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**The Accumulation of Phosphorus in Maize Biomass Treated by  
Thermally Processed Sewage Sludge**

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## **Declaration**

I declare that this diploma thesis work on “**The Accumulation of Phosphorus in Maize Biomass Treated by Thermally Processed Sewage Sludge**” is my own work and all resources I cited in it are listed in references.

Prague, 23<sup>rd</sup>, April 2021

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## Abstract

A three-year (2018 - 2020) pot experiment with maize plant and two soils (Žamberk and Citov) has been set up at the outdoor precipitation-controlled vegetation lobby at the department of Agro-environmental Chemistry and Plant Nutrition, Czech university of life science to investigate the effect of sewage sludge and sewage sludge biochar on the yield and uptake of P by the maize crops. For this purpose, 12 treatments: control, no sludge (NK), fresh sludge, oven dry sludge, biochar produced at 5 different temperatures (BC 220, 320, 420, 520 and 620 °C), triple super phosphate (TSP) 100% P, TSP 50% P, and rock phosphate (RP) 100% P have been established. Eight maize plants were sown at the beginning May, thinned to four at the 14 days after sowing, regularly irrigated to 60% of the respective soil maximum water holding capacity. The maize plants were then harvested at the full maturity, dry biomass weighed, the concentration of P analyzed, and the total removal of P calculated. In the acidic Žamberk soil (pH = 5.2), all the amendments (fresh and dry sludge, all biochars) and P fertilizer treatments had higher maize yield than no sludge (NK) treatment at all three-growing seasons except the TSP 50% at 2019. However, in the neutral Citov soil (pH = 7.3), RP 100% in 2018, all P fertilized treatments in 2019 and all amendments except BC 520 in 2020 had lower maize biomass than no sludge (NK) treatments of the respective year. Comparison between all biochar treatments the BC 220 had the highest maize biomass yield. Comparing biochar and P fertilized treatments, the TSP 100% had higher maize yield than all other biochars, but the TSP 50% and RP 100% had equal or less biomass yield than all biochar treatments. The cumulative removal of P in Žamberk over three years was higher in all amendments and P fertilized treatments than the no sludge (NK) treatments. It was also evident that the highest portion of P removed was at the first growing season. However, in Citov soil the higher cumulative maize biomass compared to no sludge (NK) treatment was only at the TSP 100%, BC 320, BC 420 and BC 620 treatments, while the rest exhibiting lower P removal than the no sludge (NK) treatments. This was consistent with the PUE, in which the positive PUE was only at the TSP 100%, BC 320, BC 420 and BC 620 treatments. Therefore, based on the findings of this study, the better performance of sewage sludge and sewage sludge biochar in acidic soil could be expected with a possible effect of longevity up to three years. Additionally, the sewage sludge and sewage sludge biochar could potentially substitute TSP and RP fertilizers.

**Key word:** Sewage sludge, Sewage sludge biochar, P fertilizers, Maize yield and Uptake of P

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## 1. Introduction

The fast growth of human population promotes worldwide food deficiency, which is leading to intensive utilization of phosphate fertilizer and continual misuse of phosphate rocks in the planet. In addition to this, the considerable fixation and loss of phosphate fertilizer in the soil makes P unavailable while making the phosphate mineral assets decreases (Yang et al., 2021). Global food production is subject to consistent supply of phosphorus to the soil. Currently, world agriculture is enormously dependent on phosphate-rock, which is a very limited asset. Generally, more than 30% of world arable land is P lacking to supply efficient crop production and the world P resource is expected to be totally drained by 2050. Therefore, looking for an alternative sustainable source of P is essential to keep feeding the growing human population. And due to the reason of finding a sustainable source of P, there is a high interest in agricultural to utilize sludge acquired from wastewater treatment plants (Sommers, 1977). But sewage sludge by itself contains considerable amounts of both organic and inorganic contaminates, which could pass to human food chain very easily (Singh and Agrawal, 2008; Brookman et al., 2010). For this reason, conversion of sewage sludge to a form with less content of contaminants is needed. For this purpose, the conversion of sewage sludge to biochar seems very promising. For example based on the study of Zielińska and Oleszczuk, (2015), 99.8% of polychlorinated biphenyls (PCBs), PAHs and endocrine-disrupting and hormonal compounds were degraded by the production of biochar at 600 C from the sewage sludge. When we come to nutrients, biochar produced from sewage sludge has also a considerable amount of P, N, K and Ca (Zielińska et al., 2015). Hence, the maximum release of P from sewage sludge and investigation of biochar produced at different temperature is needed. Therefore, this thesis work investigates the release of P from sewage sludge biochar produced at different temperatures, compares with P fertilizers and determine their effect on the yield and uptake of nutrients by crops.

## **2. Literature review**

### **2.1.Plant nutrients**

All plants require nutrients from the soil or any other growth medium for their metabolism and growth (Mitra, 2017). For the efficient development and growth plant uptake of nutrients is mostly require in an inorganic form (Naeem et al., 2017). According to Fageria et al. (2011), 18 elements, C, H, O, N, P, K, Ca, Mg, S, Fe, Zn, Cu, Mn, B, Cl, Mo, Co, and Ni, have been considered as essential for plant nutrition. The essential nutrients are very crucial for plants, so that plants cannot complete their lifecycle in the absence of them, they cannot be replaceable by any other elements, and they directly involve in the metabolism of plants (Kirkby, 2012). Among these essential nutrients, the first group members are carbon (C), hydrogen (H), and oxygen (O) called basic structural nutrients, which plant and animals are mainly composed and basis for carbohydrates such as sugars, starch and are also sources of energy for the plant. Plant obtains them from the air ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ) (Whitehead, 2000). The second group of essential nutrients called macronutrients, needed in a higher amount than is known as micronutrients. This macronutrient element includes N, P, and K, S, Ca, and Mg. The third group essential of elements called micronutrients, needed in smaller amounts by plants and contain: Zn, Fe, Mn, Cu, B, Mo, Cl, Co, and Ni (Naeem et al., 2017).

#### **2.1.1. Nitrogen**

Nitrogen is the most widely distributed element in nature, present in lithosphere, atmosphere, and hydrosphere. The uptake of nitrogen by plants is in the form nitrate ( $\text{NO}_3^-$ ) ion or ammonium ( $\text{NH}_4^+$ ) ion depending on plant species and the properties of soil like pH and redox state. Availability of ( $\text{NO}_3^-$ ) and ( $\text{NH}_4^+$ ) in the nutrient medium determine uptake rate of both. The translocation of nitrogen in plants takes place mainly as nitrate and amino acids through the xylem from the roots towards the upper plant parts (Mengel and Kirkby, 2010). Nitrogen is very mobile element, typically taken by plants through mass flow, dissolves easily in water and transported within the plant in the flow of water. The concentration of N-containing solutes, mainly nitrate may change rapidly due to processes such as active uptake by plant roots and microorganisms,

leaching and denitrification. Ammonium is mostly high in anaerobic soils (flooded soils) and regularly very low in aerobic soils because of rapid nitrification of  $\text{NH}_4^+$ . Nitrogen-sufficient plants contain 1 – 5% of N (Karthika et al., 2018). There are different sources of nitrogen for plants, such as biological N fixation and the organic and industrially available inorganic N resources (Naeem et al., 2017). Nitrogen has a very vital benefit in the development and growth of plants, and it is a component of proteins, amino acids, purine, and pyrimidine rings of nucleic acids, chlorophyll, and enzymes. Furthermore, major plant activities such as photosynthesis by chlorophyll are affected by the sufficient supply of N in soils. Otherwise, the deficiency of N could result in limited growth, yellowish color on the leaves of plants (Naeem et al., 2017).

### **2.1.2. Phosphorus**

P is one of the most essential elements for all life on our planet (Desmidt et al., 2015). Among six major macronutrients, P is the one with the least availability and have limited reachability in the soil but it is required in higher amount (Barreto et al., 2018; Soetan et al., 2010). From the total P, more than 90% of P found as insoluble and fixed forms including primary phosphate minerals, insoluble phosphates of Ca, Fe and Al and P fixed by hydrous oxides and silicate minerals. Adsorption of Phosphate declines in relation to increasing pH until a pH of 6-6.5 is reached (Fageria et al., 2010). Phosphorus occurs in soil mostly in the form of orthophosphate with total P concentrations often in the range of 500 - 800  $\text{mg kg}^{-1}$  dry soil. P concentration in the soil solution is often low (2 to 10  $\mu\text{m}$ ) (Raghothama, 1999). High  $\text{H}^+$  concentrations shift the equilibrium to the more protonated form in relation to the equation (Fageria et al., 2010). Around 200 P minerals occur in nature, apatite are the sole important group. Inorganic phosphorus present in soil solution either in homogeneous equilibria or heterogeneous equilibria thus in liquid phase only or being between the solid and liquid phases. In a solid phase of soil, the bulk of P is found in three forms, which are in form of organic compounds, in form of adsorbed on the surface of soil particles, and in form of sparingly soluble minerals. P is also present in a lattice of clays and other silicate minerals. Plant roots obtain P as phosphate primarily in the form of  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ , from soil solution (Vance et al., 2003). Transportation of P in soil solution is by three means, (a) mass flow (with the flowing of water), (b) the action of soil organisms, and (c) diffusion (thermal movement along a concentration gradient). The thinner, longer and denser of plant root, the more

in contact with the phosphate in the soil solution. Roots of higher plants as well as numerous microorganisms (*Aspergillus*, *Penicillium*, *Mucor*, *Rhizopus*, *Bacillus*, *Pseudomonas*) produce enzyme phosphatase. Phosphate is easily mobile in plants and can move upward or downward directions opposite to the soil, where it is less mobile. Translocation of phosphate by root is via xylem mainly to fast growing young leaf where P is needed for leaf expansion and growth . The P concentration in plants with sufficient P varies from 0.1 - 0.4% by weight (Rattan, 2015) and in cytosol of plant cells, the concentration of phosphate is in the range between 5 and 8 mmol L<sup>-1</sup> (Lauer et al., 1989). At the beginning, the deficiency symptoms of P make the plants to look weak, make them slowly grow, and are then hindered growth. Under P deficiency, the leaves and stems become purple, and the lack of P can be the reason for poor seed and fruit development and retard maturity (Schachtman et al., 1998; Barreto et al., 2018; Soetan et al., 2010).

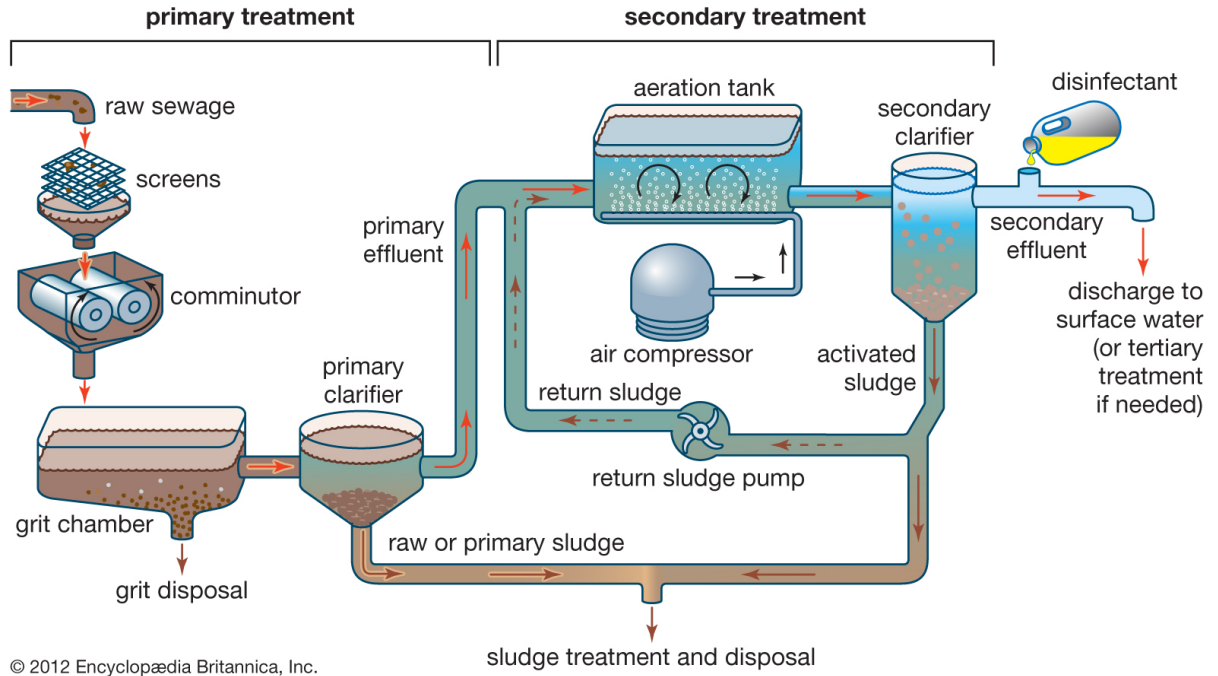
### **2.1.3. Potassium**

One of essential element for plants growth and development is potassium. The greatest portion of soil K<sup>+</sup> is bound in primary minerals and in the secondary clay minerals. The main source of K<sup>+</sup> for plants growing under natural conditions comes from the weathering of K<sup>+</sup> bearing minerals. Potassium released by minerals into the soil solution can then be taken up directly by plant roots or be adsorbed by soil colloids. An equilibrium may thus be set up between adsorbed K<sup>+</sup> and the free K<sup>+</sup> in soil solution. The K<sup>+</sup> level in the soil solution resulting from this equilibrium depends very much on the selectivity of the adsorption sites. Potassium is taken by plants in the form of K<sup>+</sup> ion. Potassium is highly mobile in plants and long-distance transport occurs in xylem and phloem (Fageria et al., 2010). K is the most important cation species in plants for both physiological and biochemical functions. It is crucial for the synthesis of simple sugars and starch, translocation of carbohydrates, and helps in normal cell division, plays a role in the maintenance of turgor pressure in plant cells as well as in the formation of oils, and in the enhancement of disease resistance (Marschner, 2011) and contribute for the survival of plants exposed to various biotic and abiotic stresses (Wang et al., 2013). K deficiency could be invisible at the beginning.

Then it slightly reduce plant growth rate and later on it could causes chlorosis and necrosis (Fageria et al., 2010).

