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Effect of Pyrolysis on the Improvement of Sewage Sludge Properties

Diploma Thesis

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Declaration

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Prague, 12th April 2019 Marcela Ulloa Murillo

Aknowledgement

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Effect of Pyrolysis on the Improvement of Sewage Sludge Properties

SUMMARY

As a result of the wastewater treatment process, the gradual population growth has resulted in a further higher production of sewage sludge. High levels of toxic elements may be found in the sewage sludge, the pyrolysis process allows the usage of the resulting biochar as soil amendment, which is a promising alternative. Different temperatures of pyrolysis are commonly used, and its effects have been studied in the past. In this study, we tested the combined effects of three pyrolytic temperatures (600ºC, 700ºC, and 800ºC) and two temperature increment rates (Fast and Slow) on the pyrolysis of sewage sludge sourced from two Wastewater Treatment Plants of Czech Republic. The sewage sludge derived biochar (SDBC) was analyzed in terms of the total and available content of selected elements in four groups: Toxic elements (As, Cd, Cr, Pb), Macronutrients (Ca, K, Mg, P, S), Micronutrients (Cu, Fe, Mn, Mo, Ni, Zn) and other elements (Al, Be, Sr, V). The total weight loss and ash content were also determined.

The temperature increase significantly affected the final total concentration of certain toxic elements. The final concentration of Cr, for example, showed an increase when a combination of fast rate and higher temperatures was used, going from 3004 mg/kg at 600ºC to 3438mg/kg at 800ºC for the SDBC from sludge 1 and 99.6 mg/kg at 600ºC to 112.7 mg/kg at 800 ºC for the SDBC from sludge 2. The concentration of Pb and Cd seemed to be more influenced by the temperature alone. A similar behavior of Pb and Cd was observed in the respect to the available content of the two elements where no influence of rate was noted. The macronutrients in the SDBC from sludge 1 showed that the combination of 700 ºC and fast rate produced increases in the total concentration of Ca, Mg, P, S. For SDBC from sludge 2, the total concentration of all macronutrients, except S, increased slightly when a slow rate was used at 800ºC. Micronutrients in both sludges showed different behavior depending on the rate. The use of a fast rate in SDBC from sludge 1 caused an increase of concentration with temperature, in this case the minimum concentration of Cu (41.30 mg/kg), Ni (532 mg/kg) and Zn (12854 mg/kg) were above the allowed standard for the Czech and European regulations. In the case of the SDBC from sludge 2, Cu showed a close positive relationship with temperature, with the highest concentrations found at 800ºC, the opposite behavior was observed in Zn which showed a negative relationship with temperature with the maximum value found at 600 ºC. Regarding the ash content, it was observed a different behavior for both sludges. The highest values in sludge 1 were observed at 800ºC when using a fast rate (37%) and 700ºC when using a slow rate (31%). The highest value in sludge 2 was observed at 800ºC for the 18% rate and 600ºC for the 19% rate. The Sludge 2 reported the higher biochar yield corresponding to 56 % when using a combination of 600 °C and fast temperature increment rate. The yields varied depending on the temperature increase.

This study shows that during the pyrolysis of sewage sludge, the temperature increment rate can have a major impact both on the total and available levels of some of the elements and on the ash content. Nonetheless, temperature was the principal factor for some other elements and for the total weight loss, in these cases the temperature increment rate played a secondary role.

KEYWORDS: Pyrolysis, sewage sludge, biochar, nutrients, toxic elements

Vliv pyrolýzy na zlepšení kvality kalů z čistíren odpadních vod

Obash

Nárůst světové populace vedl k postupnému zvyšování produkce čistírenských kalů v důsledku nakládání s odpadními vodami. Tyto kaly mohou obsahovat vysoké koncentrace toxických látek. Jednou z alternativ jak minimalizovat obsah těchto látek je jejich pyrolýza, která napomáhá využít vzniklý materiál jako půdní přídavky. Rozdílné teploty pyrolýzy ovlivňují kvalitu produkovaného materiálu a účinky této metody byly v minulosti již studovány. V této studii jsme testovali tři různé teploty pyrolýzy (600°C, 700°C, 800°C) a dvě rychlosti nárůstu teploty (rychlá a pomalá) a zjišťovali jejich společný účinek na pyrolýzu čistírenských kalů z dvou čistíren odpadních vod v České republice. Z kalu vzniklá hmota byla analyzována a dělena dle chování jednotlivých prvků do čtyř skupin: toxické prvky (As, Cd, Cr, Pb), makroživiny (Ca, K, Mg, P, S), mikroživiny (Cu, Fe, Mn, Mo, Ni, ZN) a ostatní prvky (Al, Be, Sr, V). Zároveň se zjišťovala celková ztráta masy a obsah prachu.

Rychlost nárůstu teploty měla velký vliv na konečné obsahy některých toxických látek. Finální koncentrace Cr byla například mnohem vyšší při kombinaci rychlého nárůstu teploty a vyšších teplot. Ze 3004 mg/kg při 600°C obsah Cr stoupl na 3438 mg/kg při 800°C v biocharu z kalu 1 a z 99,6 mg/kg při 600°C na 112,7 mg/kg při 800°C v biocharu z kalu 2. Koncentrace Pb a Cd se zdá být ovlivněna především samotnou teplotou. Podobný vztah mezi těmito dvěma látkami byl pozorován co se týče účinku rychlosti zvyšování teploty, která u nich neměla žádný význam. U makroživin obsažených v biocharu z kalu 1 bylo vypozorováno, že kombinace 700°C a rychlého nárůstu teploty celkově zvýšila obsah Ca, Mg, P, S. V biocharu z kalu 2 byla celková koncentrace všech makroživin (kromě S) lehce vyšší při pomalém nárůstu a teplotě 800°C. Mikroživiny prokázaly rozdílné chování v obou kalech v závislosti na rychlosti nárůstu teploty. V biocharu z kalu 1 použití rychlého nárůstu zapříčinilo zvýšení koncentrace látek spolu s teplotou, v tomto případě minimální obsah Cu (41,30 mg/kg), Ni (532 mg/kg) a Zn (12854 mg/kg) převyšovaly limity povolené českými a evropskými vyhláškami V dalším případě pak Cu ukázala pozitivní návaznost s teplotou v biocharu z kalu 2, kde se nejvyšší obsah Cu objevil při 800°C, naopak Zn měl obrácenou návaznost - maximální obsah byl nalezen při 600°C. Obsah popela a jeho chování při zvyšování teploty pyrolýzy se lišil v obou kalech. V kalu 1 se nejvyšší obsah objevil při 800°C a při rychlém nárůstu teploty (37%) a při 700°C a pomalém nárůstu (31%). V kalu 2 byly nejvyšší obsahy evidovány (18%) při 800°C a při 600°C byl obsah 19%. Nejvyšší výtěžek biocharu 56% byl nalezen v kalu 2 při kombinaci 600°C a rychlého nárůstu teploty. Výtěžek se lišil v závislosti na zvyšování teploty.

Tento test dokazuje, že rychlost nárůstu teploty během pyrolýzy čistírenských kalů může významně ovlivnit jak celkovou dostupnou koncentraci některých důležitých prvků , tak i obsah popela . Nicméně u některých látek a zjišťování celkové ztráty masy byla teplota hlavním faktorem, zatímco rychlost nárůstu hrála menší roli.

Klíčová slova: Pyrolýza, čistírenský kal, biomasa, toxické látky

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1. INTRODUCTION

The actual increase of the world's population, and the higher protection for the environment have led to a gradual increase of sewage sludge production during wastewater tratment process. For instance, in the European Union, the annual production of sewage sludge in dry weght has been stimated in 8.7 M tons, representing approximately 17 kg per inhabitant (European Commision 2017), for the particular case of the Czech Republic, in 2017 the wastewater sludge production (tons of dry matter) was 178077 tons, the amount used for agricultural purposes was 75451 tons, for composting 60930 tons, for landfill disposal 11809 tons, and for incineration treatment 4736 tons (Czech Statistical Officce 2018).

The composition and characteristics of wastewater sludge vary and are mainly dependent on treatment characteristics for wastewater and pollutants (original wastewater sources) and the components can cover a broad range of toxic substances, including heavy metals (HMs), organic material, pathogens, inorganic compounds and pharmaceuticals, which limit the use of wastewater sludge in agriculture. (Zaker et al. 2019).

Because of its efficiency in the volume of waste reduction and its toxicity, the development of thermochemical conversion approaches such as pyrolysis has received considerable attention, due to its efficient reduction of the volume of waste, and its capacity to transform the raw sewage sludge into a feedstock that can enhance the features of of the soil in posterior uses, for instance as soil amendment.

Attractive alternatives for waste disposal have often been pyrolysis and combustion, as these techniques lead a decrease on the production by volume of waste and involve profitable energetic and/or chemical products. The pyrolysis temperature, heating rate (HR), and sludge composition have been known as major factors on the pyrolysis process for the resulting quality of the biochar (Conesa et al. 2009).

Biochar as soil amendment has many advantages in terms of enhancing soil characteristics for example porosity, texture, structure, density and particle size distribution, Added biochar has been shown to increase crop growth rates, and also contributes to the reduction in nutrient leaching associated with a higher water retention capacity (Rehman & Razzaq 2017).

The aim of this Diploma Thesis will be to analyze under pyrolysis condition two different sewage sludges with distinct properties at temperatures 600, 700, and 800 °C and under different temperature-increment rates (fast and slow) during the process. Focus will be put on evaluation of mentioned pyrolytic conditions on chemical properties of resulting wastewater sludge derived biochar, in terms of total and bioavailable contents of toxic elements, ash content and weight loss analysis were also included.

KEYWORDS: Pyrolysis, sewage sludge, biochar, toxic elements

2. Objectives of work

- To evaluate the effect of pyrolytic temperature and temperature increment rate on the total content of elements in the produced biochar.

- To evaluate the effect of pyrolytic temperature and temperature increment rate on the available content of elements in the produced biochar.

- To identify the effect on the pyrolytic temperature and temperature increment rate on the losses of material and ash content.

Hypothesis:

1. The total content of the elements in the biochar is dependent on both, the temperature and temperature-increment rate of the pyrolysis and is presumed that this effect will be dissimilar for different elements.

2. The available content of the elements in the biochar is dependent on both, the temperature and temperature increment rate of the pyrolysis and is presumed that this effect will be dissimilar for different elements.

3. The losses of material and ash content in the biochar is affected by the temperature and temperature increment rate of the pyrolysis.

3. Literature Review

3.1Sewage Sludge Production

Sewage sludge can simple be defined as the semi solid resulting material from the municipal or industrial wastewater treatment process. The sewage sludge regarding its provenance is a complex and heterogeneous mixture of microorganisms, undigested organics (residues from plants, paper, stool, oil, inorganic material and moisture), this type of material contains a complex combination of materials such as lipids, polysaccharides, proteins and peptids, plant macromolecules with aliphatic structures (e.g. cutins or suberins) phenolic structures (e.g. tannins or lignins), sideways with organic micropollutants (e.g. dibenzofurans or polycyclic aromatic hydrocarbons) (Fonts et al. 2012).

Currently the sewage sludge produced in the EU, has been estimated in about 25 kg person equivalent (P.E) per year (corresponding to 6.8 g/ P.E x day), there is also a great variation with the sewage sludge production around the world, Brazil produces 5.4 and China 6.2 g/ P.E x day, this differences are related with the differences in the systems and treatment level for the wastewater (Mininni et al. 2015). Several countries, for instance the Czech Republic, Estonia, Bulgaria, Lithuania, Latvia, Poland, Romania, Slovakia, Malta and Hungary, presented an increase on production of 100 % (2.5 million tons DM of sludge in total) for yearly production, resulting from the release and implementation of more stringent municipal wastewater treatment and sludge management regulations and directives (Świerczek et al. 2018).

Figure 1 is possible to appreciate on the top of the list the countries that produces the higher amounts of sewage sludge in EU, between them is possible to identify that Germany, the United Kingdom and France have a sludge production between 1000 to 25000 (10^3 ton DS/year), this in contraposition with the countries with the lowest generation values, Slovakia, Estonia and Latvia, the production of this countries is between 25 to 50 (10^3 ton DS/year). Most than 70 % of the sludge produced in Europe is from five countries, Germany, the United Kingdom, France, Spain and Italy (Kacprzak et al. 2017)

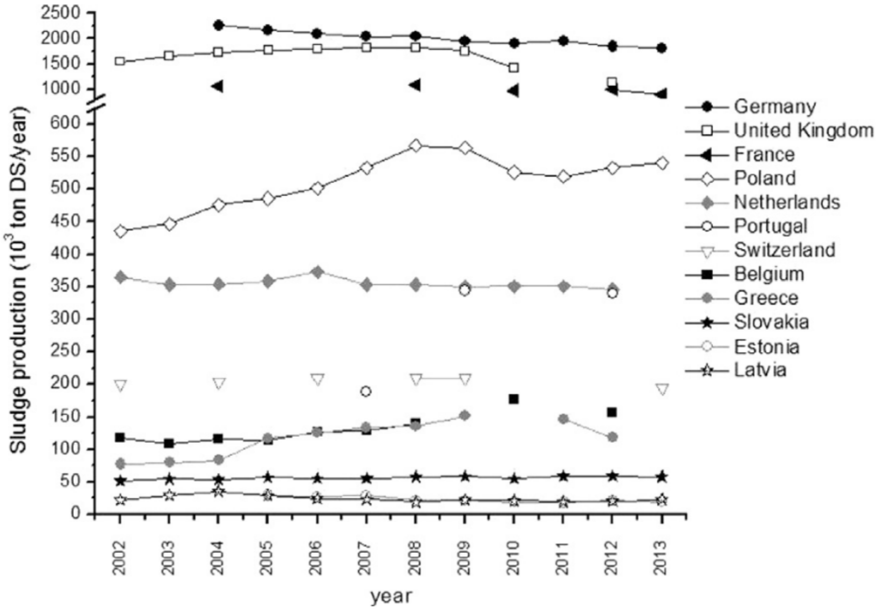


Figure 1 Sewage sludge production in some countries of the EU (Kacprzak et al. 2017)

3.1.1 Basic technological steps for sewage sludge production

Sludge production is based on wastewater treatment systems designed for treating the liquid phase, as is not specialized in treating the solid portion, the different settings in the WWTP will produce different types of sludges, for instance the primary sludge is produced from the sedimentation of the raw materials in a primary settlement tank and the secondary sludge, also known as biological sludge, produced by biomass growth due to microbiological activities; the resulting sludge are subsequently treated and processed for final disposal or reuse (Grady et al. 1999; von Sperling 2007).

Figure 2 shows the wastewater treatment steps and the types of sludge that can be generate in a WWTP , this sludge is the result of the chemical oxygen demand (COD) transformation, and posterior conversion into biosolids, this portion typically consists on 1 to 2 % of the volume from wastewater used in the treatment process (Youcai & Ziyang 2017).

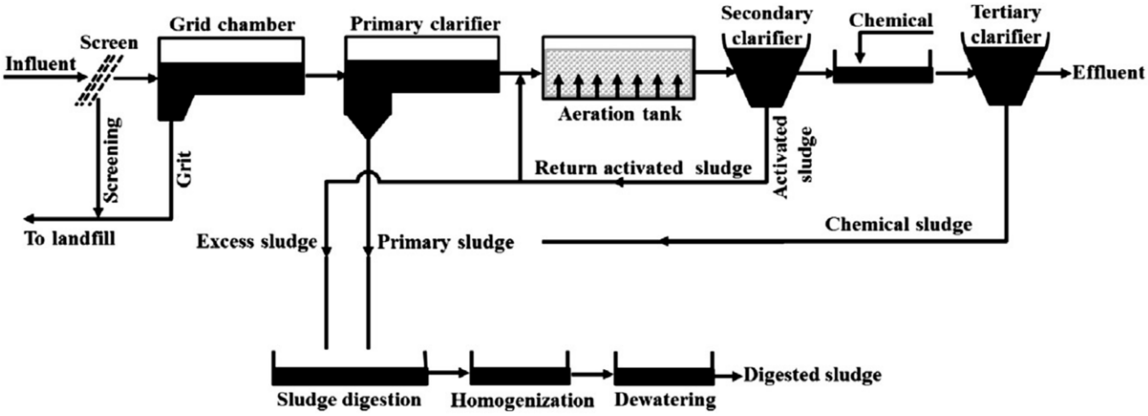
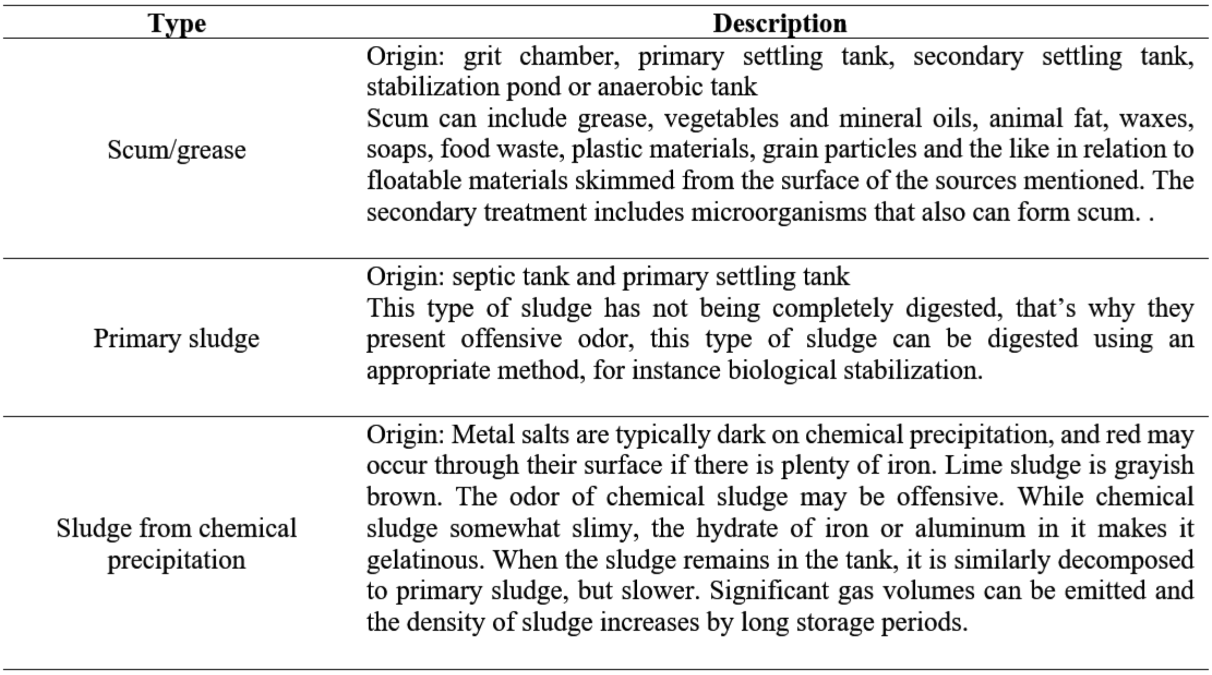


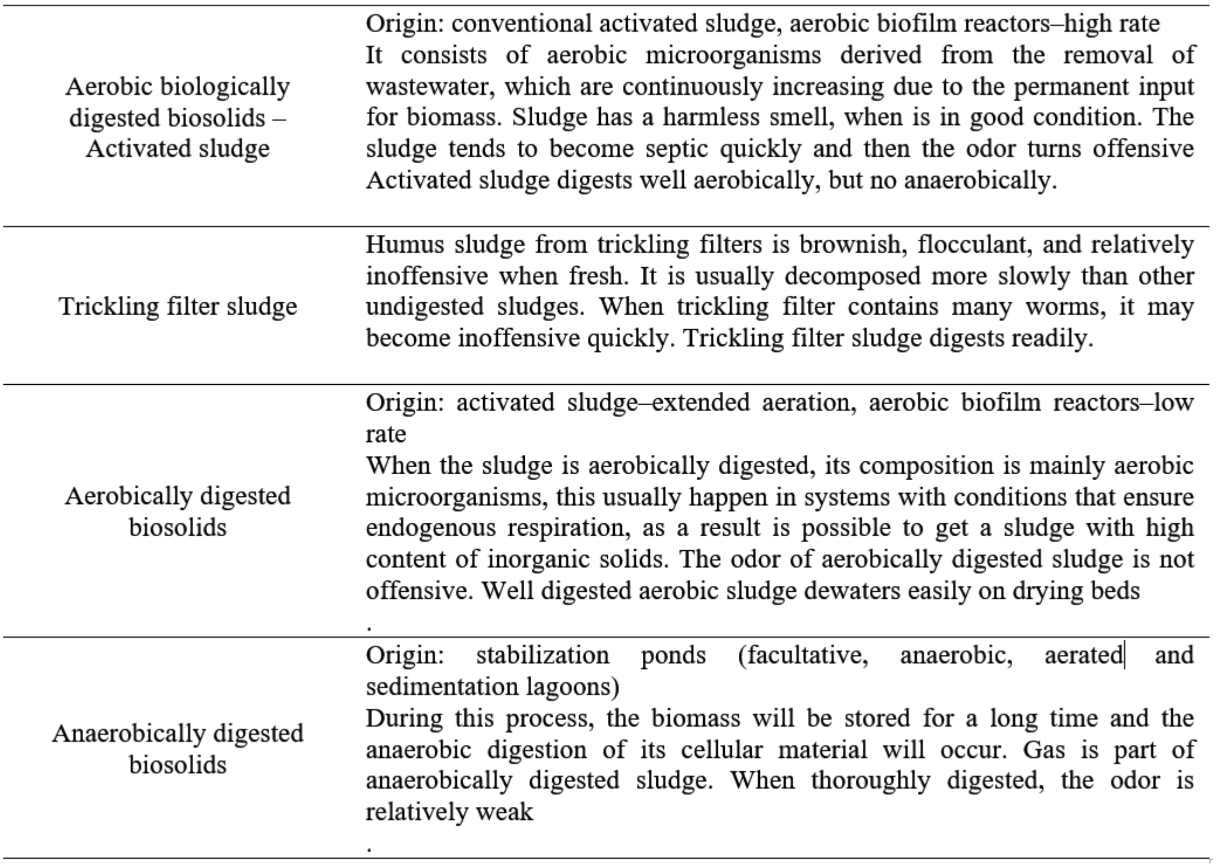
Figure 2 Sewage sludge generation paths in wastewater treatment plants (Youcai & Ziyang 2017)

Depending on the process stage, the sludge will produce different kinds of solid by-products depending mainly on the origin of wastewater, for wastewater treatment, pre-treatment is the first step and screened material is produced from here, since the primary sludge is only produced in the primary sedimentation tank, secondary sludge is the result of biological process (activated sludge, anaerobic reactors) (von Sperling 2007). Table 1 presents the differences in waste water treatment and specification among the stabilized and non-stabilized sludge.

