.000	637.000

Nitrogen extraction has been calculated according to the extractions during three years of cropping, using the rotation of maize, oilseed rape and hemp, without considering losses by lixiviation and run-off.

Table 57. Sludge and manure dosage according to nitrogen extraction (as dry matter).

Dry matter	Dosage kg ha^{-1}
Forssa (S)	24.001,51
JKL (S)	17.989,27
Kouvula (S)	23.063,00
Vaasa (S)	21.162,79
Viikki (S)	21.578,59
Kalmari (M)	21.134,70
Maanika (M)	28.086,42

All those dosages are referred to dry matter, to calculate the real application dosage it must be divided by its dry matter content.

Table 58. Sludge and manure dosage according to nitrogen extraction (as fresh).

Fresh	Dosage kg ha^{-1}
Forssa (S)	85.780,95
JKL (S)	60.366,68
Kouvula (S)	72.031,28
Vaasa (S)	71.643,05
Viikki (S)	92.725,06
Kalmari (M)	215.340,80
Maanika (M)	172.905,37

6.5.2. -Fertilization dosage according to Phosphorus extractions

Using phosphorus extraction, fertilization dosage is:

Table 59. Phosphorus extractions in maize, oilseed rape and hemp.

	Maize	Oilseed	Hemp	Total
P (g ha^{-1})	24.500	30.200	92.000	146.700

Phosphorus extraction has been calculated according to the extractions during three years of cropping, using the rotation of maize, oilseed rape and hemp, without considering losses by lixiviation and run-off.

Table 60. Sludge and manure dosage according to phosphorus extraction (as dry matter).

Dry matter	Dosage kg ha^{-1}
Forssa (S)	6.566,70
JKL (S)	7.240,87
Kouvula (S)	6.560,82
Vaasa (S)	6.985,71
Viikki (S)	4.876,99
Kalmari (M)	7.729,19
Maanika (M)	10.834,56

All those dosages are referred to dry matter, to calculate the real application dosage it must be divided by its dry matter content.

Table 61. Sludge and manure dosage according to phosphorus extraction (as fresh).

Fresh	Dosage kg ha^{-1}
Forssa (S)	23.469,26
JKL (S)	24.298,22
Kouvula (S)	22.330,91
Vaasa (S)	23.680,37
Viikki (S)	16.100,99
Kalmari (M)	72.167,97
Maanika (M)	86.815,38

6.5.3. -Fertilization dosage according to Potassium extractions

Using potassium extractions, fertilization dosage is:

Table 62. Potassium extractions in maize, oilseed rape and hemp.

	Maize	Oilseed	Hemp	Total
K (g ha^{-1})	77.500	34.000	105.000	216.500

Potassium extraction has been calculated according to the extractions during three years of cropping, using the rotation of maize, oilseed rape and hemp, without considering losses by lixiviation and run-off.

Table 63. Sludge and manure dosage according to potassium extraction (as dry matter).

Dry matter	Dosage kg ha^{-1}
Forssa (S)	103.603,39
JKL (S)	105.123,11
Kouvula (S)	103.827,97
Vaassa (S)	104.386,15
Viikki (S)	104.254,95
Kalmari (M)	90.664,68
Maanika (M)	96.406,47

All those dosages are referred to dry matter, to calculate the real application dosage it must be divided by its dry matter content.

Table 64. Sludge and manure dosage according to phosphorus extraction (as fresh).

Fresh	Dosage kg ha^{-1}
Forssa (S)	23.469,26
JKL (S)	24.298,22
Kouvula (S)	22.330,91
Vaasa (S)	23.680,37
Viikki (S)	16.100,99
Kalmari (M)	72.167,97
Maanika (M)	86.815,38

6.6. -Nutrient balance after fertilization and cropping

6.6.1. -Nutrient balance after Nitrogen based fertilization and cropping

Table 65. Nutrient balance after nitrogen base dosage using sludge and manure.

Balance	Forssa (S) kg ha^{-1}	JKL (S) kg ha^{-1}	Kouvula (S) kg ha^{-1}	Vaassa (S) kg ha^{-1}	Viikki (S) kg ha^{-1}	Kalmari (M) kg ha^{-1}	Maanika (M) kg ha^{-1}
P	**389,49**	**217,76**	**368,99**	**297,72**	**502,38**	**254,44**	**233,59**
C	- 14.568	- 16.462	- 15.029	- 15.262	-15.701	- 13.037	- 10.294
N	-	-	-	-	-	-	-
As	0,07	0,04	0,07	0,06	0,06	0,09	0,14
Cd	0,01	0,00	0,01	0,01	0,01	0,01	0,01
Cr	0,47	0,30	0,46	0,38	0,41	0,62	0,91
Cu	6,24	4,61	6,00	5,48	5,62	0,57	1,09
K	**- 166,34**	**- 179,45**	**- 168,41**	**- 172,61**	**- 171,69**	**- 166,03**	**- 153,43**
Ni	0,44	0,41	0,41	0,66	0,38	3,09	4,10
S	- 122,31	- 122,83	-122,44	- 122,51	- 122,52	-123,62	- 123,45
Si	340,93	243,98	325,32	295,37	302,12	19,49	68,71
Zn	1,91	0,89	2,18	1,33	1,63	- 2,28	- 2,06

As we can observe in the balance, there is an important deficit of potassium when we based the dosage according to nitrogen extractions. In the other hand there are important accumulation of phosphorus (Table 65).