## **2.2.Sewage sludge**

Sewage sludge, which is also known as biosolid or domestic wastewater residuals is a by-product of a waste water treatment process (Singh and Agrawal, 2008; Demirbas et al., 2017). Due to the difference in the method used for the treatment of waste water the solid content of sewage sludge could varies from 0.25 – 12% by weight of the total sewage weight (Metcalf et al., 1979). Worldwide there is large production of sewage sludge. For example in Europe the amount of dry weight sludge resulted from waste water treatment is about 90 g per person per day (Davis, 1996). Wastewater treatment process is combination of chemical, physical, and biological removal processes of solids, organic matter and often, nutrients and contaminants from wastewater. For the improved efficiency of treatment, there are different level of wastewater treatment process, mainly primary and secondary. Primary treatment is the first step of the process with the aim of taking away of larger materials, coarser solids and heavy inorganic solids called grit, which consist of pieces of paper, garbage, wood, cloth, sand, metals and glasses found in wastewater (Figure 1). The objective of primary treatment is removing organic and inorganic solids by the physical processes of sedimentation and flotation. About 25 - 50% of the incoming bio- chemical oxygen demand, 50 - 70% of the total suspended solids and 65% of the oil and grease are removed during primary treatment. Secondary treatment designed for further treatment of the effluent from primary treatment to remove the residual organics and suspended solids. According to the size of the solids, the distribution is approximately 30% suspended, 6% colloidal and about 65% dissolved solids. Biological treatment of wastewater includes in these treatment levels and uses different types of microorganisms in a controlled environment. Various aerobic biological processes are used for secondary treatment differing primarily in the manner in which oxygen is supplied to the microorganisms (Sonune and Ghate, 2004). Then final treatment, may use single or combination of composting, drying, line addition, incineration, wet oxidation, pyrolysis or disinfection, storing, transportation, and finally, it could be land filled, used in agriculture or other possible uses.



**Figure 1.** Primary and secondary treatment of wastewater (Britannica, 2020)

### 2.2.1. Properties and composition of sewage sludge

Both properties and composition of sewage sludge widely varies depending on the source and processing stage of the sludge (Table 1). In most cases, pH of sewage sludge ranges from slightly acidic to slightly alkaline. On general bases, a sewage sludge contains organic compounds, both macro and micro-nutrients, heavy metals, organic micro pollutants and also microorganisms (Singh and Agrawal, 2008; Brookman et al., 2018; Zhang et al., 2017). Sewage sludges has mostly a high content of organic matter and wide range based on the source of the sludge. The organic matter content of air dried sewage sludge was 19.8% in sewage sludge from Thailand (Parkpain et al., 1998), 43.4% (dry weight) from Spain (Fernando et al., 2002) and 23.2% (dry weight) from India (Nandakumar et al., 1998). Similarly, a wide range of nutrient content and properties of the sludge based on the treatment stage of the sludge and source of the sludge. Activated sludge is usually reported to have higher percentage of nutrients (N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O) from the total dry solid than both untreated and digested primary sludge (Metcalf et al., 1979). The composition and



reaches of sewage sludge with plant nutrients have been confirmed by many studies (Lakhdar et al., 2010; Singh and Agrawal, 2010; Latare et al., 2014; Lemming et al., 2016).

**Table 1.** Physico-chemical properties, heavy metal and organic pollutant contents of thermally dried sewage sludge

Parameter	Units	Value
Dry matter	%	94.5
WHC	%	74.7
pH	water, 1:5 (v/v)	6.9
Electrical conductivity	dS m <sup>-1</sup> , 25 °C	3.57
Organic matter	g kg <sup>-1</sup>	687
Stable organic matter	%	40.4
N	g kg <sup>-1</sup>	60.6
Non-hydrolyzable N	g kg <sup>-1</sup>	19.1
Hydrolyzable N	g kg <sup>-1</sup>	41.5
NH <sub>4</sub> -N	g kg <sup>-1</sup>	8.0
P	g kg <sup>-1</sup>	20.5
K	g kg <sup>-1</sup>	2.2
Cd	mg kg <sup>-1</sup>	1.3
Cr	mg kg <sup>-1</sup>	30
Cu	mg kg <sup>-1</sup>	645
Hg	mg kg <sup>-1</sup>	0.95
Ni	mg kg <sup>-1</sup>	53
Pb	mg kg <sup>-1</sup>	3747 <sup>a</sup>
Zn	mg kg <sup>-1</sup>	952
DEHP	mg kg <sup>-1</sup>	27
LAS	mg kg <sup>-1</sup>	331
NPE	mg kg <sup>-1</sup>	76 <sup>b</sup>
PAH	mg kg <sup>-1</sup>	0.3
PCB	mg kg <sup>-1</sup>	0.029
PCDD/F	ng TEQ kg <sup>-1</sup>	13.7

The values were expressed as dry weight basis, except for dry matter and water holding capacity (WHC). DEHP: ¼di(2-ethylhexyl)phthalates; LAS¼: linear alkylbenzenesulphonates; NPE: ¼nonylphenols; PAH: ¼polycyclic aromatic hydrocarbons; PCB: ¼polychlorinated biphenyls; PCDD/F: ¼Polychlorinated dibenzodioxins and dibenzofurans (Ramírez et al., 2008).

### 2.2.2. Adverse effect of sewage sludge

One of the risks associated with the use of sewage sludge in agriculture is high levels of organic pollutant and heavy metals release in the soil and their possible uptake by plant and/or limiting growth of crops. Sludge of any source of country and at any stage of processing have a considerable amount of heavy metals with specific amount differing per specific source and stage of processing (Table 2) (Hsiau and Lo, 1998; Černe et al., 2019).

**Table 2.** Content of chemically fixed metals in sewage sludge.

Parameter	LS	LSS	CS	CSS	S	NSSS	ANSSS	ASSS
Cr (mg kg <sup>-1</sup> sludge)	52.2	62.9	73.4	86.3	89.9	21.1	88.6	30
Pb (mg kg <sup>-1</sup> sludge)	81.1	82.3	93.9	85.6	138	32.8	51.2	42
Zn (mg kg <sup>-1</sup> sludge)	622	517	625	498	1089	650	1112	917
Cu (mg kg <sup>-1</sup> sludge)	119	96.1	112	96.8	202	103	393	186

S: untreated sludge; LS: lime-treated sludge; LSS: lime–sodium silicate-treated sludge; CS: cement-treated sludge; CSS: cement–sodium silicate-treated sludge (Hsiau and Lo, 1998). NSS: No biological stabilization; ANSSS: Anaerobic stabilization; ASSS: Aerobic stabilization (Černe et al., 2019).

The higher content of heavy metals in sewage sludge could end up in increased uptake of those metals. For example based on the study of (Singh and Agrawal, 2010), higher concentration of Ni and Pb in the grain of mung bean (*Vigna radiata* L.), was reported, which was higher than the allowable limit of the metals in the specific country of the study (India). Other study also shows increment of yield, however it brings risk of food contamination by Ni and Cd accumulated in rice grains and aboveground parts of the rice exceeding allowed Indian safe limits (Singh and Agrawal, 2010). In addition to heavy metals, other harmful toxics can be present in sewage sludge. Some of the organic compounds are as DEHP (di(2-ethylhexyl) phthalate), NPEs (sum of nonylphenol and nonylphenol ethoxylates with one or two ethoxy groups) and PCBs (sum of polychlorinated biphenyl) also presented (Aparicio et al., 2007). According to [Sánchez-Brunete et al., \(2008\)](#), sludge samples from province Madrid municipality contained aldrin and  $\alpha$ -BHC in higher amount, followed by DDT and its metabolites, and also levels of organochlorine pesticides (OCs) found

alike to other authors reports. According to Jelic et al. (2011), over two years 72 sludge samples collected from three conventional wastewater treatment plants and the sample were analysed and obtained the presence of 32 organic compounds (e.g. NSAIDs) in wastewater influent and 29 in effluent, in concentrations ranging from low  $\text{ng L}^{-1}$  to a few  $\mu\text{g L}^{-1}$  from the total obtained, 21 pharmaceuticals accumulated in sewage sludge from all three waste water treatment plants in concentrations up to  $100 \text{ ng g}^{-1}$ .

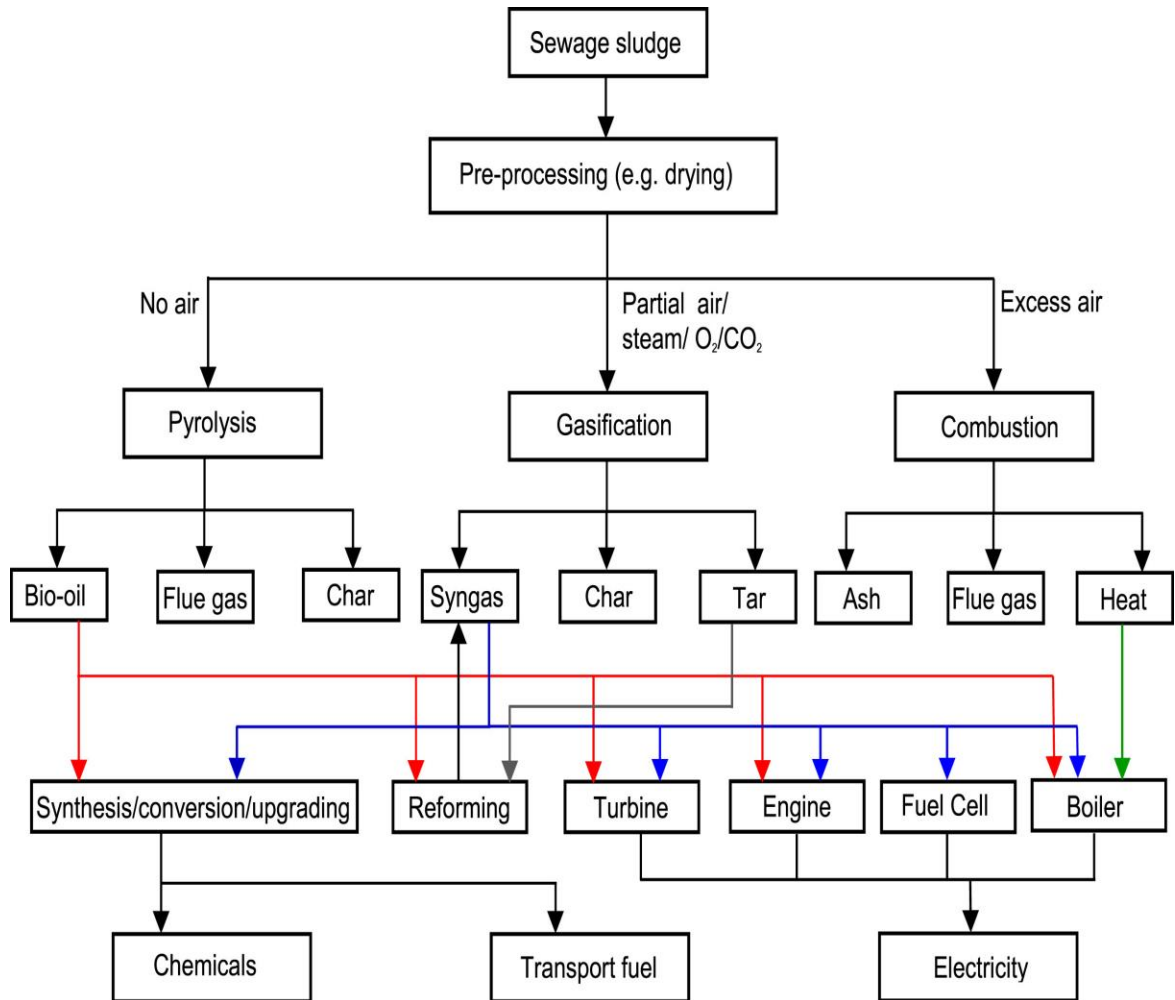
### **2.2.3. The effect of sewage sludge on the yield and uptake of nutrients by crops**

Vast majority of sewage sludge end up in agriculture as source of fertilizer in most countries (Yu, 2011; Westerhoff et al., 2015; Wang et al., 2020). The effect of sewage sludge on the properties of soil could depend on the initial properties of sludge. Sewage sludge was reported to decrease pH of soil, when applied to soil having alkaline pH (7.9 pH  $\text{H}_2\text{O}$ ) (Fijalkowski et al., 2018). The decline in the pH of soil with the addition of sewage sludge is mainly linked due to the acidification effect of humic acid resulted from the decomposition of sewage sludge in the soils. Sewage sludge application to soil had a positive effect on the increasing the uptake nutrient and yield of crops. Based on the study of Singh and Agrawal, (2010), shoot length, leaf area and total biomass had improved after the application of sewage sludge. The uptake of nutrients mainly N, P, K, Ca, Na and Mg also increased by the application of sewage sludge. Similarly, based on the study of Singh and Agrawal, (2010), the application of sewage sludge increased number of leaves, leaf area and total biomass yield of rice compared to control. The increment in the yield of at the highest sewage sludge application rate of  $12 \text{ kg m}^{-2}$  (dry weight) acquired up to 137% of increment in the yield. This was again in agreement with the finding of (Latare et al., 2014), where they reported up to 45% increment of rice yield at sewage application rate of  $40 \text{ t ha}^{-1}$  (dry weight). On different study, the application of sewage sludge increased the soil content of P and nitrate N, this intern increased the yield of sunflower (Lavado, 2006).

#### 2.2.4. Treatments of sewage sludge

Usage of sludge in agriculture within the European Union (EU) is currently regulated only by the limits of heavy metals (Cd, Cu, Hg, Ni, Pb and Zn) listed in Council Directive 86/278/EEC. It also states that the use should be by avoiding any chance of harmful effects on soil, vegetation, animal and humans (Council, 1986). Therefore, the use of untreated sewage sludge is not allowed in agriculture. The pH (alkalinity and organic acid content), heavy metal content, content of pesticides and hydrocarbons are the most important parameters of sewage sludge, which must be determined before its use in agriculture (Hall, 1995). Now a days there are a thermal way of handling sewage sludge such as pyrolysis, gasification, wet oxidation, incineration and combustions (Wang et al., 2020). Thermochemical conversion of sewage sludge is one of the promising methods including decomposition of nearly all organic parts of the sludge either biodegradable or not by using controlled heating and/or oxidation, convert to energy and fuel immediately. According Syed-Hassan et al. (2017), there are three principal ways of thermochemical conversion are pyrolysis, gasification and combustion (Figure 2).

Combustion is a process of burning organic materials in the presence of excess air. In this process, stored chemical energy is converted into heat as a source of thermal energy (e.g. for electricity generation using steam turbine). Gasification is the exothermic thermochemical alteration of organic material optimized to produce high yield of an energy rich gaseous mixture ( $H_2$ , CO,  $CO_2$  and light hydrocarbons) through a series of chemical reactions. The process is conducted at high temperature (800–900 °C or even higher) in an oxygen deficient environment (Syed-Hassan et al., 2017). Among those the pyrolytic result of sewage sludge under very limited or total absence of oxygen is called sewage sludge biochar and we will discuss in more detail about sewage sludge biochar in the following chapters. Treatment of sewage sludge by pyrolysis have numerous advantages over other thermal treatment process. Firstly, there is very smaller production of gases (hydrogen, methane, carbon monoxide, carbon dioxide). Secondly, the final product char contains very small number of inert materials and mainly it is composed of pure carbon. The liquid fraction consists of oil such as acetic acid, acetone, and methanol. Those methods are in use today to generate energy, and to decrease at least the need of large disposal areas and destroy organic pollutants (Metcalf et al., 1979).

