Czech University of Life Sciences Prague

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Nutrient dynamics in soil amended with contrasting biochars

BACHELOR THESIS

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Thesis title

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Objectives of thesis

The thesis aims to evaluate the dynamics of nutrients and metal pollutants in agricultural soil in response to a biochar amendment made from different ratios of sludge char and wood char. The final goal is to determine the optimal ratio between those two chars, allowing to: (i) improve nutrient content and mobility, and (ii) reduce metal input from sludge char.

Methodology

To answer the objectives of the thesis, an incubation experiment was performed in the laboratory. Six ratios of the two chars were tested, i.e. 100% sludge char, 95% sludge char / 5% wood char, 90% sludge char / 10% wood char, 80% sludge char / 20% wood char, 70% sludge char / 30% wood char, and 60% sludge char / 40% wood char. Those different ratios were added at 2% to an agricultural Regosol. A control without biochar was also prepared. The substrates were watered and maintained at 70% field capacity, and soil solutions were collected at different intervals, to measure: pH, Eh, and total nutrient, metal and organic carbon contents.

The proposed extent of the thesis

30-40 pages

Keywords

Agricultural soil, Fertility, Biochar, Sewage sludge, Incubation

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Recommended information sources

Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, L. & Zheng, B. (2016). Biochar to improve soil fertility. A review. Agronomy for sustainable development, 36, 1-18.

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Dean

Prague on 27. 03. 2024

Author' statement

I hereby declare that I have independently elaborated the bachelor/final thesis with the topic of: "Nutrient dynamics in soil amended with contrasting biochars" and that I have cited all of the information sources that I used in the thesis as listed at the end of the thesis in the list of used information sources.

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Abstract

Biochar has consistently been shown to improve soil properties, resulting in higher soil fertility and crop yield. Biochar characteristics are feedstock-dependent and can vary significantly. Generally, biochar abounds with high carbon content, large surface area and high porosity, which provides a suitable habitat for microorganisms. However, some types of biochar bring along characteristics undesirable for the soil. The constraints of a particular biochar type may be overcome by mixing it with another type, resulting in a synergistic effect, as is intended for in this experiment. This thesis investigates the effects of biochar amendments, which include varying ratios of sludge (SB) and wood biochar (WB), on nutrient dynamics and metal pollutant levels in agricultural soil. SB enriches the soil of important nutrients, however, it tags along some pollutants, including heavy metals. A high level of carbon comes from WB, which also acts as a sorption material to the present pollutants, making them immobile. This experiment was conducted as a laboratory incubation experiment, in which six different SB/WB ratios were added to a Regosol soil, soil solution were sampled three times during 55 days. Tested ratios were WB0%, WB5%, WB10%, WB20%, WB30% and WB40%, in which the number stands for the percentage of WB in the biochar mix. results reveal significant effects on pH, redox potential (Eh) and total nutrient, metal, and organic carbon contents in the soil solution, highlighting the potential of this biochar mix to improve nutrient retention and reduce metal pollution. Findings demonstrate that higher WB ratios, particularly WB40%, effectively conserve carbon, reduce nitrogen leaching, and increase macronutrient availability. WB40% also shows the most effective reduction in leached metals, indicating the potential for soil metal immobilization and improved soil quality. This research provides valuable insights into optimizing biochar amendments for enhancing soil fertility, crop productivity, and environmental sustainability. Further exploration of higher WB ratios could deepen understanding and optimize biochar efficacy in agricultural systems.