Table 1 Characteristics of sludge and biosolids produced during wastewater treatment



Type	Description
Scum/grease	Origin: grit chamber, primary settling tank, secondary settling tank, stabilization pond or anaerobic tank Scum can include grease, vegetables and mineral oils, animal fat, waxes, soaps, food waste, plastic materials, grain particles and the like in relation to floatable materials skimmed from the surface of the sources mentioned. The secondary treatment includes microorganisms that also can form scum. .
Primary sludge	Origin: septic tank and primary settling tank This type of sludge has not being completely digested, that's why they present offensive odor, this type of sludge can be digested using an appropriate method, for instance biological stabilization.
Sludge from chemical precipitation	Origin: Metal salts are typically dark on chemical precipitation, and red may occur through their surface if there is plenty of iron. Lime sludge is grayish brown. The odor of chemical sludge may be offensive. While chemical sludge somewhat slimy, the hydrate of iron or aluminum in it makes it gelatinous. When the sludge remains in the tank, it is similarly decomposed to primary sludge, but slower. Significant gas volumes can be emitted and the density of sludge increases by long storage periods.



Aerobic biologically digested biosolids – Activated sludge	Origin: conventional activated sludge, aerobic biofilm reactors–high rate It consists of aerobic microorganisms derived from the removal of wastewater, which are continuously increasing due to the permanent input for biomass. Sludge has a harmless smell, when is in good condition. The sludge tends to become septic quickly and then the odor turns offensive Activated sludge digests well aerobically, but no anaerobically.
Trickling filter sludge	Humus sludge from trickling filters is brownish, flocculant, and relatively inoffensive when fresh. It is usually decomposed more slowly than other undigested sludges. When trickling filter contains many worms, it may become inoffensive quickly. Trickling filter sludge digests readily.
Aerobically digested biosolids	Origin: activated sludge–extended aeration, aerobic biofilm reactors–low rate When the sludge is aerobically digested, its composition is mainly aerobic microorganisms, this usually happen in systems with conditions that ensure endogenous respiration, as a result is possible to get a sludge with high content of inorganic solids. The odor of aerobically digested sludge is not offensive. Well digested aerobic sludge dewaters easily on drying beds .
Anaerobically digested biosolids	Origin: stabilization ponds (facultative, anaerobic, aerated and sedimentation lagoons) During this process, the biomass will be stored for a long time and the anaerobic digestion of its cellular material will occur. Gas is part of anaerobically digested sludge. When thoroughly digested, the odor is relatively weak .

(Metcalf & Eddy 2003; von Sperling 2007)

3.2Sewage Sludge Composition

The properties and components of the wastewater sludge are understandable in terms of production mass and volume, this is necessary in order to be able to understand the connection between solid level and the water content due to the effect of this last characteristic on the mechanical properties and the processes of management and disposal of the sewage sludge. (von Sperling 2007), In general, the weight of the solids for sludge varies between 0,25 and 12% according to the operations and processes used (Metcalf & Eddy 2003)

Sewage sludge is a heterogeneous material, comprising a mixture of several components such as pollutants, mineral nutrients, microorganisms, cellulose, inorganic matter, among others. The components can be divided into six groups(Shao et al. 2010; Zaker et al. 2019):

(1) nontoxic organic carbon compounds, mainly from biological origin (60 % on dry basis)
(2) Components which contains nitrogen and phosphorous
(3) A big variety of toxic inorganic pollutants, counting toxic elements, heavy metals (Copper, Zinc, Cadmium, Lead, Nickel, Chromium and Mercury. Also, organic compounds are included in this group, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), linear alkylbenzene sulfonates (LAS),

polychlorinated dibenzodioxins (PCDDs), brominated fire retardants (BFRs), polychlorinated dibenzofurans (PCDFs), and alkylphenols (APs)

(4) Microbiological pollutants, which includes pathogens, bacteria, virus and protozoa
(5) Inorganic compounds, corresponding to compounds that contains Magnesium, silicates, and aluminates, and calcium
(6) Pharmaceuticals and their decay products
(7) Water.

Typically the composition of sludge, comprises 59 – 88 % w/v (on dry basis) of organic matter, in the biodegradable fraction, which is composed usually by Carbon 50 – 55 %, Oxygen 25 – 30 % and Hydrogen 6 – 10 % (Raheem et al. 2018). The total Nitrogen content can be variable, between <0.1 % and 18 %, for mineral Nitrogen it can build up to 6.7 %, for Phosphorus the same behavior is encountered, on dry weight, the content can vary from <0.1 % to 14 %, As was mentioned the contents of these elements are based on the source of the sludge and the method of sludge treatment. It is found in the phosphorus content of sewage sludge and their corresponding fraction in the inorganic percentage, that the sludge stabilization compounds used, have an observed an impact on the bioavailability of this element (Kacprzak et al. 2017; Zaker et al. 2019).

Table 2 shows ranges data for the chemical composition of untreated primary and activated sludge from municipal waste water systems.

Table 2 Characteristics of municipal sewage sludge

Parameter	**Type of sludge**			
	Untreated primary sludge		**Secondary sludge**	
	(Kacprzak et al. 2017)	(Metcalf & Eddy 2003)	(Kacprzak et al. 2017)	(Metcalf & Eddy 2003)
Total dry solids (TS), (%)	2.0 – 8.0	1 – 6	0.8 – 1.2	0.4 – 1.2
Volatile solids (% of TS)	60 – 80	60 - 85	59 – 88	60 - 85
Grease and fats (% of TS)	7 – 35	5 - 8	5 – 12	5 - 12
Protein (% TS)	20 – 30	20 - 30	32 – 41	32 - 41
Cellulose (% of TS)	8.0 – 15.0	8 - 15	7 – 9.7	-
Phosphorus (P2O5 % of TS)	0.8 – 2.8	0.8 – 2.8	2.8 – 11.0	2.8 – 11.0
Nitrogen (N % of TS)	1.5 – 4	1.5 - 4	2.4 – 5.0	2.4 – 5.0
Potassium (K2O% of TS)	0 – 1	0 - 1	0.5 – 0.7	0.5 – 0.7
pH	5.0 – 8.0	5.0 – 8.0	6.5 – 8.0	3.5 – 8.0

(Metcalf & Eddy 2003; Kacprzak et al. 2017)

3.2.1 Toxic elements content

Toxic elements are those inorganic chemical elements that, in very small quantities can be essential or detrimental to plants and animals. The term “heavy metals” is used to denote several of the trace elements present in sludge and biosolids (Metcalf and Eddy, 2003). HMs are a main focus in the regulations for the sewage sludge usage in agricultural land, this elements: zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb), mercury (Hg) and chromium (Cr), this elements are characterized for their ability of accumulation in human tissues, bioaccumulation and biomagnification through the food chain, makes this a principal problem. In Table 3 and Table 4 are presented some toxic elements concentrations found in several sewage sludges analyzed during some pyrolysis researches, which aimed to improve the sewage sludge characteristics for the land application of the produced biochar, from this studies it can be seen that the composition of the sewage sludge can vary greatly depending of its origin. The binding and the specific for in which the HMs can be found in the sewage sludge determine its mobility and availability, which is related with the toxicity to plants. It is known that HMs content that is fixed the sewage sludge during wastewater treatment is approximately 50–80% of the original content present in wastewater, and this is why some specific metals present high concentrations in sludge. (Fytili & Zabaniotou 2008; Agrafioti et al. 2013).

Table 3 shows the average content of some toxic elements in different sewage sludge samples. The content of this elements varies depending on the wastewater from which the sludge was generated, this responds to a different characteristics, for the studies listed the WWTPs were for municipal wastewater treatment for medium and large size cities with secondary or tertiary treatment, such as activates sludge and anaerobic-anoxic-aerobic process, and the sludges were digested anaerobically. From the results it can be observed the following content sequence Pb > Zn > Cu > Cd > Cr > Ni.

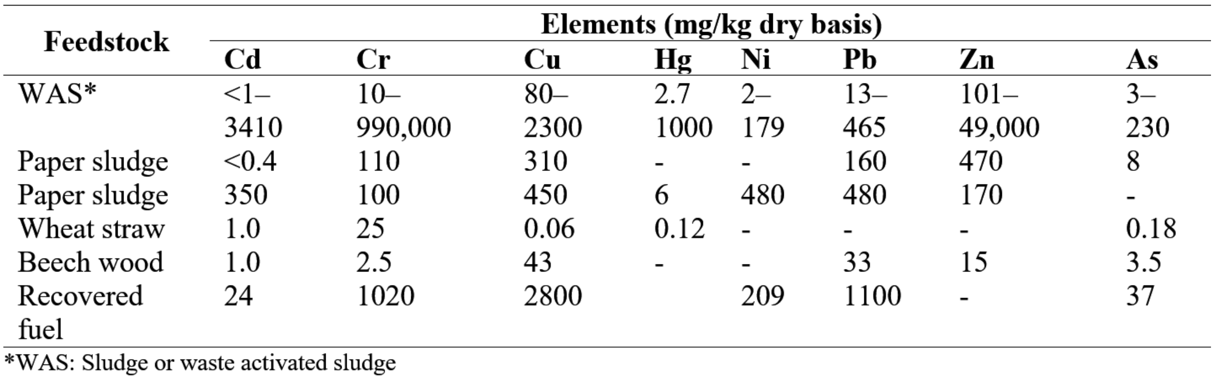
Domestic wastewater usually contains low HMs contents, however the mixing with an industrial wastewater flow would increase in great proportion the concentration of this elements in sewage sludge, this is due to the particular industrial characteristics (Lu et al. 2016).

Table 3 Average content of potentially toxic elements in sewage sludge from wastewater treatment plants

Source	**Element (mg/kg Dry Matter)**					
	Cu	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**
(Lu et al. 2016)	172 ± 3.4	735 ±14.1	3740 ± 27	169 ± 4.3	72.4 ± 2.8	100 ± 2.0
(Jin et al. 2016)	1217 ±29.31	2579 ±106.6	95.11 ±2.51	-	112.1 ±6.23	449.2 ±25.71
(Yuan et al. 2015)	172 ± 14.4	735 ± 24	3740 ± 27	169 ±7.3	72.4 ±5.8	100 ± 8.9
(Liu et al. 2014)	79.3	442	38.2	2.13	-	67.5
(Agrafioti et al. 2013)	5.51	-	1.04	-	2.23	0.40
(Hossain et al. 2011)	22.75 ±4.64	297.5 ±59.91	86.5 ±1.04	2.07 ±0.06	70 ± 0.91	81 ±0.70
(He et al. 2010)	312.3 ± 25.3	2107.8 ± 83.2	119.6 ± 14.3	5.2 ± 1.1	-	-

Table 4 contains data corresponding to the content of potentially toxic elements in different biomass materials corresponding to sewage sludge, paper sludge, wheat straw, beech wood and recovered fuel. This data allows to identify the differences on the content of the elements, which is linked mainly to the nature of the biomass.

Table 4 Potentially toxic elements contents in different biomass materials



Feedstock	Elements (mg/kg dry basis)							
	Cd	Cr	Cu	Hg	Ni	Pb	Zn	As
WAS*	<1–3410	10–990,000	80–2300	2.7 1000	2–179	13–465	101–49,000	3–230
Paper sludge	<0.4	110	310	-	-	160	470	8
Paper sludge	350	100	450	6	480	480	170	-
Wheat straw	1.0	25	0.06	0.12	-	-	-	0.18
Beech wood	1.0	2.5	43	-	-	33	15	3.5
Recovered fuel	24	1020	2800		209	1100	-	37

*WAS: Sludge or waste activated sludge

(Raheem et al. 2018)

3.3 Sludge Stabilization

Raw sludge contains a large portion of microorganisms that can cause offensive odors that are released with its decay. The stability process aims to digest the biodegradable portion of the organic substance in the sludge, reducing the presence of pathogens, offensive odours and decreasing on the subsequent degradation. A good stabilization process prevents the microorganisms from reproduce in the organic fraction of the sludge by reducing the volatile content and adding chemical composite materials to the sludge. (Metcalf & Eddy 2003).

The process of stabilization comprehends: biological stabilization (aerobic and anaerobic digestion), chemical stabilization (chemical products addition), and thermal stabilization (incorporation of heat).

Biological stabilization

Anaerobic digestion is the production of methane and CO_2 by hydrolysis, fermentation and methanogenesis of organic matter. It is the most common process for sludge stabilization. Aerobic digestion is a less used method, it is conducted in an open tank and produces carbon dioxide, ammonia and water in the endogenous phase of microorganisms. The stabilization of active sludges from WWTPs with the biological removal of nutrients can be achieved through this process. Anaerobic digestion generates a biosolid, which can be used as a conditioning or fertilizer for soils with certain restrictions in agricultural lands. Composting processes are also widely used in the treatment of solid waste in urban areas and they are performed in an enclosed reactor or piles which are capable of reaching temperatures within pasteurization range (50-70 ° C). (Metcalf & Eddy 2003; von Sperling 2007).

Chemical Stabilization

Also called lime stabilization, generally during alkaline stabilization, the pH of the mixture of wastewater solids and alkaline material (lime) is 12 und (U.S. EPA 2007), that promotes pathogens destruction.

Thermal stabilization

Thermal stabilization includes removal of the organic part of sludge that only results in the final disposal of the ash produced. The product may have high nitrogen levels and is pathogen-free. Because of the high moisture content of the sludge, a large part of the energy consumed was necessary to reduce the sludge water content (Fytili & Zabaniotou 2008).

3.4 Sewage Sludge Disposal Alternatives

During the waste water process (primary, secondary and advanced), waste sludge is generated, and it is important to ensure adequate handling of this substance in order to prevent harmful environmental effects. Is recommended to treat municipal sewage sludge before disposal in large and centralized WWTP using the following treatment set: preliminary treatment, primary thickening, liquid sludge stabilization, secondary thickening, conditioning, dewatering, final treatment (drying, composting, incineration, etc.), storage, transport and final destination (landfill, agriculture, other uses) (Fytili & Zabaniotou 2008).

Currently, the most important means for disposing of wastewater sludge are divided into three categories: agricultural use, incineration and landfill, Figure 3 provides the various alternatives for waste treatment and disposal; in large parts, the sludge is dewatered and digested anaerobically prior to their use in composting, drying and incinerating processes, to obtain some building materials from the combustion ash.

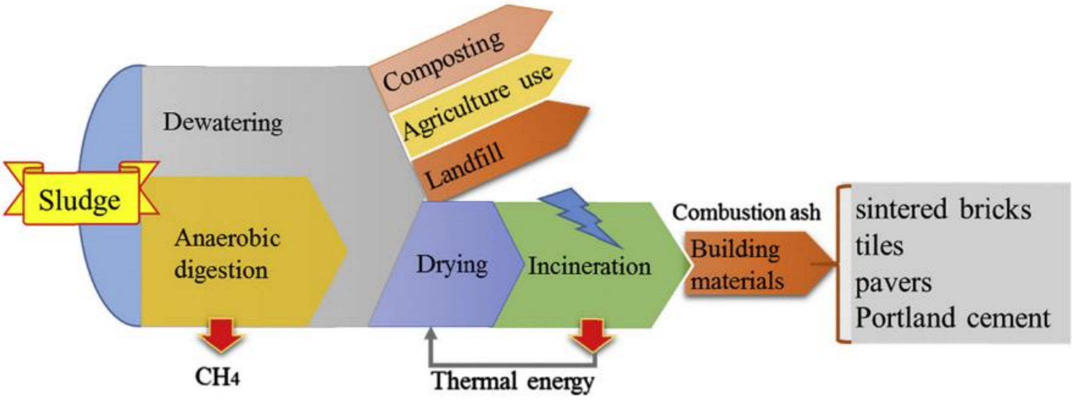


Figure 3 Treatment and disposal of sewage sludge (Youcai & Ziyang 2017)

Council Directive 1999/31/EC has set a specific objective to reduce the amount of organic waste disposed of in landfills in Europe by 65% by July 2016, compared to original value from the total amount of organic solid municipal waste produced in EU countries in 1995. It states that the amount of biodegradable organic waste disposed of in landfills should be reduced by 65% by the year 2016. (Council Directive 1999).

3.4.1 Agricultural use

This method for sludge disposal is the most used, consisting of spreading the material on the surface of the ground, and can be used in agriculture, disturbed land and forest land. Biosolids can be used to improve their soil properties (structure, water retention capacity, water infiltration) because of their organic matter content, thus increasing their cation exchange capacity (CEC). This allows the soil to hold potassium. (Metcalf & Eddy 2003).

The sludge properties are the reflect of the technologies implemented on the WWTPs, which can have nitrification and denitrification phases during the process, the resulting sludge contains phosphorus, nitrogen and organic matter, these are nutrients very important and gives to the sludge fertilizing characteristics, because this elements are essential for plants and their availability impact development and plants growth (Razaq et al. 2017). Nonetheless the sludge may also contain a great variety of elements, among them toxic elements, such as heavy metals can be identified, which are harmful if they bioaccumulate and reach the food chain (Fytili & Zabaniotou 2008; Fonts et al. 2012).

There are a range of properties, including macro, micronutrient and organic content, the toxic elements and pathogens, as well as the phosphorus, nitrogen and potassium content that should be evaluated before use of sludge as a soil conditioner.

Small technologies (composting, earthworm stabilization, pool stabilization) represent a recognized advantage for sludge use within agriculture. There are some limitations to this application, such as it can only be used in soil conditioning and fertilizers. It was the risk of pollution by high heavy metals, pathogens and aromatic hydrocarbons. (Raheem et al. 2018).

3.4.2 Incineration

Sludge incineration is the thermal decomposition process by oxidizing the material in which volatile solids are burnt in the presence of oxygen and converted into CO_2. and H_2O. Also, the fixed solids are changed into ashes. These ashes must be disposed without beneficial posterior uses (von Sperling 2007).

In Europe, current legal limitations on disposal in landfills have become incineration in the most attractive method of treatment for sludge, with several advantages, for example, the large reduction in volume of sludge, after the mechanical dewatering which is possible, after incineration, and neutralizing offensive odors approximately 10 %. The ash generated also contains a few toxic elements and is usually sunk (ash contains around 30% of the solids originally present) (Fytili & Zabaniotou 2008).

3.4.3 Sanitary Landfill

According to the Directive 1999/31/EC landfill is a waste disposal site used for its deposit into land. The sludge is disposed mixed with soil by compaction in ditches or trenches, which are sealed, its possible to dispose (von Sperling 2007). The production of leachate and the CO_2 emissions to the atmosphere are influenced directly by the disposal of sludge in landfills (Kacprzak et al. 2017). The high moisture content of dewatered sludge (around 80 %) makes very difficult its handling, for this reason it is recommended to take for disposal sludge with moisture content below 60 %, this will prevent sliding and it will make easier the equipment operation (Youcai & Ziyang 2017).

Given the current situation of the sewage sludge disposal routes, as described above, high demands can be expected in the short term on new alternative sludge management methods. Thermal processes such as wet oxidation, pyrolysis or gasification were recently investigated and proposed as possible alternatives.

The Figure 4 shows the sewage sludge disposal methods used mostly for selected countries, where is possible to determine that the most used methods for sludge disposal are agriculture, which goes up to 50 % of the total mass percentage for countries like Czech Republic, USA and Australia, this can be implemented either directly or indirectly through composting; another widely used method is incineration, being a major practice in the case of Japan goes up to 80 % of the sewage sludge production, agricultural use is very low, but landfilling is almost not used; composting is mainly used in Hungary, where almost 80% of the sludge production is composted. The variability of data is the result of the different social, economic and politic interactions in the different nations.

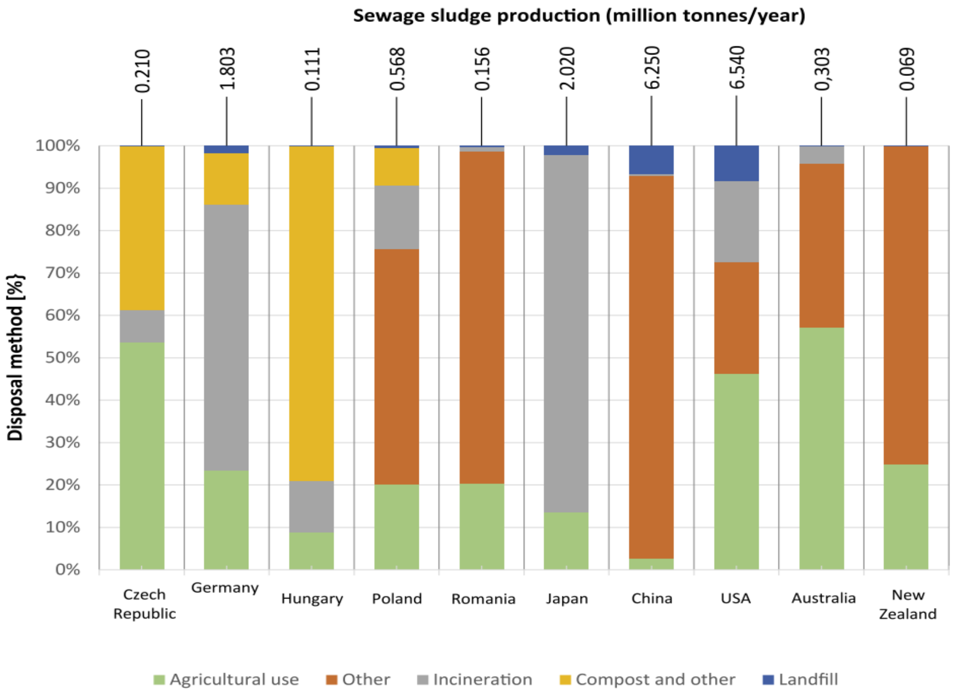


Figure 4 Sewage sludge disposal by type of treatment (Świerczek et al. 2018)

3.5Policy on Sewage Sludge Utilization

Over the last two decades, the production of sewage sludge has increased twice, with this growth being reported in China over the past five years. In this area, implementation and adoption of specific directives is mandatory for all EU Member States, and these regulations were established worldwide to prevent, control and protect the public from the potentially toxic components of waste sludge. These regulations have also been adopted throughout the world. .