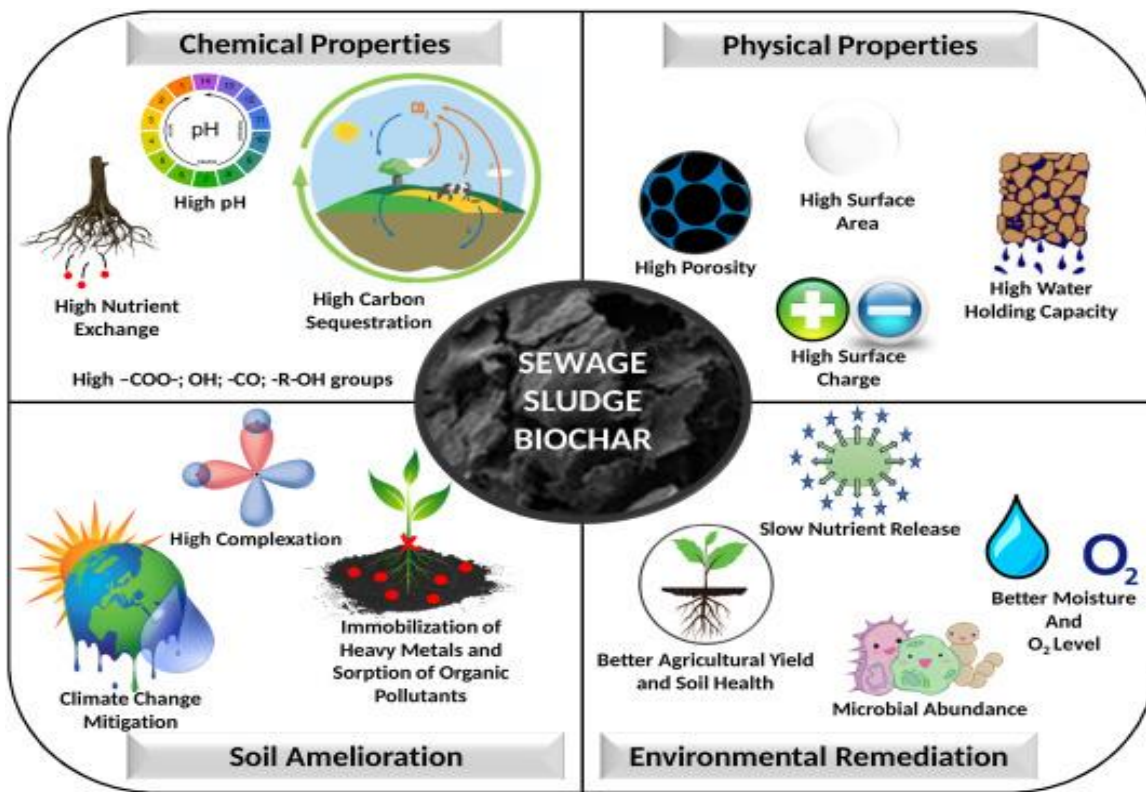


**Figure 2.** Potential applications of thermochemical conversion of sewage sludge (Syed-Hassan et al., 2017).

### 2.3.Sewage sludge biochar

An efficient way of sewage sludge management is very demanding due to the production of very high amount of municipal waste especially in the case of big cities (Khanlari et al., 2020). For example based on the report of Gendebien et al. (2010), around 10.1 million tons of sewage sludge per year is estimated to be produced only in Europe. In addition to its higher production amount, the pathogenic nature and the high accumulation of heavy metals and organic compounds make disposal of sludge hardly. Therefore, the conversion of sewage sludge to biochar and its use in agriculture could be an efficient way of sewage sludge disposal. Biochar is a pyrolytic result of

biomass under very limited or total absence of oxygen. In general, the biochar yield and properties are highly dependable on the production temperature and feedstock used for the production. Both factors again affecting biochar performance in soil effect the yield and uptake of nutrients. The use of different production temperature from different feedstock could also result in biochar with very different properties (Li et al., 2019). The general properties and use of sewage sludge biochar are stated on (Figure 3) (Singh et al., 2020). The use of sewage sludge for better crop production could arise from its higher pH, high nutrient exchange capacity, high surface area, porosity and water holding capacity, efficient carbon sequestration and immobilization of heavy metals.



**Figure 3.** The properties of sewage sludge biochar and effect in soil (Singh et al., 2020).

Sewage sludge biochar has different effect on soil physical properties. Sewage sludges are basically solid, nonporous material and the pyrolysis results in the development of different surface texture. Increasing in surface area can vary widely, from 6 to almost 40 times, which can be cause high water holding capacity and surface charge. The application of biochar to soil could increase soil pH, increase nutrient exchange capacity, and efficiently sequester carbon. The environmental

remediation capabilities of biochar is again mainly rise from its capability to increase soil pH, increase CEC, surface properties and functional groups such as carboxylic groups (Zheng et al., 2012; Hailegnaw et al., 2019; Chen et al., 2014). The physical and chemical properties of sewage sludge could varies depending on the source of sewage sludge and biochar production temperature (Zielińska et al., 2015). Important properties of sewage sludge biochar as affected by the source of sewage sludge and production conditions are described below in details.

### **2.3.1. Yield and surface properties of sewage sludge biochar**

The increment of biochar production temperature is expected to decrease the biochar yield mainly due to the decomposition of the feedstock material at the higher production temperature and loose of volatile organic matters (Onay, 2007); (Gao et al., 2014); Agrafioti et al., 2013; (Lu et al., 2013). The increment of sewage sludge biochar production temperature from 300 - 700 °C decreased yield from 72.3 - 52.4% (Hossain et al., 2011). The decline in the yield of biochar with the increment in the pyrolytic temperature is associated with the primary decomposition of sewage sludge organic matter and secondary reaction which results in higher loose of H, N and O (Zielińska et al., 2015). Surface area of biochar derived from sewage sludge fertilizer has tripled as the temperature of production increased from 400 - 950 °C (Bagreev et al., 2001). Based on their finding, the increment of porosity or total pore volume from 0.075 to 0.15 cm<sup>3</sup> g<sup>-1</sup> is responsible for the increment of surface area with production temperature (400 – 950 °C). Furthermore, the increase in the porosity is linked due to the loose of the volatile fraction of the organic matter of the sludge. The study of Hossain et al. (2011), clearly revealed the decline of volatile matter in the raw sludge accounting 50% of the total dry mass to 33.8 and 15.8% at the biochar production temperature of 300 and 700 °C, respectively.

### **2.3.2. pH and cation exchange capacity (CEC)**

The pH of biochar could vary from acidic to alkaline values based on the type of feedstock used and production conditions (pyrolysis temperature, speed of pyrolysis and holding time). For example, based on the study of Zhang et al. (2017), the lowest pH was attributed from pine wood

biochar. The increment of biochar production temperature from sewage sludge has increased from 5.5 - 8.0 (Table 3) as the temperature rises from 220 to 620 °C (Mercl et al., 2020). Similarly the increment of sewage sludge biochar production temperature from 300°C to 700°C increase pH from 8.2 to 12 (Khanmohammadi et al., 2015). Analogous to previous studies, pH of sewage sludge biochar increased from 7.8 – 8.7 with increment of production temperature (400 – 600 °C) (Méndez et al., 2013). Again a clear increment of pH of sewage sludge biochar from 5.3 - 12 has been reported as the production temperature rises from 300 - 700°C (Hossain et al., 2011).

**Table 3.** The effect of sewage source and biochar production temperature on the concentration of elements (Zielińska et al., 2015).

	SSKN	BCKN			SSKZ	BCKZ			SSCM	BCCM		
		500	600	700		500	600	700		500	600	700
<b>Yield</b>	-	54.29	51.27	48.66	-	50.37	46.4	43.69	-	54.45	51.1	49.46
<b>pH</b>	7.08	7.13	11.04	12.23	7.19	7.08	11.45	12.38	7.01	7.17	11.33	12.44
<b>Ash</b>	55.83	73.56	77.77	79.08	61.32	68.09	70.27	74.28	58.08	68.98	70.22	71.99
<b>N</b>	0.52	0.16	0.05	0.03	0.18	0.14	0.07	0.01	0.39	0.17	0.13	0.12
<b>P</b>	3.4 ±0.25	5.4 ±0.37	5.92 ±0.40	6.31 ±0.42	3.53 ±0.26	5.88 ±0.39	6.48 ±0.42	6.86 ±0.44	3.42 ±0.25	5.47 ±0.37	5.31 ±0.37	5.6 ±0.38
<b>K</b>	0.54 ±0.05	0.92 ±0.08	1.01 ±0.08	1.09 ±0.08	0.8 ±0.07	1.4 ±0.11	1.55 ±0.12	1.64 ±0.12	0.75 ±0.07	1.25 ±0.10	1.34 ±0.11	1.34 ±0.11
<b>Ca</b>	5.41 ±0.35	8.27 ±0.51	9.18 ±0.56	9.71 ±0.59	4.04 ±0.27	6.75 ±0.43	6.02 ±0.38	7.42 ±0.46	7.41 ±0.46	12 ±0.70	11.4 ±0.61	12 ±0.70
<b>Mg</b>	0.57 ±0.06	0.94 ±0.09	1.08 ±0.09	1.13 ±0.10	0.88 ±0.08	1.47 ±0.12	1.65 ±0.13	1.78 ±0.14	0.69 ±0.06	1.13 ±0.10	1.25 ±0.10	1.27 ±0.10
<b>Fe</b>	6.83 ±0.43	11.5 ±0.68	12.5 ±0.73	13.2 ±0.76	5.2 ±0.34	9.35 ±0.57	10 ±0.60	10.7 ±0.64	1.38 ±0.11	2.41 ±0.17	2.51 ±0.19	2.57 ±0.19
<b>S</b>	2.8 ±0.22	3.55 ±0.27	3.97 ±0.29	4.51 ±0.32	3.8 ±0.28	4.68 ±0.33	3.64 ±0.27	5.17 ±0.36	2.26 ±0.18	2.71 ±0.22	2.24 ±0.18	2.3 ±0.19
<b>Al</b>	2.18 ±0.17	3.33 ±0.24	3.7 ±0.27	3.86 ±0.27	1.77 ±0.14	2.31 ±0.18	2.58 ±0.19	2.74 ±0.21	2.4 ±0.18	3.21 ±0.23	3.39 ±0.24	3.44 ±0.24

SSKN: sewage sludge from Poland Koszalin (54°11\_25\_N 16°10\_54\_E), SSKZ sewage sludge from Poland Kalisz (51°45\_45\_N 18°05\_23\_E), and SSCM sewage sludge from Poland Chełm (51°07\_56\_N 23°28\_40\_E) BCKN, BCKZ, and BCCM are biochar per respective regions from which the sewage sludge is collected.



The main reason for the increment of pH with production temperature of biochar from sewage sludge biochar is due to the increment of ash content and the polymerization/condensation reaction, which result in the loose of acidic surface functional groups (Gascó et al., 2005). Likewise to the pH of biochar, the ash content of the same biochar has increased from 52.8 to 72.5% as the temperature rises from 300 to 700 °C. Similarly, the study of Bagreev et al. (2001), a significant increment of ash from sewage sludge fertilizer derived biochar from 61.7 to 80.7% has been reported with an increment of biochar production temperature from 400 to 950 °C. Cation exchange capacity decreased with biochar production temperature. Based on the study of Méndez et al. (2013) the CEC decreased from 29.90 cmol<sub>(+)</sub> kg<sup>-1</sup> at 400 °C to 11.67 cmol<sub>(+)</sub> kg<sup>-1</sup> 600 °C. The decline of CEC with the increment in the production temperature of biochar is mainly due to the loose of oxygen containing functional groups (Hailegnaw et al., 2019; Méndez et al., 2013).

### **2.3.3. Content of nutrient**

The composition of nutrients in the sewage sludge is also clearly affected by both the source of sewage sludge and production temperature Table 2. (Zielińska et al., 2015). The concentration of N in sewage sludge biochar from 3 different sewage sludge source decline with an increase of biochar production temperature (Zielińska et al., 2015). As indicated by the study of (Yuan et al., 2013), the relative enrichment (concentration in the biochar/concentration in the feedstock) of N was lower than 1, while higher than 1 in the case of P and K. This indicating there is a relative loose of N during the pyrolysis temperature, while P and K are relatively retained in the biochar (Hossain et al., 2011). The decline in the content of total N is directly linked to the volatilization of N (Bagreev et al., 2001; Yuan et al., 2015). When we come to P, the total content of P increased by 43% after the pyrolysis of sewage sludge at 700 °C. This is a very clear indicative of P association with the inorganic fraction of sewage sludge than the organic portion, which is volatilized during the process (Hossain et al., 2011). Numerically, the available P increased from 493 to 527 mg kg<sup>-1</sup> as the temperature of production increased from 300 - 700 °C. The effect of temperature on both total and available content of P was also clearly evident in the study of (Mercl et al., 2020). Based on their finding, the total content of P increased with the increment of pyrolysis

temperature from 220 - 620 °C. However, the available content was able to increase up to the pyrolysis temperature 320, while decline when the temperature rises above this point. Even if the total content of K in the sewage sludge is very small its concentration slightly increased with an increment of production temperature (Hossain et al., 2011). This finding is in agreement with Mercl et al. (2020), where the total content of K increased as the temperature rises toward 620 °C. Once more, the total content of Ca, Mg and S has also increased with an increment of pyrolysis temperature toward 620 °C. Biochar could always have higher concentration of metals as compared to the original sewage sludge. This is due to the volatilization of the volatile organic matter, which are mainly composed of O and H, however the metal retaining in the biochar (Figueiredo et al., 2019;. Beesley and Marmiroli, 2011; Yuan et al., 2015; Lu et al., 2016).

#### **2.3.4. Content of trace element**

Bioavailability of heavy metals in biochar decreased as compared to their respective sewage sludge (Liu et al., 2014; Figueiredo et al., 2019). Based on the study of Figueiredo et al. (2019) the available content of Co declined from 97.8 to 83.5, Cr from 90.6 to 88.9, Cu from 111 to 82.9, Pb from 106 to 83.4 and Zn from 90.2 to 87.7 as the production temperature increases from 300 toward 500 °C. This is mainly due to their binding with other elements triggered by pyrolysis. For example, an increased level of ZnS and phosphate bounded Pb was reported in biochar as compared to the original feedstock used for the biochar production (Lin and Lee, 2017; Wu et al., 2017).