Key words

Agricultural soil, Fertility, Biochar, Sewage sludge, Incubation

Název

Dynamika živin v půdě obohacené kontrastními typy biouhle

Abstrakt

Kvality biouhle prokazují zlepšení vlastností půdy, což má za následek vyšší půdní úrodnost a výtěžnost plodin. Charakteristiky biouhle závisí na surovině a mohou se významně lišit. Obecně má biohuel vysoký obsah uhlíku, velkou povrchovou plochu a vysokou pórovitost, což poskytuje vhodné prostředí pro mikroorganismy. Nicméně některé typy biouhle mají nežádoucí vlastnosti pro půdu. Nedostatky konkrétního typu biouhle lze překonat smícháním s jiným typem, což může vést k synergickému účinku. Tento synergický efekt je očekáván od tohoto experiment, v kterém jsou zkoumány účinky aplikace biouhle na dynamiku živin a obsah těžkých kovů v zemědělské půdě. Konkrétně je testován biohuel vyrobený z kalu (SB) a ze dřeva (WB). SB obohacuje půdu o důležité živiny, avšak s sebou nese vyšší množství znečišťujících látek, včetně těžkých kovů. Vysoký obsah uhlíku dodává půdě WB, který také působí jako sorpční materiál na přítomné znečišťující látky, čímž je znehybní. Pro výzkum byl proveden laboratorní inkubační experiment, přičemž šest různých poměrů biouhle bylo aplikováno na vzorky půdy Regosol. Proběhly tři testování během 55 dnů. Jmenovitě byy použity poměry biouhle WB0%, WB5%, WB10%, WB20%, WB30% a WB40%, kde číslo udává procento WB ve směsi biouhle. Výsledky odhalují významné účinky na pH, redukční oxidační potenciál (Eh) a celkový obsah živin, kovů a organického uhlíku v roztoku půdy, které zdůrazňují potenciál této směsi biouhle zlepšit zadržení živin a snížení znečištění kovy. Výsledky ukazují, že vyšší poměry WB, zejména WB40%, efektivně uchovávají uhlík, snižují vyplavování dusíku a zvyšují dostupnost makroživin. WB40% také ukazuje nejúčinnější snížení vyplavených kovů, což naznačuje potenciál pro imobilizaci půdních kovů a zlepšení kvality půdy. Tato studie poskytuje cenné poznatky pro optimalizaci úprav biouhle pro zlepšení úrodnosti půdy, výnosnosti plodin a environmentální udržitelnosti. Další zkoumání vyšších poměrů WB by mohlo prohloubit porozumění a optimalizovat účinnost biouhle v zemědělských systémech.

Klíčová slova

Zemědělská půda, Úrodnost, Biouhel, Kal, Inkubační experiment

Table of Contents

1. Objectives

The thesis aims to evaluate the dynamics of nutrients and metal pollutants in agricultural soil in response to a biochar amendment made from different ratios of sludge char and wood char. The final goal is to determine the optimal ratio between those two chars, allowing to: (1.) improve nutrient content and mobility, and (2.) reduce metal input from sludge char.

2. Methodology

To answer the objectives of the thesis, an incubation experiment was performed in the laboratory. Six ratios of the two chars were tested, the ratios were based on the charred mass i.e. 100% sludge char, 95% sludge char / 5% wood char, 90% sludge char / 10% wood char, 80% sludge char / 20% wood char, 70% sludge char / 30% wood char, and 60% sludge char / 40% wood char. Those different ratios were added at 2% to an agricultural Regosol. A control without biochar was also prepared. The substrates were watered and maintained at 70% field capacity, and soil solutions were collected at different intervals, to measure: pH, Eh, and total nutrient, metal and organic carbon contents.

3. Introduction

As the global population experiences exponential growth, the demand for food production intensifies, leading to a critical need to increase crop production while safeguarding the ecosystem. The Food and Agriculture Organization (FAO) estimates a doubling of the world's need for cereal production between 2000 and 2050 (FAO, 2009). Effective plant growth, crucial for food production, is up to now dependent on the use of fertilisers for plant growth acceleration and pesticides to minimise crop losses (Drechsel, P., n.d.). However, crop production that is both effective and sustainable long-term is rooted in maintaining healthy soil.

Sir Albert Howard, a pioneer of organic agriculture, emphasised that "a soil teeming with healthy life in the shape of abundant microflora and microfauna will bear healthy plants, and these, when consumed by man, will confer health on man" (Bates, 2010). This underscores the vital connection between healthy soil and the well-being of species, including humans, highlighting the essential role of soil in providing food security and climate resilience.

Since the mid-20th century, there has been a continuous increase in the worldwide production of fertiliser minerals, reaching approximately 188 million tonnes in global fertiliser consumption by 2018–2019 (Randive et al., 2021). The growing demand for fertilisers is evident in the global fertiliser outlook, which shows a rising trend between 2018-2022, as seen in Figure 1 (FAO, 2019).

