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Carbon stability and nutrient bioavailability of pyrolysis treated sewage sludge

Diploma Thesis

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Declaration

I declare that the Diploma Thesis 'Carbon stability and nutrient bioavailability of pyrolysis treated sewage sludge' is my own work and all the sources I cited in it are listed in the References.

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Acknowledgement:

Abstract:

The production of sewage sludge has increased over the years and its disposal in a safe manner is an important environmental problem. Its high content of organic matter, as well as nutrients makes it a favorable raw material for its use in agriculture. However, they usually contain a large variety of pollutants whose concentrations must be considered. Thermal treatment transforms the nutrients of sewage sludge and also favor the degradation of some of the pollutants present. The product resulting from the heat treatment is biochar, which is a material rich in C and nutrients that can be released into the soil. The properties of biochar depend to a great extent on the raw material used and the conditions of its production as well as the temperature used. The stability of the biochar is closely related to the stability of the carbon.

This study investigated the total and available contents of K, P and S and the relative content of stable C in 23 different samples of sewage sludge from water treatment plants in the Czech Republic. The effect of pyrolysis at low temperatures (220ºC and 320ºC) on the elements and properties of these samples has also been studied. The results obtained showed a high total content of nutrients and stable C in the sludge. The concentration of available nutrients in the sludge presents a great variability between the different samples. Phosphorus was the nutrient with the highest total and available concentration from the three nutrients studied. The mean of total concentration of P was 26816 g/kg and the mean of the available P concentration was 5039 mg/kg. The total mean concentration of S was 13422 mg/kg and the mean of available S concentration was 3143 mg/kg. Finally, the total mean concentration of K it was 3965 mg/kg and the mean of available K concentration was 1469 mg/kg. The pH of the raw sludge was maintained in the range from 6.47 to 7.63. During the thermal treatment, a loss of mass increases with the increase in temperature being 12.7 % the mean of loss of mass for the treatment carry out at 220ºC, and 33.8 % the mean of loss of mass for the treatment carry out at 320 ºC. The bioavailability of nutrients in the pyrolyzed samples varies in the different sludges. The percentage of stable C increases in the samples when the temperature increases, obtaining the highest percentages of stable carbon in the pyrolyzed samples at 320ºC. The pyrolyzed samples show a slightly lower pH than that of the raw samples.

Key words: Thermal treatment, sewage sludge, nutrients, carbon, bioavailability

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1. Introduction

The amount of sludge produced in society has increased over the years. The elimination of these sludges safely is an environmental problem that should be considered by everyone (Agrafiotia et al., 2016; Singh and Agrawal, 2008). According to EUROSTAT data, the countries with the highest production of sludge are Germany, United Kingdom, France, Spain and Italy (EUROSTAT, 2015). The concentration of sludge produced in 2015 in the Czech Republic was 210 thousand tons (EUROSTAT, 2015). Within the existing processes for the elimination or use of sludge, its use in agriculture offers a cost-effective use. Due to the properties of the sludge and its high concentration of macro elements and nutrients, it has a positive effect on both the soil and the plants (Spanos et al., 2014). On the other hand, it cannot be forgotten that they also contain toxic components that can be dangerous for the environment and for organisms (Yoshida et al., 2018). The European Union established some directives with limitations for the use of sewage sludge in the ground, highlighting Directive 86/278 / EEC (Directive 1986).

Nevertheless, sewage sludge could be a good raw material for the production of biochar. Biochar is a pyrolyzed component rich in carbon that can be produced from different organic sources. Both the raw material and the pyrolysis process will result in different types of qualities and characteristics for the biochar (Chen et al. 2014). The pyrolyzed biomass has important and positive properties for the soil such as carbon sequestration and its stabilization in the soil or the availability of nutrients and its high retention capacity (Laird et al., 2009). The high concentrations of organic matter, N, P, K, Ca, Mg, S and micronutrients of the biochar and its possibility of being released directly favor the enrichment of the soil. In addition, the biochar also favors the remediation of soils (Esposito, 2013; Lehmann et al., 2003). However, it must be considered that the biochar can also contain polluting and toxic compounds from the raw material (Wang et al., 2017; Lyu et al., 2016). At present, there are different processes and machinery to produce the biochar and as mentioned above, this will also affect the final properties of the product.

The degradation of biochar in the soil occurs slowly and can remain in the soil for hundreds of years, which makes it difficult to study. Its stability is closely linked to carbon mineralization (Lehmann and Joseph, 2009). The carbon in the biochar can be classified into labile fraction and recalcitrant fraction (Lehman et al., 2006). The high stability of the recalcitrant fraction

complicates knowledge about the total carbon stability of the biochar. In addition to the type of raw material and the process of pyrolysis, there are several factors to consider that may affect its degradation. Many experiments have been carried out to know the stability of biochar in the soil. Different properties can be studied to know the stability of the carbon in a direct or indirect way, they could be divided in the analysis of the carbon structures, the analysis of the carbon fuel and the stable carbon fraction and the incubation and modelling (Leng et al., 2018). Each of these types of studies can be carried out according to different methods.

2. Work Objectives and Hypothesis

Sewage sludge is a source of organic matter, nutrients and can contain toxic compounds. Its origin as well as its location can affect its properties and the percentages of each of its elements. In addition, pyrolysis helps the transformation of organic matter and nutrients into more stable compounds.

For the study of these transformations the following objectives were established:

1. To evaluate differences in the content and bioavailability of nutrients among different sewage sludge samples.

2. To evaluate differences in carbon stability among sewage sludge samples.

3. To determine the effect of low- temperature pyrolysis on carbon stability and nutrient bioavailability of different sewage sludge samples.

Hypothesis:

We can expect that produced Sewage sludge from different waste water plants has important content of organic matter and nutrients, they differ significantly.

We can assume, that the amount of stable C and the concentration of available nutrient will change when sewage sludge is thermally processed.

3. Literature Review

3.1. Sewage sludge

Sludge is a waste output result of water treatment in waste water treatment plants (WWTPs). The waters that reach these plants have diverse origins such as rural, industrial, municipal or natural. Through the sewage network, water is collected from stores, residences, establishments and so on, and they are combined with rainwater, underground and surface water, and collectively flow to the WWTPs where they are processed (European Communities, 2016; Sludge News, 2019; Center for Food Safety, 2019). After the processing of the water there remain solid insoluble residues known as biosolids or sewage sludge (SS).

The increase in the world population as well as the increase in the number of households connected to the sewage network have resulted in an intensification of sludge production. In addition, in some countries, wastewater treatment follows strict guidelines (Agrafiotia et al., 2016). The elimination of these sludges in a safe way is one of the main environmental issues to be treated around the world. Different processes have been carried out, among which are: land application, landfills and incineration or dumping into the sea (Singh and Agrawal, 2008). The use of these sludges for agricultural purposes offers a cost-effective elimination of this waste product, besides being a form of recycling of organic matter, nutrients and macro-elements that are a favorable source for agriculture (Spanos et al., 2014). Waste that is broken down by microorganisms in the soil has a positive effect on plants. The nutrients are released, rendering them available for plants to uptake via their root systems (Andersson and Nilsson, 1972).

The sewage sludge has a high concentration of organic matter, N, and P, which are important nutrients for plants. Therefore, after an appropriate treatment, the sewage sludge is suitable for application on land as fertilizer. However, the risk of soil contamination must be considered (Yoshida et al., 2018). These sludges may contain significant amounts of toxic compounds such as organic chemical as absorbable organic halogen compounds (AOX), 4-nonylphenole (NPE), linear alkylbenzene sulphonates (LAS), polychlorinated biphenyls (PCBs), Polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs), Di-2-(ethyl-hexyl)-phthalate (DEHP), polycyclic aromatic hydrocarbons (PAHs). Also, there is a certain concentration of heavy metals and pathogenic microorganisms, which can present a danger to the environment and even to living beings (Spanos et al., 2014).

3.1.1. Production of sewage sludge

The general treatment of water cleaning and whereby the sludge is obtained can be divided into three sub-processes: primary treatment, secondary treatment and tertiary treatment. The primary treatment eliminates the organic and inorganic solid sediments and materials that is in suspension or floating. The effluent from this process is known as primary sludge. In the secondary treatment, it is intended to eliminate biodegradable organic matter through biological aerobic treatments. The sludge obtained in this process is known as secondary sludge and is usually mixed with primary sludge to continue sludge processing (Pescod, 1992; Gerbalan and Pepper, 2009). The third treatment is physicochemical and is not always carried out. It is about eliminating more concrete substances of organic, inorganic or refractory or dissolved substances (Iyyanki et al., 2017).

Common methods for treating and stabilizing sludge treatment can be summarized in three main different processes that are thickening, dewatering, and digestion processes. In some cases, due to the type of sludge, more steps can be added in the treatment. In many cases, before starting the treatment, a preliminary treatment is carried out that consists of crushing and detecting the undesirable substances of large size (Karagiannidi et al., 2011). Thickening is a process where the size and quantity of solids is increased to facilitate the rest of the treatment. It is a physical process in most cases and can be performed in various ways such as co-settling, gravity settling, flotation, centrifugation, gravity belt, and rotary drum. With dewatering process, it is intended to achieve a solid fraction (Metcalf and Eddy, 1997). It can be done through different processes that are air drying on sand beds, centrifugation and filtration. Both filtration and centrifugation can cause the loss of some nutrients (Stehouwer, 2010).

The stabilization of sewage sludge can be carried out by anaerobic digestion, aerobic digestion or lime/alkaline stabilization. The stabilization of the sludge is accomplished to reduce pathogens, bad odors, and to reduce the potential for putrefaction. Where the potential for putrefaction are situations that occur when microorganisms appear in the organic fraction of the sludge. With these processes an increase in the solids content is also achieved. In the case of aerobic digestion, some losses of N can occur, while with anaerobic digestion the nutrients of the plants are conserved effectively (Stehouwer, 2010; Kacprzak et al., 2017; Ambulkar, 2018). The process of stabilization of the sludge before its application to the soil is important since it will affect the mineralization of C and N. Better stabilization of this material will favor a longer residence period of N and C in the soil (Yoshida et al., 2018; Ambulkar, 2018).

3.1.2. Sludge disposal and related legislation in EU

The total amount of sewage sludge produced in 2010 by the countries of the European Union was approximately 9,500 thousand tons according to the data obtained by EUROSTAT (EUROSTAT, 2015). Based on this data, a great difference can be observed in the production of these sludges between the different countries of the European Union. United Kingdom, Germany, Italy, France and Spain are leaders in their production. Table 1 shows the evolution in sludge production from year 2007 to 2015 in the different countries of the European Union.

Table 1: Evolution of sewage sludge production in EU countries from 2007 until 2015 (thousand tons of dry matter) (EUROSTAT, 2015).

Country	Year								
	2007	2008	2009	2010	2011	2012	2013	2014	2015
Belgium	129	140	-	176	-	157	-	-	-
Bulgaria	39.9	42.9	39.4	49.8	51.4	59.3	60.3	54.9	57.4
Czech Republic	216	220	207	196	218	263	260	239	210
Denmark	140	108	-	141	-	-	-	-	-
Germany	2040	2052	1949	1893	1946	1848	1808	1837	1820
Estonia	28.8	22.2	21.8	18.8	18.3	21.7	18.8	-	-
Ireland	86.4	103	107	90	85.7	72.4	64.6	53.5	58.4
Greece	134	136	152	-	147	118	113	116	-
Spain	1152	1156	1205	1205	-	1082	-	-	-
France	-	1086	-	966	-	987	887	962	-
Croatia	-	-	29.6	30.3	31	42.1	32.1	16.3	17.9
Italy	-	-	-	1102	-	-	-	-	-
Cyprus	7.8	7.5	9.2	7.0	6.8	6.5	6.1	6.2	6.7
Latvia	23.3	19.3	22.3	21.4	19.7	20.1	22.8	-	-
Lithuania	-	-	-	51.3	51.8	45.1	41.4	40.7	42.9
Luxembourg	16.2	12.8	-	9.7	-	7.7	-	-	9.16
Hungary	205	172	149	170	168	159	170	167	157
Malta	0	0.1	0.8	1.24	6.06	10.5	9.64	8.5	8.44
Netherlands	353	353	350	351	351	346	339	344	-
Austria	-	254	-	263	-	266	-	239	-
Poland	533	567	563	527	519	533	540	556	568
Portugal	189	-	344	-	-	339	-	-	-
Romania	99.6	79.2	121	82.1	114	85.4	173	192	211
Slovenia	21.2	20.1	27.3	30.1	26.8	26.1	27.2	28.3	29.1
Slovakia	55.3	57.8	58.6	54.7	58.7	58.7	57.4	56.9	56.2
Finland	147	144	149	143	141	141	-	-	-
Sweden	217	214	212	204	200	208	208	201	198
United Kingdom	1825	1813	1760	1419	-	1136	-	-	-

(-) Not available data

Table 2 shows the total amount of sludge available in 2010 and the amount that was destined for each purpose in every EU country. Although all the data is not available, it can be observed that the main destination for sludge is the use in agriculture. The country with the largest amount of sludge destined for agriculture is the United Kingdom with 1118 thousand tons followed by Spain with 995 thousand tons.

Table 2: Sludge disposal and destination in EU countries (thousands of tons of dry matter) (EUROSTAT 2010).

Country/2010	Sludge disposal - total	Sludge disposal - agricultural use	Sludge disposal - compost and other applications	Sludge disposal - landfill
Belgium	131	17.3	0	0
Bulgaria	39.7	13.6	0	14
Czech Republic	196	101	56.9	16.3
Denmark	115	74	-	1.4
Germany	1889	568	317	0
Estonia	16.7	2.7	11.5	2.6
Ireland	90	82.7	7.1	0.2
Greece	-	-	-	-
Spain	1205	995	-	95.7
France	950	727	-	42.3
Croatia	-	-	-	-
Italy	954	316	-	462
Cyprus	7.0	5.3	0	0
Latvia	21.4	9.3	2.2	1.3
Lithuania	20.8	7.9	11.2	0.482
Luxembourg	6.7	5.2	-	0
Hungary	131	4.81	77.2	39.2
Malta	1.2	0	0	1.2
Netherlands	333	0	0	0
Austria	263	44.4	83	20.8
Poland	527	109	30.9	58.9
Portugal	-	-	-	-
Romania	45.5	1.9	1.3	40.5
Slovenia	30.1	0.5	0.2	3
Slovakia	54.8	0.92	35.29	6.7
Finland	143	7.5	132	2.8
Sweden	186	50.5	65.2	7.5
United Kingdom	1390	1118	-	8.8

(-) Not available data

In 1975 the Waste directive called on member states to manage waste that focused on the elimination, prevention and protection of the environment. Directive 86/278/EEC on sewage sludge focuses on promoting the use of sewage sludge in agriculture (Directive 1986). The necessary precaution must be taken to avoid negative effects on the soil and vegetation, as well as on animals or human beings. In soils, only treated sludge may be applied and are

defined as those that have been subjected to biological, chemical or thermal processes with the intention of reducing the fermentation capacity and other hazards that may affect health. Directive 86/278/EEC sets out the limits of heavy metals in sludge designated to the use of agriculture. There are some national regulations in some countries that expose particular and more stringent limits for the concentration of heavy metals. Denmark, Finland, the Netherlands and Sweden are the countries with the strictest regulations as can be observed in table 3. At the other extreme, the United Kingdom is the only country in which no limit values are specified for heavy metal concentrations in sludge (Directive 1986).