#### **2.3.5. Composition of organic pollutants**

Composition of organic compounds is also highly dependent on the source of the sludge, pyrolysis temperature and holding time of the biochar (Tomczyk et al., 2020). For example, Di-(2-ethyl-hexyl) phthalate (DEHP), nonylphenol, nonylphenol mono- and di ethoxylates (NPEs) and polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and other

organic pollutants are present in sludge and need monitoring (Ramírez et al., 2008). DEHP is one of the main concern organic pollutant frequently found and detected in municipal sewage sludge and its concentration in dewatered sludge cake was more than the recommended value (100 mg kg<sup>-1</sup> dry matter base) by European Union (EU) for land application. DEHP is widely used as a plasticizer in the production of polyvinylchloride to impart flexibility to the product. Because of its mutagenicity and carcinogenicity, the presence of DEHP in sludge limits the application of sludge as a soil fertilizer (Aparicio et al., 2007). According to Cheng et al. (2000) it was found that the amounts of DEHP present in the different types of sewage sludge samples were all high and exceeded the limitation value (50 mg kg<sup>-1</sup>) of sludge land application. Based on the study of Hale et al. (2012) content of polycyclic aromatic hydrocarbons (PAH) varied from 0.07 µg g<sup>-1</sup> to 3.27 µg g<sup>-1</sup> for the slow pyrolysis biochars dependent on biomass source, pyrolysis temperature, and time. The effect of production temperature was very clear that it greatly decreased the concentration of PAH in the biochar as the production temperature rises. Similar study has shown a decline in the solvent extractable Σ16PAH, which were 3.8 mg kg<sup>-1</sup> in the original sewage sludge toward 0.9 mg kg<sup>-1</sup> in the biochar produced at 550 °C at the holding time of 8 h. Based on the study of Tomczyk et al., (2020), the content of C<sub>tot</sub> Σ16 PAHs in the biochar was up to 95% lower than the content in the original sewage sludge. Among, which the 3-ring PAHs was constituting the major proportion up to 52% of the total PAHs.

#### **2.4.Benefit of sewage sludge biochar in crop production**

The benefit of biochar for crop production is attributed from its benefit in improvement of soil properties like soil pH, CEC and also direct release of nutrients (Sousa and Figueiredo, 2016; Yue et al., 2017; Faria et al., 2018; Fathi Dokht et al., 2017; Khanmohammadi et al., 2017). The application of sewage sludge could induce both a decline and incremental effect on soil pH. Based on the study of Zuo et al. (2019) and Moreno et al. (1997) soil pH declined due to the application of sewage sludge biochar to soil. Contrary to those studies, the addition of biochar from sewage sludge to soil (pH = 5.9) increased soil pH to 6.8, 6.8 by biochar produced at 400 and 600 °C, respectively (Méndez et al., 2013). Similar increment of soil pH after the application of biochar

from sewage sludge has been reported (Bai et al., 2017). The increment of pH was mainly due to the higher content of ash in the biochar and its increment with the increment of pyrolysis temperature (Titova and Baltrėnaitė, 2020).

#### **2.4.1. Release of phosphorous and other nutrients in soil**

Content of plant essential nutrients such as P, N, Ca, Mg, K and Na concentrations of biochars is always dependent on the elemental content in the feedstock used (Enders et al., 2012). Induced increment in soil content of P and S (Waqas et al., 2014). The application of sewage sludge biochar at the rate of 1 and 2% has increased both H<sub>2</sub>O and CaCl<sub>2</sub> extractable P. The amount of both total and available P in soil increased directly as the amount of applied sewage sludge biochar increased (Gondek et al., 2019). Increment of Ca and Mg was also evident with the addition of the sludge biochar. Based on the two- year study of Faria et al. (2018) the application of sewage sludge at the rate of 15 Mg ha<sup>-1</sup> significantly increased soil content of N, P and Mg. The amount of P supplied by their sewage sludge biochar produced at 300 °C was as much as 60.7 kg ha<sup>-1</sup>. The reason for this was due to high total content of O in the original sewage sludge and its more concentration in the biochar as the sludge losses its volatile matters. Other beneficial factor associated with P getting retained in biochar ss due to P presence in the sludge in volatilization resistant form. Almost 70% of the total P in sewage sludge is in its inorganic form ( aluminium phosphate), which is very resistant to the volatilization (Torri et al., 2017). The positive impact of sewage sludge biochar is not only associated with having substantial amount of P, but also on its effect on the properties of soil. For example, the addition of biochar to soil could increase soil pH, sorb cations like Al<sup>3+</sup> and Fe<sup>3+</sup> (Xu et al., 2014; Hailegnaw et al., 2019) meaning that the adsorption of P in soil will be greatly slowed down. In some other studies, biochar was able to release N, P and K and increased yield of soybean (Dokht et al., 2017). Based on their finding the release of P, N and K was even evident after the harvest of soybean.

## **2.4.2. Yield and uptake of nutrients by crops**

Better yield of crop is always dependent on the constant supply of nutrients in the soil. Therefore, finding safe and environment friendly organic fertilizer is crucial. For this, sewage sludge biochar could be a potential source of plant nutrients for increased crop growth. The application of sewage sludge biochar at the rate of 10% in the acidic paddy soil increased shoot biomass up to 92.2% and grain yield up to 175% (Khan et al., 2013). Total biomass of sorghum increased up to 40% by the application of 250 t ha<sup>-1</sup> of sewage sludge biochar (Zuo et al., 2019). In other study the application of sewage sludge biochar produced at 450 °C (1% w/w) increased both the biomass, grain yield and uptake of K and P by wheat crop (Rehman et al., 2018). The highest release of P to soil in relation to the total content of P in the sewage sludge biochar have been also related to the improved uptake of P and then increased biomass yield of *Poa pratensis* L. (Gondek et al., 2019). Similarly, the application of sewage sludge biochar at the rate of 20 t ha<sup>-1</sup> increased the uptake of N, P, K and yield of soybean in a fine texture loess soil (Dokht et al., 2017). The higher rate of their sewage sludge biochar application rate, which is 2% was always associated with the highest uptake of P. Apart from the uptake of nutrients and yield of crops, the growth improvement of different plant tissues has been widely reported. For this the study of Kong et al. (2019) it was evident that the shoot and root length of wheat increased by 4.88% and 11.4%, respectively when sewage sludge biochar is added to soil. Sewage sludge has been also proposed to partly replace NPK fertilizers, due to substantial increase on the uptake of nutrients and increment in the yield of crops (Figueiredo et al., 2019; Faria et al., 2018).

## **2.5. Adverse effect associated to sewage sludge biochar in crop production**

### **2.5.1. Heavy metals**

The production of biochar from sewage sludge could mostly enrich the resulting biochar with risk elements and their amount could further increase with the pyrolysis temperature (Kong

et al., 2019). Based on the study of Zielińska and Oleszczuk, (2015) the amount of metal in sewage sludge biochar has increased relative to the sewage sludge was by 1.2 to 1.7% for Cd, from 1.3 to 1.7% for Pb, from 1.6 to 2.1% for Ni, from 1.7 to 2.4% for Zn and Cr, and from 1.9 to 2.4% for Cu as compared to the sewage sludge used for the biochar production. But even if, sewage sludge biochar is enriched with heavy metals compared to the original sewage sludge their release in soil and uptake by plants remained soil and source of sewage sludge specific. For example based on the study of Chagas et al. (2021), the application of sewage sludge was able to reduce availability of Cd, Cr, Pb and Co in the soil. However, in other studies the opposite was true. For example, based on the study of Zuo et al. (2019), the accumulation of Cd, Cu, Mn, Pb and Zn in both soil and sorghum has increased with the increased application rate of sewage sludge biochar. The toxicity of potential of risk elements from sewage sludge biochar could increase with the rate of biochar addition rate to the soil (Kong et al., 2019).

### **2.5.2. Organic pollutants**

Sewage sludge could contain a wide variety of pollutants from this Polyaromatic hydrocarbons, personal care and pharmaceutical products are major ones. Therefore, we could expect residual content of those compounds in their respective biochars and the application of sewage sludge biochar to soils could potentially lead to their assimilation by plants. The content of organic pollutant in the sewage sludge biochar is highly dependent on the production temperature of the sewage sludge. This agrees with Kong et al. (2019), the total contents of PAHs were reduced as the pyrolysis temperature increased from 300 toward 700 °C. However, some studies also reported an efficient removal of organic compounds. For this, the study of Moško et al. (2021), could be evident that they were able to remove up to 99.8% of polychlorinated biphenyls, polycyclic aromatic hydrocarbons and pharmaceuticals from sewage sludge by the process of pyrolysis. Surprisingly, they were able to remove pharmaceuticals below the detection limit of gas chromatography-mass spectrometry (GC-MS EVOQ; Bruker, MA, USA) they used only at the pyrolysis temperature of 400 °C sewage sludge for 2 h. By further increasing the pyrolysis temperature above 600 °C, they were able to remove 99.8% of polychlorinated biphenyls

(PCBs), PAHs and endocrine-disrupting and hormonal compounds. Thermal treatment of sewage sludge at higher temperature has the potential to cause thermal degradation of those organic compounds making them no more toxic for soil application (Zielińska and Oleszczuk, 2015). This procedure of pyrolysis could be recommended for the efficient removal of those organic pollutants, therefore the risk associated could be potentially reduced.

### **2.5.3. Benefit of sewage sludge biochar over the use of fresh sewage sludge**

Even if the amount of metals such as (Cd, Cu, Pb and Zn) is more concentrated in the biochar than the sludge of its own, the application of sewage sludge biochar lowered the content of metals in radish and corn plant than the corresponding applied sludge (Zhang et al., 2021). This was also confirmed by the study of Waqas et al. (2014), where the application of sewage sludge biochar reduced the accumulation of As, Cu, Pb and Zn in *Cucumis sativa* L than its fresh sewage sludge used for biochar production. The application of sewage sludge could potentially increase the soil content of PAHs much more than the respective biochar. Based on the study of Tomczyk et al. (2020) the addition of sewage sludge to the soil had changed soil content of mutagenic and cancerogenic 5-ring compounds. Soil content of  $\Sigma 16$  PAHs has increased up to 94.7% after the addition of sewage sludge to the soil. But their biochar induced effect on the PAH were not significant as that of the sewage sludge. In addition to that, biochar is more stable than sewage sludge, in which organic matter usually mineralizes within several months from its incorporation into soil. Therefore, the effect of reduced toxicity was more pronounced for the biochars than for sewage sludges (Wang et al., 2017; Zielińska and Oleszczuk, 2015). Furthermore, the addition of sewage sludge biochar produced at 600 °C to sewage sludge amended soil decreased  $\Sigma 16$  PAHs in the soil (Stefaniuk and Oleszczuk, 2016). Moreover, the use of biochar rather than sewage sludge have a diverse benefit including carbon sequestration, contaminant immobilization, greenhouse gas reduction, soil fertilization and improvement of water retention (Racek et al., 2020).

### **3. Scientific hypothesis and objectives**

#### **3.1. Hypothesis**

We expect that the release of nutrients and their uptake could be affected by the production temperature of biochar made of sewage sludge and therefore maize yield can be affected as well.

We expect that the effect of biochar on the release and uptake of phosphorus could be long lasting and visible at least up to the third growing season.

#### **3.2.Objectives**

This study aims to investigate the effect of biochar production temperature from sewage sludge on the availability of phosphorus to maize.

To determine the longevity of phosphorus release from sewage sludge biochar.



## **4. Material and method**

### **4.1. Soil collection**

In 2018, two contrasting soils with different chemical properties, were collected from the top 20 cm agricultural field of Zamberk (Cambisol), and Citov (Fluvisol) Czech Republic. Žamberk soil has a pH value of 5.2 and available P (MehlichIII) content of 35 mg kg<sup>-1</sup> and that of Cítov (Fluvisol) soil have a pH value of 7.3 and available P (MehlichIII) content of 14 mg kg<sup>-1</sup>. The collected soils were then air dried, sieved by 10 mm sieve and homogenized for further use.

### **4.2. Collection of Sewage sludge and biochar production**

Fresh sewage sludge was collected from local wastewater treatment plants of the Czech Republic. The collected sewage sludge was then anaerobically stabilised and dewatered by decanter centrifuge (dry matter content 24 wt. %). After that, the samples were air-dried at 105 °C until constant mass was obtained. After all the dried sewage sludge was milled and passed through a 1 mm stainless sieve before the use of biochar production or any analysis. Then the pyrolysis of sewage sludge was done at inert atmosphere of N<sub>2</sub> (99.99%) using an electric laboratory tube furnace (GHA 12/600, Carbolite Gero Ltd., Hope, UK) by putting of measured amount of air dried sewage sludge in a ceramic holders of a quartz tube, which is connected to the stream of N<sub>2</sub>. The inlet flow of N<sub>2</sub> rate was set to be 100 L h<sup>-1</sup>. The samples were pyrolysed for 30 minutes at 220, 320, 420, 520 and 620 °C temperature (measured from the moment of reaching the target temperature inside the quartz tube). The available and total content of P in the biochars and sewage sludge is presented (Table 4).

**Table 4.** The available (0.11 mol L<sup>-1</sup> CH<sub>3</sub>COOH (1 : 100 w/v)) and total content of P (g kg<sup>-1</sup>) in sewage sludge and biochars produced at different temperatures.

	<b>Total P</b>	<b>Available P</b>
<b>SS</b>	32.6 ± 0.3	5.99 ± 0
<b>BC 220</b>	36.4 ± 0.4	7.31 ± 0.11
<b>BC 320</b>	44.0 ± 0.54	7.65 ± 0.05
<b>BC 420</b>	54.2 ± 0.67	3.68 ± 0.01
<b>BC 520</b>	57.8 ± 0.94	2.34 ± 0
<b>BB 620</b>	60.8 ± 0.39	1.87 ± 0.03

SS: sewage sludge, BC 220, BC 320, BC 420, BC 520, BC 620 represents biochar produced at temperatures of 220, 320, 420, 520 and 620 °C, respectively.

### 4.3. Experimental design

A three-year pot experiment was designed in 2018 by thoroughly mixing a 5 kg of air-dried and homogenized soil with fresh sludge, oven dry sludge, biochar produced at 6 different biochar, triple super phosphate (100%) triple super phosphate (50%) and rock phosphate (100%) at the rate of giving an equal amount of total P content in all treatments (Table 5). All pots were sated up in a completely randomized block design with four replications. Every year, all pots except control were further fertilized by additional N and K. N was applied as NH<sub>4</sub>NO<sub>3</sub> in a dose of 100 mg N kg<sup>-1</sup> soil and K was applied as KCl at 88 mg K kg<sup>-1</sup> of soil. The amendments and P-fertilizers was applied in a dose of supplying 60 mg P kg<sup>-1</sup> soil at the beginning of the experiment in 2018, while the treatment TSP 50% received 30 mg P kg<sup>-1</sup> of soil in the form of TSP.

**Table 5.** The experiment design with 12 treatments each had 4 replicates and 2 soils.

	No sludge (NK)	Fresh sludge	Oven dry sludge 105 (°C)	Biochar (°C)					TSP 100%	TSP 50%	RP 100%	No fertilization (Control)
				220	320	420	520	620				
Žamberk	1,2,	5,6,	9,10,	13,14,	17,18,	21,22,	25,26,	29,30,	33,34,	37,38,	41,42,	89,90,
	3,4	7,8	11,12	15,16	19,20	23,24	27,28	31,32	35,36	39,40	43,44	91,92
Cítov	45,46,	49,50,	53,54,	57,58,	61,62,	65,66,	69,70,	73,74,	77,78,	81,82,	85,86,	93,94,
	47,48	51,52	55,56	59,60	63,64	67,68	71,72	75,76	79,80	83,84	87,88	95,96

TSP: triple super phosphate, RP: rock phosphate. N and K applied in all treatments in all three years except in the control treatment. Sludge, biochar, TSP% and RP 100% was applied to supply 60 mg P kg<sup>-1</sup> soil. TSP 50% received TSP at the rate of 30 mg P kg<sup>-1</sup> of soil.