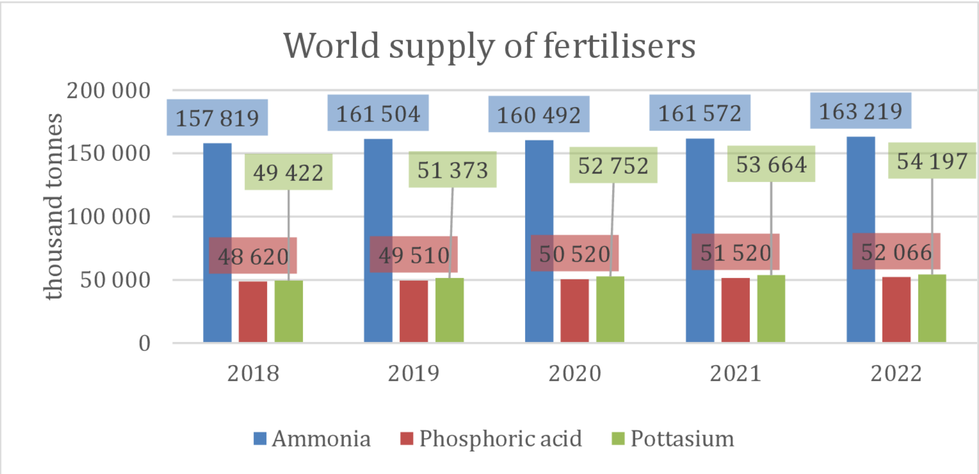

Figure 1 The world supply of ammonia, phosphoric acid, and potassium, during the period 2018-2022 (in thousand tonnes) (FAO, 2019; Randive et al., 2021).

While fertilisers address nutrient deficiencies in soil (Uchida, n.d.), their excessive use can lead to adverse effects on soil health, impacting plant growth and, subsequently, human health (Kulkarni & Goswami, 2019). Heavy metals, introduced through fertilisers, impair soil microorganisms (Wyszkowska et al., 2007) and bioaccumulate in crops, entering the food chain. Cadmium, known for its ability to translocate nutrients, has been extensively studied for its detrimental effects on human and animal health (Kulkarni & Goswami, 2019).

Fertiliser use also contributes to environmental challenges, such as soil run-off and nutrient leachate, posing threats to water quality and causing eutrophication. Annual losses of phosphorus from croplands, estimated at 10.5 million metric tons (Liu et al., 2008), and substantial losses of added nitrogen during rain or irrigation underscore these concerns. A sufficient nutrient supply to the soil doesn't guarantee their availability for plants to uptake (Kulkarni & Goswami, 2019). And shortage of nutrients leads to impaired root growth, which disables roots to access water in soil.

Therefore maintaining soil fertile leads to more efficient use of water and availability of nutrients to plants (Drechsel, P., n.d.).

Such agricultural practices aiming to enhance crop production efficiency pose long-term threats to soil health. A more sustainable approach to agriculture is imperative to feed humanity while preserving a healthy environment (Page et al., 2020). Biochar emerges as a promising alternative to traditional fertilisers, offering a sustainable soil amendment with less detrimental impact on soil health.

4. Theoretical part

4.1 Soil

4.1.1 Soil properties

Soil is a material composed of minerals, organic matter, water, and air. The average proportion of each component present in the soil is detailed in Figure 2. Minerals and organic matter constitute the solid portion, while air and water are located in the pore space in soil (McCauley, n.d.). In standard agricultural soil, the solid particles and pores account for approximately 50% each (this can be seen in Figure 2). The exact proportions of the individual elements in the soil will determine the soil texture, structure and porosity, which are the key determinants of the soil quality (Tomczyk et al., 2020). Soil texture, specifically its porosity, plays a crucial role in regulating water and air movement, influencing plant water utilisation and growth. Changes in the distribution of pores filled with water or air impact water retention.

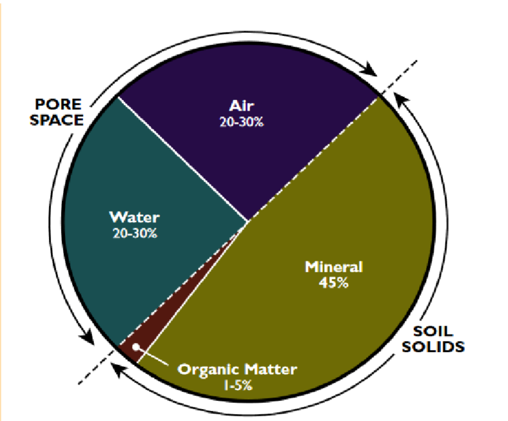

Figure 2 The main components of soil and their properties (McCauley, n.d.).

The pH of soils is another factor determining their fertility. Soil pH can impact the surface charge of colloids, which induces changes in nutrient availability and microbial activity, impacting the overall soil health (McCauley, n.d.).