Figure 5 outlines the characteristics of the main directives or regulations relating to methods used for the management of wastewater: bio-and chemical stabilization and thermal stabilization, including various uses such as agricultural use, waste disposal, raw material recovery and use in the construction sector.

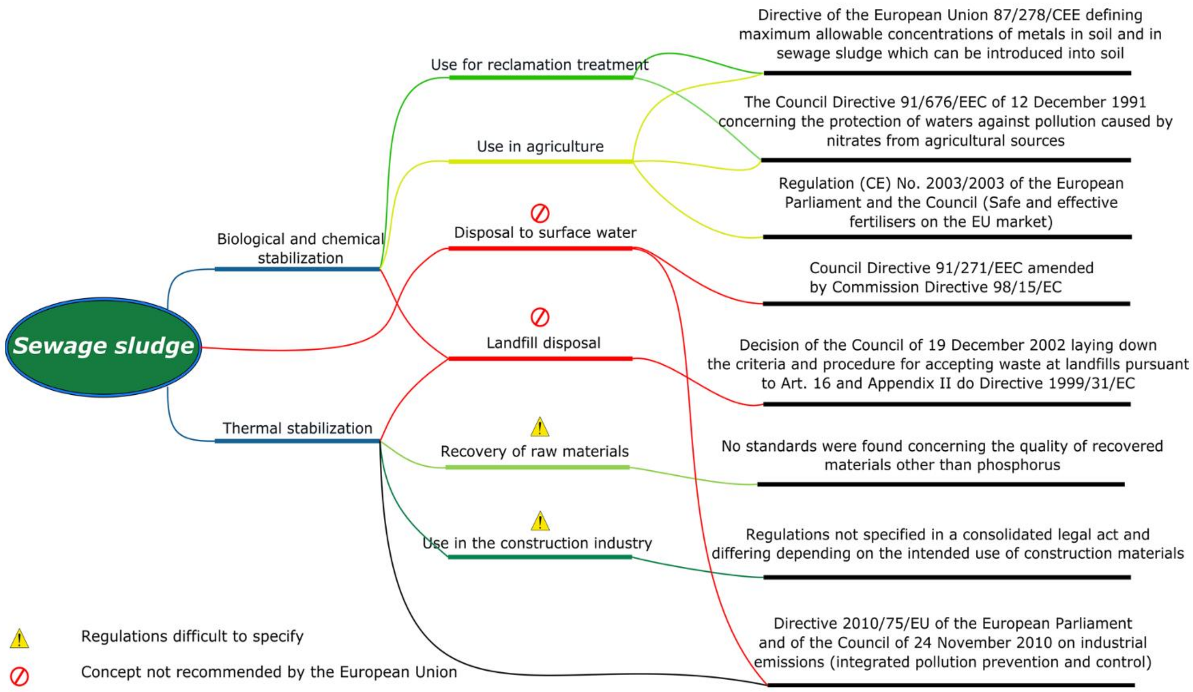


Figure 5 Regulations for sewage sludge management methods
(Cieślik et al. 2018)

3.5.1 United States of America

The U.S Environmental Protection Agency (U.S. EPA) issued United States standards for using or disposing of sewage waste 40 CFR part 503. The Land Application subparagraph B sets out standards that consist of general requirements, pollutants limits (section 503.13), management practices and operational standards, for the final use or disposal of waste generated during domestic sewage treatment in treatment plants. Standards for waste sludge appliance to the soil, the disposal on a surface or for its incineration are included in this section. (U.S. EPA 1993). Sewage sludge shall not be used on land if the concentration in material of any pollutant exceeds the ceiling concentration for each of the elements described in Table 5. Table 5.

Table 5 Pollutant ceiling concentrations of sewage sludge 40 CFR part 503

Pollutant	Ceiling concentration mg/kg dry weight
Mercury	57
Molybdenum	75
Nickel	420
Selenium	100
Zinc	7500
Arsenic	75
Cadmium	85
Chromium	-
Copper	4300
Lead	840

(U.S. EPA 1993)

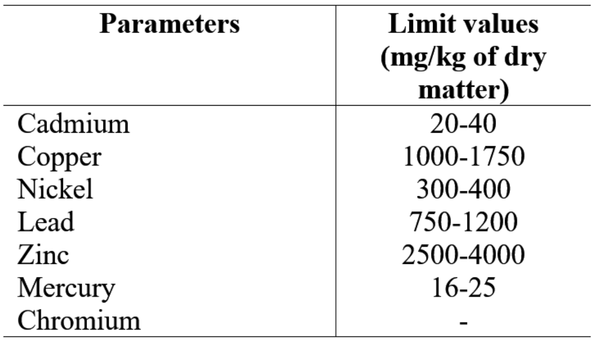
3.5.2 European Union

The directives released in the EU for management of sewage sludge are based mainly on a system of alerts. Furthermore, those directives usually set restrictions proportioning limit for selected elements when the sludge is going to be used in agricultural land, for instance.

Council Directive 86/278/EEC, on environmental protection and soil protection, when sewage sludge is used in agriculture. The purpose of this Directive is to regulate the use of sewage sludge in agriculture and to create an environmentally comprehensive framework that prevents harmful impacts and encourages its proper utilization.

The limits of heavy metal content for sewage sludge used in agriculture are presented in Table 6. It must be noted that these parameters contain limits over a broad range and that these elements restrict the consideration of the sewage sludge as a not dangerous material.

Table 6 Limit values for heavy metal concentrations in sludge for use in agriculture Directive 86/278/EEC



Parameters	Limit values (mg/kg of dry matter)
Cadmium	20-40
Copper	1000-1750
Nickel	300-400
Lead	750-1200
Zinc	2500-4000
Mercury	16-25
Chromium	-

(Council Directive 1986)

The Water Framework Directive on collecting, processing and disposed of urban waste water and certain industrial waste water sectors, as amended by Commission Directive 98/15/EC, is laid down by Council Directive 91/271/EEC. The monitoring of treatment of wastewater and the quality of the wastewater sludge obtained also requires. The purpose of this directive is to protect the environment from the hostile effects generated through inadequate waste water discharges and prevents inadequate disposal of sludge into water surfaces.

Council Directive 1999/31/EC on the landfill of waste, which obliges EU Member States to reduce the storage in landfills of biodegradable municipal waste setting up a national strategy, aimed to accomplish the targets: (a) in five years reduce to 75 % of the total amount produced in 1995, (b) eight years reduction of 50 %, (c) fifteen years reduction of 35 %. This is defined in the article 5, waste and treatment not acceptable in landfills.

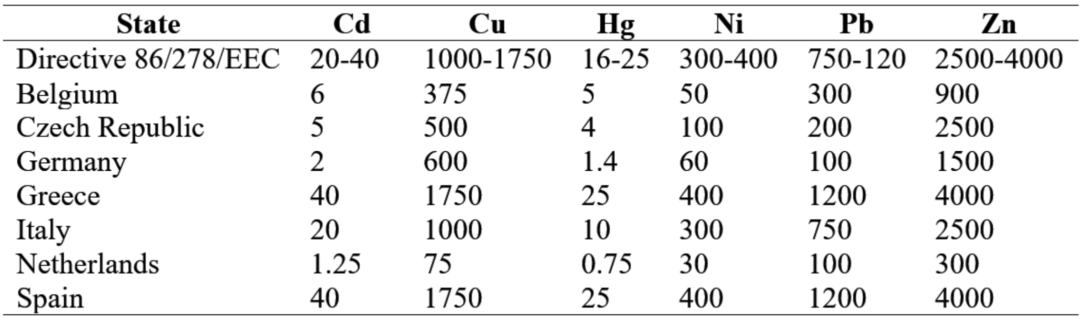
Directive 2000/60/EC of the of the European Parliament and Council of Europe sets the joint Community action in the field of Water Policy. This Water Framework Directive (WFP) states that sewage sludge should be reused, making this sludge being treated as a product other than a waste.

Some other regulations that are related to a minor extent with sewage sludge have been released in order to prevent environmental pollution:

- Council Directive 91/271/EEC of 21 May 1991 concerning waste water treatment.
- Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain directives.
- Directive of the European Parliament and the Council 2008/50/EC of 21 May 2008 on ambient air quality and cleaner air for Europe.
- Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control).

Using as a basis the Directive 86/278/EEC all the EU countries have set more struct limit values for toxic elements and substances present in sewage sludge, which want to be used in agricultural land, some countries even set limit values for toxic elements that are not include in the Directive. From Table 7 it can be observed that countries that keep limit values close to the Directive are: France, Greece, Spain and Ireland, and the countries which get more strict limits are: Czech Republic, Belgium, Germany, and Netherlands (Mininni et al. 2015).

Table 7 Limit values - toxic elements for sludge use in agriculture (mg/kg DM of sewage sludge). Selected EU countries



State	Cd	Cu	Hg	Ni	Pb	Zn
Directive 86/278/EEC	20-40	1000-1750	16-25	300-400	750-120	2500-4000
Belgium	6	375	5	50	300	900
Czech Republic	5	500	4	100	200	2500
Germany	2	600	1.4	60	100	1500
Greece	40	1750	25	400	1200	4000
Italy	20	1000	10	300	750	2500
Netherlands	1.25	75	0.75	30	100	300
Spain	40	1750	25	400	1200	4000

(Mininni et al. 2015)

3.5.3 Czech Republic

The regulations in the Czech Republic for the agricultural land use of the sludge are stricter that the Council Directive 86/278/ECC, is very valuable that some other hazardous substances of interest are included: Arsenic, adsorbable organic halogen compounds (AOX), Polycyclic Aromatic Hydrocarbons (PAH), and Polychlorinated Biphenyls (PCB). This permit to the Czech Republic to go a long way towards showing competence and growing effectiveness on the legislation concerning to the sludge usage in agricultural land.

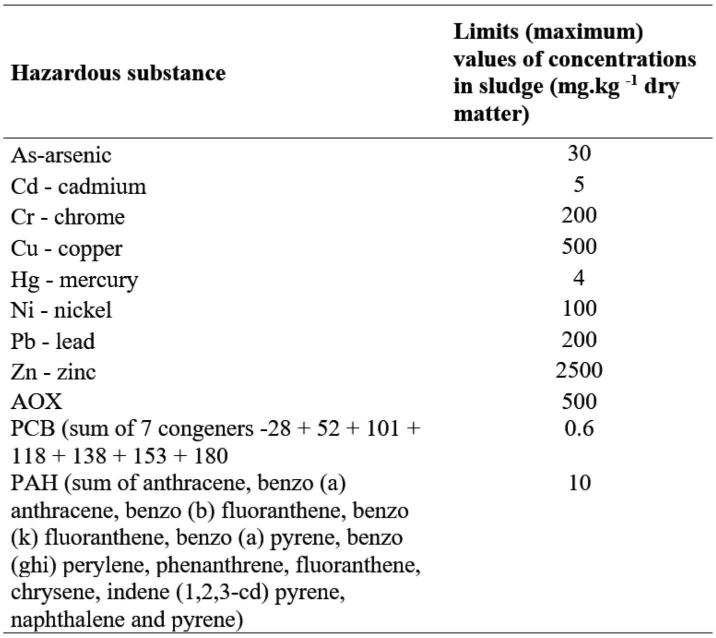
Decree No. 383/2001. Decree of the Ministry of the Environment on details of waste management. The regulation includes provisions on technical requirements on equipment to be used for waste and hard-wash operation, collections, purchases, recovery and disposal, including waste from waste disposal (incineration of hardazous waste) (Ministry of the Environment 2001).

Decree No. 294/2005. Decree on the conditions of waste disposal in ladfills and their use on the ground surface and amending Decree 383/2001 (originally in czech vyhlášky č. 294/2005 Sb., o podmínkách ukládání odpadů na skládky a jejich využívání na povrchu terénu a změně). The purpose is to provide conditions for the stockpiling and use of waste on waste dumps and on land surfaces and to provide basic concepts, technical requirements for dumps, and operating conditions, including waste management requirements from hard waste incineration. The technical conditions for the use of waste on the ground surface are explained in Title V. (Ministry of the Environment 2005).

Decree No. 341/2008. Decree on the details of the management of biodegradable waste and on the amendment to Decree No. 294/2005 (originally in czech vyhlášky č. 341/2008 Sb., o podrobnostech nakládání s biologicky rozložitelnými odpady a o změně). This Decree provides details of the management of biologically degradable waste, a list of the waste quality requirements, equipment requirements and treatment operation depending on the quantity and type of biowaste. (Ministry of the Environment 2008).

Decree No. 437/2016. Decree on the conditions of use of treated sludge on agricultural land and amendment to Decrees 383/2001, and 341/2008 (originally in czech Vyhláška č. 437/2016 o podmínkách použití upravených kalů na zemědělské půdě a změně). This Decree incorporates the technical conditions for the use of treated sludge on agricultural land, such as the minimun content of dry matter (18 %), minumun distance from drinking water sources (50 m), and minimal distance from housing development (300 m), among others. This regulation also contains limit values of concentrations of selected risk substances in soil and hardazous substances that can be added to agricultural land within 10 years (Table 8), also limit vales for microbiological criteria; the sludge and soil analysis procedures and the sampling methods. The sludge application program is also described, and conditions for storage of the sewage sludge before its use is contained in this Decree (Ministry of the Environment 2016).

Table 8 Limit values for concentrations of hazardous substances and elements in sludge for use on agricultural land – Czech Republic



Hazardous substance	**Limits (maximum) values of concentrations in sludge (mg.kg $^{-1}$ dry matter)**
As-arsenic	30
Cd - cadmium	5
Cr - chrome	200
Cu - copper	500
Hg - mercury	4
Ni - nickel	100
Pb - lead	200
Zn - zinc	2500
AOX	500
PCB (sum of 7 congeners -28 + 52 + 101 + 118 + 138 + 153 + 180	0.6
PAH (sum of anthracene, benzo (a) anthracene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (ghi) perylene, phenanthrene, fluoranthene, chrysene, indene (1,2,3-cd) pyrene, naphthalene and pyrene)	10

(Ministry of the Environment 2016)

3.6 Pyrolysis of sewage sludge

Pyrolisis is a thermal process, that allows to transform and decompose organic sustances where relatively high temperatures (300 - 1000°C) are applied to sewage sludge, under low-oxygen ot anoxic conditions or inert atmosphere, producing three basic products, syngas, bio-oil and biochar (Carey et al. 2015; Frišták et al. 2017). The gaseous fraction contains H, CH_4, CO, CO_2 and some other gases, the liquid franction, consists of in tar/oil, containing acetic acid, methanol and acetone, and finally the solid fraction is char, which is a solid carbonaceus residue combined with some inert materials; the proportion of the production of gas, oil and char dependes on severa factors, such as temperature, residence time, pressure, among others (Fytili & Zabaniotou 2008).

The resulting solid carbonactic waste (char) safely contains heavy metals (like mercury and cadmium), which is less pollutant than more conventional methods such as incineration or combustion. Pyrolysis products for several applications such as petrochemicals can be used as fuels or as feedstock (Karayildirim et al. 2006).

Pyrolysis is different from gasification, which mainly converts organic material in syngas or gas, where a range of oxygen used in total combustion ranges between 20% and 40% is required during the process, while pyrolyses are aimed mainly at producing carbohydrate, gas and liquid called bio-oil, which can also be used as fuel. (Fonts et al. 2012).

Figure 6 drafts the low-temperature pyrolysis method, which is run under temperature range of 400 – 500 °C transforms about 50 % of the biomass in biochar and this can be returned to soil, also it can be a way to produce energy from biomass, this process is exothermic (Lehmann 2007)

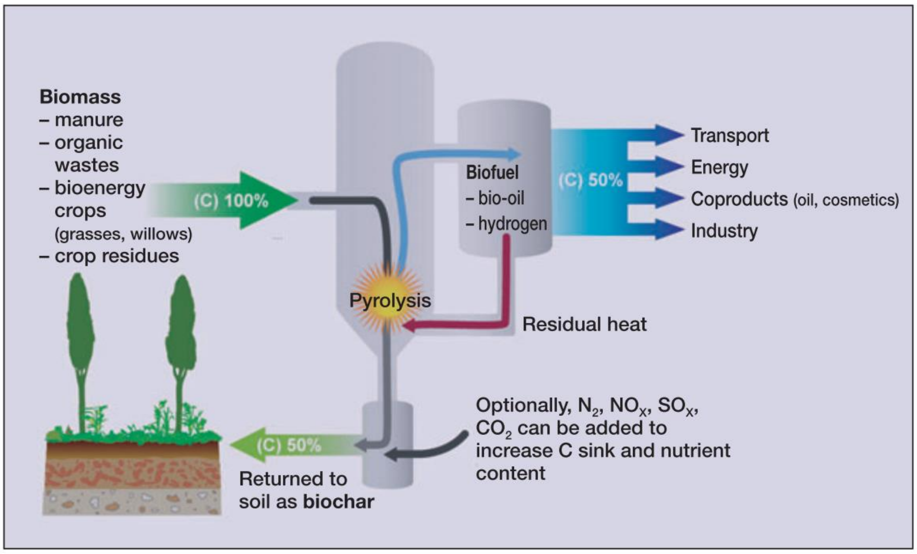


Figure 6 Low-temperature pyrolysis scheme
(Lehmann 2007)

3.6.1 Biochar

Biochar is a carbon rich product obtained from thermal decomposition of organic material with the main application as soil amendment or fertilizer. Two aspects make biochar valuable for this use: its high stability against decay and its superior ability to retain nutrients as compared to other forms of soil organic matter. The application of biochar to soil can increase soil C sequestration, reduce atmospheric CO_2 concentrations, improve physico-chemical soil quality and alter the content and availability of nutrients (Lehmann 2007; Frišták et al. 2017).

The definition of biochar according to the European Biochar Certificate (Peter 2012) implicates that pyrolyzed sewage sludge is a pyrogenic carbonaceous material (PCM). Sewage sludge-derived PCM provides valuable contents of nutrients such as P, N, K and organic matter as well as an improvement in total soil fertility and soil microbial activity (Frišták et al. 2017). Biochar has practical advantages and can be an effective product to improve the environment sustainably. Biochar has been shown to increase the quality of the soil and to remove carbon from the atmosphere. Biochar as soil amendment promotes development and activity in beneficial microbial communities and helps preserve nutrients for increased crop development and prevents runoff of water. (Lehmann 2007; Carey et al. 2015).

The feedstock in pyrolysis may affect the properties of the produced biochar, for example, cropping residue, as feedstock produces a nutrient rich biochar, biochar at high temperatures decreased in acidity of the surface and CEC compared to low-temperature biochar production. The impact of pyrolitic temperature was tested for sewage sludge derived from biochar (Lu et al. 2013).

3.6.2 Pyrolysis Condtions

Conditions for pyrolysis are mainly pyrolytic temperature, heating (HR) and gas residence (GRT); according to the change in its characteristics the pyrolysis may be classified as fast and slow.

Slow Pyrolysis

Is carried out at lower heating rate, which is about 0.1 to 1 °C/s, and is used low pyrolytic temperature, on the range of 300 to 400 °C, and the gas residence time is about 5 – 30 min (Raheem et al. 2018)

Fast Pyrolysis

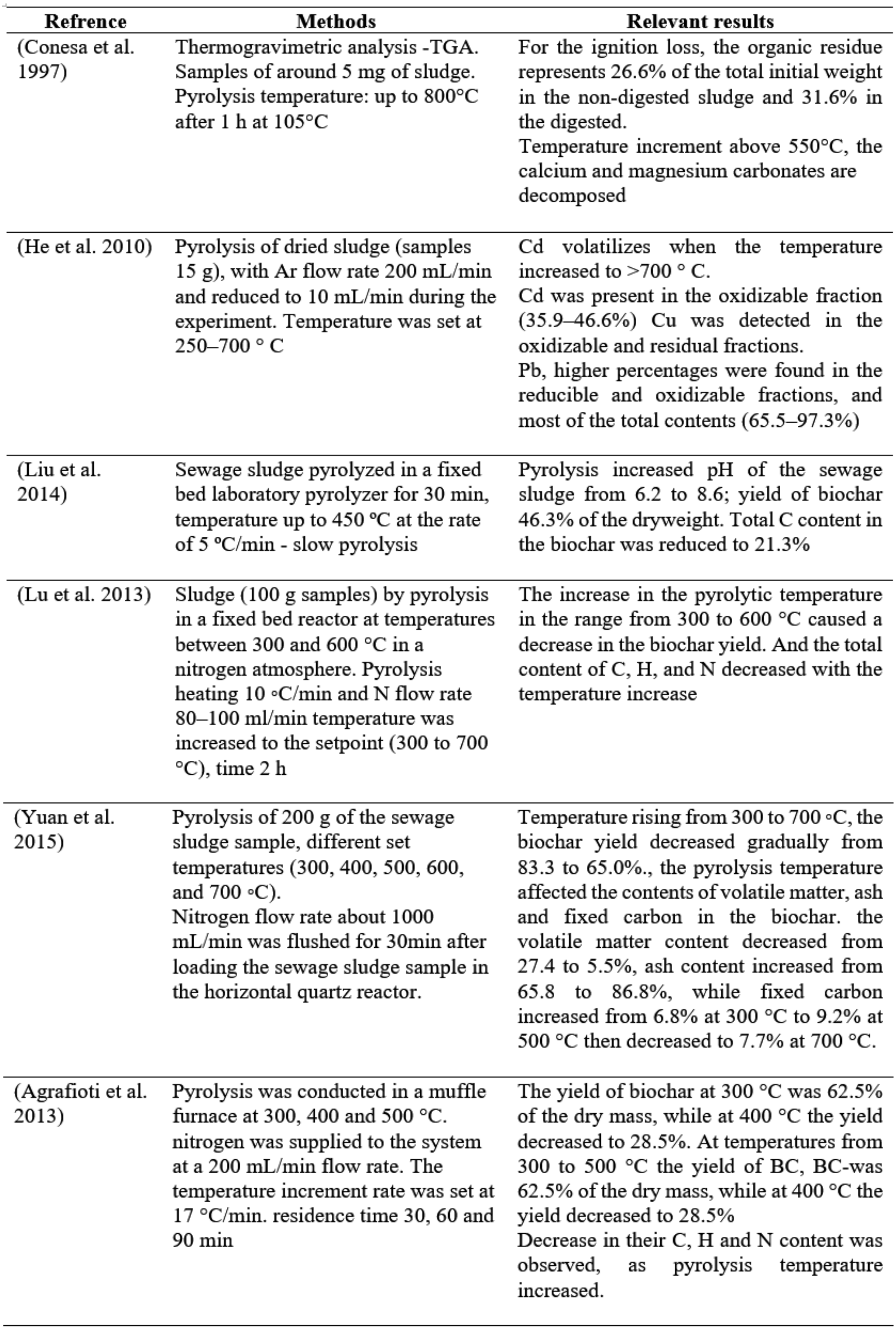
A pyrolysis reaction with higher heating rate, 10 - 200 °C/s, higher pyrolytic temperature 450 – 600 °C and the gas residence time is 0.1 – 0.3 s. This pyrolysis method is used mainly when its required higher yields on the production of gas and bio-oil/tar (Raheem et al. 2018). Polycyclic aromatic hydrocarbons (PAH) can also occur at high temperatures, its presence constitues a non desired contamination (Conesa et al. 2009).