#### **4.4.Crop cultivation and fertilization**

A pot experiment was set up at the outdoor precipitation-controlled vegetation lobby of the department of Agro-environmental Chemistry and Plant Nutrition. Plants of maize (*Zea mays* L.) were planted in 6L plastic pots filled with soil weighing 5 kg (dry weight) then a sewage sludge, biochars and fertilizer were applied according to the experimental design (Table 5) and mixed uniformly. Eight maize seeds were planted on June 06.2018. Then the plants were thinned to 4 plants at fourteen days after planting. Irrigation was also applied after sowing on regular base to 60% of maximum water holding capacity for each soil. Then plant parts (upper biomass, cob and root separately) were harvested at the full maturity. The same principle was followed for the years 2019 and 2020. P fertilizer was applied before sowing only in 2018. Samples of soil solution were collected 4 times each year, 3 at the plant growing stage and 1 after the harvest, using Soil Moisture Samplers - Rhizons (Rhizosphere, Netherlands) which were installed in the pot while loading up with soil.

#### **4.5.Plant and Soil plant analysis**

The harvested plant biomass and grain were oven dried at 60 °C and grinded to 2mm size. From the grinded plant biomass and grain 0.5 g were weighed and then digested with a mixture of 7 ml concentrated (65% v/v) HNO<sub>3</sub> (Analytika) and 2 ml (30% v/v) H<sub>2</sub>O<sub>2</sub> (Analytika) in Ethos 1 microwave oven (Milestone). Then concentrations of nutrients were determined by an optical emission spectrometer with inductively coupled plasma ICP-OES (Varian Vista Pro, Varian Australia). And that of available P in both soil solution and soil were measured by ICP-MS.

#### **4.6.Statistical methods**

Data were compared using one-way analysis of variance followed by Tukey test. All statistical analyses were done using SPSS 19. MS Excel 2020 was used for the calculation of means

and standard deviations and developing figures. The uptake of P by maize was calculated based on Eq. (1).

$$\text{P uptake (mg pot}^{-1}\text{)} = \text{maize dry matter yield (g pot}^{-1}\text{)} \times \text{shoot nutrient concentration (mg g}^{-1}\text{)}$$

Eq. (1)

P use efficiency (PUE) was calculated according to Eq. (2).

$$\text{PUE (\%)} = \frac{\text{P}_{\text{FT}} - \text{P}_{\text{CT}}}{\text{P}_{\text{ap}}} * 100$$

Eq. (2)

Where,  $\text{P}_{\text{FT}}$  is the P uptake in fresh sludge, oven dry sludge, sludge biochars and P treatments,  $\text{P}_{\text{CT}}$  is the P uptake in no sludge (NK) treatment, and  $\text{P}_{\text{ap}}$  is the P applied in soil in the form of fresh sludge, oven dry sludge, sludge biochars and P treatments.

The percentage of increment in maize biomass and P removal was calculated according to Eq. (3).

$$\% \text{ of yield and/or P removal increment} = \frac{\text{Yield or P removal in T} - \text{yield or p removal in N}}{\text{yield or P removal in N}} * 100$$

Eq. (3).

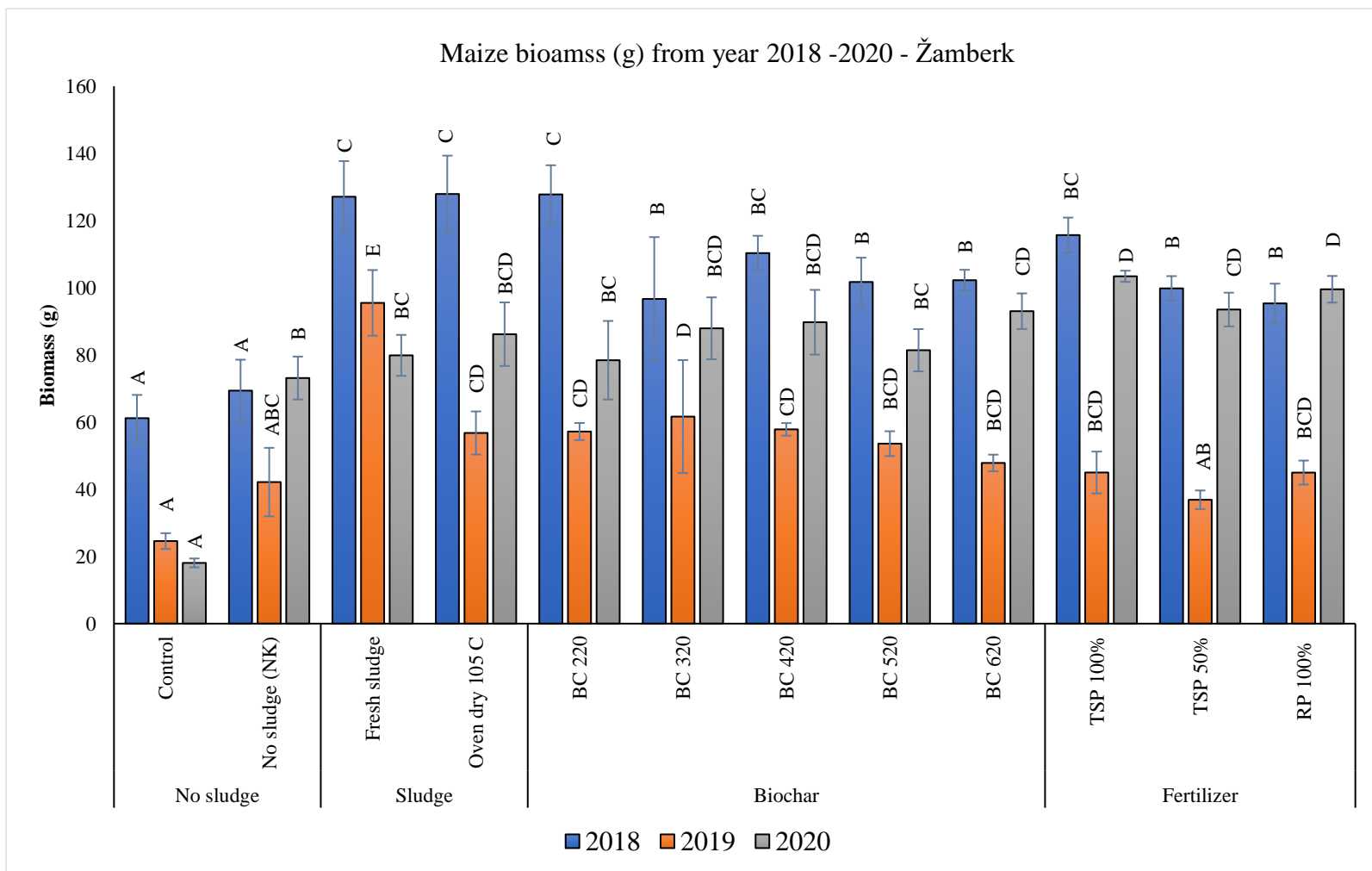
Where T is treatments of amendment and/or P fertilized treatments and N is No sludge (NK) treatment

## 5. Result

### 5.1. Maize biomass yield

#### 5.1.1. Žamberk soil

In Žamberk soil at the first growing season (2018), the application of sewage sludge, all biochars and both fertilizers (TSP 100%, 50% and RP 100%) had significantly higher maize biomass yield as compared to the no sludge treatment (Figure 4). The same year (2018) the application of fresh sludge, oven dry sludge and BC 220 produced significantly higher maize biomass yield compared to TSP 50% and RP 100%, while insignificant difference with the TSP 100%.



**Figure 4.** The effect of fresh sludge, biochar and fertilizers on maize biomass in Žamberk soil. Different letters show significant difference between treatments of the same year.

The same way in 2019, the addition of sludge, biochars and fertilizers (TSP 100% and RP 100%) had again significantly higher yield as compared to no sludge (NK) treatment. Moreover, the addition of oven dry sludge, BC 220, BC 320, and BC 420 had significantly higher maize biomass yield compared to TSP 50%, while insignificant difference with TSP 100% and RP 100%. When we come to 2020, the addition of fresh sludge, biochar and all fertilizers produced significantly higher biomass yield than control. In addition, the addition of RP 100% had a significantly higher biomass than BC 220 and BC 520, while no significance differences have been observed in other treatments.

**Table 6.** The increment of maize biomass compared to no sludge (NK) in percentage.

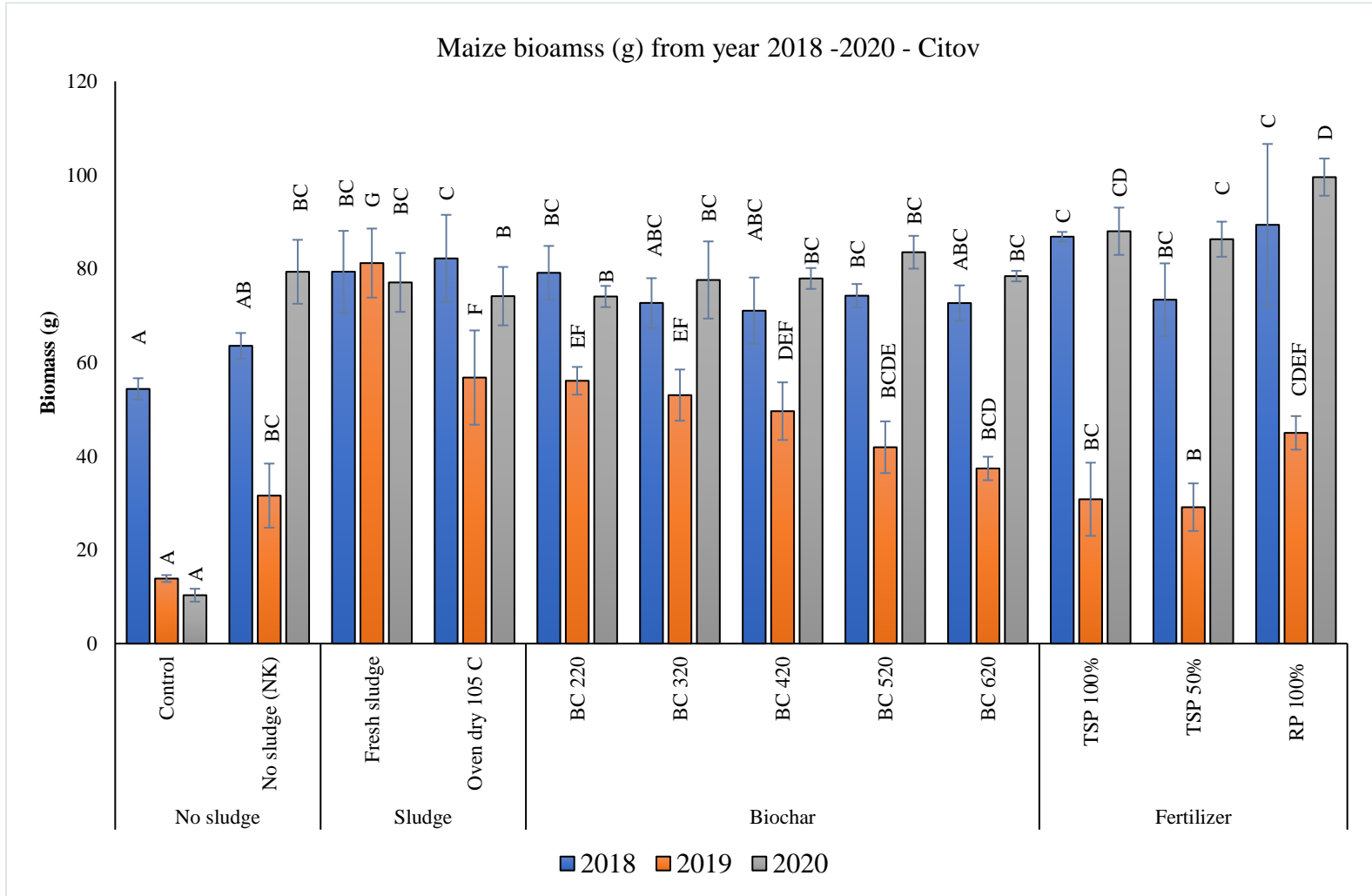
		Sludge		Biochar					Fertilizer		
		Fresh sludge	Oven dry 105 C	BC 220	BC 320	BC 420	BC 520	BC 620	TSP 100%	TSP 50%	RP 100%
<b>Žamberk</b>	2018	83	84	84	39	59	47	47	67	44	37
	2019	127	35	36	46	37	27	14	7	-13	7
	2020	9	18	7	20	23	11	27	41	28	36
	SUM	64	47	43	33	40	28	32	43	25	30
<b>Citov</b>	2018	25	29	25	14	12	17	14	37	15	-2
	2019	157	80	78	68	57	33	18	-2	-8	-5
	2020	-3	-7	-7	-2	-2	5	-1	11	9	10
	SUM	36	22	20	17	14	14	8	18	8	3

**SUM:** sum of all the years

In the year 2018, the highest maize biomass increments as compared to no sludge (NK) was from oven dry sewage sludge and BC 220 both by 84%, while the lowest was from RP 100% by 37% (Table 6). While, the year 2019, the highest maize biomass increments as compared to no sludge (NK) was from fresh sludge by 127%, and the lowest was from TSP 100% and it declined by 13%. In the case of year 2020, the highest maize biomass increments as compared to no sludge (NK) was from TSP 100% by 41%, and the lowest was from BC 220 by 7%. While in case of the sum of total yield, the highest maize biomass increment compared to no sludge (NK) was from and fresh sludge by 64%, and the lowest was from TSP 50% by 25%.

### 5.1.2. Citov soil

In Citov soil, during the year 2018, after the application of sludge, all biochars and both fertilizers (TSP 100%, 50% and RP 100%) had significantly higher maize biomass yield as compared to the no sludge treatment (Figure 5), while there was no significance difference of maize biomass yield between the biochars and fertilizers treatments.



**Figure 5.** The effect of fresh sludge, biochar and fertilizers on maize biomass in Citov soil. Different letters show significant difference between treatments of the same year.

In the year 2019, the fresh sludge treatments produced significantly higher biomass yield. Additionally, oven dry sludge, BC 220, BC 320 and BC 420 produced significantly higher biomass yield compared to both TSP 100 and 50%. At the third growing year 2020, all treatments had

significantly higher maize biomass compared to no sludge (NK) treatments. The RP 100 % produced significantly higher biomass yield as compared to all biochar treatments, while the TSP 100 and 50% had significantly higher biomass only over the oven dry and BC 220 treatments. When we come to the percentage of yield increment in 2018, the highest maize biomass increment compared to no sludge (NK) was from TSP 100% by 37%, while the lowest was from RP 100% by - 2% (Table 6). In the second growing season (2019), the highest maize biomass increment was from fresh sludge by 157%, and the lowest was from TSP 100% by -8%. In case of year 2020, the highest maize biomass increment was at TSP 100% treatment by 11 %, then from RP 100% by 10%, TSP 50% by 9% and BC 520 by 5% while a decline form the rest of the treatments. And for the total sum of maize biomass yield over the three years, the highest increment was from fresh sludge application by 36%, and the lowest was RP 100% by 3%.