6.6.2. -Nutrient balance after Phosphorus based fertilization and cropping

Table 66. Nutrient balance after phosphorus base dosage using sludge and manure.

Balance	Forssa (S) kg ha^{-1}	JKL (S) kg ha^{-1}	Kouvula (S) kg ha^{-1}	Vaassa (S) kg ha^{-1}	Viikki (S) kg ha^{-1}	Kalmari (M) kg ha^{-1}	Maanika (M) kg ha^{-1}
P	-	-	-	-	-	-	-
C	- 19.233	- 19.167	- 19.294	- 19.099	- 19.794	- 18.081	- 16.864
N	**- 462**	**- 380,60**	**- 455**	**- 426**	**- 493**	**- 404**	**- 391**
As	- 0,01	- 0,01	- 0,01	- 0,01	- 0,02	0,00	0,03
Cd	- 0,00	0,00	0,00	0,00	- 0,00	0,00	0,00
Cr	- 0,07	- 0,04	- 0,06	- 0,06	- 0,12	0,05	0,18
Cu	1,52	1,70	1,52	1,63	1,07	0,04	0,26
K	**- 202**	**- 201**	**- 202**	**- 202**	**- 206**	**- 198**	**- 192**
Ni	0,08	0,14	0,08	0,18	0,05	1,10	1,55
S	- 123	- 123	- 123	- 123	- 123	- 124	- 123
Si	60,73	71,44	60,49	67,49	33,61	- 21,29	- 1,01
Zn	- 1,59	- 1,38	- 1,46	- 1,50	- 1,88	- 2,67	- 2,58

If we base the dosage in phosphorus extraction, there are important deficit in phosphorus and potassium (Table 66).

6.6.3. -Nutrient balance after Potassium based fertilization and cropping

Table 67. Nutrient balance after potassium base dosage using sludge and manure.

Balance	Forssa (S) kg ha^{-1}	JKL (S) kg ha^{-1}	Kouvula (S) kg ha^{-1}	Vaassa (S) kg ha^{-1}	Viikki (S) kg ha^{-1}	Kalmari (M) kg ha^{-1}	Maanika (M) kg ha^{-1}
P	**2.167**	**1.983**	**2.174**	**2.045**	**2.989**	**1.574**	**1.158**
C	6.728	5.466	5.845	7.258	4.559	13.126	15.722
N	**2.112**	**3.085**	**2.230**	**2.505**	**2.440**	**2.095**	**1.549**
As	0,45	0,47	0,47	0,48	0,46	0,53	0,58
Cd	0,04	0,04	0,05	0,04	0,04	0,04	0,04
Cr	2,90	3,06	2,99	2,91	3,02	3,53	3,76
Cu	27,83	28,23	27,94	28,08	28,18	3,34	4,38
K	-	-	-	-	-	-	-
Ni	2,08	2,66	2,04	3,45	2,06	13,43	14,19
S	- 115	- 115	- 115	- 115	- 115	- 121	- 121
Si	1.620	1.642	1.621	1.633	1.631	230	344
Zn	17,86	19,26	19,97	18,00	19,01	-0,22	- 0,02

Making the dosage according to potassium exportation, there are huge accumulation of nitrogen and phosphorus (Table 67).

DISCUSSION

7. -Discussion

7.1. -Chemical characterization

7.1.1. -Phosphorus fractions

Results of phosphorus fractions showed that dairy cow manure had the highest level of soluble P fraction; in both cases the range was around 5 g kg^{-1}. The sludge soluble phosphorus was much lower than in dairy cow manure, indeed they were even lower than soluble phosphorus in the soil (0.08 g kg^{-1}). High levels of soluble P can easily lead to the P leachate and run-off (Carpenter, 2005). The differences in P contents were mainly caused by the treatments that have done on the sludge during the different production process. For example, the chemical precipitation and biological treatment decreases the soluble P so they can reduce the eutrophication risk (Fytili and Zabaniotou, 2008).

Aluminum bound phosphorus was higher in dairy cow manure (Kalmari; 6.75 g kg^{-1}), than in the dairy cow manure obtained from Maanika (3.37 g kg^{-1}). On the other hand Al-P ranged from 0.49 g kg^{-1} in sludge obtained from Kauvula to 3.58 g kg^{-1} in sludge obtained from Vaasa. Al-P is less available for the plant compared to the soluble phosphorus (Smil, 2000), but it releases the phosphorus to the soil slowly.

Iron bound phosphorus (Fe-P) was higher in sludge samples than in the dairy cow manure samples. The highest Fe-P was found in sludge obtained from Viikki (21.1 g kg^{-1}), while the lowest value was obtained from the dairy cow manure that obtained from Kalmari (5.91 g kg^{-1}) and Manninka (1.92 g kg^{-1}). This fraction as aluminum fraction is less available than soluble phosphorus and is released slowly (Smil, 2000). The soluble phosphorus can be precipitated into the Al-P or Fe-P due to the acidity of the soil (Smil, 2000), which can caused by the sludge or the manure application into the cropland.

Calcium bound P (Ca-P) was higher in the sludge than in the dairy cow manure. Sludge obtained from Viikki had the highest Ca-P (8.35 g kg^{-1}), while the lowest Ca-P was found in the dairy cow manure that obtained from Kalmari (1.17 g kg^{-1}). Such fraction is low in the availability in the soil for plants (Payne et al., 1965).