Soil serves multiple crucial roles, encompassing social, economic, and environmental aspects. Its functions include water filtration and storage, food production, and carbon storage. Remarkably, the soil holds three times more carbon than the atmosphere and five times more carbon than forests. This carbon is primarily stored in the form of organic matter, which plays a pivotal role in determining the overall quality of the soil (Hornung et al., 2021). Despite its critical functions, the sustainability of these roles is jeopardised by the ongoing loss of soil fertility. While enhancing crop yield is undeniably crucial for ensuring global food security, a fundamental prerequisite is the preservation of soil health.

Effective plant growth is determined by the required supply of essential elements. Apart from carbon and oxygen that are derived from the atmosphere, the elements are obtained from the soil. All essential elements are equally important, only varying in the required amounts. Scientists have recognized these 18 elements found in Table 1 as essential for plant growth. Other elements considered important are also sodium (Na), silicon (Si), and vanadium (V) (A.O. Abaye, n.d.).

Table 1 Essential elements in soil (A.O. Abaye, n.d.).

Element	Symbol	Form Absorbed by Plants
Carbon	C	CO_2
Hydrogen	H	H^+, OH^-, H_2O
Oxygen	O	O_2
Nitrogen	N	NH_4^+, NO_3^-
Phosphorus	P	HPO_4^{2-}, $H_2PO_4^-$
Potassium	K	K^+
Calcium	Ca	Ca^{2+}
Magnesium	Mg	Mg^{2+}
Sulfur	S	SO_4^{2-}
Iron	Fe	Fe^{2+}, Fe^{3+}
Manganese	Mn	Mn^{2+}, Mn^{4+}
Boron	B	H_3BO_3, BO_3^-, $B_40_7^{2-}$
Zinc	Zn	Zn^{2+}
Copper	Cu	Cu^{2+}
Molybdenum	Mo	MoO_4^{2-}
Chlorine	Cl	Cl^-
Cobalt	Co	Co^{2+}
Nickel	Ni	Ni^{2+}

4.2 Biochar

4.2.1 Biochar and its properties

Biochar, a solid carbon-rich product, is obtained through the thermal decomposition of organic material in a process called pyrolysis, conducted under low oxygen conditions. The raw material, or so-called feedstock, used for biochar production can be any kind of plant or animal waste, such as woodchip waste, agricultural residues, sewage sludge, manures and more (Tomczyk et al., 2020).

Although the specific characteristics of each biochar depend on the feedstock material, pyrolysis temperature and residence time, biochar generally stands out for its high proportion of carbon, large specific surface area and high cation exchange capacity (Dejene & Tilahun, 2019). Biochar also attracts attention for its high porosity. Large pores provide habitats for microorganisms and create release routes for pyrolytic vapours, hence are particularly helpful in improving soil quality (Tomczyk et al., 2020). Apart from that, pores also serve to store water. Biochar generally contains carbon and other essential nutrients, whose contents are dependent on the type of feedstock. Upon biochar addition to soil, the nutrients degrade, which contributes to the organic matter content (Tomczyk et al., 2020).

Regarding the pH values, in general, biomass tends to be acidic or neutral (Tomczyk et al., 2020). According to a study on pyrolytic temperatures (W. Ding et al., 2014) the pH shifts towards alkalinity upon biochar formation at higher temperatures due to reduced acidic groups and the release of alkali metal salts from the biomass's organic matrix.

Biochar is applied as a soil amendment to increase water retention, prevent soil erosion and ensure long-term fertility of agricultural land, all of which lead to improved plant health (Gul et al., 2015).

4.2.2 Biochar preparation: influence of pyrolysis conditions and feedstock

A wide range of biochar materials exist, depending on the feedstock and the pyrolysis conditions (*e.g.,* residence time, temperature, heating rate). This chapter will provide a further description of those two influencing factors.

4.2.2.1 Pyrolysis

The use of pyrolysis for char production, whether it is charcoal or biochar, is an old industry that is ongoingly evolving to improve production efficiency and reduce pollution (Brown, 2009). Apart from carbon production, the process of pyrolysis has been utilised to produce a large variety of other compounds, including activated carbon, methanol, synthetic gas and petrol (Husain et al., 2008).

Pyrolysis is the chemical decomposition of any organic substance. It takes place under anaerobic conditions (Cremers, n.d.). However, a small amount of oxygen always occurs, because it is not possible to create an entirely oxygen-free environment (European Commission. Joint Research Centre. Institute for Environment and Sustainability., 2010). In general, pyrolysis involves the thermal treatment of the chosen biomass at a temperature in the range of 400-1000 °C. In this process, an organic substrate is transformed into different components, *i.e.,* gas (*e.g.* syngas), solid (*e.g.* biochar) and liquid (*e.g.* oil). The temperature and residence time of pyrolysis are chosen according to the desired end product (Bridgwater, 2003), as they affect the proportions of obtained gas, solid and liquid.