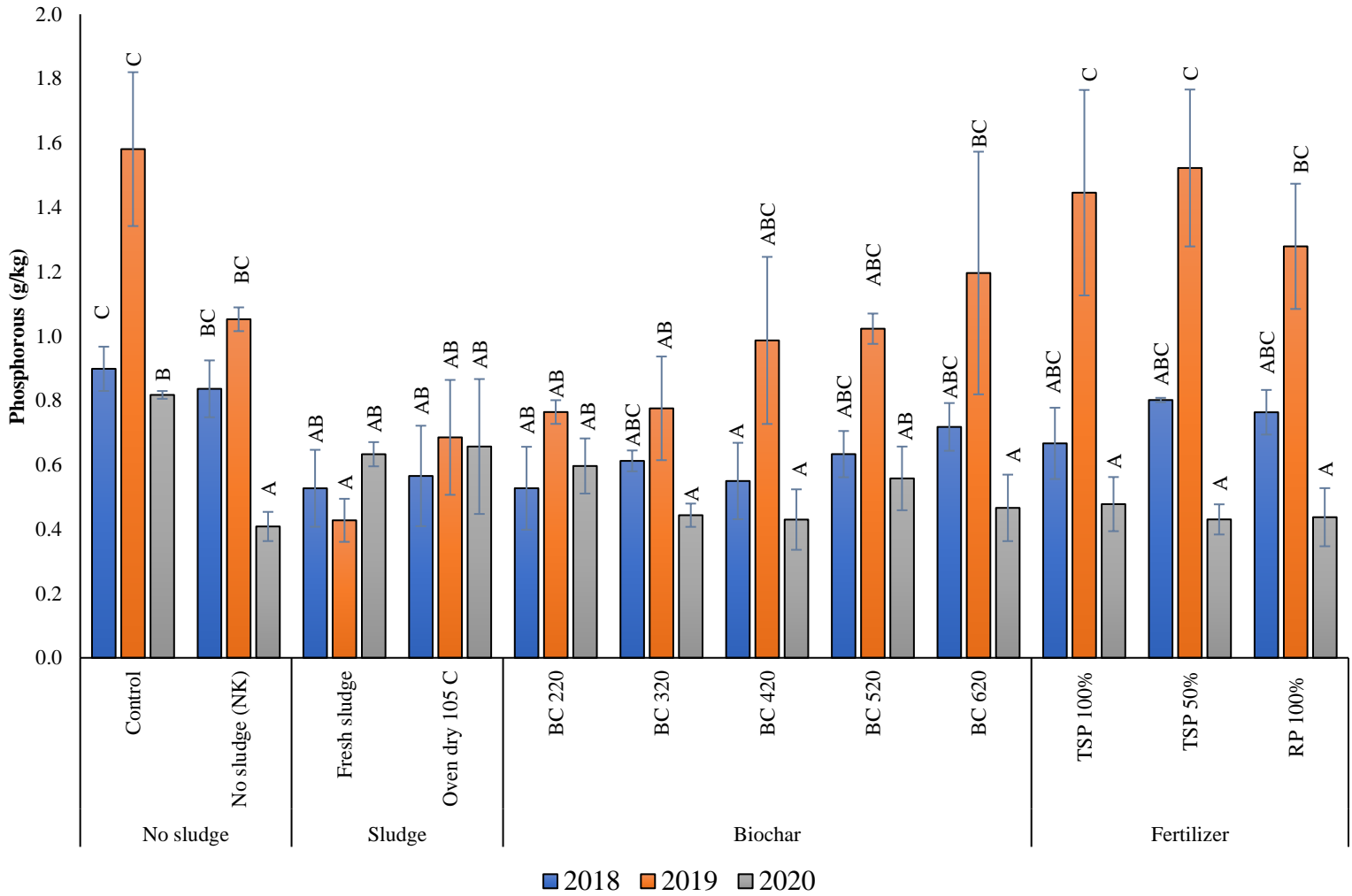
## **5.2. Concentration of phosphorous in maize biomass**

### **5.2.1. Žamberk soil**

The concentration of P in the maize biomass also have been measured for all tree years. In the year 2018 for Žamberk soil, there was not any significant difference between biochar and fertilizer treatments (Figure 6). However, the concentration of P in maize grown on control treatment was significantly lower than the concentration of P in the fresh sludge, oven dry 105 C, BC 220 and BC 420 treatments. Again in 2019, there was no significant difference of P concentration between BC 420, BC 520, BC620 and fertilizer treatment. However, the concentration of P was significantly higher in the TSP100 and TSP 50% compared to BC 220 and BC 220 treatments. The concentration of P in maize grown on control treatment was significantly higher than the concentration of P in fresh sludge, oven dry, BC 220 and BC 320 treatments. In 2020, there was no much significance difference between all treatments, except maize biomass grown on the no fertilization treatment have significantly higher P concentration than all other treatments.



Concentration of P in maize biomass 2018 - 2020 Žamberk

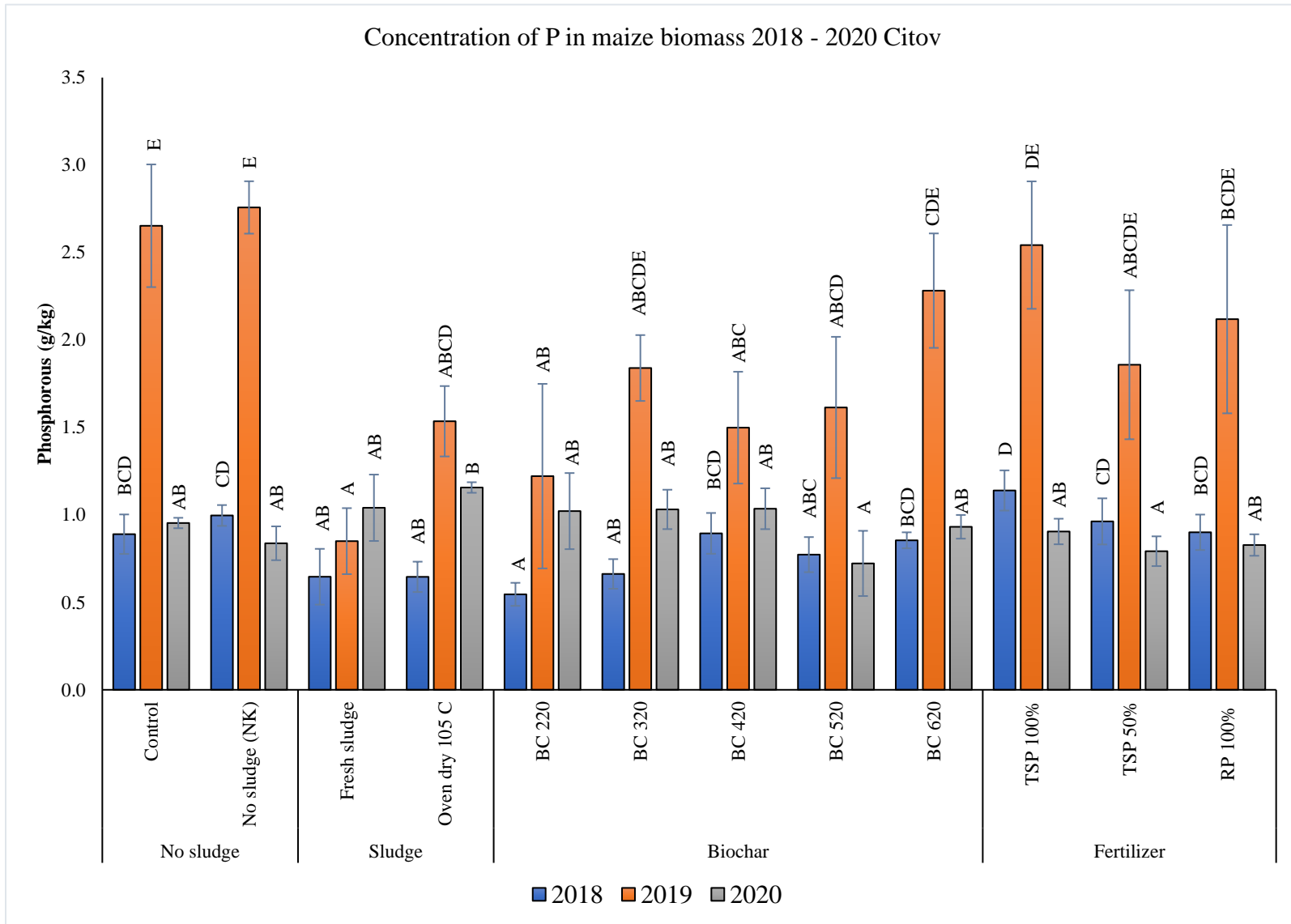


**Figure 6.** The effect of fresh sludge, biochar and fertilizers on the concentration of phosphorous in maize biomass in Žamberk soil. Different letters show significant difference between treatments of the same year.

### 5.2.2. Citov

In the case of Citov soil 2018, the concentration of P in maize biomass was significantly higher in TSP 100 and TSP 50% as compared to the BC 220 and BC 320 treatments, while both TSP treatments was not able to induce significance difference with the treatments of BC 420, BC 520 and BC 620 (Figure 7). In 2019, the concentration of P in maize biomass, there was no

significant difference between biochar and fertilizer treatment except BC 220, BC 420 treatments had significantly lower P concentration than TSP100%. On top of that, there was no significance difference in the concentration of P between the no sludge and all fertilizer treatments. In 2020 soil, there was no significance difference between the concentration of P in maize biomass between the biochar and fertilizer treatments, while there was significantly higher P concentration in no sludge treatment than the BC 520 and TSP50% treatments.

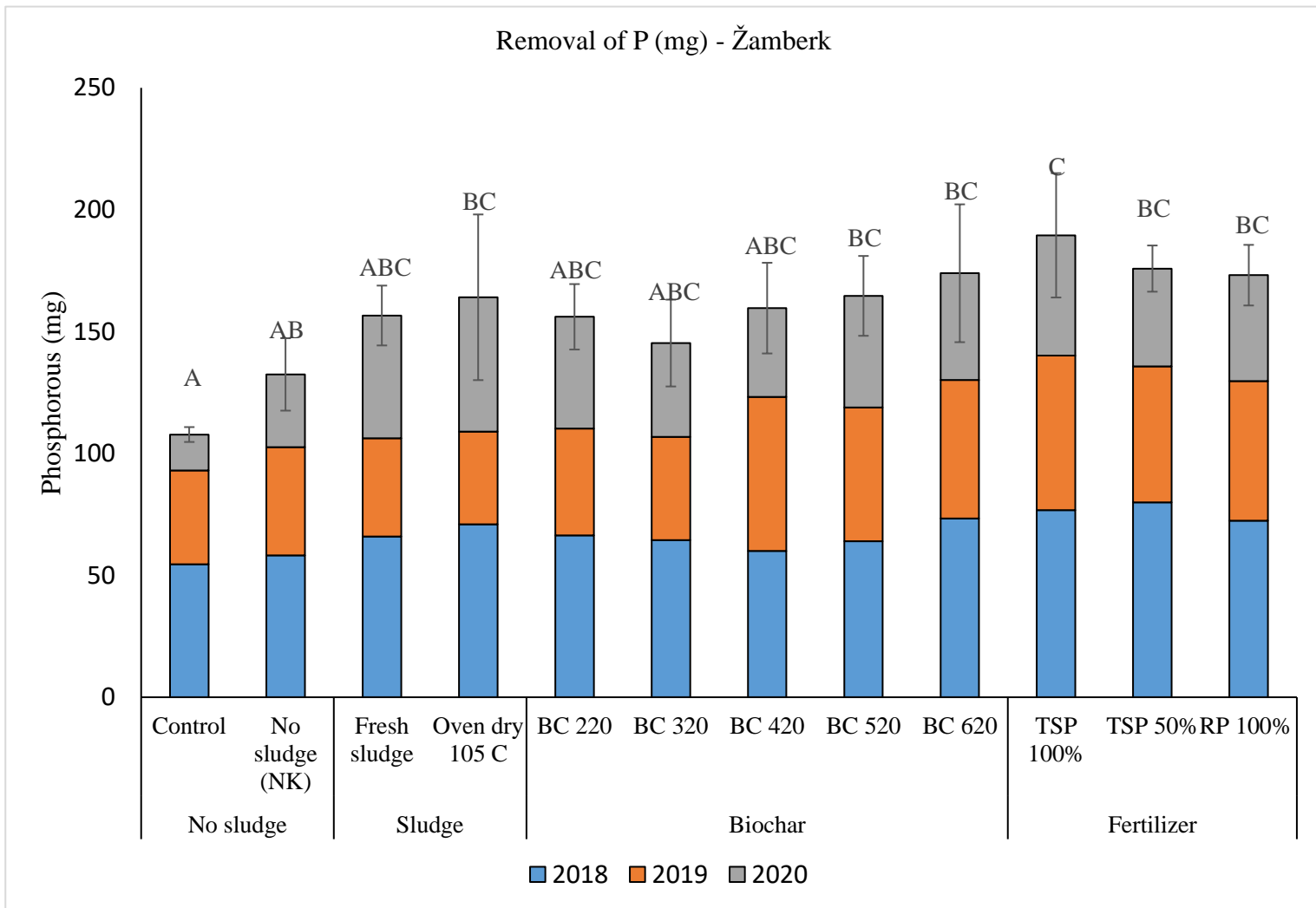


**Figure 7.** The effect of fresh sludge, biochar and fertilizers on the concentration of phosphorous in maize biomass in Citov soil. Different letters show significant difference between treatments of the same year.

### 5.3. Removal of phosphorous by maize over the three years

#### 5.3.1. Žamberk soil

The overall sum of P removed over the three years was slightly higher in the TSP100% treatments than all other treatments however the increment was insignificant with all except control and no sludge treatments (Figure 8).



**Figure 8.** The effect of fresh sludge, biochar and fertilizers on the removal of phosphorous by maize Žamberk soil. Different letters show significant differences between treatments of the same year.

When we come to the percentage of P removed as compared to no sludge (NK) treatment over the year 2018, the highest was from TSP 50% by 37, while the lowest was from BC 420 by 3% (Table 7). In the year 2019, the highest P removed was from TSP 100% treatment by 43%, while the lowest was from oven dry treatment and it was by 14%.