Table 3: Limit values for concentrations of heavy metals in sludge of different countries (mg/kg dry matter) (Stylianou et al., 2008).

Metal	86/278/EEC (range)	Sweden	Netherlands	France	Czech Republic
Zn	2500-4000	800	300	3000	2500
Cu	1000-1750	600	75	1000	500
Ni	300-400	50	30	200	100
Cd	20-40	2	1.25	20	5
Pb	750-1200	100	100	800	200
Cr	-	100	75	1000	200
Hg	16-25	2.5	0.75	10	4
Mn	-	-	-	-	-

(-) Not available data

In the case of organic compounds, Directive 86/278/EEC does not offer limit values, but some countries have national regulations that expose the requirements in this area. The table 4 shows the limits imposed in Austria, Denmark, France, Germany and Sweden.

Table 4: Limit values for concentrations of organic compounds in sludge of different countries (mg/kg of dry matter) (European Commission 2009; Decree No. 437/2016).

Organic compounds	EU	Denmark	Sweden	Lower Austria	Germany	Czech Republic
AOX	500	-	-	-	500	500
DEHP	100	50	-	-	-	-
LAS	2600	1300	-	-	-	-
NP/NPE	50	10	50	-	-	-
PAH	6^1	3^1	3^3	-	-	10
PCB	$0,8^2$	-	$0,4^4$	$0,2^5$	$0,2^5$	0.6
PCDD/F (ng TEq[6]/kg d.w.)	100	-	-	100	100	-

(-) Not available data

AOX: Adsorbable organic halides
DEHP: di(2-ethylhexyl) phthalate
LAS: linear alkylbenzene sulphonates
NP/NPS: Nonylphenols
PAH: Polycyclic aromatic hydrocarbons
PCB: polychlorinated biphenyl
PCDD/F: Polychlorinated dibenzo-p-dioxins and dibenzo-furans

[1] Sum of acenapthene, phenanthrene, fluorine, fluoranthene, pyrene, benzo(b+j+k) fluoranthne, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3- c,d)pyrene
[2] Sum of 6 congeners PCB 28, 52, 101, 138, 153, 180
[3] Sum of 6 compounds
[4] Sum of 7 congeners 28, 52, 101, 118, 138, 153, 180
[5] Each of the six congeners PCB 28, 52, 101, 138, 153, 180.
[6] TEq- Toxicity equivalents

Table 5: Limit values of pathogens (dry matter) (European Commission 2009).

	Salmonella	Other pathogens
Denmark	No occurrence	Faecal streptococci-< 100/g
France	8 MPN/10 g DS	Enterovirus- 3 MPCN/10 g of DS Helminths eggs- 3/10 g of DS
Finland	Not detected in 25 g	Escherichia coli <1000 cfu
Italy	1000 MPN/g DM	-
Luxembourg	-	Enterobacteria- 100/g no eggs of worm likely to be contagious
Hungary	-	Faecal coli and faecal streptococci decrease below 10% of original number
Poland	Sludge cannot be used in agriculture if it contains salmonella	-

(-) Not available data

MPN: most probable number

DM: Dry matter

Directive 86/278/EEC also does not include limits on the concentration of pathogens in sludge but, as with organic compounds, there are several countries that have their own regulations that limit their concentration (Table 5).

In 1991, new regulations were established in European Union for the use and application of hazardous waste. In addition, Directive 91/271/EEC dealing with urban wastewater implements new quality rules for wastewater and requires monitoring in the municipal treatment of wastewater and the total elimination of municipal sewage sludge for agglomerations (Kacprzak et al., 2017). This directive was modified in 98/15/EC and finally became operational in 2005. The most important article in directive 91/271/EEC is number 14, which talks about the sludge produced in the course of wastewater treatment and its reuse in the most convenient situation to avoid environmental pollution or health hazards. With this article, the member states are also obliged to guarantee the suppression of sludge in the surface waters by dumping of ships or other means such as the release of pipes before December 31, 1998 (Kacprzak et al., 2017).

The Directive of the European Parliament and Council 2008/98/EC of November 2008 on waste was responsible of sewage sludge. In addition, it establishes that the priority is the prevention of the creation of waste, followed by a good disposal of the waste already produced, looking for the most optimal forms of recycling or recovery, speaking both of the energy consumed in the process and of organic recycling. Finally, the elimination of these wastes must be considered, since it is not possible to suppress their production.

Examples of legislative directives for the quality of sludge can be found as follows. The directive 2010/75/EC of November 24, 2010 dealing with industrial issues is responsible for updating several directives as well as their combination (Commission, 2010). Among the Directives that help to compose the directive 2010 are the Directive 2008/1/EC which deals with the issue of pollution and control, Directive 2001/80/EC which is responsible for the regulation of pollutant emissions from air pollution control facilities. Air combustion, Directive 2000/76/EC dealing with the incineration of waste and the Directive of the European Parliament and Council 2009/28/EC which is responsible for the promotion of energy from renewable sources.

It is important to consider two more documents, the Technical Report for the End-of-Waste Criteria in Biodegradable Residues Subject to Biological Treatment and the Third Working Document in which sewage sludge is selected as part of the positive waste list and its positive role as fertilizer is clarified.

The Czech Republic has the following specific decrees for the treatment and disposal of sewage sludge:

Decree No. 383/2001. Decree of the Ministry of the Environment on details of waste management (originally in czech vyhlášky č. 383/2001 Sb., o podrobnostech nakládání s odpady a změně). This degree aims to address the necessary requirements in equipment for addressing the treatment of waste in terms of acquisition, rehabilitation, incineration of hazardous waste (sewage sludge treatment) and disposal of waste and hazardous waste.

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). This ordinance objective is to provide some guidelines on technical requirements in terms of utilisation of waste on ground surface (Title V) along with basic concepts and operating conditions of waste disposal in landfills.

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 regulation provides specific details on how to manage biodegradable waste (biowaste) in terms of quality of waste for direct utilisation and requirements for waste treatment determined by the extent and type of biowaste.

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 explains the sludge application program and the conditions on the preferred facilities, necessary technical requirements and treatment for sludge storage.

3.1.3. Properties of raw sewage sludge and its chemical composition

Sludge is a heterogeneous material and its composition is different in each zone or city where they are produced (Sommers, 1997; Lampert et al., 2007). In general, there are several factors that influence the characteristics of the sludge and affect its behavior and management. Among them are the composition of the wastewater, the treatment to which they are subjected and time between production and treatment (Fytili and Zabaniotou, 2008; Baroutian, et al., 2013). The principal component of sewage sludge is water. The dry matter is the second most abundant component and are composed of organic and inorganic substances. The amount will vary throughout the process depending on whether we speak of primary, secondary or tertiary sludge and will also depend on whether the stabilization is carried out aerobically or anaerobically (Lenntech, 2019).

There is a significant content of organic compounds in sewage sludge. The organic compounds present in the sludge are carbohydrates, lignin, soaps (Ca/Mg salts of fatty acids) and proteins (Werle and Dudziak, 2014; Di Bonito, 2016). Some of the organic compounds in the composition of the sludge have hydrophobic characteristics and one of the main ways to remove them from the wastewater is through their absorption to the sludge solids (Harrison et al., 2006; Werle and Dudziak, 2014). The organic compounds of the sewage sludge have a high calorific value and produce a high amount of biogas during the digestion of the sludge (Kijo-kleczkowska et al., 2012).

In the sludge there is also a high concentration of nutrients for plants such as N, P, S, Cu, Zn, B, Mn, Fe, Mo. Usually the concentration of N and P is high, but in the case of nitrogen, its concentration can vary and is not directly available to plants (Tabatabai and Frankenberger, 1979). On the other hand, sludge also contains toxic elements such as Ni, Cr, Cd, Se, As, Co, Pb, and Hg. Although Ni is considered a nutrient for plants, it can also be considered as a toxic element. Sludge is also composed by some organic chemicals which are toxic and hazardous as synthetic detergents, phenols and their derivatives, dioxins and furans, polychlorinated biphenyls (PCBs), organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), adsorbed and extracted chloro derivatives (chloroanilines, chlorobenzenes), sex hormones, to name a few (Werle and Dudziak, 2014; Strandberg et al., 2001). The amount of trace elements, present in organic and inorganic matter, present depends very much from one site to another. It is important to be aware of their concentration before you give the sludge a destination (Tabatabai and Frankenberger, 1979; Harrison et all., 2006).

3.2. Pyrolysis and biochar production

Pyrolysis is a thermal treatment carried out at high temperatures and under absence of oxygen and in which a decomposition of organic matter occurs (Rofiqul Islam et al., 2008). As a result of this process, we obtain a solid fraction (biochar), a liquid fraction composed of an aqueous fraction with organic water-soluble components and gaseous fraction. The organic compounds in the liquid phase depend on the composition of the biomass as well as the amount of lignin and cellulose in the raw material (Lee et al., 2016). The liquid phase, also called bio-oil, has a variable composition, but it is known that more than 300 types of organic compounds can be found. Acids, alcohols, ketones, aldehydes, phenolics, hydroxyaldehydes, carboxylic acids, hydroxyketons, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds are elements that can be part of the liquid phase (Bruckman et al., 2016). The gaseous fractions main components are CO_2, CO, H_2, O_2, N_2 and C_xH_y (Inguanzo et al., 2002). The reaction that takes place can be expressed as (Chen et al., 2014):

$$C_xH_yO_z + Q \rightarrow Biochar + Liquid + Gas + H_2O$$

Where Q is the heat that needs to be applied in the reactor so that the reactions can take place. Q includes the fractions: heat of vaporization of humidity (Q_1), required heat of pyrolysis (Q_2), and loss of radiation from the reactor to the surroundings (Q_3). Biochar is a carbon-rich component, derived from organic matter and obtained after the thermal decomposition of organic material in the absence/low concentration of oxygen (solid fraction). The temperatures used during pyrolysis cover a wide range (Lehmann and Joseph, 2009), for example in the experiment carried out by Yuan et al. (2011) the pyrolysis was done with three different temperatures 300ºC, 500ºC and 700ºC. The type of biomass used for its production together with the pyrolysis conditions are determining factors in the properties and quality of the biochar (Demirbas, 2004).

The biochar can be produced with different organic sources as raw material, among which are organic residues of different origins such as forest and agricultural biomass (Harsono et al., 2013), urban solid waste (Chen et al., 2014) or livestock waste (Cely et al., 2015). The chemical composition of each raw material, the volume of production, its dispersion as well as other economic elements will be factors of competition between the different types of biomass (Verheijen, et al., 2010). Unlike other types of organic matter, biochars have a high content of aromatic carbon compounds (Zielinska et al., 2010). This property can be considered defining

in terms of chemical composition, since it has not been possible to reach a complete definition because of its diversity (Schmidt and Noack, 2000).

Main biochar element is carbon, other elements present in the biochar are oxygen, hydrogen, sulphur, base cations and heavy metals. These elements can be found in different concentrations. In addition, the biochar stands out for its high porosity and its large surface area, which favors the retention of water (McElligott, 2011). The pyrolyzed biomass has several positive effects, (Laird et al., 2009) among which stand out are the carbon sequestration in the soil in the long term and the stable fraction of C in the biochar. This means that carbon can be kept in the soil for hundreds of thousands of years, thanks to the recalcitrant capacity of biochar. It is also used in remediation; due its absorbing potential it can be used as an amendment of contaminated soils (Lehmann, 2007; Laird et al., 2009; Roberts, et al., 2009; Steinbeiss, et al., 2009). On the other hand, it is a form of energy generation. The renewable energy produced by the biochar is found both in the heat produced and in the gases that are released during the process (Lehmann et al., 2003). In addition, in the case of using wastes as a source, after pyrolysis there is a reduction in the volume and weight of these waste materials, which is considered as a biomass waste management (Laird et al., 2009).

In the soil, biochar produces other positive effects, providing an increase in moisture retention, and the capacity of cationic exchange increases with time, when the biochar is in contact with oxygen and water (Karhu et al., 2011; Laird et al., 2009). It has been also shown that there is greater retention of nutrients due to its absorption capacity (Lehmann et al., 2003; Novak et al., 2009b). Other components that can also be found in the biochar are some pollutants that usually have originated from the raw material, as in the case of sludge. During pyrolysis, these pollutants are converted and, in some cases, eliminated. However, during this thermal process new contaminants may also appear as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dioxins and furans (PCDD/DF) (Wang et al., 2017; Lyu et al., 2016). This information is important with regards to the damages that can occur in the soil when coming into contact with these harmful elements (Lievens et al., 2009). In order to know the quality of the biochar destined to agricultural activities, Kuwagaki and Tamura (1990) fixed 7 properties that must be studied: pH, volatile compound content, water retention capacity, apparent density, pore volume, the specific surface and trace elements and contaminants contents.

3.2.1. Pyrolysis technology

Current pyrolysis techniques seek to achieve some general objectives that improve efficiency, both economically and energetically. There are common characteristics for the pyrolysis techniques used nowadays (Chen et al., 2014). Most commercialized pyrolysis technologies are combined with other processes by gasification. Another characteristic is a pre-treatment of the materials to dispose of the unwanted materials that are usually made before the pyrolysis. In the process of pyrolysis there are a variety of machines that allow to carry out the pyrolysis of the biomass at the desired temperatures. Kilns, reactors and retorts, are some examples. Depending on whether the pyrolysis will be fast or slow, a certain device will be used.

Rotary kilns

Rotary kiln is one of the main kilns used (Fig. 1). They are especially employed in the pyrolysis of fuels and they are usually used for slow pyrolysis; the heating rate is usually not higher than 100ºC min-1 and the residence times are usually 30 min or 1 h. One of its main advantages is that solids of different sizes, shapes and heating values can be treated in this type of furnace, it also allows a continuous treatment and has a heat transfer to the biomass better than other equipment (Czajczynska et al., 2017; Kerna et al., 2012). Another one of its positive features is that due to the shape of the oven and the slow rotation, a good mixture of waste is produced (Chen et al., 2014).
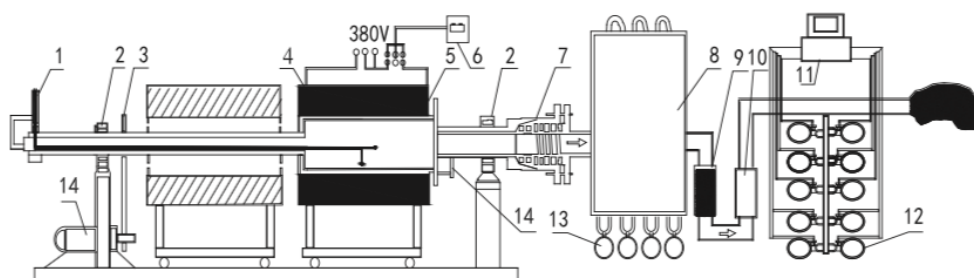
Rotary kiln pyrolysis system (1-thermometer; 2-bearing; 3-gear transmission; 4-electrical furnace; 5-rotary kiln; 6-temperature controller; 7-seal; 8-two-steps condenser; 9-filter; 10-accumulative flowmeter; 11-computer; 12-gas sampling device; 13-feed and discharge opening; 14-speed adjustable electrical machinery)

Figure 1: Rotary kiln pyrolysis system (Dezhen et al., 2015).