Moreover, the process of pyrolysis may transform some heavy metals present in the raw material into a product with less toxic forms of heavy metals. On the other hand, the pyrolysis process may generate carcinogenic compounds under some conditions, especially when using a polluted feedstock (Tomczyk et al., 2020). According to different conditions, three types of pyrolysis are distinguished: fast pyrolysis, slow pyrolysis (also called bio carbonization) and gasification. Table 2 summarises the differences in pyrolysis processes and their operating conditions.

Table 2 Proportion of final products; gas, solid (biochar) and liquid under different conditions of pyrolysis. (Tomczyk et al. 2020).

Product	***Temperature (°C)***	***Residence time***	***Average proportion of final products (%)***		
			Gas	***Solid (biochar)***	***Liquid***
Fast pyrolysis	*400-600*	*seconds*	*13*	*12*	*75*
Slow pyrolysis	*350-800*	*seconds-hours*	*35*	*35*	*30*
Gasification	*700-1500*	*seconds-minutes*	*85*	*10*	*5*

Environments with conditions of lower temperatures and longer residence time, referred to as slow pyrolysis, are the most suitable to produce solid materials, meaning biochar (35 % of the dry biomass on average). Higher temperatures alongside longer residence time promote gas production, indicating the name of this process - gasification. The conditions of the fast pyrolysis process are moderate temperatures and short residence time, which promotes liquid production (Bridgwater, 2003).

There are other methods derived from those three principal pyrolysis processes. One of those is hydrothermal carbonization, which is based on pyrolyzing the biomass at 180°C-290°C in water for 30 minutes to 16 hours. Hydrothermal carbonization resulted in relatively high biochar output, specifically 36-72% of solid product (Yoganandham et al., 2020).

As previously discussed, pyrolysis temperature and residence time play a crucial role not only in determining the quantity of the end product but also in shaping the physicochemical attributes of the biochar, encompassing its structural and textural features. Changes in pyrolysis parameters result in a broad spectrum of biochar characteristics, including pH, specific surface area, pore volume, cation exchange capacity, volatile matter, and carbon content (Tomczyk et al., 2020).

It has been proven that the rise in pyrolysis temperature leads to an expansion in pore volume. With increasing temperature, biochar's apparent density slightly decreases. However, its surface area increases and is mainly attributed to the decomposition of organic substances and the formation of micropores at high temperatures (W. Ding et al., 2014). The most notable increase in surface area seems to occur from 500 to 600 °C, with a minimal yield loss, indicating that higher pyrolytic temperatures fostered the development of a porous structure in biochars, leading to a greater internal surface area (W. Ding et al., 2014). As the pyrolysis temperature rises, biochar's carbon and ash contents also increase. The elevated carbon content at higher temperatures indicates a greater degree of polymerization, potentially retaining original organic plant residues like cellulose (Tomczyk et al., 2020). Research also suggests that higher temperatures of pyrolysis result in an increase in the contents of total base cations and carbonates, thereby contributing to an elevation in pH levels (Tomczyk et al., 2020).

A summary of parameters increasing versus decreasing with pyrolysis temperature is depicted in **Error! Reference source not found.**, pH levels, pore volume, surface area, and carbon content are all elevated after pyrolysis, whereas the apparent density of yielded biochar decreases.

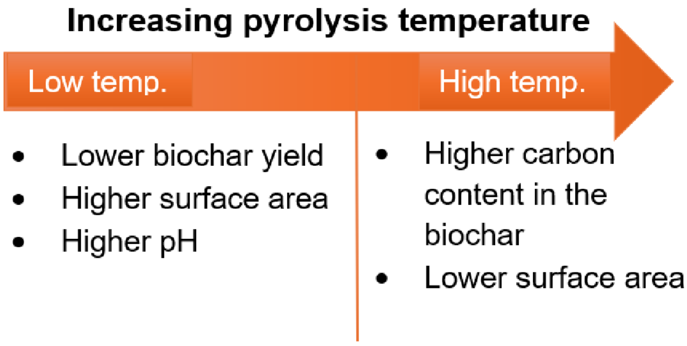

Figure 3 Parameters impacted by the pyrolysis temperature, comparing low temperatures to high temperatures.