The results showed that the soluble form was the highest in the dairy cow samples, and the lowest Fe-P and Ca-P fractions due to the difference in the pH, since the Ca-P can be enhanced with the increase of pH (Smil, 2000). Sludge had the most of P in iron or aluminum forms, which means that it will be less available for the plant (Payne et al., 1965). However, the slow release of these fractions makes the sludge suitable as fertilizer on the long term.

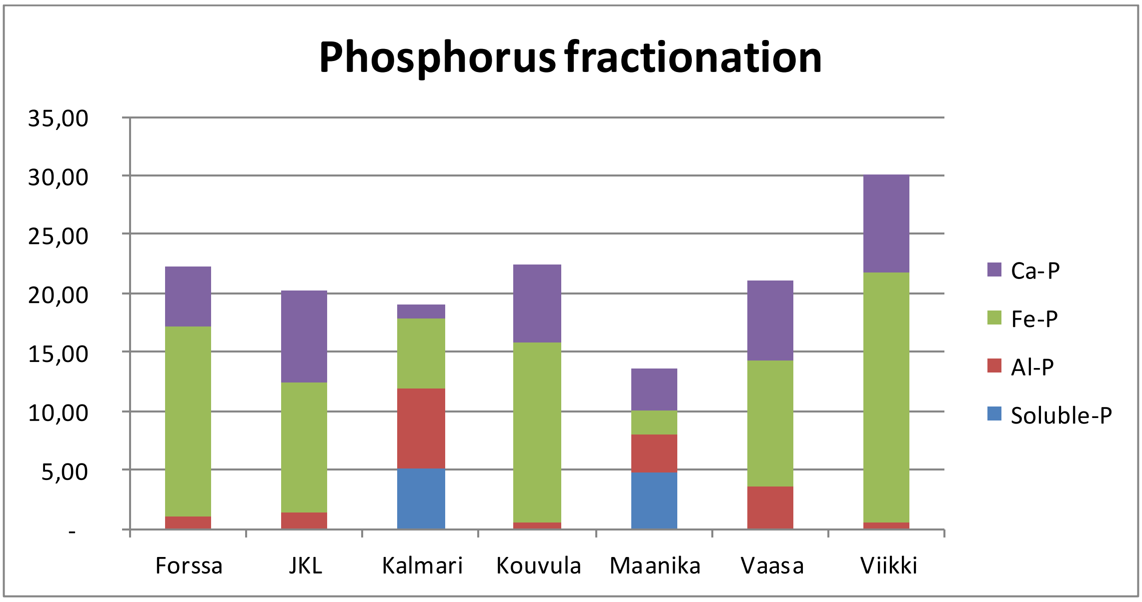

Figure 14. Phosphorus fractionation.

This figure shows clearly how phosphorus is divided into different fractions. As we can see sludge has most of the phosphorus in secondary mineral forms, and manure have higher amount of non-secondary mineral forms.

7.1.2. -Nitrogen and Carbon content

In the literature, nitrogen usually contain between 15 and 40 g kg^{-1} (Fytili and Zabaniotu, 2008; Casado-Vela, 2007; De Saavedra et al, 2000) and the results shows a range of 26,54 to 35,41 g kg-1- So the results are similar to the data obtained from literature. In manure the range was 22,68 to 30,14 g kg^{-1}, and the literature shows values of 18,4 g kg-1 (Pomares and Canet, 2001), so the results were higher than the data from literature.

According to the literature, manure has a CN ratio of 13,9 (Pomares and Canet, 2001), and in Kalmari the result is quite close (12,5) but in Maanika is higher (16,8). Regarding sludge, literature shows a CN ratio of 12,7 (Casado-Vela, 2007) which is much higher than the results, that's rages from 7,11 to 10,6.

Generally, the sludge obtained from Viikki, Vassa and Kalmari contained the highest total N in comparison to other products, which means that they are recommended on the cropland application as a nutrient source for plant growth. C content in the dairy cow manure was about 380 g kg^{-1} and in the sludge ranged from 245 to 275 g kg^{-1}. The difference in C content could be due to the different in the diet, dairy cow diet which could contain higher fiber than human diet, and this can result in higher C content in manure than in sludge (Dao and Schwartz, 2010).CN ratio reflects the differences of C content from dairy cow manure to sludge. As a result, the highest value was found in dairy cow manure that obtained from Maanika, while the lowest CN ratio was obtained in dairy cow obtained from Jyväaskylä.

7.1.3. -Electrical conductivity and pH

Sludge usually shows neutral pH or slightly acid pH (Fytili and Zabaniotou, 2008) or also can be slightly basic (Casado-Vela, 2007). The result shows a range from 6,91 to 7,73, similar to the literature data. Manure has been characterized with basic pH, around 8-9 (Pomares and Canet, 2001) and the results also shows a pH in this range.

Result of conductivity measurements showed that sludge had lower conductivity than dairy cow manure. However, the EC values were varied in sludge samples and these differenced could be due to the chemical used in sludge production. For example, Fe salts have higher EC than Al salts. pH values of sludge were lower in sludge samples than dairy cow manure samples. The lower pH of sludge can enhance the precipitation of P to Al-P and Fe-P forms instead of Ca-P form. The P is more available for the plant in the soil with low pH (Choi et al., 2009). However, the low pH can enhance the bioavailability of heavy metals such as Al, Cd, Zn (Morera et al., 2002; Hossain et al., 2010). Soil pH was slightly lower than sludge pH, while it was much lower than manure pH. This means that the manure will increase soil pH compared to sludge, causing increase in the Ca-P which can reduce the eutrophication risk (Hossain et al., 2010; Morera et al., 2002).