Fixed bed sheets

This type of reactors is widely used thanks to its simplicity of design (Fig. 2). The heating rate for these ovens is low due to low heat transfer coefficient. They have an external heat source that heats the reactor where the raw material is located. The pyrolysis in this case is carried out in the presence of an anaerobic atmosphere (Czajczynska et al., 2017; Wang et al., 2005). The main drawback of this type of equipment is that by maintaining the static sample during combustion, not all areas will receive the same heat.

Fixed bed pyrolysis system (1-furnace; 2-pyrolysis reactor; 3-thermocouple; 4-temperature controller; 5-N_2 pipe; 6-liquid gathering tank; 7-thermometer; 8-condenser; 9-pressure gauge; 10-sampling vent)
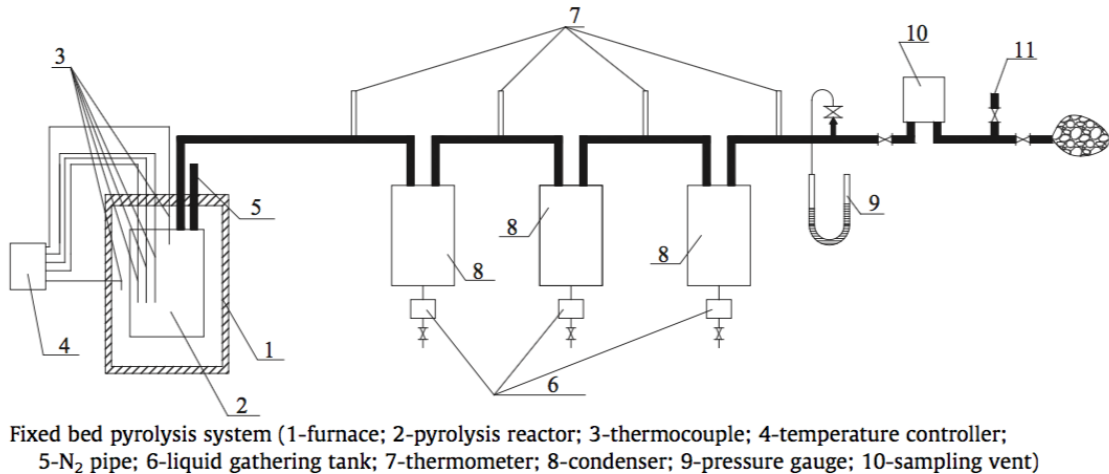
Figure 2: Fixed bed pyrolysis system (Dezhen et al., 2015).

Fluid bed

The fast pyrolysis can be carried out with several different reactors but the most used is the fluid bed (Fig. 3). Their heating temperature is characterized by being high. They are appropriate to study how affects the influence of temperature and residence time on the raw material. This type of kilns has a cyclone that traps the ashes at the exit of the pyrolysis reactor where the raw material is incinerated. Ash can be reused as chemical fertilizer for soils (Zhanga et al., 2011). For the pyrolysis of municipal solid wastes is not the most appropriate technique, since it requires small material and also can produce certain problems in the separation of char with the bed. (Czajczynska et al., 2017; Chen et al., 2014). Since the residence time is shorter than in slow pyrolysis techniques, the biochar produced will show different characteristics (Lehman and Joseph, 2009).
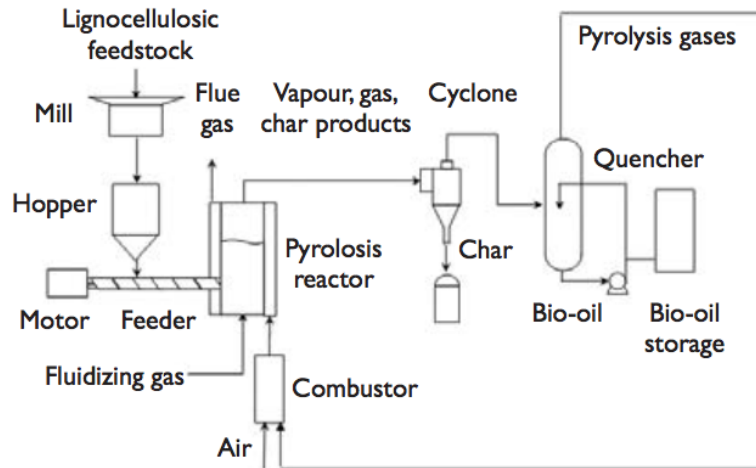
Figure 3: Fluidized-bed fast pyrolysis reactor (Lehmann and Joseph, 2009).

Tubular reactors

Tubular reactors (Fig. 4) are formed by a series of fixed walls through which the raw material advances. The movement of biomass through the tube can be done in different ways as with the help of the action of a rotating screw. The source of heating is external although in some cases a heat carrier such as sand, is used to heat. It is important to know the heat transfer coefficient to get a good performance. The operation is continuous and contributes to a large heating surface (Chen et al., 2014; Lehman and Joseph, 2009).
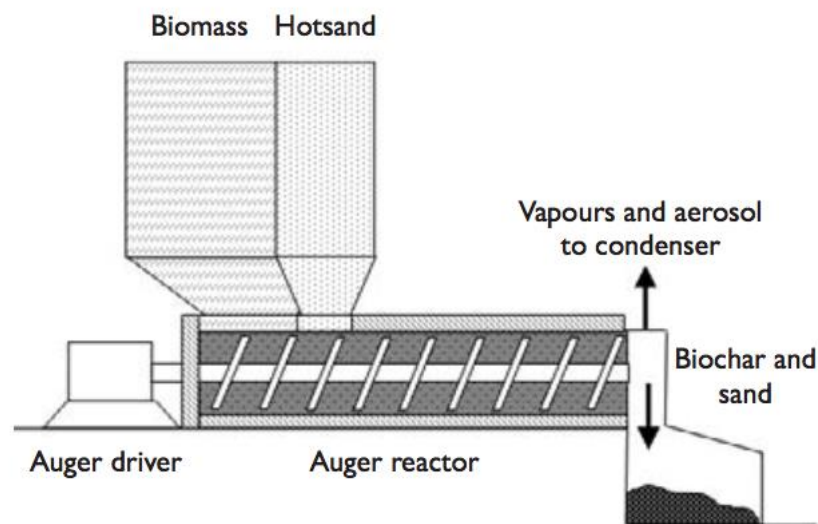
Figure 4: Screw pyrolyser with heat carrier (Lehmann and Joseph, 2009).

3.2.2. Biochar properties based on pyrolysis conditions

The properties of biochar are affected mainly by the raw material used and by the pyrolysis conditions. The yield, the size of the pores, the concentration of nutrients, the pH, the surface area or the ratio H:C, O:C, are some of the properties that vary depending on the conditions of the carbonization process. The treatment temperature and the pyrolyzed time are two of the factors that influence the final characteristics of the biochar the most (Chen et al. 2014; Manyà et al., 2014; González el al., 2017). Numerous studies and experiments have been carried out in order to know to what extent and in what areas these factors are affected.

In the case of the treatment temperature, the studies carried out by Hossain et al., (2011) and Kim et al., (2012) showed that an increase in temperature leads to a decrease in biochar yield and an increase in the gaseous fraction, in the case of the liquid fraction, a small increase was observed at 450 ºC to 650 ºC, but at higher temperatures it kept constant. This could result in a reduction in yield. Also, in the experiment carry out by Devi (2014) this effect on the yield can be observed (Fig. 5).
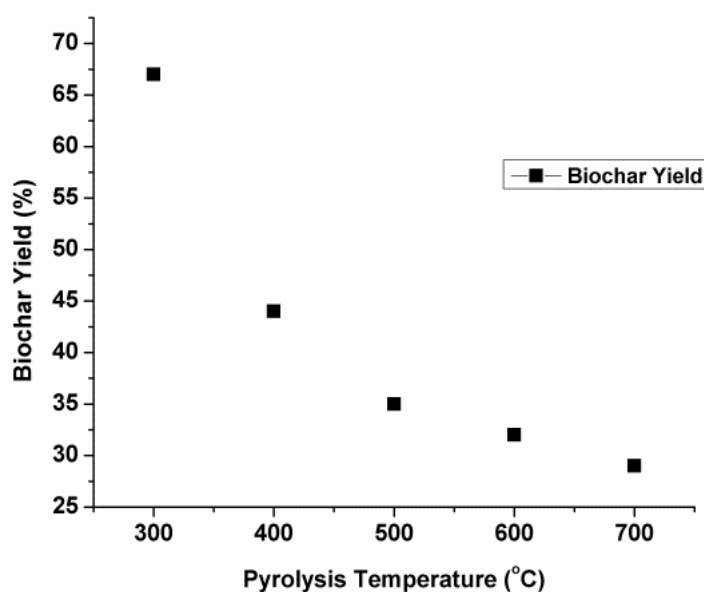
Figure 5: Biochar yield due pyrolysis temperature (Devi, 2014).

In the experiment carried out by Ahmad et al. (2012), in which soybean stover and peanut shells were used as raw material and pyrolysis was carried out at two different temperatures, at 300 °C and at 700 °C, a reduction in the yield in the process carried out at 700 °C was also observed. On the other hand, Downie et al. (2009) indicated that the loss of the solid fraction is closely related to the source material. The biomass that is going to be pyrolyzed is composed, in broad strokes, mainly by hemicellulose, cellulose and lignin. The hemicellulose is degraded around 200-260 °C and the cellulose degrades between 240-350

°C, during its decomposition organic acids and phenolic substances are produced that lowered pH of the products. In the case of lignin decomposition, it starts around 280ºC, but it depends on the nature of the biomass (Cao and Harris, 2010; Jouhara, 2017; Nassar and MacKay, 1993). It has been observed in the study carried out by Sumiyaki Association (1991) a great loss of cellulose in temperatures between 180-250 ºC, while the loss of lignin was almost linear, this is closely related to the temperature of degradation of each element. The pH of the biochar can vary from basic to acid according to the pyrolysis conditions. Some acid functional groups such as carboxyl are degraded at high temperatures; increasing the temperature of the treatment results in higher pH values of the biochar. At 700 ºC, they are alkaline; while those produced at low temperatures between 300 and 400 ºC are acidic (Yuan et al., 2015; Hossain et al. 2011; Wei et al., 2017; Abe et al., 1998). Table 7 shows the pH values of the raw material and the pyrolyzed biochar at 5 different temperatures in the experience carried out by Yuan et al., 2015.

Table 6: pH of sewage sludge and biochar pyrolyzed at different temperatures (Yuan et al., 2015).

	Sludge	300ºC	400ºC	500ºC	600ºC	700ºC
pH	5.67	6.66	7.4	7.5	8.1	8.4

The surface area and the amount of ash increased at high temperatures in the study developed by Wang et al. (2013). The surface area increases due to the removal of volatile materials resulting in increased micropore volume (Lee et al., 2010). The treatment time is another fundamental parameter that affects the final properties of the biochar. We can talk about 3 different types of pyrolysis due to time. Slow pyrolysis uses temperatures that vary between 300 ºC and 800 ºC and lower heating rates (0.1-1 ºC s^{-1}). The amount of solid fraction is greater than in rapid pyrolysis. The increase in residence times causes an increase in the surface area and the amount of ash (Wang, et al., 2013). Rapid pyrolysis is carried out at temperatures close to 500ºC, characterized by high heating rates > 1000ºC/s (Bridgwater, 2007). Flash pyrolysis is the third class of pyrolysis, it is a type of rapid pyrolysis with higher heating rates (Onay and Kockar, 2003). The distribution of the main products is similar to that obtained in rapid pyrolysis.

The different types of sources under biochar is produced affect significantly the properties of the pyrolyzed material. In the study conducted by Aragao de Figueredo et al. (2017) biochar

was produced from sugarcane, eucalyptus and sewage sludge. Two different temperatures were used, 350 °C and 500 °C. Sugar bagasse with 5.5 g/kg and eucalyptus bark with 5.3 g/kg showed to have a slightly higher amount of K than the sewage sludge with 1.2 g/kg. The difference between them increased significantly after pyrolysis at 500 °C, obtaining a result of 39 g/kg for sugarcane bagasse, 26 g/kg for eucalyptus bark and only 0.1 g/kg for sewage sludge. However, the sewage sludge showed a higher concentration of both P and S than the other types of raw material as well as after pyrolysis. The biochar of sewage sludge and sugarcane showed a decrease in carbon content with the increase in temperature. In the case of the biochar produced by sewage sludge, most of the C was oxidized by dichromate. Biochar produced by eucalyptus showed a more stable fraction.

In the experiment carried out by Brendova et al (2012) the biochar of three different raw materials, wood, corn and meadow hey and three different pyrolysis temperatures 450 ºC, 500 ºC and 550 ºC were studied. In this study it was observed that biochar produced of wood has higher carbon content than that produced with corn or meadow hey, which indicates that biochar produced with raw materials of herbaceous origin have lower carbon yield. On the other hand, it was observed that the specific surface of the three types of biochar increases directly with the increase in temperature.

3.2.3. Availability of nutrients from biochar

Due to its characteristics, biochar plays an important role in the presence of some nutrients in the soil, as well as the absence of them (Esposito, 2013; Lehmann et al., 2003; Cheng et al., 2008). There is a clear certainty of the improvement in soil nutrients after applying the biochar, but it has been observed that these benefits vary according to soil type, climate and other conditioning factors (Pandit et al., 2018).

Within the biochar composition there are available nutrients that can be released into the soil. The concentrations of N, P, K, Ca, Mg, S and micronutrients present and with the possibility of being released play an essential role for the enrichment of the soil. Each one of them has different speed of release that would depend largely on their availability (Esposito, 2013). Some studies show that biochar produces changes in the available concentration of N and P and K. The total amount of these nutrients is not totally linked with their available forms for plants, ammonia $(NH_4)^+$, nitrate (NO_3^-), phosphate (PO_4^{3-}) and K but they do have a relationship (Ding et al., 2017). An increase in available forms of retention as NH_4^+ has been seen (Glaser et al., 2002; Lehmann et al., 2003; Novak et al., 2009a). The increase in the amount of ash leads

to a greater amount of nutrients such as Ca, Fe, Mg, S, Cu and Zn that compact the ash. The ash increase is considered beneficial for the plants (Cao and Harris, 2010; Hossain et al. 2011; Shinogi and Kanri, 2003). Also, the increase in the availability of K is due to its high concentration in biochar ash. On the other hand, in some studies, there has been a clear increase in the availability of nutrients such as Ca or Mg after the application of biochar, in others, this increase has not been visible (Pandit et al., 2018).

In addition, biochar has a high capacity for nutrient retention. This makes this product very useful for soil remediation. It also increases its water retention capacity, making it especially suitable for nutrient rich soils and arid areas (Esposito, 2013). A high available concentration of Al is toxic to plants, the biochar manages to reduce this concentration in many soils that act as a liming agent (Glaser et al., 2002; Major et al., 2010; Martinsen et al., 2014; Yamato et al., 2006). In addition to being a potential source of P, Yao et al. (2013) suggests that BC can play a role in the retention of P applied in fertilizers.