The available technologies for fast pyrolysis are, (1) Ablative pyrolysis, this process uses larger particles of material and is typically limited by the rate of heat supply to the reactor, (2) Fluid bed and circulating fluid bed pyrolysis, which transfers heat from a heat source to the material by a mixture of convection and conduction and (3) Vacuum pyrolysis which has slow heating rates but removes pyrolysis products as rapidly as in the previous methods (Bridgwater et al. 1999).

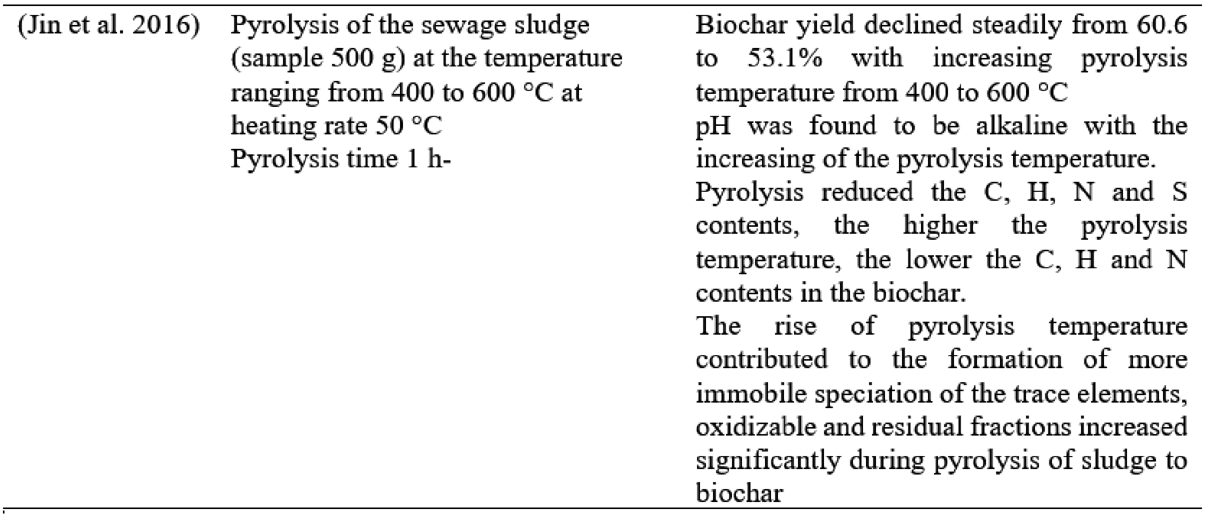
The conversion through pyrolysis of sewage sludge provides a secondary raw material, or by product, that consist on a potential source of nutrients (Frišták et al. 2017). Some toxic elements, such as Cd, Cr, Cu, Ni, Pb and Zn, are expected to occur in significant concentrations, it is very important to track their variation in mobility, solubility and availability; for a number of studies presented in Table 9, the behavior of these elements in biochar, the total and bioavailable contents of sewage sludge and sludge biochar, and the general deduction of key studies in this matter is fact that some toxic elements are fixed, immobilized and potentially stable in biochar matrix

The optimal pyrolysis conditions are observed to depend on future biochar application, for example the biochar produced at lower temperatures is best suited to agricultural use, although higher pyrolysis temperatures produced by biochar have a better porosity, and this characteristic helps to improve the capacity for adsorbing pollutants in soils (Agrafioti et al. 2013)

Table 9 Summary of sewage sludge pyrolysis conditions



Refrence	Methods	Relevant results
(Conesa et al. 1997)	Thermogravimetric analysis -TGA. Samples of around 5 mg of sludge. Pyrolysis temperature: up to 800°C after 1 h at 105°C	For the ignition loss, the organic residue represents 26.6% of the total initial weight in the non-digested sludge and 31.6% in the digested. Temperature increment above 550°C, the calcium and magnesium carbonates are decomposed
(He et al. 2010)	Pyrolysis of dried sludge (samples 15 g), with Ar flow rate 200 mL/min and reduced to 10 mL/min during the experiment. Temperature was set at 250–700 ° C	Cd volatilizes when the temperature increased to >700 ° C. Cd was present in the oxidizable fraction (35.9–46.6%) Cu was detected in the oxidizable and residual fractions. Pb, higher percentages were found in the reducible and oxidizable fractions, and most of the total contents (65.5–97.3%)
(Liu et al. 2014)	Sewage sludge pyrolyzed in a fixed bed laboratory pyrolyzer for 30 min, temperature up to 450 ºC at the rate of 5 ºC/min - slow pyrolysis	Pyrolysis increased pH of the sewage sludge from 6.2 to 8.6; yield of biochar 46.3% of the dryweight. Total C content in the biochar was reduced to 21.3%
(Lu et al. 2013)	Sludge (100 g samples) by pyrolysis in a fixed bed reactor at temperatures between 300 and 600 °C in a nitrogen atmosphere. Pyrolysis heating 10 ◦C/min and N flow rate 80–100 ml/min temperature was increased to the setpoint (300 to 700 °C), time 2 h	The increase in the pyrolytic temperature in the range from 300 to 600 °C caused a decrease in the biochar yield. And the total content of C, H, and N decreased with the temperature increase
(Yuan et al. 2015)	Pyrolysis of 200 g of the sewage sludge sample, different set temperatures (300, 400, 500, 600, and 700 ◦C). Nitrogen flow rate about 1000 mL/min was flushed for 30min after loading the sewage sludge sample in the horizontal quartz reactor.	Temperature rising from 300 to 700 ◦C, the biochar yield decreased gradually from 83.3 to 65.0%., the pyrolysis temperature affected the contents of volatile matter, ash and fixed carbon in the biochar. the volatile matter content decreased from 27.4 to 5.5%, ash content increased from 65.8 to 86.8%, while fixed carbon increased from 6.8% at 300 °C to 9.2% at 500 °C then decreased to 7.7% at 700 °C.
(Agrafioti et al. 2013)	Pyrolysis was conducted in a muffle furnace at 300, 400 and 500 °C. nitrogen was supplied to the system at a 200 mL/min flow rate. The temperature increment rate was set at 17 °C/min. residence time 30, 60 and 90 min	The yield of biochar at 300 °C was 62.5% of the dry mass, while at 400 °C the yield decreased to 28.5%. At temperatures from 300 to 500 °C the yield of BC, BC-was 62.5% of the dry mass, while at 400 °C the yield decreased to 28.5% Decrease in their C, H and N content was observed, as pyrolysis temperature increased.



(Jin et al. 2016)	Pyrolysis of the sewage sludge (sample 500 g) at the temperature ranging from 400 to 600 °C at heating rate 50 °C Pyrolysis time 1 h-	Biochar yield declined steadily from 60.6 to 53.1% with increasing pyrolysis temperature from 400 to 600 °C pH was found to be alkaline with the increasing of the pyrolysis temperature. Pyrolysis reduced the C, H, N and S contents, the higher the pyrolysis temperature, the lower the C, H and N contents in the biochar. The rise of pyrolysis temperature contributed to the formation of more immobile speciation of the trace elements, oxidizable and residual fractions increased significantly during pyrolysis of sludge to biochar

3.7 Reduction and Immobilization of toxic elements in Sewage Sludge Products

About 50 to 80 % of the toxic elements content present in wastewater is fixed into the sewage sludge, and this is the reason why the sewage sludge contains such high trace elements concentration (Agrafioti et al. 2013). As is mentioned by Raheem et al. (2017) toxic elements usually exist in pyrolysis products. Its volatilization is mainly associated to their boiling point. Subsequently, higher gasification temperatures divergent to pyrolysis result in an bigger risk of contamination risk for gaseous products, Because of this is very important monitoring this toxic elements distribution in the pyrolysis products. He et al. (2010) conducted the pyrolysis with a sequential extraction procedure in electric furnace, mainly focusing on fractionation of heavy metals (such as Zn, Pb, Cu and Cd) in WAS and its residues which were generated after pyrolysis at temperatures ranging from 250 to 700 °C. The Cd was volatilized at 700 °C and decreased in the residues. Additionally, Cu, Pb and Cd in the WAS and pyrolysis residues, were primarily bounded to organic matter and sulphides, whereas Zn was bounded to Fe and Mn oxides

The mean values for concentrations of toxic components analyzed in SDBC at different temperatures are presented in Table 10, these values were repositioned in prior reserarches, the temperature increase influenced the concentration of toxic components in a resulting biochar. It is not possible to determine a unique behavior for the different SDBC obtained and its toxic components vary depending on the temperature, a reduction tendency with the increasing temperature was reported by He et al. (2010), different from the data obtained for Lu et al. (2016), which presented a porportional increasing in the toxic elements concentration along with the increasing temperature.

Table 10 Mean values of toxic elements content in biochar produced at different pyrolysis temperatures

Biochar	Element (mg/kg dry matter)					
	Cu	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**
(Lu et al. 2016)						
SDBC 600 °C	209±3.4	1090±16.1	5250±37	229±5.8	101±4.4	406±2.0
SDBC 700 °C	227±3.5	1090±18.2	5250±46	123±5.6	103±4.6	103±2.1
(Jin et al. 2016)						
SDBC 600 °C	1697±79.92	3368±90.7	110.7±13.52	-	218.6±16.12	1374±108.42
(Yuan et al. 2015)						
SDBC 600 °C	1.41±0.004	73.6±4.2	-	-	-	-
SDBC 700 °C	0.41±0.002	39±2.6	-	-	-	-
(Hossain et al. 2011)						
SDBC 700 °C	-	-	132±2.5	-	195±6.45	83±3.36
(He et al. 2010)						
SDBC 600 °C	407.5±23.5	2563.7±97.1	151.5±25.3	8.1±2.3	-	-
SDBC 700 °C	425.4±24.2	2412±105.3	168.2 □ 26.3	3.9±1.1	-	-

SDBC: Wastewater sludge-derived biochar

4. Material and Methods

4.1Sewage Sludge

In this study the sewage sludge feedstocks for the preparation of the sludge derived biochar (SDB) were sourced from two different Wastewater Treatment Plants (WWTPs) located in Central Bohemia, Czech Republic. Both WWTPs provided the samples only on condition of anonymity and are therefore labeled as Sludge 1 and Sludge 2. In common, the sewage sludge was centrifuged for dewatering after anaerobic stabilization. Sludge 2 was dried after dewatering in a industrial, low-temperature drier.

Sludge 1 is from WWTP in a larger town; with 22% of dry matter in the collected sludge.

Sludge 2 is from WWTP in a medium size town; with 96% of dry matter in collected sludge. No further information about the source of the sludges is present as this research work is subject to data protection agreement with the producers.

After retrieving the sludge samples from the WWTP they were frozen at –42°C and freeze-dried until use. For both the slow and fast pyrolysis experiments, the dried sludge was milled to a particle size < 1 mm (Shao et al. 2010; Luan et al. 2013; Barry et al. 2019) using an IKA A11 basic analytical mill (IKA-Werke GmbH & Co. KG) in order to maintain the particle size.

4.2Pyrolysis

Figure 7 presents the schematic diagram of the experimental device set for pyrolysis. SDBC preparation was pyrolysis with the temperature range going from room temperature to 1000 °C. The system used a horizontal quartz tube, Nitrogen cylinder and volatiles collection system.

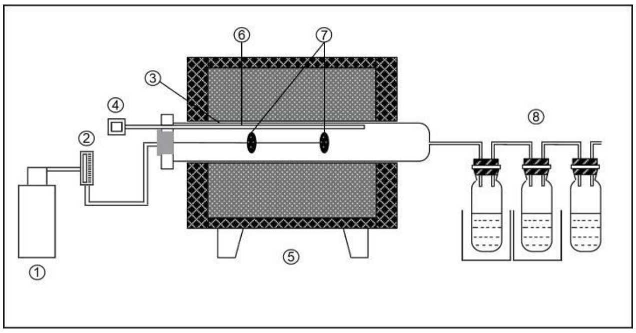


Figure 7 Schematic diagram of sewage sludge pyrolysis experiment. 1) Nitrogen, 2) Gas flowmeter, 3) Quartz tube, 4) Thermometer, 5) Furnace, 6) Thermometer probe, 7) Sample holder, 8) volatiles collecting system

For SDBC production in laboratory furnace Carbolite® Typ 301 (Carbolite Gero; UK) was used (Figure 8).

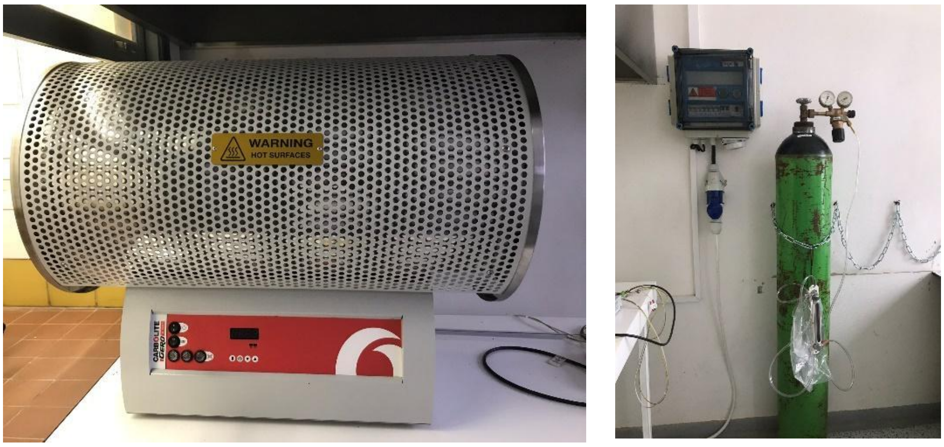


Figure 8 Furnace Carbolite® Typ 301 and Nitrogen source

Well-mixed milled samples by duplicates (4 g, particle size <1 mm) were placed in crucibles (ceramic-made). This samples were put into a cylindrical tube, made of quartz with 4.5 cm internal diameter and 95 cm length, giving a total reactor volume of 0.6711 L (Figure 9). The sample was kept in the operating furnace for 30 min, to maintain an oxygen-free atmosphere during the process, nitrogen (99.99 %) was supplied to the system at a rate of 100 L/h.

Figure 9 Sample setting

Each run was executed with three different set temperatures; 600 °C, 700 °C and 800 °C according to the temperature increment rate which were:

Slow: The sample was introduced in the quartz tube at room temperature, the furnace was then heated to the desired final pyrolysis temperature (600 °C, 700 °C and 800 °C). Once the final reaction temperature was reached, it was maintained for 30 minutes before cooling the furnace back to room temperature. During the process the quartz tube was injected with a continuous stream of nitrogen, which was permanently manually controlled. The SDBC were then removed from the furnace, air dried, weighted and stored in airtight plastic containers.

Fast: The furnace was pre-heated, and once the set temperature was reached (600 °C, 700 °C and 800 °C), the tube was then loaded with the sample and injected with a continuous stream of nitrogen, which was permanently manually controlled, the sample stayed under these conditions for 30 minutes and from there the same procedure as *slow* pyrolysis was used.

The volatiles were absorbed on three conical flasks filled as follows: the first two by chloroform ($CHCl_3$) and the third one by nitric acid (HNO_3). These were kept in ice bath to collect condensable vapors (Figure 10). After the condenser the gases were vented.

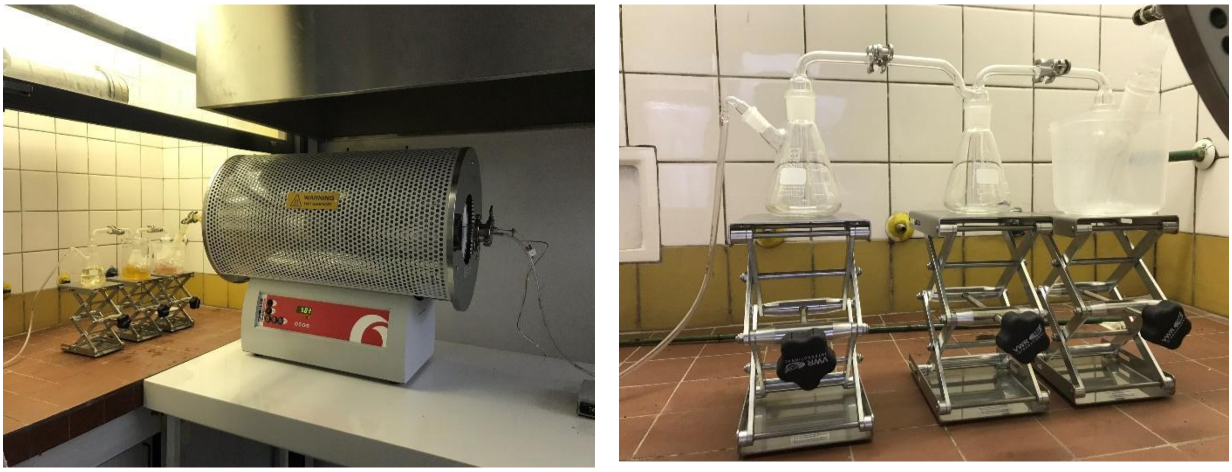


Figure 10 Volatiles collecting setting

4.3 Total content of elements

Total contents of elements in SDBC samples were determined by inductive coupled plasma-optical emission spectrometry (ICP-OES; Agilent 720, Agilent Technologies Inc., Santa Clara, CA) after dry ashing by sequential burning at different temperatures and times.

The dry sample is inserted onto a cold hot plate, starting with a temperature of 170 °C, after 1 h the temperature was increased to 230 °C, one hour later to 290 °C, and after one hour to 380 °C, this temperature was set for one hour and then the hot plate was turned off. The samples were transferred to a cold muffle furnace, at 350 °C, this temperature was raised up to 400 °C after 30 min, following step was to increase temperature to 450 °C and after another 30 min to 500 °C, then the samples were left at this temperature overnight (16 h) (Mader et al. 1998).

According to Mader, Száková, & Miholová (1998), were the total content of elements analyzed after the dry ashing described before, the insoluble ash portion are washed, and then were mixed and boiled with HF + HNO_3 (45 mL per 1g of sample), after this procedure there was still some portion that remained insoluble, the material was then transferred to diluted *aqua regia* solution, and the part of the analytes which were dissolved were determined by ICP-OES.

4.4 Bioavailable fraction of elements

The mobility of TEs (As, Cd, Cr, Cu, Ni, Pb, and Zn) was determined by means of sequential extraction. 0.3 g of SDB samples was mixed with 25ml of 0.11M CH_3COOH acetic acid (pH 2.0) and was shaken (120 rpm) for 16 h at room temperature, following by centrifugation at 6000 rpm for 10 minutes, the supernatant samples were filtered with nylon syringe filters (Whatman 0.45 µm) to remove fine particles and transferred to test tubes for posterior analysis. The concentrations were determined by an inductively coupled plasma optical emission spectrometer, ICP-OES, Agilent 720 (Agilent Technologies Inc., USA) (Pukalchik et al. 2018).

4.5 Total organic matter (TOM)

Ash content was determined using a loss-on-ignition (L.O.I.) procedure. 0.1 – 0.2 g samples were dried at 105 °C for 24 h (moisture content) and then transferred to a muffle furnace at 550 °C for 12 h. Ash content was calculated from the ratio of pre- and post-ignition sample weights (Antizar-Ladislao et al. 2006).

4.6Elemental Analysis

Total C, H, and N the samples were determined using an elemental analyzer (CHNS Vario MACRO cube, Elementar Analysensysteme, Hanau, Germany) (Košnář et al. 2019).

The elemental components of the sample (C, H, N, S) are converted into gaseous oxidation products (CO2, H2O, NOx and SO2) in an oxidation / digestion stage at high temperatures in organic elemental analysis. Quantitative measurement is done using an appropriate detector (TCD, IR, etc) after gas treatment and separation (ELEMENTAR 2014).

4.7Statistical and data analysis

All experiments were conducted in duplicate. The effects of the rate and temperature on the final concentration of the elements linear models were adjusted using the function lm in R 3.5.0 (R Development Core Team and R Core Team, 2017). The response variable was the concentration in mg/kg of each element. The rate of the pyrolysis and temperature were used as fixed-effect explanatory variables. For the assumption of the models, normality of the residuals was tested using quantile-quantile plots finding no significant departure from normality. The homogeneity of variance was also tested. There were some cases for some elements that showed difference in variance among groups, we decided not to transform the data since this will models more difficult to interpret.

The fit of the models was tested using the F-statistic with an alpha value of 0.05, this statistic compares the variance explained by the parameters in the model and the residual unexplained variance and gives information about whether the variable used explain the behavior of the response variable better than a null model. In our case from the 72 models fitted the f statistic found 61 models with significant better fit than the null model.

Linear Model

Regression analysis provides an explanation and allows to model the relationship between a single variable Y or a dependent variable and one or more independent variables; studies changes to a variable based on changes to another variable. It is called a simple regression when p=1 in case p>1 in some cases is called a multiple or multivariate regression (Faraway 2009; Lavine 2013).

The response variable must be continuous, but in the case of the explanatory, they can be continuous, categorical or discrete. The possible objectives of the regression analyses, according to Faraway (2009), can be:

- Prediction of future behaviors
- Evaluation of the connection between explanatory variables and the response
- A general description of data structure

5. Results

The sewage sludge derived biochar (SDBC) was analyzed in terms of the total and available content of twenty elements, which were congregated in four different groups: Toxic elements (As, Cd, Cr, Pb), Macronutrients (Ca, K, Mg, P, S), Micronutrients (Cu, Fe, Mn, Mo, Ni, Zn) and other elements (Al, Be, Sr, V).

Analysis were made on the raw sewage sludge, being called Sludge 1 and Sludge 2, and on the resulting SDBC from these two mentioned feedstocks. Each sample was under tree different set temperatures 600, 700 and 800 °C and was subjected to two different temperature increment rates, fast and slow.