**Table 7.** The increment of P uptake by maize biomass compared to no sludge (NK) treatment in percentage.

		Sludge		Biochar					Fertilizer		
		Fresh sludge	Oven dry 105 C	BC 220	BC 320	BC 420	BC 520	BC 620	TSP 100%	TSP 50%	RP 100%
<b>Zamberk</b>	2018	13	22	14	11	3	10	26	32	37	24
	2019	-9	-14	-1	-5	42	24	28	43	25	29
	2020	69	85	54	29	22	54	47	65	35	46
	SUM	18	24	18	10	21	24	31	43	33	31
<b>Citov</b>	2018	-20	-16	-31	-24	0	-9	-2	56	11	-13
	2019	-21	-1	-20	12	-15	-23	-2	-12	-40	-28
	2020	20	30	14	20	22	-9	10	20	4	9
	SUM	-8	4	-13	4	1	-15	2	18	-11	-12

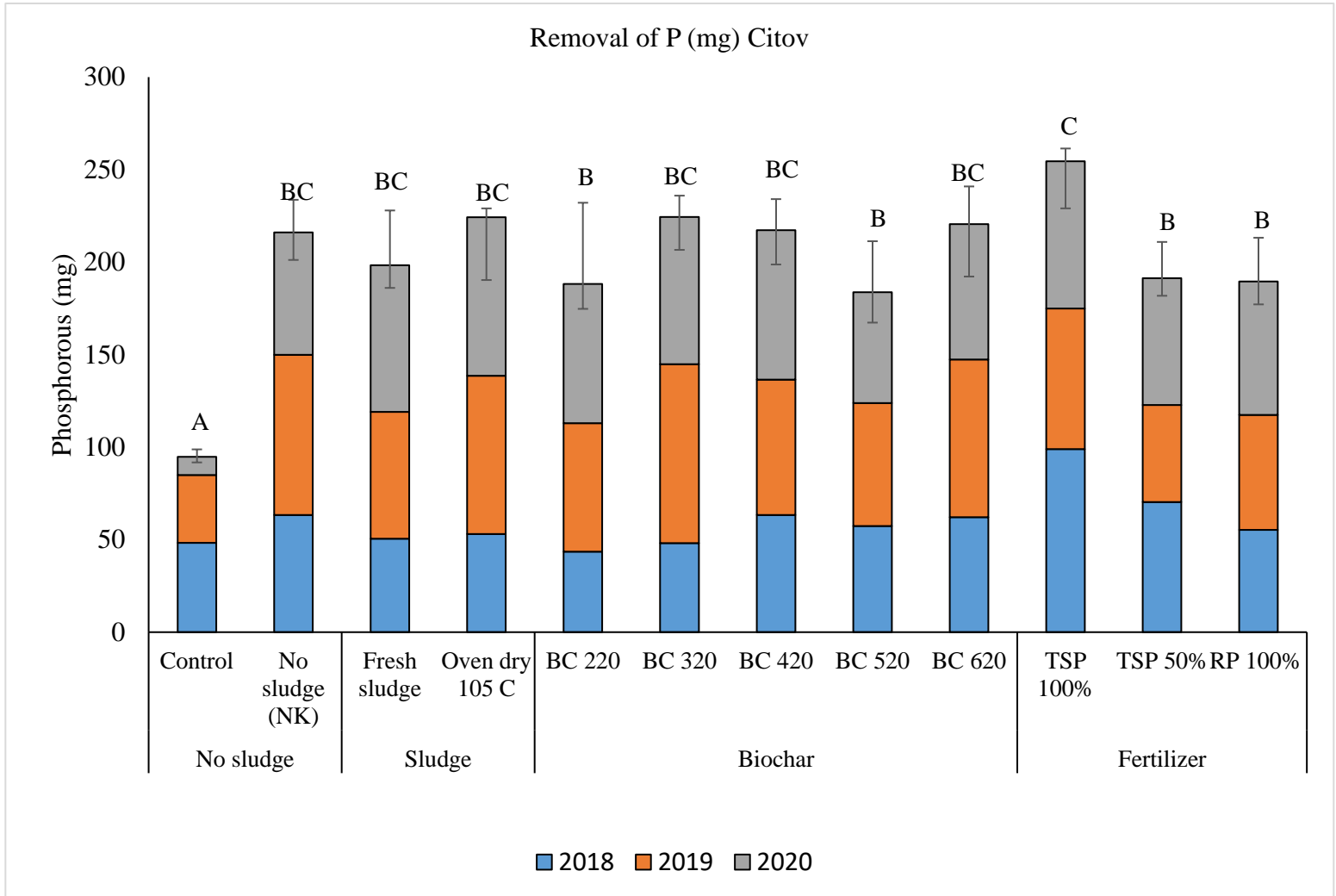
**SUM:** sum of all the years

And for the year 2020, the highest P removed by maize as compared to no sludge (NK) treatment was from oven dry 105 C by 85%, and the lowest was from BC 420 by 22%, while in case of total sum of P removed over the three years, the highest was TSP 100% treatment by 43%, and the lowest was from BC 320 treatment by 10%.

### 5.3.2. Citov soil

The total sum removal of P over three years by maize biomass was higher in TSP100% treatment but it is significantly higher only over TSP50%, RP100%, control, BC 220 and BC 520 treatments (Figure 9). The removal of P by maize grown on the control treatments was significantly

lower than all other treatments. For all biochar treatments the removal of P was lower at the first growing season 2018 than 2019 and 2020, while it was higher for TSP100, TSP 50% and no fertilization treatments. However, there was no significant difference of total P removal between all biochar treatments.



**Figure 9.** The effect of fresh sludge, biochar and fertilizers on the removal of phosphorus by maize Citov soil

At the first growing season (2018), the amount of P removed increment was registered only at TSP 100 and 50% by 56 and 11%, respectively as compared to no sludge (NK) treatment, while a decline in other treatments ranging up to 31% at BC220 compared to the no sludge (NK) (Table

7). In the year 2019, the P removed as compared to no sludge (NK) treatment declined in all treatments, the highest decline was in TSP 50% by 40% and the lowest decline in the oven dry sludge by 1%. At the the year 2020, the highest P removed was from oven dry 105 C by 30%, while decline in the BC520 by 9%. While in case of the total sum of P removed over the three maize growing period declined at BC 520, BC220, RP 100%, TSP 50% and fresh sludge by 15, 13, 12, 11 and 8% respectively as compared to no sludge (NK) treatment.

The PUE is presented on (Table 8) the PUE was calculated based on Eq 2, and no sludge (NK) treatment was considered as a reference because NK fertilizer is applied in all treatments including no sludge (NK) treatment except the control. And taking control as a reference for the calculation of PUE will be false leading as the application of NK by itself will improve the uptake of P. The highest PUE by maize was at 100 % of TSP by 19 and 12.8% in the Žamberk and Citov soils, respectively. However, comparing two soils, the PUE of all treatments were generally higher in Žamberk soil as compared to Citov soil and in Citov soil the PUE declined in all treatments except oven dry sludge, BC 320, BC 620 and TSP 100%. In Žamberk soil, the addition of BC 520 and BC 620 has comparably the same PUE as TSP 50% and 100% RP additionally the BC 620 has higher PUE than all other biochars including both fresh and oven dry sludges.

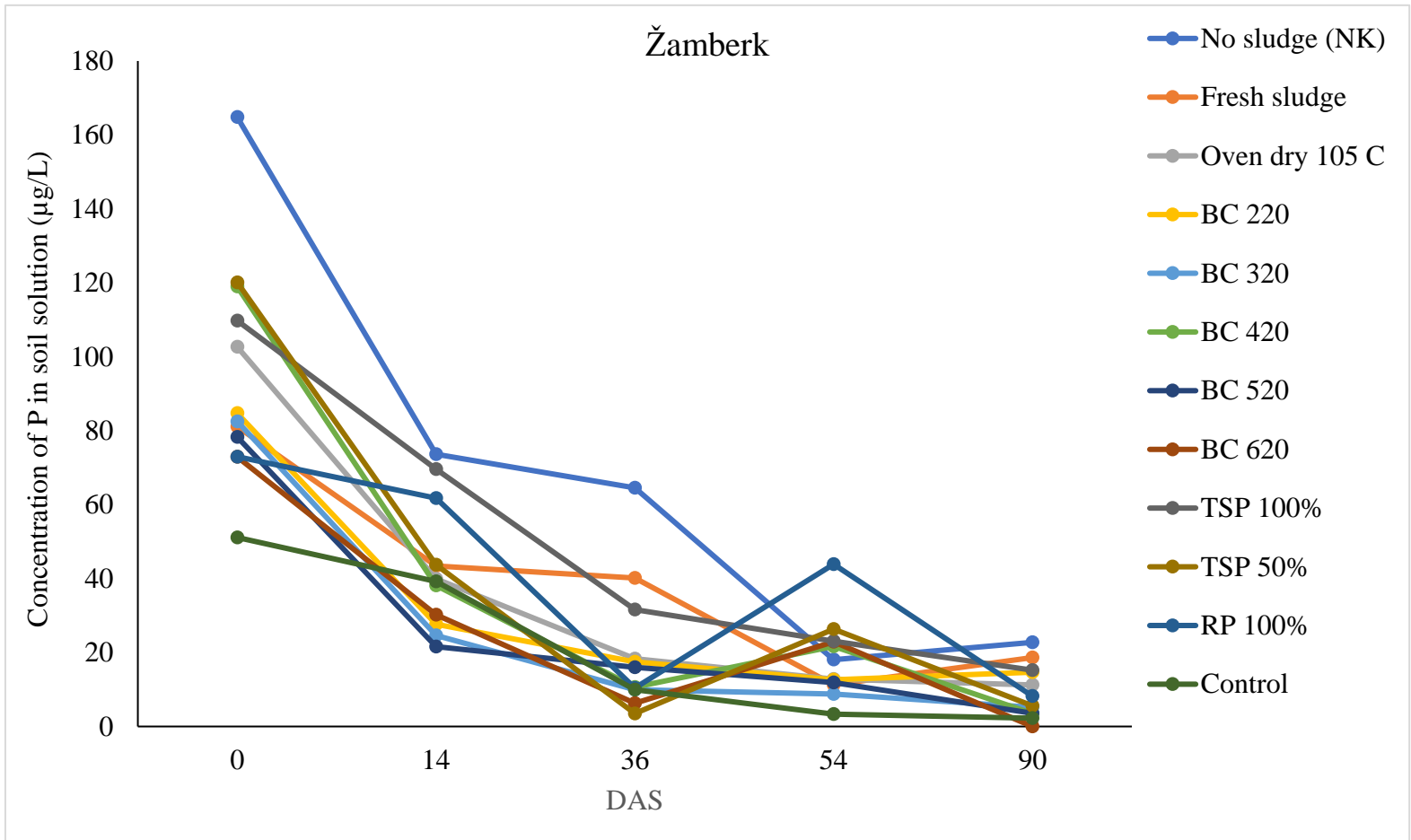
**Table 8.** Phosphorous use efficiency as affected by different treatments.

	<b>Fresh sludge</b>	<b>Oven dry 105 °C</b>	<b>BC 220</b>	<b>BC 320</b>	<b>BC 420</b>	<b>BC 520</b>	<b>BC 620</b>	<b>TSP 100%</b>	<b>TSP 50%</b>	<b>RP 100%</b>
Žamberk	8.1	10.6	7.9	4.3	9.1	10.7	13.8	19.0	14.5	13.6
Citov	-5.9	2.8	-9.3	2.8	0.4	-10.8	1.5	12.8	-8.2	-8.8

#### 5.4.The concentration of P in soil solution

The concentration of P in soil solution has been measured for the third maize growing season 2020. And the concentration of P in the soil was decreased over the collection period for

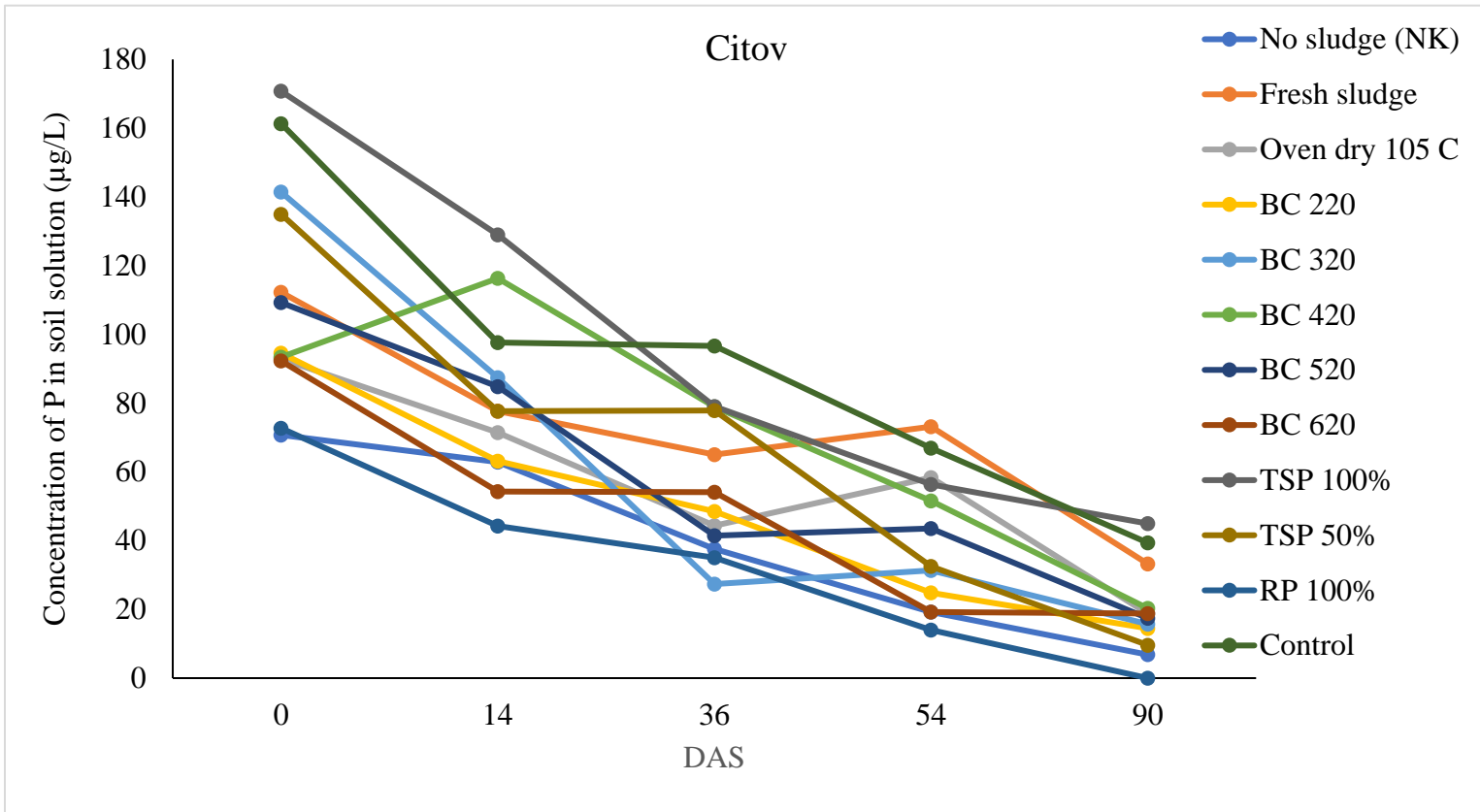
all treatments. At the first three collection period, the control treatments have slightly higher p concentration in soil solution compared to other treatments, but this effect disappeared at the fourth and fifth collection times. After the harvest time of the maize all soil treatments had almost the same level of P concentration in the soil.