The biochar relieves the stress of nutrients, which increases the cation exchange capacity of the soil, which helps the retention of active nutrients. It also helps the retention and adsorption of nutrients from fertilizers (Esposito, 2013; Cheng et al., 2008). The biochar also produces changes in the pH of the soil, reducing its acidity and this also affects the availability of nutrients. The relationship between P-Al improves when pH is improved. This improvement could be observed in the study conducted by Pandit et al. (2018). The biota of the soil is also affected by the application of biochar; changes in the metabolism of microbes and fungi will occur, and that will also produce changes in the concentration of available nutrients (Cheng et al., 2008).

3.2.4. Stability of carbon in the biochar
The C in the biochar can be found as a constituent of organic wastes, which have different mineralization ranges, which can be classified as labile fractions and recalcitrant fractions (Lehman et al., 2006). The initial properties of the raw material used for biochar will have a clear influence on its stability and longevity (Enders et al., 2012). The labile part of the biochar refers to reactive functional groups together with the non-aromatic C structures. These elements are sensitive to biochemical degradations and carbon fraction can decompose within years or decades, so knowing its stability is relatively simple. Through 14 C dating it has been shown that the charcoal of the biochar or black carbon is one of the most stable components, the

recalcitrant part can take hundreds to thousands of years (Calvelo Pereira et al., 2011; Crombie et al., 2012; Cheng at al., 2008).

This makes the knowledge about the stability of the total carbon a complicated task since stable carbon in this compound is slower than most of the other carbon sources. There have been some studies on this subject as the one carried out by Crombie et al. (2012). As it is shown in this study, the ratios of O: C and H: C have also been indicators of carbon stability. The less C:O and C:H ratios the biochar has, the more stable it becomes (Crombie, et al., 2012). In the case of biochar produced with pine raw material, a reduction in the C: O ratio was observed, being 0.29 for 350 ºC and 0.02 for 650 ºC and in the case of the atomic radio H: C the results showed that for a temperature of 350 °C 0.65 was obtained and for a temperature of 650 0.25 was obtained. Also, according to Calvelo Pereira et al. (2011), the knowledge of the labile fraction in different pedoclimatic conditions, could be an important source of information for future assessments of the proportion of stable C.

3.3. Degradation of biochar in soil

In Terra Preta (Amazonas, Brassil), soils have been found high content of pyrogenic carbon and other essential nutrients such as P, Ca and K (Glaser and Woods, 2004; Glaser et al., 2001). The hypothesis about the origin of these soils are diverse, from burning of forests to cultivating lands till causal fires, but it has been demonstrated by several studies that the indigenous people who inhabited this area benefited from the properties of the soil (Woods and Glaser, 2004).

In addition, this type of soil has been found in other places such as Borneo with an age greater than 10 thousand years (Sheil et al., 2012). Although it is difficult to estimate its stability, the discovery of these soils is a sign of the biochar stability over time. The biochar is made up of different products, which depends to a large extent on the raw material. The stability of biochar in the soil is linked to the absolute and relative stability of the components as well as the production conditions. However, stability refers to different contexts, such as mitigation to climate change or its ability to sequester carbon (Cross and Sohi, 2013). When the biochar is applied to the soil, its aging begins and its physical and chemical properties will be altered in nature. Different studies have been carried out to evaluate the physicochemical changes produced, most of them have been carried out in laboratories and only a few have been carried out in the open field (Dong et al., 2017).

It was shown that the biochar that had been applied to the soil and had begun with its aging had a greater amount of O and N on the surface while there was a reduction of 10% in the C. In addition, there was an increase in polar groups and in Al, Si, P and Ca in soil's biochar (Ren et al., 2018). The aging of biochar also affects the adsorption of pollutants. Although different results have been given in several studies. Martin et al. (2012), showed in their study a decrease in absorption of atrazine and diuron 32 weeks after the application of biochar. Due to the contrary results obtained in other experiments such as that of Jones et al. (2011) in which there were no changes in the absorption, it is deduced that there are different factors that affect this property of the biochar in the soil.

A higher concentration of aromatic structures will reduce the biochar degradation, however, a high number of functional groups with O and N produce a greater reactivity and a lower stability (Cheng et al., 2008; Lehmann and Joseph, 2015).

The degradation or loss of biochar is closely related to C mineralization. It should also be considered that some environmental and soil conditions may induce C mineralization (Singh et al., 2012).

3.3.1. Factors responsible for biochar degradation in soil

The changes of the produced biochar in the soil can be classified in a general way in abiotic, biotic and biological and physical or indirect.

- Abiotic

The surfaces of fresh biochar are hydrophobic and are also characterized by their affectation to the hydrophobicity of the soil. Pyrogenic organic matter in soil- its origin and occurrence, its chemistry and survival in soil environments. These first changes are generally abiotic. Cheng et al. (2006), consider that abiotic changes are more important than biotic ones. Biotic oxidation occurs mainly inside the pores of the biochar particles. Abiotic oxidation favors long-term microbial or biotic mineralization of highly aromatic compounds.

- Biotic

Initially, biotic changes are very slow, but as they age, other interactions between some soil components and biochar are promoted. Biochar can be degraded by microorganisms. The heterotrophic decomposition is the most characteristic (Shneour, 1966; Baldock and Smernik, 2002; Brodowski et al., 2005). Bacteria and fungi are present on the surface of the biochar and

this favors mineralization of the biochar (Brodowski, et al., 2005). Biotic oxidation occurs mainly on the surface and increases by decreasing the size of the particles.

The functions of saprophytic fungi (Wiedner and Glaser, 2013) and granular bacteria are very suitable for the degradation of aromatic and recalcitrant compounds, they have a very important role in the early consumption of biochar (Farrell, et al., 2013). In addition, Hockaday et al. (2006) confirm that there are extracellular enzymes such as β -glucosidase (BG), β-D-cellobiosidase (CB) N-acetyl- β -glucosaminidase (NAG), and phosphatase (PHOS) that result in the degradation of insoluble macromolecules into smaller molecules that are able to be microbially assimilated when added to the biochar. The different climates and ecosystems affect the biochar degradation differently although there is not a wide knowledge on how these factors influence (Cheng et al., 2008; Elzobair 2015)

- Indirects

The annual average temperature and humidity obviously affect the oxidation of carbon. At higher temperatures the decomposition is faster (Cheng et al., 2008). Erosion, leaching translocation or bioturbation also have a role in the loss of biochar. The low density of the biochar's particles can favor its movement. In addition, bioturbation can also be caused by animals (Verheijen et al., 2010; Ameloot et al., 2013)

The fragmentation of particles increases the surface vulnerability to chemical and biological changes. Rain or wind are climatological agents that cause this decrease of particles (Lehmmann and Joseph, 2009). Areas where freezing and thawing occur on a regular basis are vulnerable to particle fracture, since water enters the pores and, when freezing, increases its volume, forcing the walls of the pores (Carcaillet, 2001; Liu et al., 2018).

3.3.2. Methodological approaches for the determination of biochar stability in soil

It is difficult to estimate the degradation of biochar in the soil. Existing methods do not offer information analogous to long-term degradation processes. The long-term loss of C cannot be established efficiently since its short-term loss does not follow a first-order decomposition (Cross and Sohi, 2013).

According to the properties that are measured to assess the aging of the biochar, different techniques will be carried out. To measure the stability of the biochar, one can measure the

stability of the labile fraction of C, the functionality or the degree of aromatic condensation that indicates the abiotic and biotic degradation. Leng et al. (2018) established three types of properties or processes, valid for the determination of the stability of the biochar which can be defined as the analysis of the carbon structures, the analysis of the labile carbon and the stable carbon fraction and the incubation and modeling. In each of them, different methods and technologies are exposed to carry out the study of stability.

- Stability assessment by C structure analysis

<u>Ultimate analysis is based on the analysis of the H:C and O:H ratio.</u>

The relationship between H:C provides information on the aromaticity of biochar. The aromaticity increases when the ratio between H:C decreases (Xiao et al., 2016).

The molar ratio between O:C also provides information on the aromaticity of carbon in the biochar. The classification of the average life of the biochar according to their ratio O:C described Spokas, (2010) defines that the biochars with an O:C ratio of <0.2 are stable and usually persist for more than 1000 years, biochars with an O:C radio between 0.2 and 0.6, have an intermediate half-life that can go from 100 to 1000 years; Biochars with a C:O ratio greater than 0.6 have a half-life of approximately 100 years (Spoka., 2010).

<u>Molecular markers</u>

Molecular markers are also a method that allows to know the carbon structures of the biochar. An example of molecular marker is benzene polycarboxylic acids (BPCA), which helps to know the changes in the properties of biochar and has proved to be a good technique to know the mechanisms of absorption of organic pollutants in the biochar, this is very useful during the aging of the biochar in the soil as a method of investigation of interactions with soil elements (Chang et al., 2018).

- Stability assessment by analyzing labile/stable biochar C

<u>Nuclear magnetic resonance (NMR) analysis</u>

This technique is focused on the aromaticity of biochar. It is based on the direct polarization of C^{13} nuclear magnetic resonance spectroscopy (Verheijen et al., 2010; Budai et al., 2013; Nguyen et al., 2010).

This technique is the most used technique in laboratories for the characterization of carbon structure in biochar. To perform NMR in soil materials, it is necessary to carry out an invasive previous treatment, which will eliminate impurities (Singh et al., 2016).

X-ray diffraction (XRD) analysis

XRD is a method that provides information about C structures and is especially advantageous for biochar with high crystallinity. The XRD spectrum can be used to know the aromaticity, degree of condensation, space between layers, or three-dimensional information among other properties of the C elements present in the biochar. (Lehmann and Joseph, 2015).

Fourier transformation spectroscopy (FTIR)

This method obtains infrared spectra by collecting an interferogram of a sample signal by means of an interferometer and then a Fourier Transform (FT) is performed on the interferogram to cover the infrared spectra of broadband infrared (NIR) to far infrared (FIR). All wavelengths are collected at the same time. FTIR offers information on the functional groups of the fractions of organic matter (Newport Corporation, 2019) Based in the reduction the reduction/loss of O-containing functional groups and aliphatic C-H in comparison to the incremental aromatic C-H and C-C groups (Singh et al., 2016).

Chemical oxidation

One of the most used techniques is chemical oxidation that can be carried out with different chemical compounds. For chemical oxidation, H_2O_2 or dichromate ($K_2Cr_2O_7$) can be used between other oxidant agents. The acid dichromate $K_2Cr_2O_7$ is a powerful oxidizing agent that allows determination of the black carbon in the soil (Certini et al., 2011) knowing the degree of aromatization (Calvelo Pereira et al., 2011) as well as the recalcitrant fraction of C in the biochar (Paul et al., 1997).

Hydrogen peroxide can be useful to explain the depolymerization of carbon by the action of microorganisms. Lignin is degraded by H_2O_2, and oxidation can be accelerated thanks to this agent. Cross and Sohi (2013) used this oxidizing agent H_2O_2 at 5 % to carry out their experiment. After the application, this heat the samples at 80ºC for two days and the samples were dry and ready to analyze.

Thermal degradation

The thermal processes are intended to simulate natural combustion processes, thereby eliminating the labile carbon part of the biochar in order to measure the stable organic aromatic carbon. This allows to measure the thermal stability of the biochar. Qi et al. (2017) used a method of thermal oxidation in which the biochar were burned at 375 ºC during 24h.

Proximate analysis

Proximity analysis is a method that provides information on fixed carbon, volatile matter and the size of the ash fractions. It is a quick and simple method that helps to predict the C stability of biochar in soils. The proximity analysis has been carried out with numerous variations, this lack of protocol has made it difficult in some cases its use in research (Aller et al., 2016).

- Incubation and modelling

The best current techniques are incubation and modeling, but due to their high cost, other characteristics can be measured or studied. It provides data on the longevity of the biochar stability, but this may take decades, since the degradation of biochar in the soil is slow as mentioned above. The modeling allows to calculate a simulated degradation or MRT. In modeling exponential decay models are used as the basis for calculating the total decay rate (Lehmmann and Joseph, 2009; Leng et al., 2018).

4. Methodology

4.1. Location and sampling

This study was carried out using 23 samples of sewage sludge collected from 23 different water treatment plants around Czech Republic. Each kind of sludge was named with a different number, going from 1 to 23.

4.2. Pyrolysis

For economical and time-saving reasons, 11 samples out of the 23 different sludges were selected to be pyrolyzed at two different temperatures of 220 °C and 320 °C in order to study the effects of the heat treatment on the sludge samples (Fig. 6). To differentiate them from the samples of raw material, they were named with the number corresponding to the sample of origin plus the temperature of the thermal treatment to which they were subjected. The samples that were pyrolyzed are from number 3 to number 13.

Figure 6: Pyrolyzed samples. Source: Maite Sánchez Revuelta.

The pyrolysis was carried out in the laboratory with a furnace Carbolite® Typ 301 (Carbolite Gero, UK). The samples that were subjected to the heat treatment were previously ground (4 g, particle size <1 mm). The type of pyrolysis carried out was rapid pyrolysis, therefore the furnace was pre-heated until it reached the set temperatures of 220 ºC and 320 ºC. The samples remained

for 30 min, then the oven was cooled to room temperature. Three replicates were made per sample.

4.3. Nutrient availability

The study of the bioavailability of nutrients present in these samples was analyzed by extraction in diluted acetic acid. A sample weight of 0.3 g was added to 30 ml 0.11 M of acetic acid and the samples were shaken in a shaker for 16 h. Centrifugation at 10 000 x g for 10 minutes was used to separate the solid part and the liquid part. The solution was then introduced into test tubes and analyzed by means of inductively coupled plasma- optical emission spectroscopy (ICP-OES; Agilent 720, Agilent Technologies Inc., Santa Clara, CA). This technique uses a plasma and a spectrometer. The plasma is created at the end of a plasma torch when the argon gas is passed through it. This causes a collision between the electrons with argon atoms. The sample to be analyzed is introduced into the torch in the form of atoms, the electrons of these atoms get excited, causing the electrons to jump to higher energy levels. The energy emitted when the electrons return to their initial state is released in the form of photons that are specific to each element.

4.4. Carbon stability

The measurement of carbon stability was done for the 23 types of raw sewage sludge and the 13 types of sewage sludge pyrolyzed at 220 ºC and 320 ºC. The process was repeated 3 times per type of sewage sludge. In the case of biochar, the process was repeated once for each replicate, so that each variety of pyrolyzed sludge will have 3 samples. The experiment was based on the loss of weight of the samples after oxidation. The empty Erlenmeyer of 100 ml of volume was weighed, then approximately 0.2 g of sample were weighed into each Erlenmeyer and was weighed again. Before the oxidation, they were dried overnight in an oven (105 °C) to eliminate residual humidity and their weight was measured again (Fig. 7).

Figure 7: Samples before oxidation. Source: Maite Sánchez Revuelta.