The physicochemical characteristics of the final product are also impacted by the specific feedstock subjected to pyrolysis, which will be discussed in the next chapter.

4.2.2.2 Feedstock

Feedstock is the substrate used in the pyrolysis to create biochar. The most common types of feedstock are sewage sludges, manures, poultry litters, excrement, bones, wood chips, wood pellets, tree cuttings, bagasse, distiller grains and crop residues (Tomczyk et al., 2020). Distinct properties of each substrate result in the production of biochar with diverse attributes (Cetin et al., 2004, p. 200). Designing a suitable biochar for a desired purpose requires knowledge about the particular feedstock (Tomczyk et al., 2020).

Biochar properties are intricately linked to feedstock characteristics, particularly the organic composition of cellulose, hemicellulose, and lignin. Thermal decomposition studies reveal distinct temperature thresholds for each component, influencing biochar yield. The ash content in feedstock indirectly impacts biochar yield, affecting carbon share and heating value. Higher ash content reduces the share of carbon in the produced biochar.

In a conducted study (Enders et al., 2012), scientists compared corn, hazelnut, oak and pine feedstocks, discovering that the carbon content of the original biomass was relatively consistent (ranging from 43% to 49%), but that the carbon content of biochars derived from these feedstocks exhibited greater variability (from 60% to 91%). Upon heating, the carbon content rose in feedstocks with low ash content but declined in those with high ash content (Enders et al., 2012). This implies the variability of carbon content based on the biomass material.

The nutrient content of the biochar also varies based on the initial feedstock, particularly the concentrations of phosphorus (P), nitrogen (N), calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) (Enders et al., 2012). Apart from that, the level of salinity (Domene et al., 2015), as well as pH levels (Enders et al., 2012) were both strongly influenced by the source of the original feedstock. When observing the change in physical properties, such as porosity and surface area, it is evident they are both dependent on the feedstock type. It has been shown that the overall pore volume expands with an elevated lignin content in the feedstock biomass (Břendová et al., 2017).

Alternative feedstocks like biowaste (sewage sludge, municipal waste, chicken litter), and compost are potential options for biochar production, but their use poses risks due to the potential presence of hazardous components, including organic pollutants and heavy metals (European Commission. Joint Research Centre. Institute for Environment and Sustainability., 2010).

The feedstock used for biochar production is oftentimes waste from agriculture, industry or municipalities. Thus, biochar production provides an opportunity to reuse the biomass that would have been destined to be disposed of otherwise. Most of the biomasses used for biochar production support the circular economy by giving waste a second life (Lua et al., 2004). The feedstocks used for this particular experiment are sewage sludge and wood. Their differences and reasoning behind mixing them is elaborated on later in this paper.

4.2.3 Influence of biochar on soil and crop production

Biochar application to soil has received a lot of attention for its ability to enhance soil properties and potential to mitigate climate change (B. Singh, 2012). In my thesis, I will focus on the influence of biochar on soil properties, and will not assess greenhouse gas emissions.

When added to soil, biochar alters soil texture, pore size distribution, and bulk density, enhancing aeration and water-holding capacity (Maroušek & Trakal, 2022). The resulting soil characteristics depend on the initial soil quality, type, and composition. In clayey soils, it promotes larger pores for increased aeration, while in sandy soils, it enhances water-holding capacity and nutrient adsorption. Biochar's positive impact on soil porosity benefits microorganism habitats and protective surfaces, particularly in colloid-poor sandy soils (Kocsis et al., 2022).

The application of biochar is advocated to reduce water evaporation, lower soil bulk density, and mitigate water leaching and runoff. The reduction in water leaching, thanks to biochar's high cation exchange capacity and sorption capacity contributes to a more efficient and sustainable nutrient supply for plants. Water retention is increased by a diverse porous structure of biochar. Large pores support high microbial activity, increasing the accessibility of nutrients to plants (Kocsis et al., 2022), enhanced diversity of soil microorganisms includes nitrifying bacteria and phosphate-solubilizing bacteria, which helps accelerate nutrient flow between the soil and crops (Maroušek & Trakal, 2022), in other words improving nutrient bioavailability (Dejene & Tilahun, 2019).

Biochar has been also shown to improve the plants' tolerance to stress such as salinity, drought, high temperature and heavy metal pollution (Dejene & Tilahun, 2019). In addition, biochar has been reviewed to support restoration of contaminated soils (Gopinath et al., 2021).