7.1.4. -Potassium content

Potassium content in sewage sludge was lower than in manure. If we compare that data with others studies, we can see that according to Fytili and Zabaniotou, in the study run in 2008 they observed that their samples had around 4.000 mg kg^{-1}, two times the average quantity recorded in the samples, if we compare with other studies like the study done by Casado-Vela in 2007, were they measured 7890 mg kg^{-1}, the difference is even higher. That difference can be explained to the different way of obtaining the data, in the study of Fytili and Zabaniotou they measured the potassium content as K_2O and the ICP analysis measured the content of elemental potassium. So to compare both results we have to convert the content in K_2O in total amount of elemental potassium, and doing that the results are in the same magnitude. In other study made by Wang et al in 2009 made by ICP potassium content was 820 mg kg^{-1}, almost the half of the values obtained. Erikson in 2001 also analyzed potassium content and measured a value of 31.000 mg kg^{-1}, more than ten times higher than the obtained values.

If we look to a study were potassium was analyzed in manure samples, the average was 3,4 g kg^{-1} elemental potassium and in the samples, the results were around 2,4g kg^{-1}, much lower than in the study but in the same order of magnitude (Pomares and Canet, 2001). The difference can be caused by the difference origin of the manure (Spain and Finland), changes in cow nutrition between both countries and the microbes that digest the manure.

Anyway, potassium content could not be enough to cover crop potassium requirements. Manure despite having higher amounts of potassium, could be in the same situation of lacking potassium. Is also remarkable that most of the potassium is usually unavailable for the plants, is estimated that between 90 and 98% is not available (Comu et al., 2001). Moreover the low temperatures that are common in Finland and its usual changes during autumn and spring of freeze and defrost can enhance potassium solubilization, high humidity (other climatic characteristic of Finland) also enhance this process. Regarding losses by leached, at pH lower than 7 (like this type of soil), losses by leaching decreases (Ahlberg et al., 2006).

7.1.5. -Manganese content

In manganese we can observed that there are three statically different groups, one group of sewage sludge, sewage sludge from Jyvaskyla and manure. The first group range between 247-248 mg kg^{-1} and Jyvaskyla is in 250 mg kg^{-1}. If we compare that result with other studies we can see that Fytili and Zabaniotou obteined 260 mg kg^{-1}, quite similar to the result. Goi et al. obtained different results; they found that manganese in sewage sludge ranged from 10 to 100 mg kg^{-1}, less than the half of the quantity founded in the results. Hernández et al obtained 169 mg kg^{-1}, lower than the obtained values. Results from Erikson of 2001, 310 mg kg^{-1}, are also in the same order of magnitude than the samples.

In manure the average content of manganese was significantly higher than the content in sewage sludge. If we compare the results, 275-276 mg kg^{-1}, to the average content of manganese found in manure in other study, 172 mg kg^{-1}, we can see that the values found in those samples were higher than in the literature (Pomares and Canet, 2001). Again the difference can be cause by the different management of the feed and the microbes that can live in both places (Spain and Finland).

In the soil that is studied there shouldn't be problems of manganese, despite its low content 7,6 mg kg-1, with the low pH it will be quite soluble and available for the plant. An excessive application of manganese could lead to phytotoxicity problems, but to reach that is needed from 300 mg kg-1 in soy to near 2.000 mg kg-1 of dry matter in rice, levels that are difficult to reach using sludge or manure as a fertilizer source (Ahlberg et al., 2006).

7.1.6. -Sodium content

Sodium content is significantly higher in manure than in sewage sludge, in the order of 100 mg kg^{-1} higher in sewage sludge. In manure, the study shows a content of 580mg/kg, similar to the 400-440 mg kg^{-1} founded in manure samples. To compare with sewage sludge is more difficult due to the lack of information about sodium content. Is relevant that the highest amount of sodium was founded in Forssa where the sludge is biologically digested.

Excessive amounts of sodium can lead to pH increases and salinity problems, but with this kind of soil and the concentration in sludge and manure, there shouldn´t be any problems cause by sodium (Ahlberg et al., 2006).

7.1.7. -Copper content

In most of the studies that analyze sewage sludge appears the quantity of copper. This interest for copper concentration in due to the fact that high concentrations of copper can lead to phytotoxicity and that's why the European legislation has established a limit concentration for sludge in agricultural application which ranges from 1000-1750 mg kg^{-1} (European legislation) and a total amount of copper of 12kg/ha/year. There were significantly differences between sewage sludge concentrations and manure concentration, being around 270 and 39-48 mg kg^{-1}respectively. Other studies like the one done by Wang et al in 2008 shows a content of 170 mg kg^{-1}, Hernández et al obtained in 1990 152 mg kg^{-1}, Cai et al obtained in 2007 396 mg kg^{-}1 and Goi et al found a range of 12-100 mg kg^{-1}. Erikson in 2001 also found similar values for copper, 390 mg kg^{-1}. So the results are consistent with the values that appear in the literature.

In addition, we can observe how those values of copper concentration are lower than the limit values established in the European legislation, so according to the copper limitation that sewage sludge can be apply in the field providing less than 12 kg ha^{-1} $year^{-1}$, which means that we cannot apply more than 44 ton ha^{-1} $year^{-1}$ of those sludge (in dry matter). This sludge samples showed the most limiting amount of sludge that can be legally applied in the soil in the amount of sludge limited by its copper content (Tables 42 to 46).