Hydrogen peroxide was used for the oxidation. Following the idea of Cross and Soshi (2012), it was considered that for 0.1 g of C, 0.01 mol of H_2O_2 is needed. Therefore, the amount of H_2O_2 needed for each sample was calculated according to amount of C of each sample before oxidation, which were determined by CHNS Vario MACRO cube analyser (Elementar Analysensysteme GmbH, Hanau, Germany) and its approximate weight to 0.2 g.

$$0,01 \text{ mol } H_2O_2 \rightarrow 100 \text{ mg}$$

$$X \rightarrow \text{mg of carbon of the sample before oxidation}$$

Then the bottles were filled with deionized water until reaching 40 ml to provide sufficient mixing and contact between solid and liquid phase

39 ml deionized water + x H_2O_2 µL +(1-x) deionized water µL.

All the Erlenmeyer were covered for 4 hours. During this time, they were aerated and shaken by hand every hour, until the samples were oxidized. When the 4 hours passed the samples were dried in a dryer at 80ºC for 48 hours approximately (until a stable weight measurement was gotten). Once the samples were dried the Erlenmeyer were cooled in a desiccator and they were weighted again to determine the mass losses. Finally, the residue after oxidation was collected and analyzed using CHNS analyzer (Figure10). With this type of analysis, combustion takes place at temperatures close to 1000 ºC. During this thermal process the elements are transformed, C is converted into CO2, H is transformed into HO2, N is converted into nitrogen

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oxides and S is converted into SO_2. To eliminate the oxygen that has not been consumed, the products resulting from the transformation are transported by an inert gas and passed over high purity copper heated to about 600 ºC. The quantitative measurement is done by means of a suitable detector.

4.5. pH measurement

The pH of the pyrolyzed samples at 220 °C and 320 °C were measured. This process was performed twice for each sample. 0.5g of the samples were taken and 30 ml 0.01M of $CaCl_2$ was added. The measurement was carried out with a pH meter Sentron SI400 pH meter with ISFET electrode (Sentron Europe BV, Leek, Netherlands).

4.6. Statistical analysis

The statistical analysis was carried out using one-way analysis variance (ANOVA). Tukey`s HSD (Honestly Significant Difference) test with an alpha value of 0.05 has been carried out to make the assessment of individual treatments. Statistica 12.0 software (www.StatSoft.com) has been used.

5. Results

5.1. Nutrients

5.1.1. Total nutrient concentrations

The data obtained from the total concentration of K, P and S are collected in Table 7. As can be observed all sludge samples coincide with a higher total concentration of P than the concentration of K and S. Potassium is the nutrient that has a lower concentration in all samples.

Table 7: Total content of nutrients in different individual of sewage sludge samples (mg/kg).

Number of sample	K (mg/kg)	P (mg/kg)	S (mg/kg)
1	2995± 50.3 B	27709±228 DEF	19274±56.3 J
2	4084± 16.7 EFGH	25467 ±3834 BCDE	13474±732 DEF
3	3031± 152 B	21892±639 AB	11916 ±405 BCD
4	4554 ±44.7 FGHI	25028 ±316 BCD	13760 ±92.1 DEF
5	3545± 40.3 BCDE	27658±872 DEF	10246 ±104 B
6	4321 ± 125 FGH	32210 ±944 GH	10855 ±558 BC
7	2926± 258AB	20399±1717A	14464 ±351 EFG
8	2929 ± 62.3AB	28143 ±474 DEFG	16223±245 GH
9	4640± 16.5 GHI	29853± 499 EFG	12064 ±154 BCD
10	4506 ± 19FGHI	21939 ±697AB	13613 ±917 DEF
11	3014 ±13.4 B	21727±313.4AB	14557± 214 EFG
12	3159±58.9 BC	22511 ±623 ABC	14008± 366 DEF
13	3511 ± 124 BCDE	26689 ±920 CDEF	18521±455 IJ
14	4711± 279 HI	27687 ±467 DEF	12778± 1856 CDE
15	5723±266 J	26877±683 CDEF	8020±347 A
16	7657±528 K	30570±635 FGH	10152±262 B
17	3864±32 CDEF	29009±340 DEFG	11039±169 BC
18	3923±124 DEFG	27819±668 DEFG	15563±94 FGH
19	3360±63.3 BCD	26137±491 BCDEF	11109±265 BC
20	2436±51.7A	28062±177 DEFG	15454±79.3 FGH
21	5124±75.5 IJ	27067±465 DEF	11011±174 BC
22	4228±29.3 EFGH	27842±343 DEFG	16822±26.3 HI
23	2953±448 B	34484±4668 H	13782±2034 DEF
Mean	3965	26816	13422
Median	3864	27658	13613
Max	7657	34484	19274
Min	2436	20399	8020
CV	0.29	0.13	0.21

Different capital letters indicate significant difference between total concentration of nutrients in raw samples.

The results in Table 7 show a homogeneous distribution in the total K concentration of the different sludges. The sample with the highest total K concentration is number 16 with 7657 mg/kg and it shows significant differences with respect to the total K concentration of the other samples. The sludge with the lowest concentration is number 20 with 2436 mg/kg and based on the total K concentration it shows significant similarities with samples 7, with 2926 mg/kg and sample 8, with 2929 mg/kg. The mean of K concentrations among all samples of raw sludge is 3965 mg/kg. Ten out of the 23 raw samples have a K total concentration higher than the mean (samples 2, 4, 6, 9 10, 14, 15, 16, 21 and 22). The statistical data present in Table 7 show a significant difference in the results of K total content between the different raw sludges. The analysis results in 11 homogeneous groups organized according to the similarity between the total K concentration of the samples.

Table 7 show a homogeneous distribution in the total P concentration of the different sludges. The samples with highest P total content is number 23 with 34484 mg/kg and based on the total P concentration it shows significant similarities with samples number 5 and 16. The sample with lowest total amount of P is number 7 with 20399 mg/kg, according to the total P concentration it has similarities with samples 3, 10, 11 and 12. The mean of the total amount of P of all samples is 26816 mg/kg. Samples number 1, 5, 6, 8, 9, 13, 14, 15, 16, 17, 18, 20, 21, 22, and 23 present concentrations of total content of P above the mean. There is a statistical difference in the total P concentration of the different raw samples. The results show 8 homogeneous groups organized according to the similarity in the total P concentration of each sample.

Table 7 show a homogeneous distribution between the total S concentration of the different samples. The sample with the highest concentration is number 1 with 19274 mg/kg and based on the total S concentration it shows a significant similarity with the sample 13. The lowest total S concentration belongs to sample number 15 with 8020 mg/kg and it shows significant differences with respect to the total S concentration of the other samples. The mean of total concentration of S is 13422 mg/kg. Samples number 1, 2, 4, 7, 8, 10, 11, 12, 13, 18, 20, 22, 23 show a S concentration higher than the mean concentration. The data show a significant difference in the concentrations of S of the different samples. The statistical results show 10 homogeneous groups organized according to the similarity in the concentrations of S.

5.1.2. Nutrient bioavailability

The results obtained for the bioavailability of K, P and S of the different sewage sludge are shown in the following tables. The data shows a significant difference between the available concentrations of K, P and S between all the raw samples.

Table 8: Nutrient available concentration in raw samples of sewage sludge (mg/kg).

Number of sample	K (mg/Kg)	P (mg/Kg)	S (mg/Kg)
1	2864±91.0 J	6739±43.9 O	2808±15.3 G
2	1565±10.6 G	14167±126S	2798± 28.7 G
3	954±2.2 DE	341±31.0 A	1386±6.1 B
4	1763±14.6 H	13150±51.0 R	2756±37.9 G
5	888±7.7 BCD	5112±42.1 K	1717±14.4 D
6	1126±8.2 F	2482±12.5 E	2440±34.1F
7	900±4.0 CD	4680±94.8 J	3134±56.2 HIJ
8	1606± 5.8 G	3640± 111.3H	4575± 21.8 M
9	1634±14.3 G	2886±54.9 F	3023±50.0 H
10	3415±24.5 K	5702±35.4 M	3203±35.5 J
11	921±7.0 CDE	1217±15.4 C	3069±25.2 HI
12	951±1.6 CDE	2902±39.0 F	4790±7.4 N
13	983±54.8 E	1469±59.5 D	6775±73.4 P
14	3683±16.5 L	4102±36.6 I	640±8.3 A
15	916±6.9 CDE	5478±51.0 L	3165±17.9 IJ
16	1126±4.7 F	6204±48.8 N	1926±8.8 E
17	1560±8.0 G	3374±6.5 G	6112±65.8 O
18	426±2.5 A	634±2.7 B	1510±12.9 C
19	820±4.7 B	606±4.4 B	2848±22.8 G
20	1830±11.7 HI	6112±53.2 N	2776±26.8 G
21	1899±27.4 I	10339±158 Q	4071±59.8 K
22	873±16.9 BC	4742±56.0 K	4357±87.4 L
23	1090±5.1 F	9813±124 P	2414±23.9 F
Mean	1469	5039	3143
Median	1126	4680	2847
Max	3683	14167	6775
Min	426	341	640
CV	0.57	0.75	0.46

Different capital letters indicate significant difference between available nutrient concentration in raw samples.

There is non-homogenous distribution of available K concentration between all the samples. The Table 8 depicting the K concentrations in the raw sewage sludges indicate a high concentration of K in samples 1, 10 and 14 with over 2500 mg/kg; and lowest concentration of K was found in sample 18 with lower than 500 mg/kg. The available K concentration of the sample 18 with 426 mg/kg and the available K concentration of sample number 10 with 3683 mg/kg show a significant difference with respect to the available K concentration in the other samples and with respect to the mean of the available K concentration. The mean of the available K concentration is 1469 mg/kg. The sludge corresponding to the numbers 1, 2, 4, 8, 9, 10, 14, 17, 20 and 21 have concentrations of available K above the mean. The statistical data show significant differences between the K availability among the different samples analyzed. The data obtained show that the concentrations of available K have been distributed in 12 groups organized according to the similarities of the available concentrations of K in the different sludges.

Table 8 show a non-homogeneous distribution of available P concentration in the samples. The mean of the available concentration of P is 5039 mg/kg. The concentrations can be highlighted of available P from samples 2 and 4 with 14167 mg/kg and 13150 mg/kg, respectively, with a concentration of available P significantly higher than the mean concentration. On the other hand, the concentrations of available P from samples number 3, 18 and 19 with the values 341 mg/kg, 634 mg/kg and 606 mg/kg respectively are significantly lower than the mean concentration. Ten of the samples have available P concentrations above the total mean, these samples are those corresponding to the numbers: 1, 2, 4, 5, 10, 15, 16, 20, 21, 23. Table 9 shows significant differences in the concentrations of available P between all the raw samples of the sludge. Variation coefficient show that the nutrient which present higher available concentration variability is P.

There is non-homogenous distribution of available S concentration between all the samples. Available concentrations of S can be noted to be significantly higher in samples 13 and 17 with 6775 mg/kg and 6112 mg/kg, respectively. The sample 14 shows a significantly lower available S concentration than the available concentration of the other samples, with 640 mg/kg. The mean of the available S concentrations is 3143 mg/kg. There are 8 samples that have a concentration of available S higher than the average concentration, these samples are those corresponding to numbers 8, 10, 12, 13, 15, 17, 22 and 23. The data show significant difference

of the available S concentration between the samples. There are 16 differentiated groups organized according to the similarities of the concentrations of available S in the samples.

5.1.3. Percentage of available nutrients

The percentages of available nutrients are shown in Table 9. There is a large variation of K available in the samples of the different sludges as it can be observed in the Table 10. Sample 1 shows a high percentage of available K with 95.6 % followed by 14 with 78.2 % and number 10 with 75.8 %. On the other hand, sample 18 shows a low percentage of available K, with only 10.8 % of the total. Samples 15 and 16 with 15.0 % and 14.7 %, respectively, also show a low percentage of available K.

Table 9: Relative available nutrient content in raw samples (%).

Number of sample	K (%)	P (%)	S (%)
1	95.6	24.3	14.6
2	38.3	55.6	20.8
3	31.5	1.6	11.6
4	38.7	52.5	20.0
5	25.0	18.5	16.8
6	26.1	7.7	22.5
7	30.7	22.9	21.7
8	54.8	12.9	28.2
9	35.2	9.7	25.1
10	75.8	26.0	23.5
11	30.6	5.6	21.1
12	30.1	12.9	34.2
13	28.9	5.6	36.4
14	78.2	14.8	5.0
15	16.0	20.4	39.5
16	14.7	20.3	19.0
17	40.4	11.6	55.4
18	10.8	2.3	9.7
19	24.4	2.3	25.6
20	75.1	21.8	18.0
21	37.0	38.2	37.0
22	20.6	17.0	25.9
23	36.9	28.5	17.5
Mean	38.9	18.8	24.2
Median	31.5	17	22.1
Max	95.6	55.6	55.4
Min	10.8	1.6	5
CV	0.57	0.77	0.46

Significant differences can be observed in the percentages of available P between the different sludges. The highest percentage corresponds to sludge number 2 with 55.6 % followed by sludge number 4 with 52.5 %. The sludge with the lowest percentages of available P are numbers 3 with 1.6 % and numbers 18 and 19 with 2.3 %.

Sulphur presents a significant difference in the availability percentages between the different sludges. Sample number 17 had a significantly higher percentage than the rest, with 55.4 %. The sample with the lowest percentage is the number 14 with only 5 %.

5.1.4. Regression of available nutrient concentration on total nutrient concentration

Figure 8: Regression of available K concentration (mg/kg) on total K concentration (mg/kg).
The Fig. 8 shows that the total K concentration has little to no relation with the available K concentration.

Figure 9: Regression of available P concentration (mg/kg) on total P concentration (mg/kg).

The Fig. 9 shows that the total P concentration has little to no relation with the available P concentration.
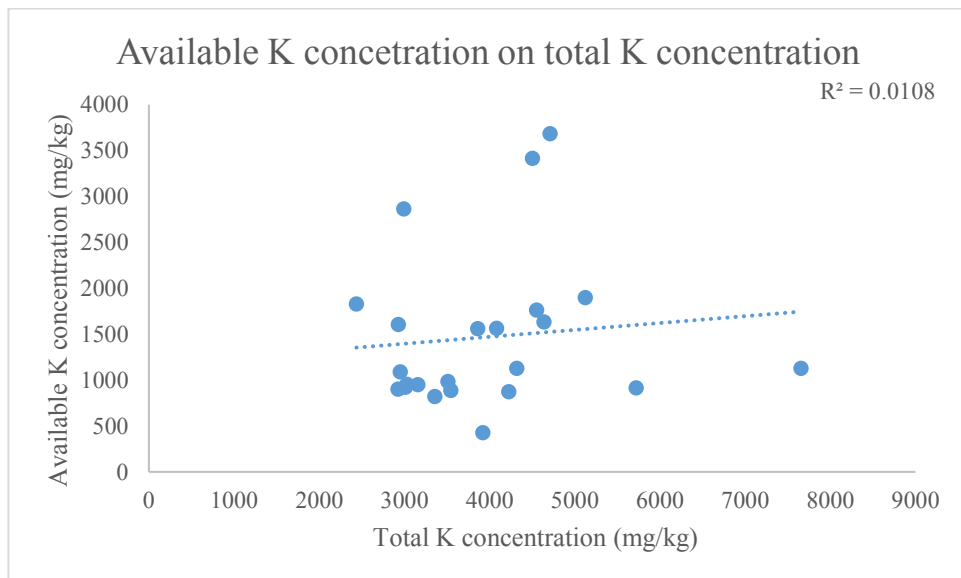

Figure 10: Regression of available S concentration (mg/kg) on total S concentration (mg/kg).