In Table 11, the initial content of toxic elements shows some differences between the feedstocks studied; Sludge 1 have higher concentrations of Cd, Cr, and Pb (Cr for example containing more than 20 times the concentration reported for Sludge 2). In Table 12, macronutrients content is shown, from here the data shows less difference between the two sludges compared to Toxic elements, in this case Ca, P and S were higher in sludge 1 and K and Mg than in Sludge 2.

Micronutrients content in Table 13, for the Sludge 1 Cu, Fe, Mo, Ni, and Zn present higher values compared to Sludge 2 (Cu is more than 10 times higher), Fe concentrations are relatively similar, and Table 14 is presented the initial content of other elements like Al and Be (20 times higher) which have in Sludge 2 significant different content from Sludge 1. From the data it is observed that the concentration of nutrients like Ca, P, K and Mg decreased with increasing levels of Toxic elements.

Table 11 Sewage sludge – Initial Toxic elements content (mg/kg of dry matter)

	Toxic elements			
Sludge	**As** mg/kg	**Cd** mg/kg	**Cr** mg/kg	**Pb** mg/kg
1	12.53 ± 1.34	14.56 ± 0.13	1148.43 ± 16.74	102.83 ± 3.99
2	37.83 ± 0.54	0.96 ± 0.03	49.81 ± 4.56	46.34 ± 5.09

Table 12 Sewage sludge – Macronutrients content (mg/kg of dry matter)

	Macronutrients				
Sludge	**Ca** mg/kg	**K** mg/kg	**Mg** mg/kg	**P** mg/kg	**S** mg/kg
1	31926.92 ± 135.38	3815.05 ± 32.52	3898.1 ± 69.08	23875.06 ± 234.14	8362.36 ± 214.77
2	20245.89 ± 63.07	7518.78 ± 54.7	4436.72 ± 126.3	19654 ± 331.05	6480.16 ± 298.01

Table 13 Sewage sludge – Micronutrients content (mg/kg of dry matter)

	Micronutrients					
Sludge	**Cu**	**Fe**	**Mn**	**Mo**	**Ni**	**Zn**
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	1632.11 ± 26.56	26828.5 ± 584.05	194.49 ± 1.38	12.58 ± 0.38	193.62 ± 2.36	4826.71 ± 85.5
2	136 ± 4.02	22374.72 ± 436.75	442.33 ± 0.96	6.46 ± 0.21	24.61 ± 0.43	646.75 ± 7.68

Table 14 Sewage sludge – Other elements content (mg/kg of dry matter)

	Other Elements			
Sludge	**Al**	**Be**	**Sr**	**V**
	mg/kg	mg/kg	mg/kg	mg/kg
1	12458.32 ± 175.24	0.48 ± 0.01	158.25 ± 2.19	24.65 ± 0.8
2	46109.05 ± 1912.84	10.61 ± 0.07	182.64 ± 4.84	31.86 ± 3.56

5.1Total Content of elements for Sewage sludge Derived Biochar (SDBC)

The effect of pyrolysis temperature and temperature increment rate is shown in the following tables. This tables reported the result of total content analysis for each SDBC produced from Sludges 1 and 2. Cadmium values were below detection limit - BDL (<0,17 mg/kg).

In Table 15, the concentration of elements had minimal variations relating to the temperatures and temperature increment rate for each Sludge. Except for Pb that showed the greater variation among the treatments from its original value in the raw sewage sludge 102.83 mg/kg for Sludge 1 and 46.35 mg/kg for Sludge 2. For SDBC from Sludge 1 and 2 fast pyrolysis at 800 °C present the lower Pb content (133.2 and 54.2 mg/kg respectively) in contrast to the higher content reported 284.8 mg/kg for SDBC from Sludge 1 (around 270 % higher that the raw sewage sludge concentration) and 84.6 mg/kg for SDBC from Sludge 2 (around 75 % higher that the raw sewage sludge concentration), and this can be attributed to the Pb volatilization temperature, which is 800 °C

Table 15 Wastewater sludge-derived biochar (SDBC) Total content – Toxic elements (mg/kg)

			Toxic elements			
SDBC	**Rate**	**Temp**	**As**	**Cd**	**Cr**	**Pb**
Sludge1	FAST	600	22.52 ± 8.37	8.36 ± 1.26	3004 ± 77.89	284.8 ± 11.24
		700	31 ± 0.55	BDL	3274 ± 3.07	275.9 ± 12.01
		800	33.72 ± 1.52	BDL	3438 ± 12.58	144.4 ± 0.31
	SLOW	600	29.97 ± 5.32	9.72 ± 0.74	3113 ± 30.83	279.8 ± 3.91
		700	20.35 ± 2.21	0.52 ± 0	3021± 26.38	262.9 ± 10.49
		800	21.19 ± 1.68	BDL	3171 ± 50.01	133.2 ± 11.65
Sludge2	FAST	600	56.39 ± 1.94	1.31 ± 0.04	99.67 ± 3.43	84.67 ± 2.92
		700	40.07 ± 1.38	BDL	107.3 ± 3.7	68.51 ± 2.36
		800	57.95 ± 0.1	BDL	112.8 ± 7.97	32.09 ± 19.27
	SLOW	700	47.86 ± 2.21	BDL	105.2 ± 17.71	82.92 ± 7.15
		800	43.83 ± 0.42	BDL	101.7± 17.18	54.2 ± 7.05

BDL: Below detection limit for Cd <0.17 mg/kg

Table 16 report the Macronutrients content in the SDBC across the different treatments, for Ca and P the concentration increases after the pyrolysis for both sludges compared with the raw sludge values, and if it observed the percentual concentration the SDBC from Sludge 1 has a higher increment. For Ca ranging from 31926.9 (mg/kg) in raw Sludge to 92103.06 (mg/kg), for 700 °C fast pyrolysis, and for P variation was reported from 23875.06 (mg/kg) to 74276.79 (mg/kg) at 800 °C fast pyrolysis, K reported a slightly higher concentration after pyrolysis. Total P and K contents of the SDBC were increased, in addition it can be expected the available P and K contents also higher.

The mentioned contents in SDBC increased with the rising pyrolysis temperature compared with the content in the raw sample, this indicates that this Macronutrients were enriched in the SDBC.

Table 16 Wastewater sludge-derived biochar (SDBC) Total content – Macronutrients (mg/kg)

			Macronutrients				
SDBC	**Rate**	**Temp**	**Ca**	**K**	**Mg**	**P**	**S**
Sludge1	FAST	600	81781 ± 2361	9488 ± 1232	10593 ± 1158	62975± 3017	15973± 1034
		700	92103 ± 407.1	9374 ± 155.7	12259± 140.8	70843± 626.3	18118± 17.03
		800	88487 ± 3981	9175 ± 49.26	11923± 591.6	74276 ± 578.2	19483± 230.9
	SLOW	600	86576 ± 625.2	8643 ± 93.49	11906± 16.77	66356 ± 558.8	16738± 258.2
		700	82422 ± 998.6	10047 ± 564.2	10023 ± 104.8	62541± 523.8	15260± 307.1
		800	86578 ± 1472	10168 ± 149.1	10573 ± 167.1	66236± 1365	15575± 911.1
Sludge2	FAST	600	37948 ± 1308	10205 ± 352	8314 ± 286.8	39078± 1347	7275± 250.9
		700	38899 ± 1341	26382 ± 910.0	7799 ± 269.0	36643± 1263	6125± 211.3
		800	40064 ± 1487	15309 ± 4695	8514 ± 868.2	40520 ± 1670	6693± 433.5
	SLOW	700	40931 ± 4439	16034± 1705	7790 ± 105.6	36067 ± 422.9	6027 ± 147.9
		800	41979 ± 3406	16323± 1357	8047± 84.14	37544± 792.7	6027 ± 118.8

From Table 17, the concentrations of Cu, Zn were slightly higher in SDBC than those reported in raw sewage sludge.

Micronutrients in both sludges showed different behavior depending on the rate. The use of a fast rate in SDBC from sludge 1 caused an increase of concentration with temperature, in this case the minimum concentration of Cu (41.30 mg/kg), Ni (532 mg/kg) and Zn (12854 mg/kg) were above the allowed standard for the Czech and European regulations. In the case of the SDBC from sludge 2, Cu showed a close positive relationship with temperature, with the highest concentrations found at 800ºC, the opposite behavior was observed in Zn which showed a negative relationship with temperature with the maximum value found at 600 ºC. Finally, Ni was higher in both the maximum and minimum temperatures tested (600°C and 800ºC).

Table 17 Wastewater sludge-derived biochar (SDBC) Total content – Micronutrients (mg/kg)

			Micronutrients					
SDBC	**Rate**	**Temp**	**Cu**	**Fe**	**Mn**	**Mo**	**Ni**	**Zn**
Sludge1	FAST	600	4130 ± 134.6	68956± 2359	475.9± 33.42	26.49 ± 0.27	532.3 ± 47.13	12854± 103.6
		700	4255± 27.5	78540± 661.5	544.4 ± 6.38	27.92 ± 0.67	600.1 ± 2.91	13426± 87.42
		800	4496± 69.59	79267± 254.2	569.5 ± 4.57	29.72 ± 0.11	646.9 ± 10.44	13004± 318.1
	SLOW	600	4109± 52.91	73646± 483.3	507.3 ± 0.45	26.23 ± 0.27	572.1 ± 0.36	12854 ± 77.95
		700	4345± 44.93	69065± 569.9	456.9± 4.5	29.08 ± 0.98	513.4 ± 8.89	13017 ± 202.6
		800	4579± 92.56	72727± 1354	484.1 ± 4.59	30.32 ± 1.74	537.2 ± 13.51	12384 ± 487.9
Sludge2	FAST	600	284.5 ± 9.81	42424 ± 1463	821.2± 28.32	8.12 ± 0.28	69.34 ± 2.39	1449± 50.01
		700	255.9 ± 8.82	41224 ± 1421	778.5 ± 26.85	11.94 ± 0.41	61.69 ± 2.12	996.7 ± 34.37
		800	256.1 ± 6.99	42657 ± 1989	808.2 ± 65.66	8.83 ± 0.46	68.85 ± 6.56	669.3 ± 309.1
	SLOW	700	245.9 ± 12.73	41169 ± 495.1	758.6 ± 17.42	10.69 ± 0.3	44.57 ± 1.09	1093± 56.03
		800	244.5 ± 10.19	42431 ± 809.9	769.8 ± 16.39	10.94 ± 1.19	43.17 ± 2.3	752.9 ± 111.6

Table 18 presents the variation in concentration after pyrolysis demonstrated for this group of elements shows the biggest change in Al at 700 °C and Fast temperature increment rate, for both sludges.

In addition, Sludge 2 presented the highest increment, going from 46109.06 for raw sludge to 91318 mg/kg for pyrolyzed material, is interesting that a similar increment was reported at 800 °C and Slow temperature increment rate, with a final concentration value of 91474 mg/kg. The percentual change in concentrations was about 4,5 % in both cases.

Beryllium, Strontium, and Vanadium had almost imperceptible increments in the final concentrations after pyrolysis in all the combinations of temperature and increment rates.

Table 18 Wastewater sludge-derived biochar (SDBC) Total content – Other Elements (mg/kg)

			Other Elements			
SDBC	**Rate**	**Temp**	**Al**	**Be**	**Sr**	**V**
Sludge1	FAST	600	31941± 205.9	1.1 ± 0.12	420.6 ± 13.36	61.6 ± 5.25
		700	35405± 268.4	1.21 ± 0.01	463.8 ± 0.43	62.41 ± 0.64
		800	29475± 4246	1.27 ± 0	484.6 ± 0.11	63.86 ± 0.83
	SLOW	600	33377± 422.7	1.15 ± 0	440.9 ± 0.55	58.12 ± 0.15
		700	32339± 357.2	1.08 ± 0.04	422.7 ± 3.79	66.77 ± 0.44
		800	34066± 796.1	1.24 ± 0.11	442.5 ± 7.99	70.32 ± 1.28
Sludge2	FAST	600	50261± 1733	19.93 ± 0.68	265.8 ± 9.16	57.41 ± 1.98
		700	91318± 3149	18.74 ± 0.64	357.9 ± 12.34	63.06 ± 2.17
		800	55047± 2574	20.28 ± 0.7	279.4 ± 21.1	59.7 ± 1.16
	SLOW	700	88394± 768.1	18.03 ± 0.29	348.7 ± 7.42	62.38 ± 0.74
		800	91474± 1744	18.52 ± 0.38	359.9 ± 7.33	64.55 ± 1.05

5.2 Bioavailable Content of elements for Sewage sludge Derived Biochar (SDBC)

The reported result for the effect of pyrolysis on the availability of elements and its behavior under the different treatments combining sludge, temperature and temperature increment rate is shown in this section. Table 19 presents data obtained for availability percentage in raw sludge samples are presented.

Table 19 presents the initial available content of toxic elements , it can be seen some differences between the two sludges, in the case of the Sludge 1, contained higher concentrations of Cd, which presented a value 5.4 times higher than Sludge 2 and Cr, which report a value below detection limit (<0.005 mg/L) for sludge 2 . Table 20 reported the available macronutrients content, in this case all the elements (Ca, K, Mg, P, and S) were higher in the Sludge 1, but the content difference compared with Sludge 2 is not large, for Sludge 1 in the case of Ca is 1.6 times the content in Sludge 2, K is 2 times, and Mg is 1.2 times the value reported for Sludge 2. Table 21 reported available micronutrients content, for Sludge 1 Cu, Ni and Zn presented higher values than the reported in Sludge 2, in opposite for the elements Fe, and Mn Sludge 2 presented higher content values, these were higher in around 1.5 and 3 times higher for Fe and Mn respectively compared to the amount obtained for Sludge 1. Table 22 presented the initial available content of other elements like Al, Be, Sr and V, Aluminum shows a sharp difference, obtaining for sludge 1 a content of 74.47 and for Sludge 2 211.77 mg/kg, for the rest of the elements it was observed slightly different values.

Table 19 Sewage sludge – Available Toxic elements content (mg/kg of dry matter)

Sludge	As mg/kg	Cd mg/kg	Cr mg/kg	Pb mg/kg
	Trace Elements			
1	7.303	2.155	13.159417	BDL
2	17.34	0.399	BDL	BDL

BDL: Below detection limit for Cr <0.005 mg/kg, Pb <0.02 mg/L

Table 20 Sewage sludge – Available Macronutrients content (mg/kg of dry matter)

Sludge	Ca mg/kg	K mg/kg	Mg mg/kg	P mg/kg	S mg/kg
	Macronutrients				
1	30078.67	2364.36	2942.79	5632.52	3702.34
2	18567.96	1143.23	2424.58	1358.07	2283.33

Table 21 Sewage sludge – Available Micronutrients content (mg/kg of dry matter)

Sludge	Cu mg/kg	Fe mg/kg	Mn mg/kg	Ni mg/kg	Zn mg/kg
	Micronutrients				
1	4.67	911.04	99.06	107.73	2458.35
2	3.71	1365.74	345.27	8.90	394.38

Table 22 Sewage sludge – Available Toxic elements content (mg/kg of dry matter)

Sludge	Al mg/kg	Be mg/kg	Sr mg/kg	V mg/kg
	Other Elements			
Sludge1	74.47	2682.50	73.03	0.54
Sludge2	211.77	1035.82	76.73	0.44

Table 23 contains toxic elements availability measured for As and Cd presented several values below the detection limit, data obtained for Sludge 2, ranging from 0.75 mg/kg for 700 ºC to 5.27 at 600 ºC, at slow temperature increment rate, a decreasing concentration with temperature was observed, the same behavior was pointed for fast temperature increment rate. The inversely proportional relation between temperature and concentration was presented for Cd as well. This is contrary with Cr, which augmented its concentration with the rising temperature, for SDBC from Sludge 1 at slow temperature increment rate the concentration went from 7.07 to 18.42 mg/kg, Sludge 2 presented lower concentrations, some of them even below detection limit (<0.005 mg/L).

Table 23 Wastewater sludge-derived biochar (SDBC) – Availability Toxic elements (mg/kg)

			Toxic elements			
SDBC	**Rate**	**Temp**	**As**	**Cd**	**Cr**	**Pb**
Sludge1	FAST	600	BDL	0.91±0.12	4.29±0.06	BDL
		700	BDL	BDL	8.72±0.48	BDL
		800	BDL	BDL	17.2±1.18	BDL
	SLOW	600	BDL	0.91±0.1	4.07±0.07	BDL
		700	BDL	BDL	8.28±0.24	BDL
		800	BDL	BDL	18.42±1.41	BDL
Sludge2	FAST	600	3.31±1.39	0.42±0.02	0±0	BDL
		700	BDL	BDL	0.52±0	BDL
		800	1.58±2.24	BDL	1.92±0.22	BDL
	SLOW	600	5.27±0.46	0.46±0.03	BDL	BDL
		700	0.75±1.31	0.09±0.08	0.5±0.08	BDL
		800	BDL	BDL	0.53±0.04	BDL

BDL: Below detection limit for Cd <0.001, Cr <0.005 and Pb <0.02 mg/L

Available portion for Cadmium in the SDBC from sludges 1 ad 2 was about 10 and 32 % respectively, maximum value for As was 5 % in sludge 2, 600 ºC fast temperature increment rate were the conditions that facilitate the availability of this elements (Figure 11 and Figure 12).

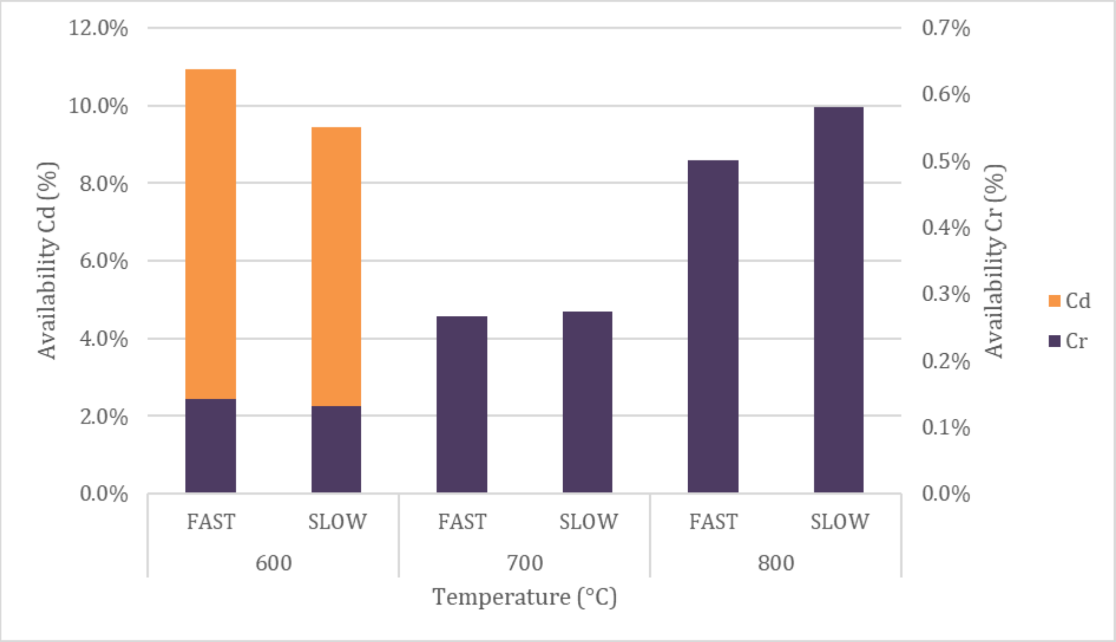


Figure 11 Wastewater sludge-derived biochar (SDBC) – Availability Toxic elements (%). Sludge 1

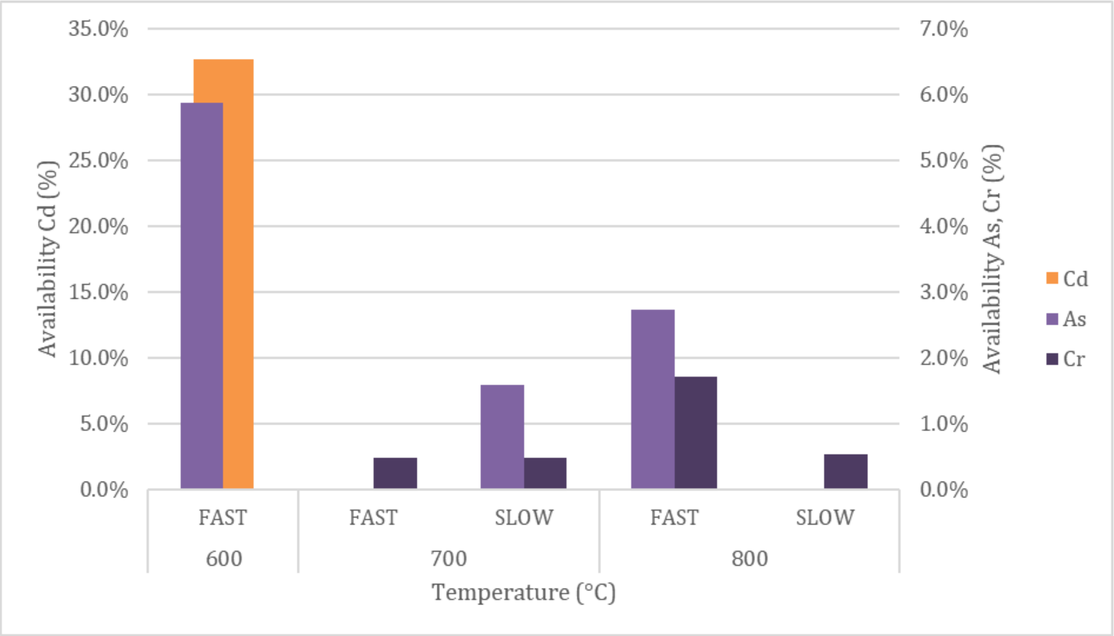


Figure 12 Wastewater sludge-derived biochar (SDBC) – Availability Toxic elements (%). Sludge 2

The availability of macronutrients is presented in Table 24, where it can be observed for Ca the maximum concentration 20924 mg/kg with the operation variables at 600 ºC and fast temperature increment rate, from this the availability decreases with the temperature. SDBC from Sludge 1 presented the highest concentrations.

Potassium availability was different for each SDBC, for Sludge 1 the concentration decreases with the temperature in both temperature increment rates, contrary with what occurred to Sludge 2, which presented higher concentrations with the temperature increase at fast increment rate, being 800 ºC the temperature with the highest concentrations, in contrast for the same SDBC at slow increment rate the concentration decreases with the temperature. Similar behavior was observed from the data for S.