Copper can be quite soluble at low pH, like in the studied soil. That could lead to a higher solubilization of copper, as a result it can have higher phytotoxicity at the same concentration in an acid soil than in a basic soil (Ahlberg et al., 2006; Doelsch et al., 2006).

7.1.8. -Chromium content

Chromium is other element that is restricted which content is restricted by the European legislation. The results obtained where much lower than some of the values observed in the literature, in the sewage sludge the values are around 31 mg $kg^{-1}$and Fytili and Zabaniotou had observed 500 mg $kg^{-1}$of Chromium, but there are other studies like the one done by Singh and Agrawal in 2007 where they found 35,5 mg kg^{-1}which is much similar to the observed values. In adittion, Erikson found in 2001 33 mg kg^{-1}, very close to the observed values.

Manure as significantly higher concentration of chromium than in sewage sludge, with values of around 41 mg kg^{-1}that are almost the half of the chromium content that is found in the literature, 24 mg kg^{-1}.

7.1.9. -Zinc content

Zinc is also restricted by European legislation and is quite usual to see zinc concentrations in chemical analysis of sludges. According to the literature the values can vary from 290 mg kg^{-1} (Wang et al., 2008), 780 mg kg^{-1} (Herández et al., 1990), 1213 mg kg^{-1}, 20-400 mg kg^{-1} (Goi et al., 2006), 785 mg kg^{-1} (Singh and Agrawal., 2007) and 550 mg kg^{-1}(Erikson, 2001). The results range from 200 to 220mg kg^{-1} in sewage sludge and are quite similar to the concentrations that appear in the literature, being more similar to the results given by Wang et al and Goi et al.

Concentrations in manure were much lower, 29 mg kg^{-1}in both cases. This value is quite lower than the concentration that appears in the literature 133 mg kg^{-1}. Again, this difference can be cause by the different environment and management of the farms.

According to European legislation any sludge that has more than 2500-4000 mg kg^{-1} cannot be used for agricultural proposes. The total amount of zinc that can be legally applied on the field is 30kg ha^{-1} $year^{-1}$. With those samples of sewage sludge the total amount of sludge that we have to apply to reach that level is 136 ton ha^{-1}.

7.1.10. -Lead content

Lead is other element of high risk of phytotoxicity and toxicity to humans and animals, that's why the amount of this element in the sludge is restricted by the European legislation and is widely analyzed in the literature. According to the literature the concentrations of lead in sewage sludge are 255 mg kg^{-1} (Wang et al., 2009), 109 mg kg^{-1} (Hernámdez et al., 1990), 57 mg kg^{-1} (Cai et al., 2007) a60 mg kg^{-1} (Singh and Agrawal, 2007) and 33 mg kg^{-1} (Erikson, 2001). Results show significant differences between sewage sludge and manure. In sewage sludge the values ranges from 19 to 20 mg kg^{-1}, and are quite smaller than the values obtained from the literature.

Manure has slightly higher concentration of lead, 26 mg kg^{-1}, than sewage sludge. Literature shows concentrations of 14 mg kg^{-1}, almost the half of the obtained concentration.

Looking at the European legislation we can see that that sludge meets with the limitation of lead concentration which is 750-1200 mg kg^{-1}. The total amount of lead that can be legally apply on the field is 15kg/ha/year, so to reach these level would be necessary to apply more than 750 ton ha^{-1}.

7.1.11. -Sulfur content

Sulfur has been barely analyzed in the literature, one study where sulfur has been analyzed was done by Erikson in 2001, and he found out that sludge has 9.000 mg kg^{-1}. There is just one study to compare, but the obtained result was much lower than this value. The results shows that manure has significantly less sulfur concentration (30-32 mg kg^{-1}) than the sewage sludge concentration (80-84 mg kg^{-1}).

Due to the humidity of the Finnish climate, there could be important losses of sulfur, but they will be less important than nitrogen losses, because of its lower solubility. In addition, water used for irrigation can have enough sulfur to cover crop needs, as an example, the water used by Casado-Vela in 2007 to irrigate sweet pepper contained 130 mg L^{-1}, higher amount than which is present in manure or the sludge.

7.1.12. -Silicon content

There is lack of information in the literature about silicon content in sludge and manure, it appears as a secondary data in the study of Fytili and Zabaniotou of 2008, where they mention a silicon content of 100.000-200.000 mg kg^{-1}, it also appear in the study done by Erikson in 2001 where he measured a value of 45.000 mg kg^{-1}. The results shows values much lower than those concentrations, in sludge they are around 16.000 mg kg^{-1} and in manure in the order of 3.000-4.000 mg kg^{-1}. Moreover, silicon isn't a key element in crop fertilization.

7.1.13. -Aluminum content

Aluminum hasn't been deeply analyzed in literature, as the case of silicon is not considered as a key element in crop fertilization. One example where aluminum has been analyzed is the study done by Erikson in 2001, and the measured concentration of aluminum was 40.000 mg kg^{-1}. The results are ten times lower, in the order oF 4.000 mg kg^{-1}.

7.1.14. -Iron content

Most of soil analysis shows values of 1.5-6 mg kg^{-1} of iron, but the result showed 150 mg kg^{-1} of iron, extremely higher than most of the soils that appear in literature. Looking at the iron concentration in manure, the result is even more inordinately higher, with concentrations of 500 mg kg^{-1}, but the manure analysis done by Pomares and Cannet showed contents of 4100 mg kg^{-1} so much higher than the results. In sludge the literature is quite confusing, some studies like Casado-Vela shows values of 5 mg kg^{-1}, but others like Fytili and Zabaniotou shows values of 2.500 mg kg^{-1}. Looking at those values, the result of a concentration of around 17.000 mg kg^{-1} is closer to the result obtained by Fytili and Zabaniotou. Comparing the results with the data obtained from Erikson in 2001, we can observe that the obtained results are quite lower than the concentration in his study, 49.000 mg kg^{-1}. Probably there has been contamination or errors in the measurement of the iron, otherwise sludge application in the soil should lead to considerable phytotoxicity problems, and the field trials doesn't show that.