The Fig. 10 shows that the total S concentration has little to no relation with the available S concentration.
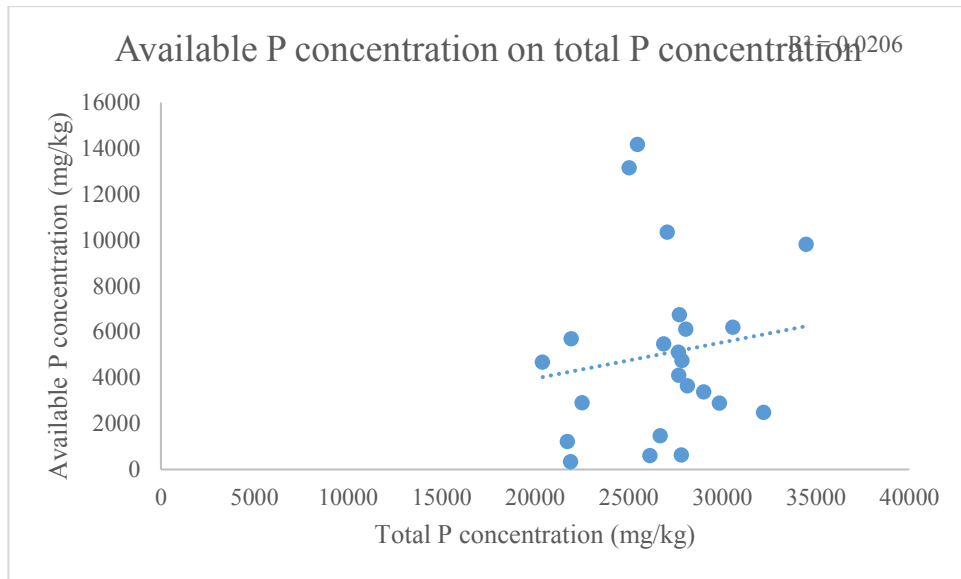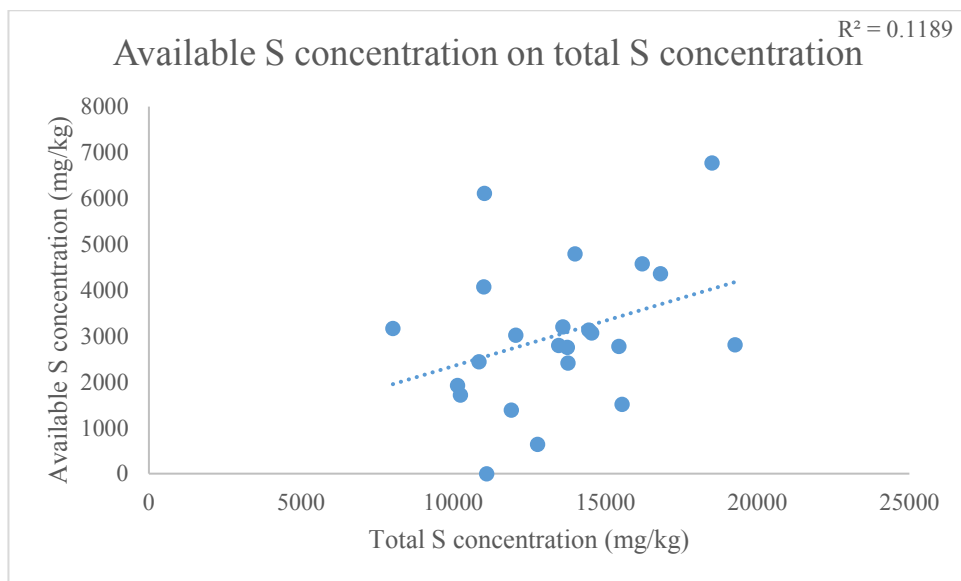
5.2. Carbon stability

Table 10 shows a homogeneous distribution on the stable C percentage. The lowest percentages of stable C are found in samples 23 with 39.7 % and in sample 11 and 12 with 40 %. On the other hand, the samples with the highest percentage of stable C are number 15 with 62.5 % and number 18 with 61.4 %. The mean of the percentages of stable C of the different raw sludges is approximately 49.7% and the median 49 %. Only 9 out of the 23 samples are above the mean of the percentage of stable C and are those corresponding to sludges number 1, 3, 4, 6, 8, 15, 16, 18 and 21.

Table 10: Concentration of stable C in sewage sludge in different raw samples (%).

Number of samples	Stable C (%)
1	58.3±1.0 FGHI
2	46.5±0.6 ABCD
3	59.4±1.6 GHI
4	54.9±0.9 DEFGHI
5	42.3±4.7 ABC
6	52.6±2.1 DEFGHI
7	48.7±2.3 ABCDEF
8	57.3±0.8 EFGHI
9	47.0±1.1 ABCD
10	49.6±2.6 ABCDEFG
11	40.±1.6 A
12	40±2.2 A
13	48.8±4.9 ABCDEF
14	49.4± 1.4 ABCDEF
15	62.5 ± 2.8 I
16	52.1± 0.9 CDEFGH
17	48.1±1.0 ABCDE
18	61.4±0.5 HI
19	46.5±3.1 ABCD
20	46.7±2.7 ABCD
21	50.9±0.7 BCDEFG
22	41.1± 7.8 AB
23	39.7±1.9 A
Mean	49.7
Median	48.8
Max	62.5
Min	39.7
CV	0.13

Different capital letters indicate significant difference between stable C percentage in raw samples.

The data present in Table 10 shows that there is a statistical difference on the stable C percentage between the different samples of raw materials. The statistical analysis shows 9 homogeneous groups organized according to the percentage of stable C.

5.2.1. Regression of available nutrient on C

The Figures number 11, 12 and 13 show that the percentage of stable C has little to no relation with the available percentage of nutrients.
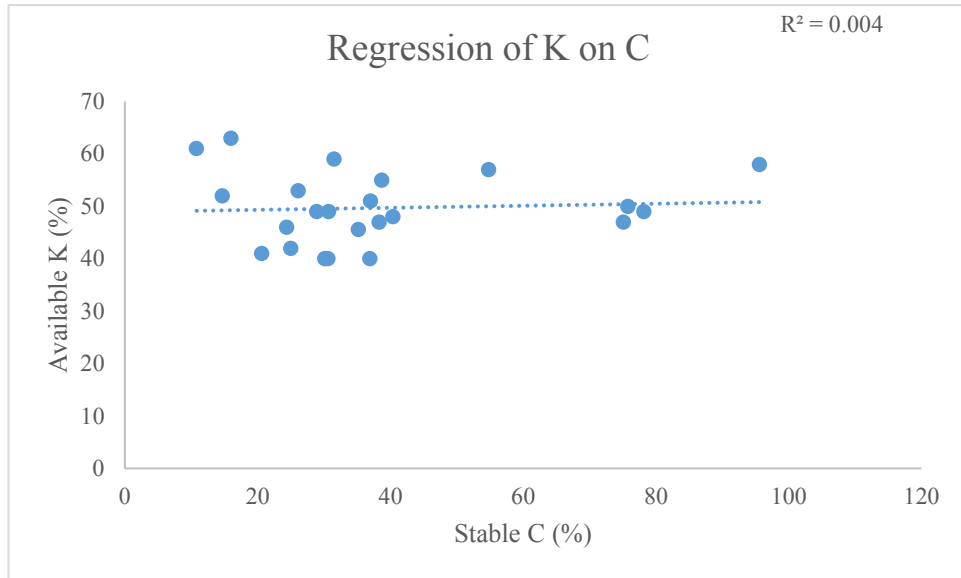
Figure 11: Regression of K on C.
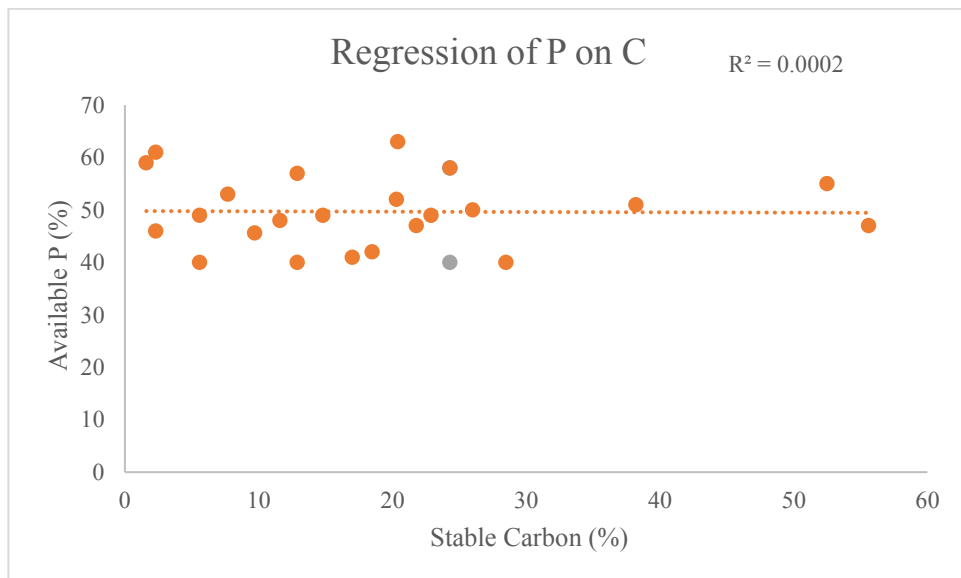
Figure 12: Regression of P on C.
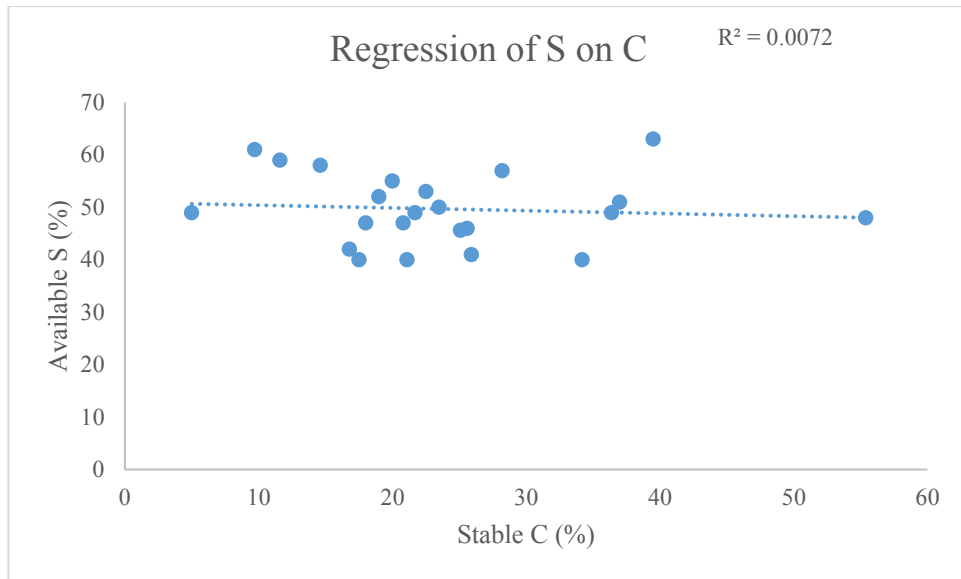
Figure 13: Regression of S on C.

5.3. pH of raw samples

Fig. 14 shows the pH of the different raw sludges. A homogeneity between the pH can be observed. The pH of sample number 15 shows a significant difference when compared to the pH of the rest of the samples, with a pH slightly lower 6.5 pH. The sludge with the highest pH is number 22 with 7.63 pH.
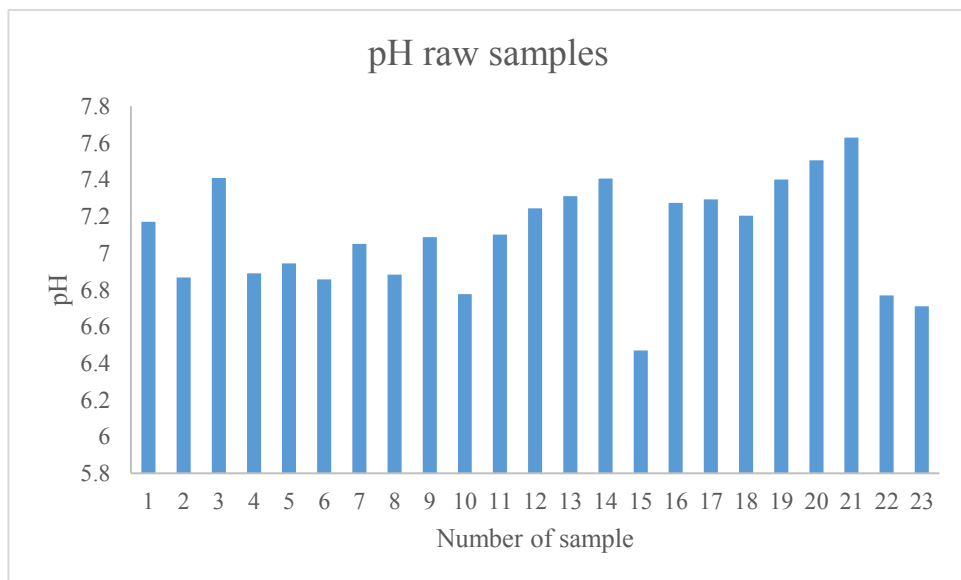
Figure 14: pH of raw sludges.

5.4. Effect of low-temperature pyrolysis on sludge properties

In the pyrolyzed samples a mass loss was observed. Table 11 shows the percentage of mass loss of the samples after the thermal process. The loss of mass increases when the temperature increases. The percentages of mass loss show a homogeneous distribution in the two temperatures. The mean of the percentage of mass loss in the pyrolyzed sludge at 220 ºC is 12.7 % and the mean of the percentage of mass of the pyrolyzed sludge at 320 ºC is 33.8 %. As it can be seen in the results, the percentage of mass loss for sludge treated at 220°C is at most 16 %, in the case of sample 8 and 10, while pyrolysis at 320 °C leads to a loss of mass of 43 % for sample 8. The largest difference between mass losses in the pyrolyzed samples at both temperatures can be seen in sample number 8 and 11 with a difference of 27 % and 30 % of mass loss respectively. On the other hand, the sample with the smallest difference in mass loss between the two pyrolysis temperatures is number 9 with a 14 % difference in mass loss between the pyrolyzed sludge at 220 ºC and the pyrolyzed sludge at 320 ºC.

Table 11: Loss of mass during thermal treatment (%).

Number of sample	Mass loss 220 ºC (%)	Mass loss 320 ºC (%)
3	12±1.64 ABC	35±1.22 CD
4	13±1.64 ABC	34.7±1.22 CD
5	13±1.64 ABC	30.7±1.22 ABC
6	13.7±1.64 ABC	31±1.22 ABC
7	11.2±1.64 ABC	33.3±1.22 BC
8	16±1.64 AB	43±1.22 E
9	12.7±1.64 ABC	27±1.22 A
10	16.3±1.64 C	41±1.22 E
11	8.67±1.64 A	39±1.22 DE
12	10.3±1.64 AB	27.3±1.22 A
13	12.3±1.64 ABC	29.7±1.22 AB
Mean	12.7	33.8
Median	12.7	33.3
Max	16.4	43
Min	8.67	27
CV	0.18	0.16

Different capital letters indicate significant difference between the losses of mass in the pyrolyzed samples.