A different behavior was identified for Mg, in SDBC from Sludge 1 the concentration increased with the temperature in higher values for fast increment rate ranging from 2196 mg/kg at 600 ºC to 2645 mg/kg at 800 ºC. In the case of SDBC from Sludge 2 the availability decreased with the increment of temperature, fast temperature increment rate presented lower values going from 1867 to 926 mg/kg at 600 ºC and 800 ºC respectively.

The high pyrolytic temperature was beneficial for the availability of Mg, K and P.

Table 24 Wastewater sludge-derived biochar (SDBC) – Availability Macronutrients (mg/kg)

			Macronutrients				
SDBC	**Rate**	**Temp**	**Ca**	**K**	**Mg**	**P**	**S**
Sludge 1	FAST	600	20924±64.79	1783±26.69	2196±4.25	4241±10.96	381.6±12.68
		700	15847±49.46	1317±13.62	1819±30.23	2311±113.3	590.6±28.31
		800	15853±71.41	2290±124.7	2645±107.8	3363±85.45	852.3±136.3
	SLOW	600	20346±401.6	1722±61.62	2103±33.99	4041±51.53	427.3±193.4
		700	15091±121	1351±73.47	1862±16.87	2343±25.72	649.1±50.63
		800	16194±629.4	2409±21.53	2711±49.25	3554±147.5	839.3±109.3
Sludge 2	FAST	600	9842±95.35	328.6±27.87	1867±41.13	988.1±15.01	190.8±34.16
		700	6474±157.9	309.9±0.99	1648±2.53	658.5±35.81	172.43±6
		800	5482±283.4	2002.8±221	926.8±0.44	1012±88.31	85.98±0.46
	SLOW	600	9364±101.5	305.4±11.5	1780±37.4	1036±4.36	229.6±8.76
		700	6039±174.7	298.7±8.96	1572±33.07	648.9±68.13	159.9±3.91
		800	5860±97.93	633.3±260.6	1490±28.08	751.9±21.35	159.3±11.9

In Figure 13 is possible to observe the percentage of availability for macronutrients, Ca, K and Mg registered the highest availability portions. SDBC from Sludge 1 presented higher Ca available portion (25 %) at 600 °C with fast temperature increment rate, K had 25 % at 800 °C with fast temperature increment rate, Mg at 800 °C with slow temperature increment rate presented 25.6 % availability, P registered a slightly higher availability at 600 °C, both temperature increment rates. From Figure 14 it can be observed that Sludge 2 presented a different behavior, from the figure Ca and Mg availability decreased with the increasing temperature, K remains approximately constant (1.2 – 3.9 %), except at 800 °C fast temperature increment rate, where it presented the highest availability (13.1 %).

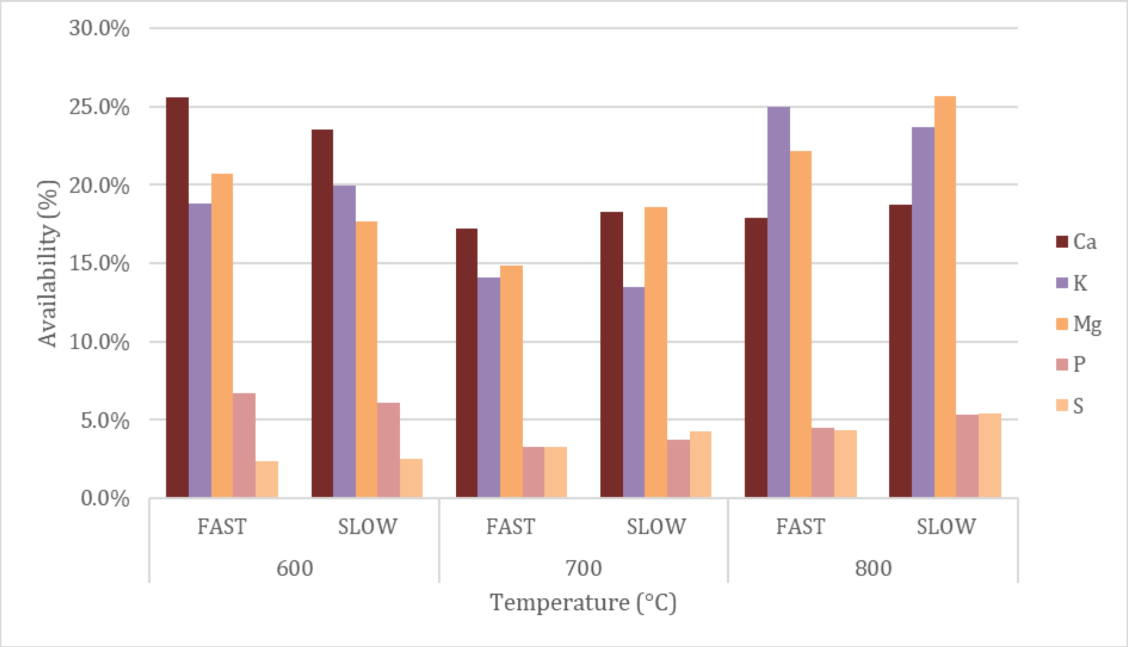


Figure 13 Wastewater sludge-derived biochar (SDBC) – Availability macronutrients (%). Sludge 1

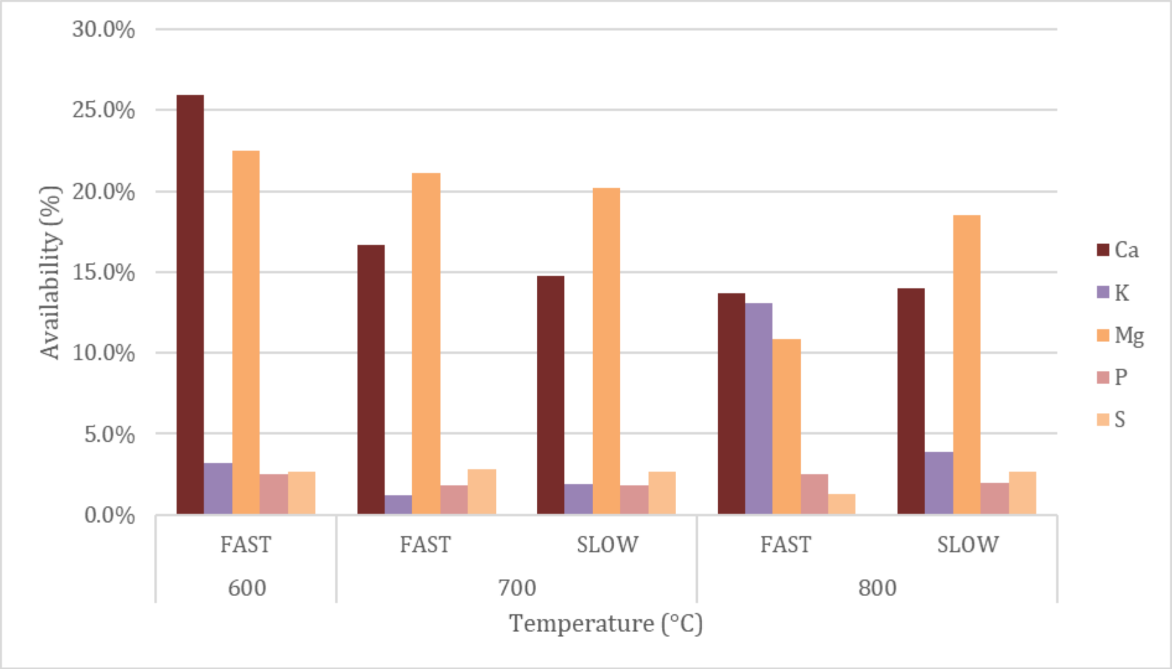


Figure 14 Wastewater sludge-derived biochar (SDBC) – Availability macronutrients (%). Sludge 2

For availability in micronutrients, presented in Table 25 is possible to observe that Cu augmented with the increasing temperature, for SDBC from Sludge 1 and 2 temperature increment rate fast and slow, in contrast with the results obtained for Fe, which decreases with the increasing temperature, SDBC from the sludge 1, at 600 and 700 °C, presented higher concentration and for both rates the values registered where approximately the same, 4.89 and 4.81 mg/kg for slow at 600 and 4.18 and 4.09 mg/kg for slow temperature increment rate. Mn and Zn in SDBC from Sludge 1 increased with the temperature increment but has the opposite comportment in the SDBC from Sludge 2. Molybdenum presented values below detection limit <0.005 mg/L in all the SDBC analyzed.

Table 25 Wastewater sludge-derived biochar (SDBC) – Availability Micronutrients (mg/kg)

			Micronutrients				
SDBC	**Rate**	**Temp**	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**
Sludge1	FAST	600	86.36±1.27	4.89±0.06	49.23±0.54	6.15±0.19	1558±0.83
		700	143.2±16.34	4.81±0.11	33.44±1.77	6.38±0.24	1076±136.9
		800	863.17±9.61	1.89±0.02	109.6±17.68	10.7±0.43	4600±299.7
	SLOW	600	86.5±13.36	4.18±0.47	48.45±2.83	5.82±0.14	1512±10.33
		700	157.2±16.13	4.09±0.28	35.81±1.16	6.24±0.06	1400±161.7
		800	900.3±37.23	1.54±0.13	143.1±13.62	10.71±0.47	5405±204.6
Sludge2	FAST	600	0.91±0.24	10.73±0.1	165.45±1.88	3.34±0.69	290.9±14.37
		700	2.59±0.25	19.96±1.4	98.96±2.62	2.91±0.2	180.4±3.56
		800	1.52±0.28	11.1±0.01	98.05±7.55	3.86±0	40.84±9.33
	SLOW	600	1.17±0.57	13.24±0.2	158.88±2.63	4.2±0.05	286.55±1.9
		700	2.83±0.38	19.4±0.33	92.64±2.14	2.91±0.47	179.9±7.1
		800	8.37±1.12	13.7±0.29	90.1±0.12	2.45±0.05	222.3±79.72

Figure 15 and Figure 16 represents the available portion of micronutrients in the SDBC analyzed. Zn recorded the highest available portions, for Sludge 1, the availability increased with the growing temperature, reaching its maximum value at 800 °C, for fast temperature increment rate 35.4 % and for slow 43.6 % availability. For SDBC from Sludge 2 the maximum percentage was 29.5 % at 800 °C slow. For Cu the proportional availability increment with temperature was identified just for SDBC from Sludge 1 (19 % at 800 °C slow and fast).

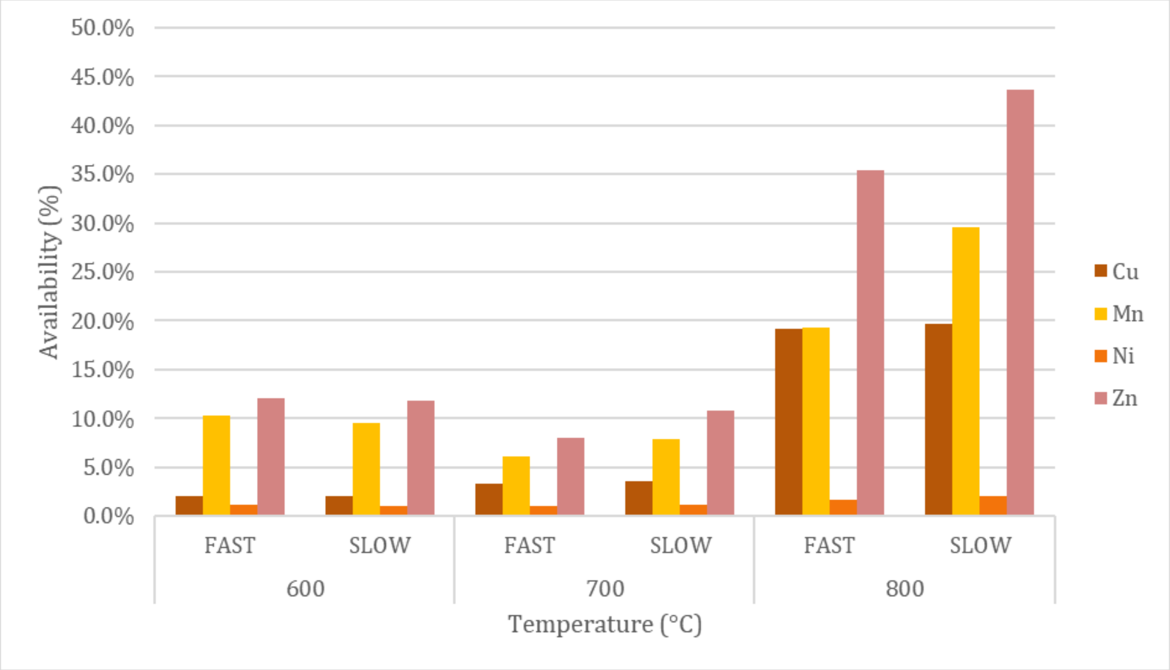


Figure 15 Wastewater sludge-derived biochar (SDBC) – Availability micronutrients (%). Sludge 1

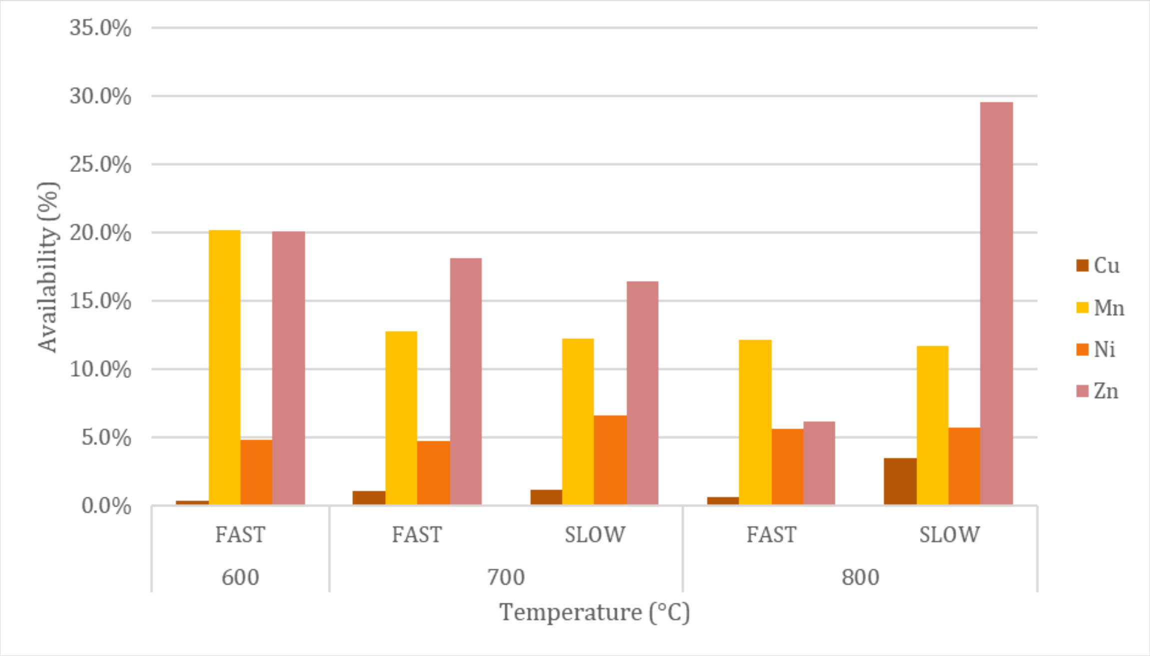


Figure 16 Wastewater sludge-derived biochar (SDBC) – Availability micronutrients (%). Sludge 2

From Table 26, Al Availability concentration presented a different behavior for the two SDBC, In the case of Sludge 1 for both temperature increment rates, at 700 °C (422.5 mg/kg - fast) it was an increment in the concentration from the value obtained at 600 °C (241.4 mg/kg - fast) and then at 800 °C a decrease was registered (203.6 mg/kg - fast). In contrast for Sludge 2 the availability increased with the temperature in both temperature increment rates.

In SDBC from Sludge 1 Na and Sr presented the same conduct, where at 700 °C it was a decrease in the concentration from the value obtained at 600 °C and then at 800 °C an increment was registered. The highest concentration was 2562.3 mg/kg at 800 °C Slow. Na in Sludge 2 decreased with temperature at Slow temperature increment rate, which presented the lowest concentration value 235.2 (mg/kg).

Data obtained for V was below the detection limit (<0.005 mg/L).

Table 26 Wastewater sludge-derived biochar (SDBC) – Availability Other elements (mg/kg)

			Other Elements		
SDBC	**Rate**	**Temp**	**Al**	**Na**	**Sr**
Sludge1	FAST	600	241.48±9.12	1859.46±11.45	44.1±0.03
		700	422.5±11.79	1257.03±38.46	32.54±0.39
		800	203.62±11.14	2360.76±137.87	54.02±0.92
	SLOW	600	212.44±21.85	1764.62±48.88	42.2±0.47
		700	364.78±18.54	1423.62±17.92	32.23±0.28
		800	190.7±18.06	2562.36±48.1	57.37±1.81
Sludge2	FAST	600	749.78±12.61	294.48±10.53	45.33±0.72
		700	1311.72±42.24	325.02±2.6	25.94±0
		800	1710.75±72.49	473.4±35.94	31.53±1.84
	SLOW	600	848.44±10.26	299.75±0.19	42.9±0.51
		700	1253.76±43.27	297.28±3.76	24.43±1.02
		800	1343.89±22.29	235.23±2.62	22.23±0.25

5.3 Losses of material and ash content

Pyrolysis yield of weighted SDBC was in average 47 % from the dry feed. The yields corresponded with what was expected.

Table 27 indicates total weight loss and the ignition loss, called ash content values for each SDBC from Sludges 1 and 2, it can be observed that the increasing of temperature is leading to a higher weight loss and the ash content is increasing as well, Sludge 2 presented the higher biochar yield with a total weight loss corresponding to 44 % at fast temperature increment rate.

Table 27 Weight loss and ash content for the Sewage derived biochar - SDBC

Rate	Temp.	SDBC Sludge 1		SDBC Sludge 2	
		Ash cont. (%)	**T. weight loss (%)**	**Ash cont. (%)**	**T. weight loss (%)**
FAST	600	32.92 ± 0.59	56.78 ± 0.03	15.87 ± 0.6	43.74 ± 0.16
	700	28.06 ± 1.27	59.08 ± 0.21	15.06 ± 1.33	44.73 ± 0.21
	800	36.67 ± 12.16	61.53 ± 0.07	18.2 ± 6.43	47.53 ± 0.22
SLOW	600	25.51 ± 8.09	56.27 ± 0.25	19.46 ± 0.37	43.52 ± 0.06
	700	31.26 ± 2.37	58.8 ± 0.02	18.41 ± 0.99	58.37 ± 27.08
	800	26.6 ± 0.64	61.15 ± 0.13	14.1 ± 1.32	44.56 ± 0.11

Figure 17 and Figure 18, shows a comparison for ash content and weight loss for SDBC from Sludges1 and 2 with respect to their temperature and temperature increment rate.

Figure 17 shows for SDBC from Sludge 1 that the total weight loss maintains an increasing linear behavior, directly proportional with temperature for slow and fast increment temperature rate. From the results obtained for SDBC from Sludge 2, for fast pyrolysis, it can be observed a positive linear behavior, they were increasing with the higher temperatures, going from 44 to 48 % for total weight loss, indicating these conditions had higher biochar yields.

Contradictory to what is shown for slow pyrolysis, where the total weight loss went from 58 % at 700 °C to 45 % at 800 °C.

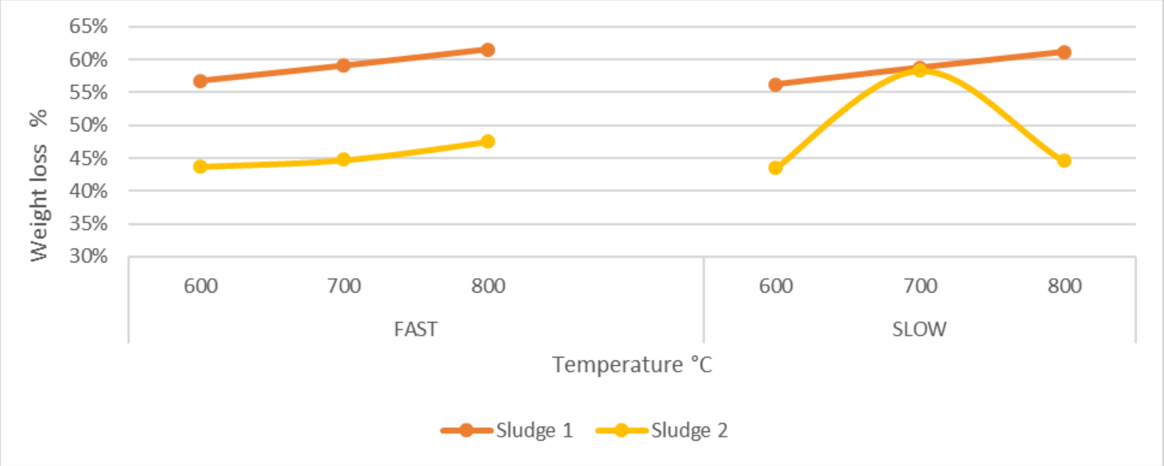


Figure 17 Comparison between total weight loss – SDBC from Sludge 1 and Sludge 2

Figure 18 shows results obtained for ash content in SDBC from Sludges 1 and 2, for fast pyrolysis. A positive linear behavior can be observed as it was increasing with the higher temperatures, going from 33 to 37 % and 16 to 18 % for Sludge 1 and 2 respectively. This is very different to what is reported for slow pyrolysis, where the ash content showed a reduction for both SDBC reported values from 700 to 800 °C.

For SDBC from Sludge 1 is it possible to follow the behavior of the ash content at 700 °C compared with 600 and 800 °C. Ash content shows a different pattern; during fast pyrolysis there was a decrease observed at 700 °C, but at the same temperature during slow pyrolysis an increase was registered.

From the results at 700 °C it is observed that the organic residue represents, 28 % and 15 % from the initial weight in Sludge 1 and 2 respectively for fast pyrolysis, compared with the slow pyrolysis, that reported 31 % for Sludge 1 and 18 % for sludge 2.