The mentioned improved soil properties lead to an increase in plant growth, therefore higher crop yields (Awad et al., 2013). The analysed scientific papers documented enhancements in yield ranging from 20% to 220%, depending on the amount and quality of biochar applied (Kocsis et al., 2022).

The lasting effects of applying biochar evolve as its physical characteristics degrade over time. Despite this degradation, biochar continues to support essential soil microbial communities, which are pivotal for maintaining prolonged soil fertility (Maroušek & Trakal, 2022).

4.2.4 Focus on two contrasting biochar feedstocks

As mentioned above in the section about feedstocks, the biomass used for biochar production is usually a waste product, providing a purpose to materials that would have been disposed of otherwise (Lua et al., 2004). Two types of biochar were used in this experiment - one made from sewage sludge and one made from wood residues. This section will provide a general characteristic of biochars derived from those two feedstocks.

4.2.4.1 Sewage sludge Biochar

Sewage sludge is the solid by-product resulting from the biological treatment of municipal waste. Disposal of sewage sludge is a pressing issue due to its potential for secondary pollution and adverse impacts on human health. Sewage sludge disposal is currently one of the global environmental concerns of modern society (Hossain et al., 2009). Current ways of disposal of sewage sludge are mainly landfilling (14%), incineration (27%) and application in agriculture (42%) (B. Singh, 2012).

Preparing a sewage sludge biochar via pyrolysis process requires a pretreatment, as sewage sludge contains more than 90% water, therefore dewatering and drying is needed before pyrolysis (Hornung et al., 2021). Drying can be carried out either at higher temperatures (around 100°C) for 24 hours or at lower temperatures (around 30°C) for a few weeks. Sewage sludge biochar is also produced via hydrothermal carbonization, which takes place in the presence of water in low-temperature environments, hence this process allows the feedstock to contain moisture (Gopinath et al., 2021).

Sewage sludge biochar is characterised by slight alkalinity- pH varying from 8.7 to 11.1 (Gopinath et al., 2021), exhibiting a contrasting feature to wood based biochar (Tomczyk et al., 2020). At the same time, sludge contains large amounts of nutrients, particularly phosphorus coming from blackwater, nitrogen and organic matter, which positively affect the soil properties. Capturing nutrients from sludge may be an efficient way to redirect them into soil, where they are needed (Maroušek & Trakal, 2022). Sewage sludge biochar is proven to enhance crop yield and improve nutrient-deficient soils (S. Singh et al., 2020). This practice also makes crops more resilient to drought. Moreover, sewage sludge biochar promotes the presence of beneficial soil microbes that further support overall soil health (S. Singh et al., 2020).

However, while sewage sludge is rich in several valuable elements, it also contains potentially toxic elements negatively impacting the whole ecosystem, such as polycyclic aromatic hydrocarbons (PAHs), heavy metals (Cr, Ni, Cu, Zn, Cd and Pb) and human bacterial pathogens (S. Singh et al., 2020), all entering the wastewater system upon domestic or industrial disposal. Application of sewage sludge directly to agriculture may be limited due to its contaminant content. However, these constraints can be addressed through thermal treatment, *i.e.,* pyrolysis (Fytili & Zabaniotou, 2008). Numerous researchers have explored the heavy metal content of sludge-derived biochar and its binding patterns of heavy metals, proving that pyrolysis effectively reduces heavy metal potential release, remaining stable within the biochar matrix to some extent (Hossain et al., 2009). Nevertheless, sewage sludge biochar still carries a potential risk in soil application due to the presence of hazardous components such as organic pollutants and heavy metals (European Commission. Joint Research Centre. Institute for Environment and Sustainability., 2010).

4.2.4.2 Wood Biochar

Wood-based biochar is characterised by low moisture, low ash, and high bulk density, which makes it distinctive from non-woody biomass. The pH of wood-based biochar is generally about two pH units lower than other types of biochar (Tomczyk et al., 2020). Unlike various biological wastes, wood biochar does not necessitate an external energy source for the pyrolysis process, as it occurs at temperatures exceeding 500°C.

Upon reviewing available knowledge, it is evident that wood biochar abounds with its carbon content and high porosity attributed to the chemical composition of the feedstock. Environmental researchers recommend using wood biochar as an approach to minimise water evaporation, reduce soil bulk density and alleviate water erosion. Its characteristic enhances the soil water retention, which enables water uptake by plants. It has been documented that the presence of finer configurations in wood biochar within the inter-pores among larger soil particles improve the vitality of diverse soil microbiota (Maroušek & Trakal, 2022).