5.4.1. Effect of low-temperature pyrolysis on available potassium concentrations

Table 12 show a non-homogeneous distribution of the available K concentration in pyrolyzed samples at 220 ºC. The maximum value for available K concentration is 3402 mg/kg in sample 10 and the lowest one is 947 mg/kg corresponding to sample 5; these two values show a significant difference with respect to the other available K concentrations. In the results of Table 12 it can be seen that the available K concentrations of the different pyrolyzed sludges at 220 °C present a significant difference that can be organized in 5 different groups according to the similarities in available K concentration. There is a non-homogeneous distribution in available K concentrations in the 320 °C pyrolyzed samples. The maximum concentration of available K in samples pyrolyzed at 320 ºC is in sample number 10 with 2348 mg/kg and it shows a significant difference with respect to the other available K concentrations of the other samples pyrolyzed at 320 ºC. The lowest available K concentration is in sample number 5 with 816 mg/kg and based on the available K concentration it shows significant similarities with the samples 11 and 12. The samples are organized in 7 different groups according to the similarities in available K concentration between the samples.

Table 12: Comparison of K bioavailability in raw sewage sludge, pyrolyzed at 220 ºC and pyrolyzed at 320 ºC (mg/kg).

Number of sample	K Raw (mg/kg)	K 220 ºC (mg/kg)	K 320 ºC (mg/kg)
3	954±2.2 Da	1145±6.2 Cc	1109±12.5 Cb
4	1763±14.6 Ha	2313±16.8 Ec	1919±8.2 Fb
5	888±7.7 Aa	947±19.4 Aa	816±134.5 Aa
6	1126±8.2 Fb	1156±4.1 Cb	1059±31.4 Ca
7	900±4.0 ABa	971±0.3 ABb	1011± 5.8 BCc
8	1606± 5.8 Gb	1764±2.9 Dc	1467±64.9 Da
9	1633±14.3 Ga	1762±53.7 Db	1717± 5.5 Eb
10	3414±24.5 Ib	3646±59.1 Fc	2348±83.1 Ga
11	921±7.0 BCa	983±13.5 ABc	951±7.8 ABCb
12	951±1.6 CDb	1042±6.5 Bc	861±20.9 ABa
13	983±9.9 Ca	1005±3.6 ABa	1005±46.9 BCa
Mean	1372	1521	1109
Median	954	1145	1059
Max	3414	3646	2348
Min	888	947	816
CV	0.65	0.55	0.39

Different capital letters indicate significant difference between available K concentration in raw and pyrolyzed materials individually (vertical) and small case letters indicate significance difference between raw material and their respective biochar production temperature of 220 ºC and 320 ºC (horizontal).

The Table 12 shows that sewage sludge pyrolyzed at 220 ºC has a higher concentration of available K than the raw samples and the pyrolyzed samples at 320 ºC in several samples. A significant difference between the available K concentrations between the raw sludge samples and the samples of the pyrolyzed sludge is observed in majority of the samples. Based on the available K concentration of the raw and pyrolyzed sludges, samples present different behaviors. Samples 3, 4 and 11 show a significant difference in available K concentration between the 3 samples (raw, pyrolyzed at 220 ºC and pyrolyzed at 320 ºC). The samples with highest available K concentration being the one pyrolyzed at 220 ºC, and the sample with lower available K concentration is the raw one. In samples 5 and 13 there is no significant difference between the three samples (raw, pyrolyzed at 220 ºC and pyrolyzed at 320 ºC). In sludge number 6 there is a significant difference in available K concentration of raw and pyrolyzed samples at 220 ºC with respect to the ones pyrolyzed at 320 ºC. There is no significant difference between available K concentration between raw samples and pyrolyzed samples at 220 ºC. In sample 7 it is shown a significant increase of available K concentration with the increase of the temperature, with the sample with highest available K concentration being the one pyrolyzed at 320 ºC, and the sample with lowest available K concentration being the raw one. Samples 8, 10 and 12 present significant differences in available K concentrations between the raw sample, the pyrolyzed sample at 220 ºC and pyrolyzed sample at 320 ºC, the highest available K concentration belongs to the pyrolyzed sample at 220 ºC and the lowest one belongs to the pyrolyzed sample at 320 ºC. In sample 9 there is a significant difference between the available K concentration in raw sample with respect to the available K concentration in pyrolyzed samples. There is no significant difference between available K concentration between pyrolyzed samples.

5.4.2. Effect of low-temperature pyrolysis on available phosphorus concentrations

Table 13 show a non-homogeneous distribution in the available P concentration in pyrolyzed samples at 220 ºC. The sludge number 4 present a significant difference in the available P concentration in pyrolyzed sample at 220 ºC, the highest one with 14884 mg/kg. Available P concentration of sample number 3 is the lowest with 829 mg/kg and shows a significant difference with respect to the other available P concentrations in the samples pyrolyzed at 220 ºC. Based on the concentrations of P available in the pyrolyzed samples at 220 ºC all samples show a significant difference.

The results of available P concentrations in samples pyrolyzed at 320 ºC show a non-homogeneous distribution. The maximum available P concentration is found in sample 4 with 13812 mg/kg, showing a significant difference with respect to the other available P concentrations of samples pyrolyzed a 320 ºC. The lowest available P concentration between samples pyrolyzed at 320 ºC correspond to the sample number 3 with 645 mg/kg and based on the available P concentrations in the samples pyrolyzed at 320 ºC, it shows significant similarities with samples 11 and 12. The available P concentrations of pyrolyzed samples at 320 ºC is organized in 5 different groups based on the similarities between the available P concentration.

Table 13: Comparation of P bioavailability in raw sewage sludge, pyrolyzed at 220 ºC and pyrolyzed at 320 ºC (mg/kg).

Number of sample	P Raw (mg/kg)	P 220 ºC (mg/kg)	P 320 ºC (mg/kg)
3	341±31.0 Aa	829±0.7 Ac	645±0.3 Ab
4	13150±51.0 Ja	14884±16.8 Kb	13812± 522 Ea
5	5112±42.1 Ha	5933±158 Hb	8091±361 Dc
6	2482±12.5 Da	3869± 270 Fa	3935±1584.0 Ba
7	4680±94.8 Ga	6424±2.9 Ib	6246±408 Cb
8	3640± 111 Fa	4218±35.2 Ga	4074±670 Ba
9	2886±54.9 Ea	3128±34.7 Db	3861.±61.3 Bc
10	5702±35.4 Ia	7340±78.2 Jb	5605±712 BCa
11	1217±15.4 Bb	1582±32.6 Cc	991± 58.5 Aa
12	2902±39.0 Ec	1281±14.9 Ba	1346±10.0 Ab
13	1469±45.5 Ca	3505±55.5 Eb	4037±204 Bc
Mean	3962	4817	4785
Median	2902	3869	4037
Max	13150	14884	13812
Min	341	829	645
CV	0.88	0.82	0.79

Different capital letters indicate significant difference between available P concentration in raw and pyrolyzed materials individually (vertical) and small case letters indicate significance difference between raw material and their respective biochar production temperature of 220 ºC and 320 ºC (horizontal).

The P concentrations of the pyrolyzed sludge are in most cases higher than that of the raw as it is shown in Table 13. The statistical results of Table 13 indicate that there are significant differences in the available P concentrations between the raw samples and the pyrolyzed samples at 220 ºC and 320 ºC. Based on the available P concentrations, samples present

different behavior due to de pyrolysis temperature. In samples 3, 11 and 12 there is a significant difference between the 3 samples (raw, pyrolyzed at 220 ºC and pyrolyzed at 320 ºC). In sample 3 the highest available P concentration belongs to pyrolyzed sample at 220 ºC and the lowest one belongs to the raw sample. The sample 11 presents the highest available P concentration in the pyrolyzed sample at 220 ºC and the lowest available P concentration correspond to pyrolyzed sample at 320 ºC. To conclude, in sample 12 the highest available P concentration is found in the raw samples while the lowest belongs to the pyrolyzed samples at 220 ºC. In samples 4 and 10 there is a significant increase in the available P concentration in the samples pyrolyzed at 220 ºC. The available P concentration between raw and pyrolyzed sample at 320 ºC has no significant difference. In samples 5, 9 and 13, there is a significant difference in the available P concentrations between the three samples. There is an increase of the available P concentration with the increase of the temperature; the sample with highest available P concentration was the one pyrolyzed at 320 ºC and the sample with lowest available P concentration was the raw one. In samples 6 and 8, there is no significant difference between the available P concentration of raw and pyrolyzed samples. In sample 7 there is significant difference between the available P concentration in raw sample with respect to the available P concentration in pyrolyzed samples. There are no significant differences between available P concentrations between pyrolyzed samples.

5.4.3. Effect of low-temperature pyrolysis on available sulphur concentrations

The results presented in table 14 show a non-homogeneous distribution between the available S concentration of samples pyrolyzed at 220 ºC. The sample 8 shows a significantly high difference with respect to the available S concentration of the rest of pyrolyzed samples at 220 ºC with 4695 mg/kg. The lowest available S concentration between pyrolyzed samples at 220 ºC belongs to sample number 10 with 2203 mg/kg and based on the available S concentration it shows significant similarities with samples number 4 and 6. The samples are distributed in 7 groups based on the similarities between the available S concentration.

The results present for available S concentration in samples pyrolyzed at 320 ºC present a homogeneous distribution (Table 14). Sample number 11 with 3562 mg/kg shows a significant difference in available S concentration with respect to the other samples pyrolyzed at 320 ºC. The lowest available S concentration is present in sludge number 10 with 834 mg/kg. The samples are distributed in 5 homogeneous groups according the similarities in available S concentration.

Table 14: Comparation of S bioavailability in raw sewage sludge, pyrolyzed at 220 ºC and pyrolyzed at 320 ºC (mg/kg).

Number of sample	S Raw (mg/kg)	S 220 ºC (mg/kg)	S 320 ºC (mg/kg)
3	1386±6.1 Aa	3226±21.5 Fc	2505± 56.9 BCDb
4	2756±37.9 Dc	2493±19.1ABCb	1823±39.0 Ba
5	1717±14.4 Bb	2542±11.0 BCDc	984± 152.4 Aa
6	2440±34.1Cb	2378±96.2 ABb	980± 140 Aa
7	3134±56.2 EFc	2887±4.4 Eb	2561±38.9 CDa
8	4575± 21.8 Gb	4695±230 Gb	2238±635 BCDa
9	3023±50.0 Eb	2717±31.2 CDEa	2748±56.0 Da
10	3203±35.5 Fc	2203±22.3 Ab	834±94.9 Aa
11	3069±25.2 Eab	2808±80.4 DEa	3562±433 Eb
12	4790±7.4 Hc	3199±52.1 Fb	2041±45.9 BCDa
13	6775±73.4 Ic	3415±192 Fb	1958± 215 BCa
Mean	3352	2960	2021
Median	3069	2808	2041
Max	6775	4695	3562
Min	1386	2203	834
CV	0.45	0.23	0.42

Different capital letters indicate significant difference between available S concentration in raw and pyrolyzed materials individually (vertical) and small case letters indicate significance difference between raw material and their respective biochar production temperature of 220 ºC and 320 ºC (horizontal).

The concentrations of S show, in most cases, a decrease in the pyrolyzed materials as it can be observed in Table 14. Based on the available S concentration of the raw sludge and the pyrolyzed sludges, the samples present different behavior. In samples 3 and 5 there is a significant difference between available S concentration between the raw sample, the pyrolyzed sample at 220 ºC and the pyrolyzed sample at 320 ºC. In sample 3 the highest available concentration belongs to the pyrolyzed sample at 220 ºC and the lowest available S concentration belongs to the raw sample. In sample 5 the highest available concentration belongs to the pyrolyzed sample at 220 ºC and lowest concentration belongs to the pyrolyzed sample at 320 ºC. In sample number 4, 7 10, 12 and 13 there is a significant difference in the available S concentration between the three samples. It can be observed a decrease in the available S with the temperature; the sample with highest available S concentration was the raw one and the sample with lowest available concentration was the samples pyrolyzed at 320 ºC. In samples 6 and 8 there is no significant difference in available S concentration between raw and pyrolyzed samples at 220 ºC, but it can be observed that there is a significant difference of

the available S concentration between these two samples and the one pyrolyzed at 320 ℃. The data shows a decrease in the available concentrations in the samples pyrolyzed at 320 ℃. In sample 9 there is a significant decrease in available S concentration in pyrolyzed samples with respect to the raw samples. Between the pyrolyzed samples there is no significant difference. In sample 11 there is a significant difference in the available S concentration between pyrolyzed samples, but there are significant similarities between the available S concentration of raw sample and the available S concentration of the both pyrolyzed samples. The highest available S concentration belongs to the pyrolyzed sample at 320 ℃ and lowest one to the pyrolyzed sample at 220 ℃.

5.4.4. Effect of low-temperature pyrolysis on stable C

The results in Table 15 shows a homogeneous distribution in the stable C percentage for samples pyrolyzed at 220 ℃. The sample number 3 shows a significantly high stable C percentage with respect to the other samples pyrolyzed at 220 ℃ with 60.7 %. The lowest stable C percentage belongs to sample number 11 with 38.9 %. The stable C percentages were distributed in 5 homogeneous groups according to the similarities

The result in Table 15 of stable C percentage in samples pyrolyzed at 320 ℃ show a homogeneous distribution. The highest percentage is 67 % and belongs to sludge number 7 and according to the stable C percentage in pyrolyzed samples at 320 ℃ sample number 7 shows significant similarities with sludges number 3, 4, 8, and 12. The lowest stable C percentage is 45.3 % and belongs to sample number 13. The data for stable C percentage for samples pyrolyzed at 320 ℃ present in Table 15 show significant differences.

Table 15: Comparison of Concentration of stable carbon in raw sewage sludge, pyrolyzed at 220ºC and pyrolyzed at 320ºC (%).

Number of sample	Stable C Raw (%)	Stable C 220ºC (%)	Stable C 320ºC (%)
3	59.4±1.6 GHIa	60.7±5.1 Ea	59.3±5.1 CDa
4	54.9±0.9 DEFGHIa	52.2±0.2 CDa	65.8±2.1 Db
5	42.3±4.7 ABCa	44.7±A1.6 BCa	51.0±5.1 ABCa
6	52.6±2.1 DEFGHIab	47.0±3.1 BCa	54.7±1.7 ABCb
7	48.7±2.3 ABCDEFa	45.1±1.0 ABCa	67.0±4.5 Db
8	57.3±0.8 EFGHIa	56.4±2.4 DEa	66.4±2.4 Db
9	47.0±1.1 ABCDa	46.0±1.5 ABCa	51.3±3.6 ABCa
10	49.6±2.6 ABCDEFGab	44.9±0.5 ABCa	51.6±2.1 ABCb
11	40.0±1.6 Aa	38.9±1.1 Aa	46.9±0.6 ABb
12	39.9±2.2 Aa	50.1±2.3 BCDb	57.2±1.5 BCDc
13	48.8±3.3 ABCDEFa	43.6±1.1 ABa	45.3±0.3 Aa
Mean	49.1	48.1	56.0
Median	48.8	46	54.7
Max	59.4	60.7	67
Min	39.9	38.9	45.3
CV	0.13	0.14	0.14

Different capital letters indicate significant difference between stable C percentage in raw and pyrolyzed materials individually (vertical) and small case letters indicate significance difference between stable C percentage in raw material and their respective biochar production temperature of 220 ºC and 320 ºC (horizontal).