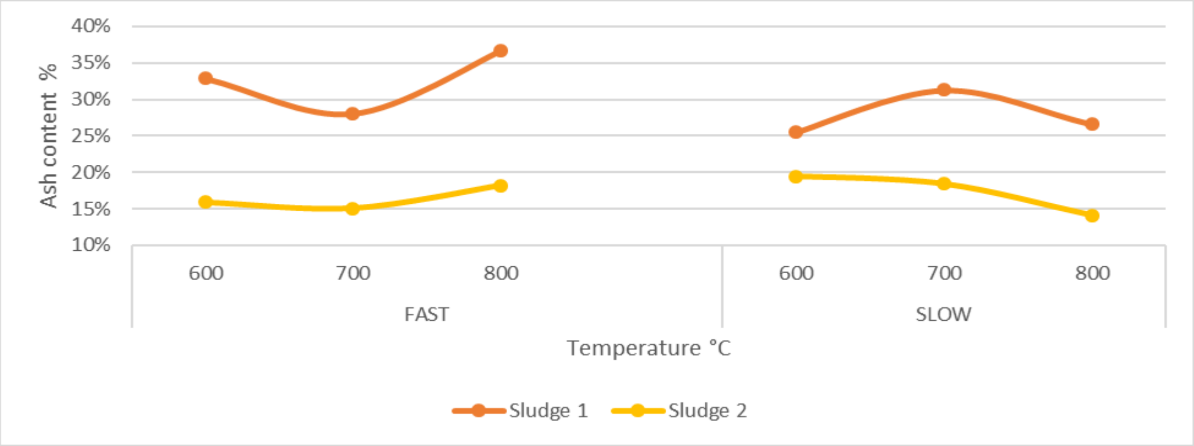


Figure 18 Comparison ash content – SDBC from Sludge 1 and Sludge 2

Univariate effects plots are presented in Figure 19 for SDBC from Sludge 1 and Figure 20 for SDBC from Sludge 2. These plots represent the way in which each factor affect the mean and its variation between the groups.

For Sludge 1 is it possible to observe that the mean value presented higher variation with the temperature, in comparison with the changes due to the temperature increment rate. Figure 19 shows ash content ranging from 28 y 33 %, but with the temperature it only varies between 29 a 1 %. In the weight loss case the most relevant factor was the temperature.

For SDBC from Sludge 2 (Figure 20) ash content has a better dependence relationship with temperature, which affect ash content percentage more than the temperature increment rate, contrary with the behavior of the Sludge 1

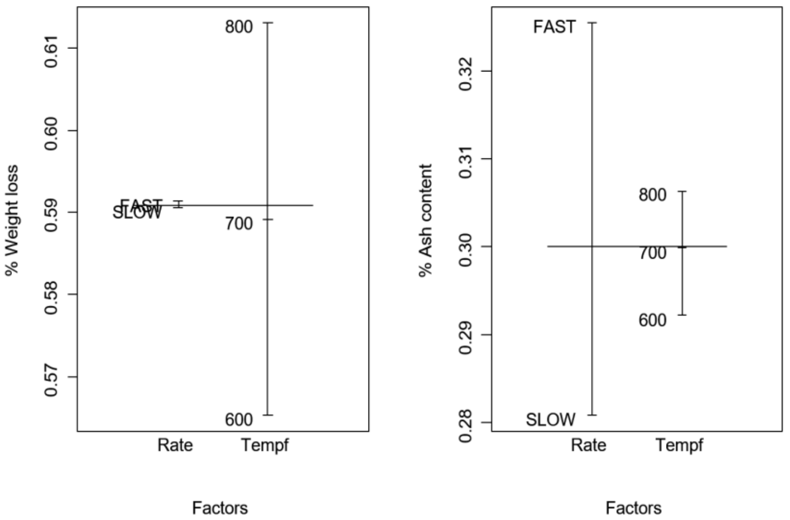


Figure 19 Univariate effects weight loss and ash content SDBC from Sludge 1

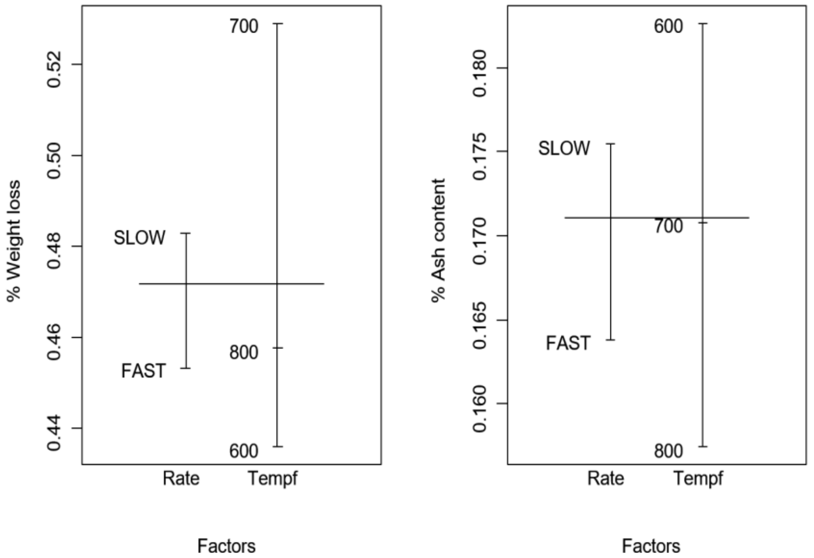


Figure 20 Univariate effects weight loss and ash content SDBC from Sludge 1

5.4 Linear Model Results

5.4.1 Effect of pyrolytic temperature and temperature increment rate on the total content of elements

Table 28 and Table 29 presents the relevant results for the model, it presents the significant influences among the relationship between temperature and temperature increment rate as factors and its influence on the total element content.

Coefficient – Estimate: is the intercept

Coefficient – t value: measures the distance in standard deviations of the coefficient estimate is away from 0. Is ideal to be far from 0 to indicate the null hypothesis rejection.
Coefficient - Pr(>|t|): is the probability of getting a value larger or equal to t.
The data presented on the following tables have codes of significance 0 '***' 0.001 '**' 0.01 (p-value).

The analysis of Table 28 for SDBC from Sludge 1, indicates that when slow rate was applied at 700 and 800 °C the model suggests a significant influence in the reduction of total concentration, indicating a negative effect on the following groups of elements: Toxic Elements (Cr), macronutrients (K, Mg, P, S), micronutrients (Mn, Ni) and other elements Sr. Conversely there was no evidence that showed significant increase of the concentration of the elements in the slow rate. This suggests that the general effect of this setting is to decrease the final concentration of elements of interest when coupled with pyrolysis temperatures superior to 700 °C.

The analysis shows that temperature higher than 700 and 800°C and the slow increment rate combined had a significant influence over the reduction in the total concentration of elements.

Table 28 Linear Model – Influence of temperature and temperature increment rate on total content of elements. SDBC from Sludge 1

As				**Ca**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
800 °C	11.19	2.931	0.01896 *	700 °C	10322	5.486	0.000583 ***
700 °C - Slow	-18.1	-3.499	0.00809 **	800 °C	6706	3.564	0.007354 **
800 °C - Slow	-19.97	-3.862	0.00479 **	700 °C - Slow	-14475	-5.682	0.000464 ***
Sr				**Cr**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	43.175	6.664	0.000158 ***	700 °C	269.81	6.548	0.000179 ***
800 °C	64.008	9.88	9.29e-06 ***	800 °C	434.01	10.533	5.75e-06 ***
700 °C - Slow	-61.424	-7.002	0.000112 ***	700 °C - Slow	-361.87	-6.486	0.000191 ***
800 °C - Slow	-62.384	-7.112	0.000101 ***	800 °C - Slow	-375.91	-6.738	0.000147 ***
S				**Mn**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	2144.7	3.479	0.008326 **	700 °C	68.515	5.455	0.000605 ***
800 °C	3510.1	5.695	0.000457 ***	800 °C	93.656	7.457	7.22e-05 ***
700 °C - Slow	-3623.1	-4.341	0.002474 **	700 °C - Slow	-119.44	-7.024	0.000110 ***
800 °C - Slow	-4672.7	-5.599	0.000511 ***	800 °C - Slow	-116.842	-6.871	0.000128 ***
K				**Mg**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
Slow	4689.8	4.069	0.00359 **	700 °C	1665.5	3.522	0.007827 **
700 °C - Slow	-14165.5	-9.078	1.74e-05 ***	700 °C - Slow	-3548.7	-5.542	0.000546 ***
800 °C - Slow	-11229.2	-7.196	9.28e-05 ***	800 °C - Slow	-2663	-4.159	0.003171 **

Fe

Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	9584.4	8.316	3.30e-05 ***
800 °C	10310.8	8.947	1.94e-05 ***

Cu

Conditions	Estimate Std.	t Value	Pr(>|t|)
800 °C	365.37	4.733	0.00148 **

Ni

Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	67.73	3.58	0.007184 **
800 °C	114.63	6.059	0.000303 ***
700 °C - Slow	-126.4	-4.935	0.001143 **
800 °C - Slow	-149.46	-5.835	0.000389 ***

P

Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	7867.4	5.86	0.000378 ***
800 °C	11301.1	8.418	3.02e-05 ***
700 °C - Slow	-11682.4	-6.427	0.000203 ***
800 °C - Slow	-11421.2	-6.283	0.000237 ***

Pb

Conditions	Estimate Std.	t Value	Pr(>|t|)
800 °C	-140.343	-14.23	5.79e-07 ***

Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01

The analysis of Table 16 for SDBC from Sludge 2, indicates that when slow rate was applied at 700 °C the model suggests a significant influence in the reduction of total concentration, indicating a negative effect on the following elements: Toxic elements (As), Macronutrients (K), Micronutrients (Mn), Other elements (Al, Sr).

The analysis shows that temperature 700 °C combined with the slow increment rate had a major influence over the reduction in the total concentration of elements. A significant positive effect was identified for pyrolysis temperature of 700 °C and slow temperature increment rate, this condition promotes an increasing behavior for Vanadium.

Table 29 Linear Model – Influence of temperature and temperature increment rate on total content of elements. SDBC from Sludge 2

Al

Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	41057	20.976	1.41e-07 ***
Slow	36428	20.387	1.71e-07 ***
700 °C - Slow	-39352	-15.573	1.09e-06 ***

As

Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	-16.323	-10.83	1.26e-05 ***
Slow	-14.12	-10.26	1.80e-05 ***
700 °C - Slow	21.917	11.265	9.70e-06 ***

K

Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	16177	7.507	0.000136 ***
700 °C - Slow	-11362	-4.084	0.004664 **

Mn

Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	3.8205	5.41	0.000998 ***
700 °C - Slow	-3.3644	-3.69	0.007753 **

Be

Conditions	Estimate Std.	t Value	Pr(>|t|)
Slow	-1.7656	-3.765	0.00703 **

Ni

Conditions	Estimate Std.	t Value	Pr(>|t|)
Slow	-25.6754	-9.132	3.88e-05 ***

Pb				**S**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
800 °C	-52.584	-5.738	0.000707 ***	700 °C	-1149.7	-5.017	0.00154 **
Si				**Sr**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	37911.1	10.873	1.23e-05 ***	700 °C	92.124	8.127	8.24e-05 ***
Slow	28538.5	8.966	4.37e-05 ***	Slow	80.602	7.789	0.000108 ***
700 °C - Slow	-35623.9	-7.914	9.76e-05 ***	700 °C - Slow	-89.804	-6.137	0.000474 ***
V				**Zn**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	5.6435	4.088	0.00464 **	800 °C	-780.58	-5.719	0.000721 ***
Slow	4.8546	3.852	0.00628 **				

Signif. codes: 0 '***' 0.001 '**' 0.01

5.4.2 Effect of pyrolytic temperature and temperature increment rate on the available content of elements

Table 30 and Table 31 presents the relevant results for the model, it shows the significant influences among the relationship between temperature and temperature increment rate as factors and its influence on the available content of elements.

According to the model, the effect of temperature and temperature increment rate combined for the SDBC from Sludge 1, shows no significant influence in the variation of the available concentration of elements, except for the Na where a slow rate at 800 °C showed a significant positive effect in the available concentration of this element. The behavior of the other elements was better explained, according to the model, by the influence of the temperature with the rate showing no significant influence (Table 30).

Table 30 Linear Model – Influence of temperature and temperature increment rate on available content of elements. SDBC from Sludge 1

Al				**S**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	181.03	11.005	4.14e-06 ***	800 °C	470.68	4.541	0.001896 **
Ca				**Cr**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	-5077.6	-14.401	5.28e-07 ***	700 °C	4.4312	5.224	0.000799 ***
800 °C	-5071.1	-14.383	5.34e-07 ***	800 °C	12.9021	15.21	3.46e-07 ***
Cr				**Cu**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
800 °C	776.805	35.486	4.35e-10 ***	800 °C	-2.996833	-12.728	1.37e-06 ***

K				**Mg**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	-465.62	-7.366	7.87e-05 ***	700 °C	-377.61	-7.72	5.64e-05 ***
800 °C	506.71	8.016	4.30e-05 ***	800 °C	448.46	9.168	1.62e-05 ***
Mn				**Ni**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
800 °C	60.3756	6.462	0.000196 ***	800 °C	4.5513	14.609	4.73e-07 ***
P				**Si**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	-1929.66	-20.97	2.81e-08 ***	700 °C	388.23	10.068	8.07e-06 ***
800 °C	-877.84	-9.54	1.21e-05 ***	800 °C	843.36	21.872	2.01e-08 ***
Na				**Sr**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	-602.43	-10.132	7.70e-06 ***	700 °C	-11.5556	-11.582	2.81e-06 ***
800 °C	501.3	8.431	2.99e-05 ***	800 °C	9.9211	9.944	8.85e-06 ***
800 °C-Slow	296.44	3.682	0.0062 **	Slow	5.2489	3.885	0.00464 **

Signif. codes: 0 '***' 0.001 '**' 0.01

Table 31 indicates a negative influence when 800 °C and slow temperature increment rate is combined, the availability decreased for majority of elements.

In contrast with the behavior observed for the SDBC from sludge 1, when no combination of factors was observed to cause a significant change in the available concentration of most elements the analysis of SDBC from sludge 2 showed a significant increase in the concentration for the elements Ca and Mg when a slow rate was used at 800 °C. In the rest of the elements significant effects in the interaction between rate and temperature were found with significant decrease of the concentration when using 800 °C at a slow rate. One element (Fe) showed a significant decrease only when using a slow rate at 700 °C. For the elements Copper, Magnesium and Zinc in which the availability increased at 800 °C slow temperature increment rate.

Table 31 Linear Model – Influence of temperature and temperature increment rate on available content of elements. SDBC from Sludge 2

Al				**Ca**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	561.94	14.483	5.06e-07 ***	700 °C	-3367.8	-21.045	2.73e-08 ***
800 °C	960.98	24.767	7.55e-09 ***	800 °C	-4359.4	-27.241	3.55e-09 ***
800°C - Slow	-465.52	-8.861	2.08e-05 ***	800°C - Slow	854.8	3.945	0.00427 **
Cu				**K**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
800°C - Slow	8.76E-01	7.51E+00	6.85e-05 ***	800 °C	1.67E+03	1.10E+01	4.18e-06 ***
				800°C - Slow	-1346.26	-6.526	0.000183 ***

Cr				**Fe**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	5.22E-01	5.615	0.000501 ***	700 °C	9.23E+00	1.65E+01	1.81e-07 ***
800 °C	1.93E+00	20.727	3.08e-08 ***	Slow	2.5136	4.499	0.00201 **
800°C - Slow	-1.39E+00	1.26E-01	4.01e-06 ***	700°C - Slow	-3.0728	-4.062	0.00362 **
Mg				**Sr**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	-2.19E+02	-7.47E+00	7.11e-05 ***	700 °C	-1.94E+01	-2.16E+01	2.22e-08 ***
800 °C	-940.84	-32.121 *	9.61e-10 **	800 °C	-13.8013	15.378	3.18e-07 ***
800°C - Slow	650.55	16.404	1.92e-07 ***	800 °C - Slow	-6.8622	-5.647	0.000483 ***
Mn				**Na**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	-6.65E+01	-2.06E+01	3.29e-08 ***	800 °C	1.79E+02	1.33E+01	9.87e-07 ***
800 °C	-67.3997	-20.834	2.95e-08 ***	800°C - Slow	-243.447	-13.345	9.50e-07 ***
Ni				**S**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
800°C - Slow	-2.2629	-4.75	0.00144 **	800 °C	-1.05E+02	-7.43E+00	7.43e-05 ***
P				**Si**			
Conditions	Estimate Std.	t Value	Pr(>|t|)	Conditions	Estimate Std.	t Value	Pr(>|t|)
700 °C	-3.30E+02	-6.67E+00	0.000157 ***	700 °C	2.62E+02	8.38E+00	3.13e-05 ***
800°C - Slow	-309.48	-4.627	0.001695 **	800 °C	750.4	24.008	9.66e-09 ***
				800 °C - Slow	-471.72	42.32	3.75e-06 ***

Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01

6. Discussion

The interaction between the pyrolysis temperature, rate and feedstock affects the biochar total and available elements concentration. All experiments were carried out with the same time setting, pyrolysis reactions have been completed within 30 minutes and longer periods of testing are not required (Agrafioti et al. 2013).

Total content of Cadmium had a higher concentration in SDBC from Sludge 2 at 600 °C - Fast, reported value from 0.96 for raw sewage sludge to 1.3 mg/kg on biochar, but the values were below the detection limit for 700 and 800 °C in both temperature increment rates. For the SDBC from Sludge 1 at 600 and 700 °C for slow rate it was reported that there was a reduction in the concentration from 9.7 to 0.5 mg/kg for 600 and 700 °C respectively, the initial decrease was observed from 14.57 mg/kg for raw sewage sludge, the behavior observed for both SDBC are in concordance with the results described by Lu et al. (2016), who obtained an increase from the content for raw sewage sludge 169 mg/kg, to the content at 600 °C of 229 mg/kg and then a reduction at 700 °C of 123 mg/kg. The behavior of the Cd at 700 and 800 °C can be explained, because During pyrolysis, the Cd tends to volatilize because it depends on factors such as temperature, feedstock concentration and interaction of various organic and inorganic components (Mancinelli et al. 2016).

Cadmium concentration values from raw sewage sludge that were reported at 600 °C, for the SDBC from Sludge 1 a reduction was observed, but in the case of SDBC from Sludge 2 an increment was detected, this doesn't match the findings reported by Hossain et al. (2011), in which the concentration of Cd in biochar increased with the increasing temperature, the reported values were: raw sewage sludge 2.07 mg/kg, for biochar at 500 °C 3.17 mg/kg, increasing to 3.22 mg/kg at 700 °C.

It was found that the toxic elements and the micronutrients in the wastewater sludge (Pb, Zn, Ni, Cd, As, Cu, Cr) were concentrated in biochar. In general, it has been observed that, irrespective of the temperature increase, the pyrolysis process increased the enrichment of heavy metals in biochar, this fact has been reported in several researches (Conesa et al. 1997; He et al. 2010; Hossain et al. 2011; Agrafioti et al. 2013; Liu et al. 2014; Lu et al. 2016; Mancinelli et al. 2016).

The heavy metals which can be found in the sewage sludge as sulfate, carbonate, chlorate, phosphate (mineral salts), sulfide and hydroxide, are able to transform into better thermostability sulfides or oxides during pyrolysis, therefore a big portion of heavy metals remains in biochar The available fraction (bioavailable) can be absorbed directly by plants. The changes in its portion reflect chemical speciation and element transformations during the pyrolysis(Lu et al. 2016).

It was found for SDBC from Sludge 1, that the available portion of Ni between 4 and 5 % for the experiment set temperatures (600, 700, and 800°C), in accordance with the findings on Lu et al. (2016), where exchangeable fraction was identified for Ni, and Zn as less than 5 % for temperatures 600°C, and 700°C. As the feedstock had a high initial total content of these elements, the resulting biochar is not suitable for posterior agricultural usage and the exchangeable fraction has good mobility, which has direct eco-toxicity and bioavailability to environment (Lu et al. 2016).

Pyrolysis conditions lead to the elimination of arsenic available portion, which was reported under the detection limit for the SDBC from both sludges (0.03 mg/L), Luan et al. (2016) reported in the case of As, an availability percentage inferior to 5% for 600°C, higher temperatures didn't registered availability of the element, Hossain et al. (2011) reported values for Arsenic below detection limit (< 3 mg/kg) for the tested temperatures (300, 400, 500, 600 and 700 °C), also Agrafioti et al. (2013) presented values for As below detection limit for biochar produced at 300, 400, and 500 °C.

For SDBC from Sludge 2 concentration of Pb, Cr, and Ni was found to be enriched on the SDBC at 700 °C, then these decreased at 800 °C, this can indicate partial defractionation or devolatilization of these elements at elevated temperatures (Hossain et al. 2011).

Chromium as trace element and Copper (Cu) as micronutrient had similar behaviors, these reported low availability percentage, in the case of Cr for SDBC from Sludge 1 ranging from 0.1 % at 600 °C to 0.6 % at 800 °C. the higher availability percentages that were reported for Cu, happened at 800 °C – Slow and Fast going up to 19 % from 201 % at 600 °C. This data corresponds to an increment of availability in biochar, compared to the raw sludges, the same result was found by Mancinelli et al. (2016), who analyzed sewage sludge samples pyrolyzed at 450 and 700 °C, and by Hossain et al. (2011) who determined nutrient concentration on biochar obtained at 300 to 700 °C. In contrast, this was in discordance with the findings by Lu et al. (2016), in this study the exchangeable portion of these two elements disappeared.

Table 32, shows the comparison of the SDBC obtained from this study with the current regulations, shows that according to the Council Directive 86/278/ECC (Council Directive 1986), the content of As, Cd, Cr, Pb, Cu, Ni, and Zn in the SDBC from Sludge 2 meets the control standards for agricultural use, in the case of SBC from Sludge 1 can’t be used because the contents of: Cu, which the higher value registered was 4579 mg/kg and the minimum reglementary range is 1000 - 1750 mg/kg (four times higher), for Ni, the higher registered value was 646 mg/kg, in comparison with the Directive limit 300 – 400 mg/kg (two times higher), and Zn limit was exceeded by five times the recommended value (13004 mg/kg for SDBC and 2500 – 4000 mg/kg Directive limit). It can be observed that the SDBC from Sludge 2 according to the Council Directive 86/278/ECC is suitable for usage in agricultural land as amendment

Table 32 Shows in red the elements and the total concentrations obtained for the following elements: As, Cd, Cu, Pb, Ni, and Zn. In blue are written the values corresponding to the elements that doesn’t meet the current regulations neither the Council Directive 86/278/ECC or the Decree 437/2016 from the Czech Republic. The red values are higher that the limits set in Decree 437/2016, and the green values are which meet both regulations.