**Figure 10.** The concentration of P in soil solution of Žamberk soil. DAS: day after sowing

Similarly, for Citov soils the concentration of P has decreased over the collection period. At the first two collection period, the TSP100% had slightly higher P concentration over other treatments but this effect disappeared as the time goes (Figure 11).

After the harvest the no fertilization, fresh sludge and TSP 100 % seems to have slightly higher P concentration in the soil solutions compared to the other treatment.



**Figure 11.** The concentration of p in soil solution of Citov soil. DAS: day after sowing.



## 6. Discussion

### 6.1. Maize yield

For both Žamberk and Citov soils, at all three year the addition of sludge, biochar and fertilizers had higher yield as compared to control treatments. The reason for this is mainly the application of N and K in those treatments yearly, while there was no N and K fertilization in control treatments. In Žamberk soil, at all maize growing season the maize biomass yield of both fresh and dry sludge, all biochars and fertilizer treatments were higher than the no sludge (NK) treatments except that of TSP 50% had lower yield than no sludge (NK) treatment at both years. Additionally, for the sum of maize biomass over the three years was higher in all amendments than no sludge (NK) treatment. In Citov soil, the same was true on 2018, except a decline at the RP 100% and on 2019, except all P treatments, while in 2020, both fresh and dry sludge and all biochar treatments had lower biomass yield than the no sludge (NK) treatments. However, the cumulative of maize yield over the three years was higher in all amendments and P fertilizers than the no sludge (NK) treatments. The general higher yield of maize biomass by sludge biochar compared to the no sludge (NK) without sludger and biochar treatment is very expected and it is also in agreement with other findings ([Agrafioti et al., 2013](#); [Song et al., 2014](#); [Yue et al., 2017](#); [Sousa and Figueiredo, 2016](#); [You et al., 2019](#)). One of the major contributing reason for the improved yield of maize biomass in sludge, biochars and P fertilizer treatment is the improved uptake of P. For example, for Žamberk soil in the year 2020, the biomass yield was significantly correlated ( $p = 0.05$ ,  $r = 0.768$ ) with the uptake of P by maize plant. Additionally, the cumulative maize biomass yield over the three years is significantly correlated ( $p = 0.05$ ,  $r = 0.735$ ) with the total uptake of P by maize over the three years. Similarly, in Citov soil for the year 2020, the biomass yield was significantly correlated ( $p = 0.05$ ,  $r = 0.654$ ) with the uptake of P by maize. In addition, the cumulative maize biomass yield is significantly correlated ( $p = 0.05$ ,  $r = 0.662$ ) with the total removal of P by maize over three years. This relation of total P uptake and biomass yield could in one way, or another explain that one of the reasons for the increment of maize biomass is the release of P from all treatments and its uptake by maize. This is in agreement with the finding of [Fachini et al. \(2021\)](#), where the improved uptake of nutrients such as P and N subsequently

improved the yield of maize. Additionally, in the sludge and biochar treatments, increment could be also due to the uptake of other nutrients. For example, the presence of considerable amount of other nutrients (Ca, K, Mg and S) from the sludge and biochar used in this study have been thoroughly discussed by [Mercl et al. \(2020\)](#). Therefore, the release of those nutrients from the fresh sludge, oven dry sludge and BC 220 could be expected and result in potential increment of maize biomass yield as compared to single application of P fertilizers. Based on the sum of total yield over the three years for both soil, the BC220 treatment had almost equal maize biomass yield with TSP 100% treatment and higher had higher yield than both TSP 50% and RP 100%. The ability of sewage sludge and sewage sludge biochar to substitute in organic fertilizer and increase maize biomass has been confirmed in two year field study (Faria et al., 2018). Based on their finding, the main reason for the improved maize biomass yield after the addition of sewage sludge biochar was the improvement of soil P, Mg, cation exchange capacity and base saturation. Based on the study of [Hossain et al. \(2010\)](#) the application of sewage sludge biochar at the rate of 10 t ha<sup>-1</sup> resulted in 64% increment of cherry tomato yield. The significant increment of shoot biomass, grain yield, number of tillers and height of the tillers have been reported in rice plant after the addition of sewage sludge biochar (Khan et al., 2013). Based on their report the increment of rice yield after the application of 10% sewage sludge biochar was up to 92%. The improved uptake of N up to 7.5% and P up to 166% by rice plant after the application of sewage sludge biochar has been reported as the main reason for the improved rice yield. Due the improved uptake of nutrients and improved yield of corn, [Faria et al., \(2018\)](#) have assumed the ability of sewage sludge biochar to replace the conventional fertilizers of N, P and micronutrients. When we come to the comparison of biochars, the total sum of maize biomass over the three year slightly declined with the production temperature of biochar. This could be potentially related to decrease in the available content of nutrients with the biochar production temperature [Mercl et al. \(2020\)](#) and their low availability in soil with the increment of production temperature. Furthermore, it was evident that the higher three years cumulative biomass yield was always in the Žamberk soil. Žamberk soil is an acidic soil with lower available P content compared to the neutral Citov soil. Therefore, better performance of sewage sludge in the acidic and low fertile soil could be expected. The mechanisms responsible for the lower performance of sewage sludge and biochar in the Citov soil regarding P release are further discussed at the next chapter.

## 6.2. The concentration and removal of phosphorous by maize

In Žamberk soil, the concentration of P in maize biomass for the year 2018 and 2020 was slightly higher in the control treatments than other treatments but not significantly different in most cases (Figure 6). This situation is simply due to the dilution effect of increased biomass yield in the sludge, biochar and P fertilized treatments. The dilution effect of increased biomass again appears in the year 2019, in a way that the concentration of P in maize biomass was always higher in the year 2019 as compared to 2018 and 2020. This is due to the lower maize biomass yield in the year 2019 as compared to both growing seasons of 2018 and 2020. Therefore, the lower yield of maize biomass resulted in 2019 increased concentration of P in maize biomass in the year 2019. The general decline in the concentration of nutrients in the tissue of plants due to the rapid plant growth is evident (Jarrell and Beverly, 1981). The same way in Citov soil, the highest concentration of P in the year 2019 is observed than the year 2018 and 20120.

The removal of P by maize plant was quite different between soils, therefore here it is discussed separately. In Žamberk, which is acidic soil, the application of sludge, all sludge biochars and P fertilizers increased the removal of P by maize at all three years compared to no sludge (NK) treatment except a decline of P removal in the fresh sludge, oven dry, BC 220 and BC 220 at the second growing season (2019). From here we can clearly observe that the P from fresh sludge and slightly pyrolyzed sludge biochar by a temperature up to 320 °C is fast releasable and could be depleted for the second growing season, while again being released at the third growing season. However, the biochar produced at the temperature of 420, 520 and 620 °C was supplying P constantly at all the three maize growing seasons (Table 7). When we come to the comparison of P removal between biochar and P fertilizers, there was no significant difference between the biochars and P treatments. Meaning, fresh sludge, oven dry sludge and all biochars were supplying P to the maize crop as much as P fertilizers supplying. However, the three highest PUE was at TSP 100, 50 % and BC 620 treatment. Generally, the increment of P uptake by crops after the application of sewage sludge agrees with other studies. For example, the application of 10% sewage sludge biochar has increased the uptake of P in rice plant by 166% compared to control without biochar treatments (Khan et al., 2013). A significant increment of P by blue grass (*Poa pratensis*) after the application of sewage sludge biochar at the rate of 2% was evident and

further correlation of P uptake with the amount of P added was observed in the study of [Gondek et al. \(2019\)](#). The application of sewage sludge biochar could simply increase the availability of P in soil due to the availability of P in the sludge biochars ([Sousa and Figueiredo, 2016](#); [Gondek et al., 2019](#); [Fachini et al., 2021](#)). For example based on the study of [Fachini et al. \(2021\)](#), 5 times increment of available P in soils applied by biochar produced at 300 and 500°C at the rate of 15 t ha<sup>-1</sup> was reported. Sewage sludge biochar could contribute for the increment of P in such acidic soils by two different mechanisms and a subsequent P uptake. Firstly, sewage sludge biochar is a source of P by itself therefore this P could be released to the soil solution and subsequent uptake by crops. Secondly, biochar could potentially adsorb cations such as Al<sup>3+</sup>, Fe<sup>3+</sup>, and Ca<sup>2+</sup> this potentially contributing for the decline of P precipitation and/or adsorption of P in soils ([Xu et al., 2014](#)).

In Citov soil quite different results was revealed. Based on the sum of total P removal over the three years, there was no significant difference between no sludge (NK) treatment and all other treatments except the control having significantly lower P removal than all other treatments. Despite the insignificant difference, there was lower P removal in sludge and all biochar treatments than no sludge (NK) treatment except BC 420 on the first and second maize growing seasons (Table 7). Citov soil is a neutral soil having pH value of 7.3 and in such neutral or alkaline soil a decline in the P content of soil after the application of biochar could be expected and this declined the uptake of P. A similar decline in the available content of P in three soils after the application of biochar was reported by [Xu et al. \(2014\)](#). The main mechanism for the decline of P after the application of biochar in such soil is the increment of soil pH in neutral or alkaline soil, which could decrease the availability of P in the soil solution. Additionally, the sorption of P could further increase with an increment of pH due to the high rate of Ca-phosphate precipitation, Ca-induced P sorption or the co-adsorption of Ca and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or HPO<sub>4</sub><sup>2-</sup> as ion complex is higher at higher pH ([Agbenin, 1995](#)). Based on the finding of [Faloye et al. \(2017\)](#) a decline in available P could be expected at alkaline pH due to the precipitation of P through chemical reaction with Mg and surface deposition on Mg crystal.

However, in both soils the total cumulative uptake of P over the three years in most cases is not significantly different between the biochar and fertilized treatments. Thus, insignificant cumulative removal of P between biochar and P fertilized treatment indicates the P fertilizing

potential of sewage sludge biochars as much as that of TSP and RP. Additionally, it was evident to observe better PUE at the BC 620 was higher than the fresh sludge at both soils. This could show the better performance of sewage sludge biochar produced at 620°C than its fresh sewage sludge. And the PUE at the BC 620 was almost equal or higher than TCP50% and RP100% treatments. This again could potentially show the better or almost the same recovery rate of P from sewage sludge biochar produced at 620 °C as the recovery rate of P from the RP. When we come to the effect of biochar production temperature on the uptake of P it was quite inconsistent over the years and between soils. For example, in Žamberk soil in 2019, the uptake of P was significantly correlated ( $p = 0.05$  and  $r = 0.08$ ) with the total content of P in biochars and the cumulative sum of total P uptake was again significantly correlated ( $p = 0.05$  and  $r = 0.08$ ) with the total content of P in biochars. While in the case of Citov, the significance correlation between the uptake of P by maize and the total content of P in biochars was only in 2018 with  $r = 0.9$  and  $p = 0.05$ . This shows that the increment in the total content of P in the biochar with the production temperature could induce an increment in the uptake of P by plants. The increment of P uptake by crops with sewage sludge production temperature is in agreement with the finding of (Tian et al., 2019). Based on their finding, the lowest uptake of P by turf grass (*Poa pratensis L.*) was at the lower production temperature 200 °C than the highest production temperature of 700°C. Above of all, many studies claimed the positive effect of sewage sludge biochar as an organic fertilizer with a potential to substitute commercial P fertilizers (Rehman et al., 2018; Faria et al., 2018; Fachini et al., 2021).

## 7. Conclusion

In this study a three-year (2018, 2019 and 2020) pot experiment has been established to investigate the effect of biochar production temperature from sewage sludge on the availability of phosphorus and to determine the longevity of phosphorus release from sewage sludge biochar. At all three years and both soils, the addition of sewage sludge and biochar produced higher maize biomass compared to the maize grown in no sludge treatment. The higher maize biomass yield as compared to no sludge treatment was from TSP and RP treatments in all three years. The effect of sewage sludge, all biochars and P fertilizers were quite different in two soils. In the acidic Žamberk soil, all amendments (sludge and biochars) and P fertilizers had higher maize biomass than the no sludge (NK) treatment except TSP 50% at the second maize growing season. Based on the collective sum of three-year maize yield, the four top highest maize yields compared to the no sludge (NK) treatment was at fresh sludge, dry sludge, BC 220 and TSP 100%, by 64, 47, 43 and 43, respectively. While the TSP 50% and RP 100% resulted in lower cumulative yield of maize biomass than all biochar treatments. For the biochar, TSP and RP treatments, the maize biomass was lower at the second growing season as compared to the first and the third growing season. However, at the neutral soil, the higher maize biomass yield was registered mostly at the first and second growing season, while at the third growing season a decline was registered in all treatments except P fertilized and BC 520 treatments. Based on the collective sum of three-year maize yield the three top highest maize yields compared to the no sludge (NK) treatment were at fresh sludge, dry sludge, BC 220 and BC 320 by 36, 22, 20, respectively. While the TSP 50 and RP 100% again resulted in lower cumulative yield of maize biomass than all biochars and sludge treatments. The sum of maize biomass yield over the three years has significant correlation with the sum of P taken up by maize ( $p = 0.05$ ,  $r = 0.735$  for Žamberk and  $p = 0.05$ ,  $r = 0.662$  for Citov soil). When we come to the biochar production temperature, for both soils there was not much clear trend and significant difference but the cumulative maize biomass was considerably higher at the lower production temperature.

Similarly, for the removal of P the treatments of sewage sludge, all biochars and fertilizers best performed at the acidic Žamberk soil than the Citov soil. In Žamberk, the cumulative removal of P over the three years was higher in all amendments and P fertilized treatments than the no

sludge (NK) treatments. The TSP had higher P removal than all other treatments, while the TSP 50% and RP 100% treatments had almost similar P removal as that of BC 620. The cumulative removal of P increased with an increment of pyrolysis temperature from 320 to 620 °C. It was also evident that the highest portion of P removed was at the first growing season. While the lowest were at the third growing season in the most cases, except the fresh, dry sludge and BC 220 had the lowest removal at the second growing season. The PUE Žamberk soil was higher at TSP 100%, followed by TSP 50%, and BC 620 in order. In Citov soil, the higher cumulative maize biomass compared to no sludge (NK) treatment was only at the TSP 100%, BC 320, BC 420 and BC 620 treatments, while the rest exhibited lower P removal than the no sludge (NK) treatments. This was consistent with the PUE, in which the positive PUE was only at the TSP 100%, BC 320, BC 420 and BC 620 treatments. Finally, it is very true that the effect of sewage sludge and sewage sludge biochar is soil specific. Better performance of sewage sludge and sewage sludge biochar could be expected in acidic soils where the uptake of P and yield response from the application of biochar was visible up to third growing season of maize. Furthermore, the results are very indicative that the application of sewage sludge biochar could potentially substitute the TSP and RP fertilizers. It is also very true that, even if the application of fresh sewage sludge has almost similar effect as that of the biochars, the use of biochar for soil application is recommended due lower impact of soil contamination by both organic and inorganic contaminants.

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