Iron increases its solubility by the decrease of pH. In the type of soil that is studied, iron is quite soluble, and there could be excessive iron available for the plant. Although there could be high precipitation rate in the form of iron phosphates, that can allow to reduce the possible negative effects that high iron content could cause.

7.1.15. -Arsenic content

Arsenic can be toxic in high concentration, but it not common to found high amounts of arsenic in the soil. Manure had higher values than sludge, but still they were below the 10 mg kg^{-1} that was reported by Fitily and Zabiniotou in 2008 in sewage sludge. In contrast the obtained values were practically the same as the obtained by Erikson in

2001. So arsenic content shouldn´t be considered as a limiting element for sludge application.

7.1.16. -Cadmium content

High concentration of cadmium can be harmful for the plants and then for the animals, that's why is included in the European legislation and included in many legislation of countries and region that regulates sludge application. European Union established a limit amount of 20 mg kg-1, in Spain is also 20 mg kg^{-1} and Finland is lower, 3 mg kg-1. The studied sludge had between 0,40 and 0,46 mg $kg^{-1}$of cadmium, bellow the limit, so it can be legally used. The soil had 0,11 mg kg^{-1} of cadmium also below the limit of 0,5 mg kg^{-1} that is established in the exigent Finnish legislation, in Spain the limit is 1 mg kg^{-1} and in Europe 3 mg kg^{-1}.

Literature shows more or less values similar to the obtained in the analysis. Pomares and Canet found 1 mg kg^{-1}in manure. Goi et al found that cadmium levels were below 2 mg kg^{-1} in all the samples that they analyzed. Casado-Vela measured 0,15 mg kg^{-1}. So all the references shows similar values. Erikson found 1,5 mg kg^{-1}, a bit higher than the obtained result.

7.1.17. -Calcium content

Comparing the data with the literature we can see that sludge results are very near to the results obtained by Casado-Vela et al in 2007, in the order of 38.500 mg kg-1. In the other hand, De Saavedra in 2000 found 76.000 mg kg-1 of calcium, but this is not measured in elemental calcium, is measured in its fertility unit (CaO) and if we extrapolate this result to elemental calcium the results shows 54300 mg kg-1, quite higher to the results, but still near. Results in manure were less close to the values found in literature, 37.400 mg kg-1 of CaO (Pomares and Canet, 2001): In a study done by ICP analysis (Erikson, 2001) the result was 28.000 mg kg^{-1}, somehow close to the results. In this case is also measured in fertility units, but if we extrapolate it to elemental calcium, the result is 26.700 mg kg-1, much higher than the 3.200 mg kg-1 found in manure.

Despite the low pH, calcium content in the soil is quite high, with more than 9.000 mg kg-1. Usually is soils with low pH, as this one, there is low calcium concentration and is necessary to apply calcium amendments, in many cases is done using manure which in this case has around 3.000 mg kg-1, but this results shows that could be more efficient sludge, due to its high content in calcium that is in the order of 38.200-38.500 mg kg-1.

7.1.18. -Magnesium content

Sludge and manure showed similar values for magnesium content, in the order of 3.400 mg kg^{-1}. Looking at literature, we can see similar values, like the 2650 mg kg^{-1} found by Casado-Vela in 2007, the result is almost the same as the result obtained by Erikson in 2001. In contrast, literature show higher values for manure 10.800 mg kg^{-1} (Pomares and Canet, 2001). The soil showed a normal content of magnesium, 109,17 mg kg-1.

7.1.19. -Nickel content

Nickel content was quite close to the limit established in the Spanish legislation of 30 mg kg-1, in the other hand was farther to the Finnish limitation of 100 mg kg-1. Manure clearly exceeded both limits with a concentration of 147 mg kg-1. This values is too high, especially if we compare it with the measured obtained by Pomares and Canet in 2001 of 20 mg kg-1. There could be cause by the different management of the farms, but considering that the obtained value is extremely high, is possible that there has been some kind of sample contamination.

Comparing the results in sludge with literature, we can see that they are similar to the results obtained by Erikson in 2001 and Goi et al in 2005. The others studies shows higher concentrations.

7.2. -Legal requirements

The soil was fulfills the legal requirements in all the studied countries. Cadmium content in the soil showed a value near to the exigent Finnish legislation, but was below the limit. The rest of the limited elements had concentrations that were far from the limit.

All the sludge samples can be legally used for agricultural proposes according to the European legislation (86/278/EEC), Spanish legislation (Minesterio de Agricultura, Pesca y Alimentación, 1310/1990) and Finnish legislation (Ministry of Agriculture and Forestry, 282/1994). In cadmium there would be needed three times higher concentration to be over the limit. Regarding chromium, the difference is even higher, in the order of ten times higher. For copper, like cadmium, there would be needed three times more copper than which is established in the most exigent legislation (Finnish). In any of the samples was detected mercury, so there aren't any problems with mercury. Nickel has the lowest value in the Finnish legislation, but still there would be needed 5 times more nickel than which is present to cannot be legally used. In the case of lead, as in most of the heavy metals, the most limiting legislation is the Finnish legislation, but to don't fulfill the legal requirements there would be needed five times more lead than the measured concentration. Surprisingly the Spanish legislation was the most exigent according to zinc concentration, but it was more than the double amount of zinc that which is present in the sample.