The assessment of results with the limit values presented in the Decree No. 437/2016, released by the Ministry of Environment in the Czech Republic, as a guideline for limit concentrations of selected hazardous substances and elements in sludge for use on agricultural land, shows categorically that none of the SDBC produced in this study is suitable for its posterior use as soil amendment, the SDBC from Sludge 2 reach all the recommended limits, except for As, which is 1.9 times higher (57.9 mg/kg) than the recommended value (30 mg/kg). In the case of SDBC of Sludge 1 the recommended concentrations are exceeded by the following elements: Cd, higher registered value was 9.7 mg/kg, 1.9 times higher than the Decree value (5 mg/kg), for As, 33.7 mg/kg, which is 12% higher than the Directive, Pb recommended value 200 mg/kg was exceeded by 2.9 times (284.8 mg/kg), Cu was the element which surpassed the limit with the higher quantity, the registered value was 4496 mg/kg, 8.9 times higher than the Directive, 500 mg/kg, Ni and Zn recommended concentration limits were exceeded by 6.4 and 5.2 times respectively.

Table 32 Comparison Wastewater sludge-derived biochar (SDBC) Total content (mg/kg) of selected hazardous substances and current regulations

SDBC	Rate	T	As	Cd	Cu	Pb	Ni	Zn
Sludge1	F	600	22.52 ± 8.37	8.36 ± 1.26	4130 ± 134.5	284.8 ± 11.24	532.3 ± 47.13	12854 ± 103.6
		700	31 ± 0.55	BDL	4255.± 27.5	275.9 ± 12.01	600.1 ± 2.91	13426 ± 87.42
		800	33.72 ± 1.52	BDL	4496 ± 69.59	144.4 ± 0.31	646.9 ± 10.44	13004 ± 318.1
	S	600	29.97 ± 5.32	9.72 ± 0.74	4109 ± 52.91	279.8 ± 3.91	572.06 ± 0.36	12854 ± 77.95
		700	20.35 ± 2.21	0.52 ± 0	4345 ± 44.93	262.8 ± 10.49	513.4 ± 8.89	13017 ± 202.5
		800	21.19 ± 1.68	BDL	4579 ± 92.56	133.2 ± 11.65	537.2 ± 13.51	12384 ± 487.9
Sludge2	F	600	56.39 ± 1.94	1.31 ± 0.04	284.5 ± 9.81	84.67 ± 2.92	69.34 ± 2.39	1449 ± 50.01
		700	40.07 ± 1.38	BDL	255.8 ± 8.82	68.51 ± 2.36	61.69 ± 2.12	996.6± 34.37
		800	57.95 ± 0.1	BDL	256.1 ± 6.99	32.09 ± 19.27	68.85 ± 6.56	669.3 ± 309.1
	S	700	47.86 ± 2.21	BDL	245.9 ± 12.73	82.92 ± 7.15	44.57 ± 1.09	1093 ± 56.03
		800	43.83 ± 0.42	BDL	244.4 ± 10.19	54.2 ± 7.05	43.17 ± 2.3	752.9 ± 111.5

BDL: Below detection limit for Cd <0.17 mg/kg. Rate: Fast (F), Slow (S)

The total content of Macronutrients as P, and S in SDBC from Sludge 1 had the higher increase under the conditions 800 °C-Fast, going from 62975 to 74276 mg/kg for 600 and 800°C respectively. From this, it can be observed that the increase in temperature led to this elements concentration increment in biochar, this can influence the retention of Macronutrients in biochar, and this might be associated to the P present in raw sewage sludge is associated with thermo-stable phosphate minerals, which are difficult to decompose, by getting more crystalized as effect of the increasing temperature (Yuan et al. 2015).

For macronutrients Potassium, Magnesium, Calcium, an increment was shown in concentration with the increasing temperature for the analyzed SDBC from Sludge 2 the higher increments were presented at 800 °C – Slow, in the case of K going from 7518 for raw sewage sludge to 16323 mg/kg for the SDBC, and for Ca from 20245 mg/kg to 41979 mg/kg in the SDBC . The enrichment of these Macronutrients in biochar was also reported for Yuan et al. (2015). Who carried out sewage sludge pyrolysis on the temperature range 300 – 700 °C, the content of K in the raw sample was 7.47 mg/kg increasing proportionally with the temperature, getting a value of 16.6 mg/kg on the biochar at 700 °C, the same situation was reported for Mg and Ca, which content augmented from 17.4 mg/kg for sewage sludge to 25.8 mg/kg for biochar at 700 °C

For the Micronutrients total content, it was observed an initial increase from the content in raw sewage sludge for all the micronutrients, except for Zn for SDBC from Sludge 2 at fast and Slow temperature increment rate, going from 646 in raw sewage sludge, 1449 mg/kg at 600 °C to 669 mg/kg at 800 °C (Fast) and for Mn at 700 °C – Slow an reduction was reported as well (442 mg/kg raw sewage sludge to 75 mg/kg at 700 °C), this last result is in concordance with the information given by Yan et al. (2015), where Mn, Fe, Zn and Cu reported a reduction on the content in biochar, using as a reference the content in sewage sludge, and the proportional decrease with the increasing temperature. For this study In the case of Cu, Ni and Zn for SDBC from Sludge 1 the experimental set that allowed to have higher concentration values was 800 °C – Slow, for the following elements, Cu, Fe and Mo; but even for fast temperature increment rate the limit values for soil application of biochar surpassed, this is due to the high presence of these elements in the feedstock. They were exceeded 4, 2 and 3 times for Cu, Ni and Zn respectively. Regarding to the Micronutrients availability, for SDBC from Sludge 2 at 600 °C-Slow, were the conditions which permit the higher availability portion of the elements in the biochar, this allow and improvement on the quality for subsequent usage in soil, biochar produced at higher temperatures (around 700 °C). It also improves soil organic matter and presents more available micronutrients to soil (Yuan et al. 2015).

Pyrolysis leads, according to Lu et al. (2016), to a decrease of Zn exchangeable fraction. In this study, higher disponible percentages have been found at 800 ° C, affecting the biochar quality in future use.

Loss on ignition for SDBC from Sludge 1, indicated an ash content that increased with the temperature, better yields on biochar production were registered at fast temperature increment rate (26 % at 600 °C and 37 % at 800°C) in both SDBC. This is in accordance with the findings of Yuan et al. (2015) and Conesa et al. (1997), who found that the loss on ignition of the organic residue represents 31.6% of the digested samples. Similar ash content was reported by Mancinelli et al. (2016), who obtained 33 % for digested sewage sludge during slow pyrolysis at set temperatures of 450 and 700 °C. Wastewater sludge derived biochar from Sludge 2 reported an ash content up to 18 % for fast and slow temperature increment rates, similar to the ash content reported for Conesa et al. (2009), who obtained 14.8 % for ash content during pyrolysis on the nominal temperature 450 to 1050°C.

Biochar yield decreased gradually with the temperature, it was found that the higher biochar yield occurred at 700 °C (46.4%) (Mancinelli et al. 2016), and the same findings were registered by Hossain et al. (2011), who reported a yield of 54.4 % at 700 °C. This coincides with the data, where higher yields were found at 600 and 700 °C (slow rate), with 44 and 41% respectively for SDC from Sludge 1, with a similar behavior for both temperature increment rates. And obtained values of 56 to 42 % for SDBC from sludge 2 at slow temperature increment rate. Being 600 °C-Slow the experimental set with higher yields reported for both sludges. The observed decrease on the biochar yield with the rising temperature can be attributed to the decomposition of more organic materials at higher temperatures, and therefore it could be ascribed to a greater primary decomposition of the initial feedstock or to the solid residue secondary reactions (Agrafioti et al. 2013). In addition, the pyrolysis temperature affects the contents of volatile matter, ash and fixed carbon on biochar, these characteristics have different influence in soil quality, enhancing soil organic carbon by applying biochar (Hossain et al. 2011).

Regarding to the linear models proposed for the evaluation of the influence of the temperature and temperature increment rate on the total content and availability of elements in the produced biochar, some findings are described: The SDBC of the Sludge1 showed that the slow rate of temperature increase had a consistent negative effect in the total concentration of some elements (As, Sr, S, Cr, Mn, Ni, K, Mg, P, Ca), however, within these elements there were different behaviors regarding temperature. For example, for the elements As, Sr, S, Cr, Mn, Ni, the decrease of concentration was higher 800 °C at slow rate than for 700 °C at slow rate, suggesting a linear negative association between the temperature and the final concentration when using a slow rate.

Nevertheless, some elements like (K, Mg, P) showed stronger decrease of concentration at 700 °C than at 800 °C suggesting that higher temperatures in a slow rate setting will probably end up in higher concentrations of these elements in the final biochar. Finally, for Calcium, a significant effect was found just for one temperature at slow rate, so no final conclusions can be made about their behavior when using different temperatures at this rate. Similar conclusions could not be drawn for SDBC from Sludge 2. despite the fact that the slow rate was associated consistently with stronger decreases in concentration for the majority of the elements. No general trend could be associated with temperature as in SDBC from Sludge 1, this because the interactions in this sludge were only just significant at 700 °C. This could mean that higher temperatures are needed to elicit strong changes in element concentration when using slow rate in the pyrolysis of SDBC from Sludge 2.

7. Conclusions

- For some elements the total concentration in the biochar is dependent of both the rate and the temperature (Toxic elements: As, Cr; Macronutrients: Ca, K, Mg, P, S; Micronutrients: Mn, Ni; other: Al Sr). While other elements showed only significant relationship to the temperature regardless of the rate (Toxic elements: Pb; Macronutrients: S, Micronutrients: Cu, Fe). This variability was also heavily dependent on the sludge used, for example within the toxic elements Cr had great influence of Combination of rate and temperature but only in the sludge 1, while in the sludge 2 no effect was observed. For the elements that had influence of both the rate and the temperature the effect was not constant, for example the combination of 700 ºC and a slow rate increased the concentration of As in sludge 2, while for the majority of elements showed smaller concentrations at this setting.

- In the same way, for few elements the available concentration in the biochar is dependent of both the rate and the temperature (Toxic elements: Cr, Macronutrients: Ca, K, Mg, P, Micronutrients: Cu, Fe, Ni, other: Al, Sr), interestingly all this effects were detected only in SDBC from sludge 2, suggesting a strong influence of the inherent characteristics of the sludge in the reaction to rate of pyrolysis. Other elements showed only significant relationship to the temperature regardless of the rate (Macronutrients :S, Micronutrients: Mn in sludge 2 and most elements in sludge 1). The reaction of the elements to the rate and the temperature varied greatly, for example both Cu and Ca showed a significative increase in concentration in the slow setting at 800ºC, while the rest of the elements had significant lower concentrations at this setting.

- Finally, the ash content showed influence of both the rate and the temperature the ash content, it was observed a different behavior for both sludges. In sludge 1 the highest values were observed at 800ºC when using a fast rate (37%) and 700ºC when using a slow rate (31%). In the sludge 2 the highest value for the fast rate was observed at 800ºC (18%) and 600ºC for the slow rate (19%). In contrast, the total yield showed only significant relation with the temperature. Higher temperatures will cause increase weight loss. This behavior was expected when comparing this result with previous studies.

8. References

Agrafioti E, Bouras G, Kalderis D, Diamadopoulos E. 2013. Biochar production by sewage sludge pyrolysis. Journal of Analytical and Applied Pyrolysis **101**:72–78. DOI: 10.1016 /j.jaap.2013.02.010.

Antizar-Ladislao B, Lopez-Real J, Beck AJ. 2006. Degradation of polycyclic aromatic hydrocarbons (PAHs) in an aged coal tar contaminated soil under in-vessel composting conditions. Environmental Pollution **141**:459–468.

Barry D, Barbiero C, Briens C, Berruti F. 2019. Pyrolysis as an economical and ecological treatment option for municipal sewage sludge. Biomass and Bioenergy **122**:472–480. DOI: 10.1016/j.biombioe.2019.01.041

Bridgwater A V, Meier D, Radlein D. 1999. An overview of fast pyrolysis of biomass. Organic Geochemistry **30**:1479–1493.

Carey DE, Mcnamara PJ, Zitomer D. 2015. Biochar from Pyrolysis of Biosolids for Nutrient Adsorption and Turfgrass Cultivation. Water Environment Research **87**:2098–2106. DOI: 10.2175/106143015X14362865227391

Cieślik BM, Świerczek L, Konieczka P. 2018. Analytical and legislative challenges of sewage sludge processing and management. Monatshefte fur Chemie **149**:1635–1645. DOI:10.1007/s00706-018-2255-2.

Conesa JA, Font R, Fullana A, Martín-Gullón I, Aracil I, Gálvez A, Moltó J, Gómez-Rico MF. 2009. Comparison between emissions from the pyrolysis and combustion of different wastes. Journal of Analytical and Applied Pyrolysis **84**:95–102.

Conesa JA, Marcilla A, Prats D, Rodriguez-Pastor M. 1997. Kinetic study of the pyrolysis of sewage sludge. Waste Management and Research **15**:293–305. DOI: 10.1006/wmre.1996 .0085

Council Directive. 1986. (86/278/ECC) On the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture.

Council Directive. 1999. Council Directive 1999/31/EC on the landfill of waste. Page 19.

Czech Statistical Officce. 2018. Sewage sludge production statistics in Czech Republic. Prague. Available from https://www.czso.cz/documents/10180/61546960/2800211811. pdf/cc0a3963-0487-4f91-8313-63a4798ae783?redirect=https%3A%2F%2Fwww.czso.cz %2Fcsu%2Fczso%2Fhome%3Fp_p_id%3D3%26p_p_lifecycle%3D0%26p_p_state%3D maximized%26p_p_mode%3Dview%26_3_groupId%3D0%26_3_keywor (accessed February 13, 2019).

ELEMENTAR. 2014. The Elemental Analyzer vario MACRO cube. Performance, Advantages, Arguments. Available from http://sales.elementar.de/downloadable/ download /sample/sample_id/664/ (accessed March 14, 2019).

European Commision. 2017. Ninth Report on the implementation status and the programmes for implementation (as required by Article 17) of Council Directive 91/271/EEC concerning urban waste water treatment. Brussels. Available from http://ec.europa.eu/ environment/water/water-drink/index_en.html; (accessed February 13, 2019).

Faraway JJ. 2009. Linear Models with R. Chapman & Hall/CRC, Washington, D.C.

Fonts I, Gea G, Azuara M, Ábrego J, Arauzo J, Esquillor M. 2012. Sewage sludge pyrolysis for liquid production: A review. Renewable and Sustainable Energy Reviews **16**:2781–2805. DOI: 10.1016/j.rser.2012.02.070

Frišták V, Pipíška M, Soja G. 2017. Pyrolysis treatment of sewage sludge: A promising way to produce phosphorus fertilizer. Journal of Cleaner Production. DOI: 10.1016/j.jclepro. 2017.12.015.

Fytili D, Zabaniotou A. 2008. Utilization of sewage sludge in EU application of old and new methods-A review. Renewable and Sustainable Energy Reviews **12**:116–140. DOI: 10.1016/j.rser.2006.05.014

Grady C, Daigger G, Lim H. 1999. Biological Wastewater Treatment, 2nd edition. Marcel Dekker, Inc., New York.

He Y, Zhai Y, Li C, Yang F, Chen L, Fan X, Peng W, Fu Z. 2010. The fate of Cu, Zn, Pb and Cd during the pyrolysis of sewage sludge at different temperatures. Environmental Technology **31**:567–574. DOI: 10.1080/09593330903514466

Hossain MK, Strezov V, Chan KY, Ziolkowski A, Nelson PF. 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. Journal of Environmental Management **92**:223–228. DOI: 10.1016/j.jenvman.2010.09.008

Jin J, Li Y, Zhang J, Wu S, Cao, Y, Liang P, Zhang J, Wong MH, Wang M, Shan S, Christie P. 2016. Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge. Journal of Hazardous Materials **320**:417–426. DOI: 10.1016/j.jhazmat.2016.08.050

Kacprzak M, Neczaj E, Fijałkowski K, Grobelak A, Grosser A, Worwag M, Rorat A, Brattebo H, Almås Å, Singh BR. 2017. Sewage sludge disposal strategies for sustainable development. Environmental Research **156**:39–46. DOI: 10.1016/j.envres.2017.03.010

Karayildirim T, Yanik J, Yuksel M, Bockhorn H. 2006. Characterisation of products from pyrolysis of waste sludges. Fuel 85:1498–1508.

Košnář Z, Wiesnerová L, Částková T, Kroulíková S, Bouček J, Mercl F, Tlustoš P. 2019. Bioremediation of polycyclic aromatic hydrocarbons (PAHs) present in biomass fly ash by co-composting and co-vermicomposting. Journal of Hazardous Materials **369**:79–86. DOI: 10.1016/j.jhazmat.2019.02.037

Lavine M. 2013. Introduction to Statistical Thought. University Press of Florida.

Lehmann J. 2007. Bio-energy in the black. Frontiers in Ecology and the Environment **5**:381–387.

Liu T, Liu B, Zhang W. 2014. Nutrients and heavy metals in biochar produced by sewage sludge pyrolysis: Its application in soil amendment. Polish Journal of Environmental Studies **23**:271–275.

Lu H, Zhang W, Wang S, Zhuang L, Yang Y, Qiu R. 2013. Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. Journal of Analytical and Applied Pyrolysis **102**:137–143. DOI: 10.1016/j.jaap.2013.03.004.

Lu T, Yuan H, Wang Y, Huang H, Chen Y. 2016. Characteristic of heavy metals in biochar derived from sewage sludge. Journal of Material Cycles and Waste Management 18:725–733. DOI 10.1007/s10163-015-0366-y

Luan J, Li R, Zhang Z, Li Y, Zhao Y. 2013. Influence of chlorine, sulfur and phosphorus on the volatilization behavior of heavy metals during sewage sludge thermal treatment. Waste Management and Research **31**:1012–1018.

Mader P, Száková J, Miholová D. 1998. Classical dry ashing of biological and agricultural materials. Part II. Losses of analytes due to their retention in an insoluble residue. Analusis **26**:121–129.

Mancinelli E, Baltrėnaitė E, Baltrėnas P, Paliulis D, Passerini G. 2016. Trace Metals in Biochars from Biodegradable By-products of Industrial Processes. Water, Air, and Soil Pollution **227**:198. DOI: 10.1007/s11270-016-2892-1

Metcalf, Eddy. 2003. Wastewater Engineering: Treatment and ReuseFourth Ed. McGraw-Hill, New York.

Mininni G, Blanch AR, Lucena F, Berselli S. 2015. EU policy on sewage sludge utilization and perspectives on new approaches of sludge management. Environmental Science and Pollution Research **22**:7361–7374. DOI:10.1007/s11356-014-3132-0.

Ministry of the Environment. 2001. Decree No. 383/2001 on Details on Waste Management. Czech Republic.

Ministry of the Environment. 2005. Decree No. 294/2005 Decree on the conditions of waste disposal in landfills and their use on the ground surface and amending Decree No. 383/2001 On waste management details. Czech Republic.

Ministry of the Environment. 2008. Decree No. 341/2008 Decree on the Details of the Management of Biodegradable Waste and on the Amendment to Decree No. 294/2005 Coll. on details of biodegradable waste management. Czech Republic.

Ministry of the Environment. 2016. Decree No. 437/2016 Decree on the conditions of use of treated sludge on agricultural land and amendment to Decree No. 383/2001 Coll., On the details of waste management and amendment to Decree No. 341/2008 Coll. On Collection of Wastes at Landfills and t. Czech Republic.

Peter H. 2012. European Biochar Certificate-Guidelines for a sustainable production of Biochar. Available from https://www.zora.uzh.ch/id/eprint/125910/1/2016_ebc-guidelines.pdf (accessed January 3, 2019).

Pukalchik M, Mercl F, Terekhova V, Tlustoš P. 2018. Biochar, wood ash and humic substances mitigating trace elements stress in contaminated sandy loam soil: Evidence from an integrative approach. Chemosphere **203**:228–238. DOI: 10.1016/j.chemosphere. 2018.03.181

Raheem A, Sikarwar VS, He J, Dastyar W, Dionysiou DD, Wang W, Zhao M. 2018. Opportunities and Challenges in Sustainable Treatment and Resource Reuse of Sewage Sludge: A Review. Chemical Engineering Journal **337**:616–641. DOI: 10.1016/j.cej.2017 .12.149.

Razaq M, Zhang P, Shen HL, Salahuddin. 2017. Influence of nitrogen and phosphorous on the growth and root morphology of Acer mono. PLoS ONE 12.

Rehman HA, Razzaq R. 2017. Benefits of Biochar on the Agriculture and Environment - A Review. Journal of Environmental Analytical Chemistry 04:3–5.DOI: 10.4172/2380-2391.1000207

Shao J, Yan R, Chen H, Yang H, Lee DH. 2010. Catalytic effect of metal oxides on pyrolysis of sewage sludge. Fuel Processing Technology **91**:1113–1118. Elsevier B.V. DOI: 10. 1016/j.fuproc.2010.03.023.

Świerczek L, Cieślik BM, Konieczka P. 2018. The potential of raw sewage sludge in construction industry – A review. Journal of Cleaner Production **200**:342–356. DOI: 10.1016/j.jclepro.2018.07.188.

U.S. EPA. 1993. 40 CFR Part 503 - Standards for the use or disposal of sewage sludge.

U.S. EPA. 2007. Alkaline Stabilization of biosolids. Page Biosolids Treatment Processes. Washington, D.C.

von Sperling M. 2007. Wastewater Characteristics, Treatment and Disposal. IWA Publishing, London.

Youcai Z, Ziyang L. 2017. Pollution Control and Resource Recovery. Chapter five Pollution Control and Resource Recovery for Landfill Gas. Butterworth-Heinemann is an imprint of Elsevier

Yuan H, Lu T, Huang H, Zhao D, Kobayashi N, Chen Y. 2015. Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge. Journal of Analytical and Applied Pyrolysis **112**:284–289. DOI:10.1016/j.jaap.2015.01 .010.

Zaker A, Chen Z, Wang X, Zhang Q. 2019. Microwave-assisted pyrolysis of sewage sludge: A review. Fuel Processing Technology **187**:84–104. DOI: 10.1016/j.fuproc.2018.12.011.