The pyrolysis of the raw sewage sludge at 220 ºC indicates great differences in concentrations of stable C, compared to the raw sewage sludge. However, the sewage sludge pyrolyzed at 320 ºC shows increased concentrations of stable C. This suggests that the stability of the stable C is closely linked to the pyrolysis temperature and increases with temperature. Based on the percentage of stable C there are significant differences in the behavior of samples. There are no significant differences in stable C percentage between the three samples (raw sample, pyrolyzed sample at 220 ºC and pyrolyzed sample at 320 ºC) in sludges number 3, 5, 9 and 13. Sample numbers 4, 7, 8 and 11 show that there is a significant difference in the percentage of stable C of the raw and pyrolyzed at 220 ºC samples with respect to the samples pyrolyzed at 320ºC but there is not a significant difference between the stable percentage of C between raw and pyrolyzed samples at 220 ºC. The C percentage in pyrolyzed sample at 320 ºC is significantly higher. In sludges number 6 and 10 there is a significant difference in the stable C between pyrolyzed samples but there are significant similarities between raw stable C percentage and the percentage of stable C of both pyrolyzed samples. The highest stable C percentage belongs to the pyrolyzed sample at 320 ºC and lowest one to the pyrolyzed sample at 220 ºC. Sample

number 12 shows a significant increase of stable C percentage between raw sample and pyrolyzed sample at 220 ºC as well as between pyrolyzed sample at 220 ºC and pyrolyzed sample at 320 ºC.

5.4.5. Effect of low-temperature pyrolysis on pH

The pyrolyzed sludge shows a lower pH than the raw sludge (Fig. 12). The lower pH is found in pyrolyzed samples at 220 °C ranging between 6.15 and 5.5. The pH of the pyrolyzed sludge at 320 ºC is slightly higher than that of the samples subjected to thermal treatment at 220 ºC and ranges from 6.75 in sample 10 to 5.7 in sample 11. The sample 11 has the same pH for the two pyrolyzed samples. The sample 10 presents an important increase of pH from pyrolyzed sample at 220 ºC, 5.65 pH, and pyrolyzed sample at 320 ºC, 6.75 pH. The rest of the samples show a similar behavior.
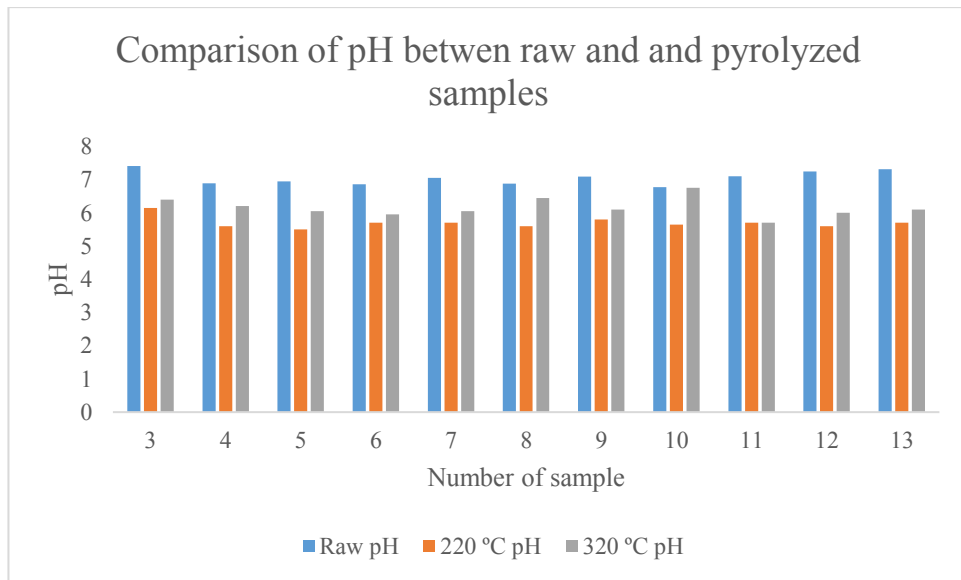

Figure 15: Comparison of pH between raw sewage sludge and pyrolyzed sludge at 220 ºC and 320 ºC.

6. Discussion

Sewage sludge is a good raw material to be used in agriculture thanks to its high content of organic matter, macro- and micronutrients, however, a main issue with sewage sludge is the potential presence of toxic elements (Logan and Harrison, 1995). The concentrations of these nutrients such as K, P and S, concentration of the toxic elements and content of organic matter is dependent on the location and can vary from one sewage sludge to another (Sommers et al., 1972). The thermal treatment favors the elimination of possible toxic elements such as organic chemical as absorbable organic halogen compounds (AOX), 4-nonylphenole (NPE), linear alkylbenzene sulphonates (LAS), polychlorinated biphenyls (PCBs), Polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs), Di-2-(ethyl-hexyl)-phthalate (DEHP), polycyclic aromatic hydrocarbons (PAHs) and in turn transforms organic matter and nutrients into compounds with different stability.

The results obtained on the total mean concentration of the P, K and S, 26816, 3965, 13422 mg/kg, respectively, can be compared to those obtained in the study carried out by Tabatabai and Frankenberger (1979), who obtained 1.2, 0.3 and 1.1 % of total P, K and S, respectively. The experiment carried out by Tabatabai and Frankenberger (1979) as well as the one conducted in this paper shows a P concentration higher than that of the other two nutrients. The second nutrient which appears in higher concentration is S and the nutrient that has a lower concentration is K. Aragao de Figueredo et al. (2017) showed in the study how the P and K concentrations of sewage sludge are higher than those from sugarcane bagasse and eucaliptus bark. With the raw sewage sludge containing 46, 1.2 and 2.2 g/kg of P, K and S, respectively, which indicates a similarity of the study conducted by Tabatabai and Frankenberger (1979) and the experiment conducted in this paper. Martinez et al. (2002) found total concentrations of 1.06 and 0.2% of P and K, respectively, in sewage sludge from Spain; while sewage sludge from India was found to have 1.34 and 0.42 % of P and K, respectively, as found by Nandakumar et al. (1998).

The results obtained in this experiment shows the sludge with the lowest total concentration of K was 2436 mg/kg and the highest was the number 16 with 7657 mg/kg. In the case of P, the sludge with a lower concentration was the number 7 with 20399 mg/kg and the one that had the highest concentration was number 23 with 34484 mg/kg. The values of the total S concentration in the samples range from 8020 mg/kg for sludge number 15 to 19274 mg/kg belonging to sludge number 1. The mean of the total concentrations of P and K in this study resemble the

concentrations obtained by Nogueira et al. (2009) in whose experiment, the nutrient concentration of sewage sludge was measured over nine years. The concentrations of P for the first year was 16000 mg/kg and the concentration was 4850 mg/kg for K. Which show that the sludges used in this study present higher amount of total P than the sludge used by Nogueira et al. (2009) and the mean of the K concentration of the different sludges used in this study (3965 mg/kg) is slightly lower than the K concentration in the sludge used in the experiment carried out by Nogueira et al. (2009).

The sludges analyses showed a high but varying available concentration of P, S and K. As shown in the results section, sample 2 has 55.6 % of the total available P, while in the sample three only 1.6 % of the total P is available. The results of the experiment carried out by Kahiluoto et al. (2015) in which a study is carried out on phosphorus in sewage sludge shows a high concentration of P available in most of the samples analyzed. The most common form of P in sludge is phosphate, however, in the experiment by Kahiluoto et al. (2015) it is shown that the treatment of sludge affects the availability of phosphate in sludge. Those treated by anaerobic digestion present a higher concentration of available P. Sulphur concentrations present in the sludges had the second highest available concentration of all the three nutrients studied and showed a great variety of concentrations throughout all the samples. It can be seen that there is a wide statistical difference between the samples. On the other hand, the percentage of S available in sludges is also variable, with the maximum concentration available in sample number 17 being 55.4 % and the minimum concentration in sample number 14 with 5 % sulfur available from the total.

The loss of mass of sewage sludge during the heat treatment shows similarity with the results obtained in the study carried out by Pulka et al. (2019). Their experiment was carried out at 6 different temperatures (200, 220, 240, 260, 280, 300 ºC), the mass loss increased by increasing the temperature in the process except for the temperature change from 200 ºC to 220 ºC where the loss of mass was of 10 % and 9 % respectively. For the pyrolysis temperature of 300 °C the mass loss was 20 %. The results of this study are comparable to those performed in this work where the mean mass loss of the pyrolyzed sludge at 220 ºC is 12% and that of the pyrolyzed sludge at 320 ºC is 34 %. This loss of mass is due to the potential of the thermal process to decompose and volatilize the solid particulates present in the sewage sludge that can affect the bioavailability of nutrients as well as the percentage of carbon (Pulka et al., 2019).

In some of the samples analyzed in this experiment it can be seen that there is a slight reduction of K available in the pyrolyzed sludge at 320 °C compared to the pyrolyzed at 220 °C. In other cases, it is the raw material that has the highest concentration of this nutrient available. In the experiment conducted by Yuan et al. (2015), in which the pyrolysis of sewage sludge at different temperatures was studied, a decrease in the available K was observed when the temperature was increased. On the contrary, the experiment carried out by Zhao et al (2017) shows that there was an increase in available potassium as well as an increase in other inorganic minerals as the temperature increased. Concentrations of phosphorus available in different sludge raw or pyrolyzed show a different behavior between all samples. As already stated in the results section, several of the sludges have the highest concentration of available phosphorus in the pyrolyzed samples at 220 °C, while others result in higher concentrations in the pyrolyzed sludge at 320 °C. In the study carried out by Yuan et al (2015) the concentration of available P increases directly with the increase in temperature, this behavior could be compared to the sludge in this experiment that shows a higher concentration after being subjected to the thermal treatment at 320 °C. The results obtained for the available S concentration are variable among the sludges. In most samples the lowest concentration is found in the pyrolyzed sludge at 320 °C. The study carried out by Cheah et al. (2009) showed a decrease of sulfate in the biochar produced at higher temperatures. In the study conducted by Knudsen et al. (2004) it is explained that the sulfur changes during the pyrolysis and it can be observed that at temperatures of 400 °C inorganic S suffered with a decrease. In a study by Hossain et al. (2011) the total mean concentration of S in sewage sludge was found to decrease when pyrolyzed at 300 °C with 4.47 % and at 400 °C with 4.72 % when compared to the raw concentration of 5.17 %. However, when pyrolyzed at 500 °C and 700 °C the concentration of S was 5.9 % and 6.17 %, respectively.

The samples of sludge analyzed do not show significant differences in the percentage of stable C in the raw material. The range of values between the sludges ranges from approximately 40 % to 60 %. The percentage of stable C increased in most of the samples pyrolyzed at 320 °C while the results of the pyrolyzed sludge at 220 °C are not as expected, and differences are not significant with respect to the raw material. This increase in the amount of stable C at 320 °C has been observed previously in other studies as in the one carried out by Cross and Sohi (2012) where the C stability increased linearly with respect to the increase in temperature. Another one of the experiments that reaffirms the increase of stable C when increasing the temperature is the one made by Singh et al. (2012). In this study, an important increase of the stable C was

observed in the biochar produced at 550 ºC with respect to the one subjected to a pyrolysis of 400 ºC. The results obtained in the experiment carried out by Al-Wabel et al. (2013) with biochar produced from *Conocarpus* shows that the stable C is increased at the same time that the temperature is increased. The most important increase was seen between the pyrolysis at 200 ºC that resulted in an approximate 45 % of stable C percentage and the pyrolysis performed at 400 ºC where this percentage increased to approximately 70 %. The increase in stable C continued to increase at higher temperatures but more moderately, reaching a maximum of approximately 80 % at a temperature of 800 ºC (Al-Wabel et al., 2013).

The pH of the raw samples ranges from 6.47 to 7.63. The pyrolyzed samples showed a slightly lower pH in the sludge treated at 220 ºC. For the pyrolyzed samples at 320 ºC, the pH increased again slightly, although in all cases it was below the pH corresponding to the sludge without previous thermal treatment. That may be caused by volatilization of ammonia and other nitrogen compounds during the thermal process (Ruiz- Echarri Rueda, 2011). In other experiments the pH decreases in the pyrolyzed biochar at different temperatures. An example of this is the study carried out by Zhao et al. (2017) in which rapeseed stem was used to produce the biochar, the results show an increase in pH when the temperature increases from 300 ºC to 500 ºC. In the results on the pH measurement of the experiment performed by Al-Wabel et al. (2013) it is also shown that the pH rises directly when the temperature increases. This study analyzed the change of pH in *Conocarpus* biochar with temperature variation among other characteristics. The lowest temperature was 200 ºC and the maximum was 800 ºC. In the results a clear increase can be observed when increasing the temperature.

7. Conclusion

The purpose of this experiment was to study the total and bioavailable P, K, and S concentrations and the percentage of stable C from various sewage sludges from different locations in the Czech Republic. The study analyzed the effect of two types of thermal treatments at low temperatures on the behavior of nutrients and stable C in the various sludges.

The results of the study indicate that total P concentrations in the sludges was the highest with a mean of 26816 mg/kg, followed by concentrations of S with a mean of 13422 mg/kg and K with a mean of 3965 mg/kg. However, a variability in the available nutrient concentrations can be noticed with P, S and K concentrations respectively ranging from 341-14167 mg/kg, 640-6775 mg/kg and 426-3683 mg/kg. The mean availability from total concentration was 18.8 % of P, 38.9 % of K and 24.2 % of S.

The percentage of stable C in all raw samples are relatively high with majority of values ranging between 45-60 % once pyrolyzed at 320 °C. The percentage of stable C shows a more regular behavior between the raw and pyrolyzed samples, being in most cases, the pyrolyzed sludge at 320 ºC which shows a higher concentration. However, the sludge treated at 220 °C did not show significant differences with the raw material. This suggests the positive effect of the higher pyrolysis temperature on the samples to achieve a higher percentage of stable C.

The pyrolyzed samples show a mass loss that is clearly greater for sludge subjected to temperatures of 320 °C than for those treated at 220 °C. The mass loss of the pyrolyzed samples at 320 °C and 220 °C respectively ranges between 27-43 % and 8.67-16.3 %. This loss of mass due to the volatilization and decomposition of compounds (such as organic compounds composed of cellulose and proteins) modifies the bioavailability of K, P and S and influences the forms of the elements in the different sludges. However, it cannot be clearly seen how these nutrients are altered since the concentrations vary from sample to sample.

The physio-chemical parameter studied in this work was pH, which shows a decrease in pH in all the pyrolyzed samples. In the samples of 220 ºC this acidification is slightly higher than in the sludge treated at 320 ºC. It is clear that the temperature of pyrolysis plays a significant role of the availability of nutrients and the stability of C. Most importantly, the composition and treatment of the sewage sludge before pyrolysis has a leading role in the availability and concentration of the nutrients and C that will be present in the biochar.

8. References

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