In manure there are problems in nickel concentration, which is slightly higher than the established in the Spanish and the Finnish legislation, but it was lower than the established in the European Directive. Despite the fact that being over the limits in the two studied countries, there wouldn´t be any legal problem to use this manure as fertilizer, due to the fact that this product is not included in those legislation. The rest of the elements were far from the limits, and if they would have been over the limits, there wouldn't be any legal problem as it was told before.

In sludge, European and Spanish legislation have more or less the same limit amount of sludge that can be applied per year. In the studied sludge, for those legislation the most limiting was copper, with a maximum of 44.000 kg ha^{-1}. However, Finnish is much more restrictive, especially in the case of copper, were the maximum amount of sludge that can be legally applied per year is 2.200 kg ha^{-1}.

Manure, as we have said before, is not regulated by this legislation, but using the same restrictions as sludge we can fix a limit for maximum dosage according to heavy metal accumulation. This manure didn´t fulfill nickel requirements, and consequently the most limiting element was nickel with a value of approximately 20.000 kg ha^{-1} in the European Union and Spain, and around 680 kg ha^{-1} in Finland.

7.3. -Fertilization dosage

7.3.1. -Nitrogen based dosage

If we make the dosage according to nitrogen extraction there will be needed 637 kg ha^{-1} of Nitrogen to compensate the nitrogen exportations during crop harvest. For most of the sludge samples it would be required the same amount, in the order of 21.000-24.000 kg ha^{-1}. If we use sludge from Jyvaskyla there would be needed less amount of sludge due to its higher amount of nitrogen. In the other hand, using manure from Maanika there would be needed 28.000 kg ha^{-1}.

According to the legislation that we have previously analyzed, there is a maximum amount of sludge that can be applied on the soil according to its heavy metal content. So in our case, the soil is located in Finland, so the maximum amount of sludge than can be legally applied per year is 2.200 kg ha^{-1}. This value is much lower than the amount needed, but this legal value is consider as an average amount of sludge applied in a period of ten years (Finnish Decree), so for example in this case we can make one fertilization per each three years, and the maximum amount of sludge that could be applied will be 6.600 kg ha^{-1}, or in the case that we left the field without cropping one year, the fertilization will be one time per each four year, and as a consequence the maximum amount of sludge that could be applied will be 8.800 kg ha^{-1}.

We can observe that even in the case of keeping one year without cropping, the maximum amount of sludge that can be legally applied is less than the half that is needed to fulfill nitrogen requirements.

If we calculate the final balance using the legal limit of 8.800 kg ha^{-1}, we obtain:

Table 68. Balance according to legal limit requirements

Balance kg ha^{-1}	Forssa (S) kg ha^{-1}	JKL (S) kg ha^{-1}	Kouvula (S) kg ha^{-1}	Vaassa (S) kg ha^{-1}	Viikki (S) kg ha^{-1}	Kalmari (M) kg ha^{-1}	Maanika (M) kg ha^{-1}
P	49,89	31,59	50,07	38,10	118,00	20,32	- 27,55
C	- 18.635	- 18.775	- 18.715	- 18.608	- 18.833	- 17.678	- 17.638
N	- 403,45	- 325,39	- 393,94	- 372,12	- 377,22	- 371,77	- 437,42
As	- 0,00	- 0,00	- 0,00	- 0,00	- 0,00	0,01	0,01
Cd	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Cr	0,00	0,01	0,01	- 0,00	0,01	0,10	0,10
Cu	2,12	2,12	2,12	2,12	2,14	0,08	0,16
K	- 198,11	- 198,38	- 198,15	- 198,25	- 198,23	- 195,49	- 196,74
Ni	0,13	0,18	0,12	0,24	0,13	1,26	1,25
S	- 123,57	- 123,58	- 123,59	- 123,55	- 123,58	- 124,02	- 124,03
Si	96,63	96,46	96,42	96,65	96,68	- 8,03	- 9,24
Zn	- 1,14	- 1,05	- 0,96	- 1,14	- 1,05	- 2,64	- 2,64

As we can observe in this balance there is an excessive phosphorus accumulation, but in the other hand there is shortage of nitrogen, potassium and sulfur, that would be supplied by other fertilizers. Is remarkable how heavy metals are balnce, according to heavy metal balance, this dosage would be the most accurate.

In contrast if this field were in Spain or in other country with laxer legislation more similar to the European legislation, the maximum amount of sludge that can be legally applied, as we have seen before is 44.000 kg ha^{-1} year^{-1}. In this case there wouldn't be needed to stay one year without cropping to increase the amount of sludge that can be applied, we can fulfill all nitrogen requirement in one application per each three years without caring about the average of heavy metals that are going to be incorporate in a period of ten years (Real Decreto, European Directive).

Making the nutrient balance using the nitrogen needs as the reference for dosage we can observe that there are an important accumulation of phosphorus that can cause eutrophication problems. There will be also important silicon accumulation, but it wouldn't cause any problems. Probably there would be needed some potassium and sulfur addition to the sludge, because it cannot supply the quantity needed by the crops. For potassium there would be needed 150-180 kg ha^{-1} and 120 kg ha^{-1} of sulfur. Regarding heavy metals there is a good balance between exportation and incorporation. Only copper shows relatively high accumulation rate, in the order of 6 kg ha^{-1} in sludge.

7.3.2. -Phosphorus based dossage

If we calculate the dosage according to phosphorus needs, the required sludge is lower than if we dosage according to nitrogen or potassium needs. But still the values are higher than the Finnish legislation, but in this case it can be solved by making the calculus for a three year period that allows incorporating 6.600 kg ha^{-1}. This limit is only slightly overpassed in Jyvaskyla and Vaasa, but is really close. Strictly talking they do not fulfill this limit, so to simplify the calculation use a higher limit by using a rotation of three years of cropping and one year of fallow, and as a result the limit will be increase up to 8.800 kg ha^{-1}. Using this limit all samples fulfill legal requirements.

In the theoretical of a field located in Spain or other European country with laxer legislation, there wouldn't be any problems with maximum amount of heavy metals that can be applied considering a ten year period.

The balance shows important deficit in nitrogen, potassium and sulfur that should be incorporate by extra fertilization. The required amount of nitrogen is 400-500 kg ha^{-1}, for potassium is 200 kg ha^{-1} and 120 kg ha^{-1} of sulfur. All heavy metals are quite balanced, excepting zinc which could become insufficient if this fertilization is used for a long period of time.

7.3.3. -Potassium based dosage

According to Finnish legislation, would be impossible to base the dosage in potassium requirement, because the established limit by the maximum amount of heavy metals that can be incorporated in the soil is too small to fulfill this requirement even in the most favorable case of three year of cropping and one year of fallow, 8.800 kg ha^{-1}.

In the other hand it would be possible to make the dosage according to potassium extraction if the field were located in Spain or other European country with laxer legislation, were the maximum amount of sludge that can be applied according to heavy metal incorporation limit is 44.000 kg ha^{-1} $year^{-1}$. So for the studied rotation of three crops the limit amount of sludge is 132.000 kg ha^{-1}. The studied sludge samples needed around 105.000 kg ha^{-1} of sludge every three year, so it fulfills the limit of 132.000 kg ha-1 extracted from European and Spanish legislation.

Making the balance for the potassium requirements we can observe that there is a huge amount of phosphorus and nitrogen that is accumulated in the soil, and as a result it will be progressively lixiviated and transported by runoff, causing eutrophication problems. In manure there isn´t important accumulation of heavy metals, only nickel can cause accumulation problems at long term. But in sludge there is important accumulation of copper and zinc, the rest of heavy metals despite its lower concentration can cause accumulation problems at long term if this fertilization dosage is used for many years.

7.3.4. Final fertilization election

To choice the best option, we must take care of the legal requirements, that don't allow using more than a determinate quantity of sludge, according to its chemical characterization. Then, we must consider the effect that excessive phosphorus fertilization can cause in the environment, so we shouldn't apply more sludge than which is needed by the crop, but also considering that not all phosphorus incorporated by the sludge is used by the plant. For the first year it will be available only the soluble fraction and some of the aluminum bound phosphorus, then iron bound phosphorus will be progressively more available and the calcium bound phosphorus will be barely available, so it will be accumulated in the soil, and slowly degraded into soluble forms. That's why we can make a fertilization plan using sludge according to phosphorus extraction based on one application per each three-four years. Due to the explained phosphorus characteristics, those phosphorus forms will be progressively released providing enough phosphorus for the plant, but this amount of phosphorus should be in the order of 15-30% (Ca-P content, Figure 3) higher than plant extraction to provide enough available phosphorus during this three-four years of cropping.

To achieve both objectives, there is only one option. Using between 16.000 and 24.000 kg ha^{-1} of sludge every cycle of four years. This system has deficit in nitrogen and potassium, and this deficit will be higher considering losses by runoff and leachate. That's why there would be needed to apply extra mineral fertilization one year after sludge application and two year after sludge application in the order of 200-250 kg ha^{-1} of nitrogen and 100 kg ha^{-1} of potassium.

CONCLUSIONS

8. -Conclusions

In general, despite few cases, standard deviations were small. That caused that there has been detected significant differences between treatment for most of the analyzed parameters. In some cases those significant differences didn´t correspond with different management of those materials.

There are significant difference in most of the studied parameters (excepting Cd, Mg and N) between sludge samples and manure.

Differences between each sludge samples are not significant, excepting phosphorus fractions, N content, Electrical conductivity, pH, Al, Ca, Cr, Mg, Mn, Na, Fe and S content.

Regarding manure samples, there are significant differences in dry matter, aluminum bound phosphorus, iron bound phosphorus, electrical conductivity, pH, nitrogen content, CN ratio, Cu, Na, Mg and K content.

Despite surpass the maximum amount of nickel that is established in sludge regulations, manure is not affected by this regulation, because is not included in those legislation. Anyway, there should be repeated Nickel content analysis and if they are correct, look for the excess nickel source and try to reduce its content.

All the sludge samples are limited by its high copper content, but all of them can be legally used for agriculture. Although phosphorus content is not included in legislation, it must be consider as a limiting factor due to the environmental effects that excessive phosphorus application can cause in the form of eutrophication.

Considering all of this measurements and limitation, it is recommended a dose base on the phosphorus extraction, using between 16.000 and 24.000 kg ha^{-1} of sludge (depending on the sludge sample) every cycle of four years. There would be needed an extra application of mineral fertilizer one year after sludge application and two year after sludge application in the order of 200-250 kg ha^{-1} of nitrogen and 100 kg ha^{-1} of potassium.

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