On the other hand, wood biochar is a product with lower nutrient content compared to sewage sludge biochar. Another potential limitation of wood based biochar usage is its high sorption ability, which potentially decreases plant nutrient availability (Lebrun et al., 2023). Nitrogen immobilisation in soils has been observed upon wood biochar addition (Nguyen et al., 2017). One factor contributing to this immobilisation is the adsorption of nitrogen on the surface of the biochar. The extent of decreased nitrogen availability remains uncertain (Nguyen et al., 2017).

4.2.4.3 Why mix sewage sludge and wood biochar?

Although both types share similar benefits, some of which are summarised in Table 3, including their affinity for retaining nutrients, particularly nitrogen, and promoting the presence of beneficial soil microbes, supporting overall soil health and leading to improved crop productivity, they still abound with different characteristics, such as moisture, bulk density, nutrient content and presence of pollutants (Gopinath et al., 2021; Maroušek & Trakal, 2022; Tomczyk et al., 2020).

Both wood and sewage sludge biochars have their drawbacks, such as low nutrient content for wood biochar and concerns about pollutants in sewage sludge biochar. Blending sewage sludge with regular biochar might reduce the bioavailability of pollutants and heavy metals (S. Singh et al., 2020), while bringing nutrients to plants.

Table 3 The characteristics and differences of wood-based and sewage sludge-based biochar, addressing the potential benefits and limitations of each.

Feedstock→ **Characteristics ↓**	**Wood Biochar**	**Sewage sludge Biochar**
Moisture	Low	High
Ash content	Low	High
Carbon content	High	Low
pH level	Slightly acidic	Slightly alkaline
Nutrient content	Lower	Higher
Sorption ability	High	-
Pollutants content	-	Pollutant and heavy metals content
Impact on soil microbes	Positive	Positive
Positive impacts on soil properties	Reduced soil bulk density Enhanced soil water retention Increased plant available water content	Large amounts of plant available nutrients
Negative impacts on soil properties	Immobilisation of important nutrients	Potential contamination

Upon reviewing current knowledge about these two types of biochar separately, their combination, which has not been studied enough yet, might provide a synergy by leveraging the strengths of each, such as nutrient retention, water availability, reduction in pollutant bioavailability and structural enhancement (Gopinath et al., 2021; Maroušek & Trakal, 2022; S. Singh et al., 2020). Hence, different ratios of wood and sewage sludge biochar must be tested to find the balance that could address the limitations of each type, to obtain an optimal product for soil fertility.

The purpose of this experiment is to find the perfect ratio of the mixed biochars that can contribute to comprehensive and sustainable soil management.

5. Materials and Methods

5.1 Soil and biochars

An agricultural Regosol from the Zvěřínek village in Czech republic (50°14'9″N, 15°2'6″E) was used. The soil was collected from 0-30 cm of the arable horizon. This soil exhibits a low organic matter content with organic carbon content of 9.33 g/kg, displays an average bulk density of 1.59 g/cm³ and a total porosity of 41.1% The soil underwent analysis using the standard hydrometer method (CEN ISO/TS 17892-4 2004, 2004) for soil particles <2 mm, which reveals a predominant composition of sand (85.5%), followed by clay (9%) and silt (5.5%). According to which it has been classified by the USDA (United States Department of Agriculture) as loamy sand. Parameters of the soil as well as the nutrient contents are detailed in Table 4.

Table 4 Parameters of the soil from Zvěřínek.

Parameters	**Soil**
Bulk Density ($g.dm^{-3}$)[a]	1590
Total Porosity (%)[a]	41.1
pH (-)	4.8
Conductivity ($mS.cm^{-1}$)	0.318
Sand (%)[b]	85.5
Silt (%)[b]	5.5
Clay (%)[b]	9.0
N_{tot} ($g.kg^{-1}$)[c]	0.54
C_{tot} ($g.kg^{-1}$)[c]	9.33
C/N	17.3
P_{tot} ($g.kg^{-1}$)[d]	0.41
S_{tot} ($g.kg^{-1}$)[d]	0.24
Mg_{tot} ($g.kg^{-1}$)[d]	0.22
Ca_{tot} ($g.kg^{-1}$)[d]	1.10
K_{tot} ($g.kg^{-1}$)[d]	8.49

[a]NF EN 13041
[b]Hydrometer method
[c]Elemental analyzer
[d]*Aqua-regia* digestion

Two biochars were used as soil amendments: 1.) biochar from wood feedstock (WB) and 2.) biochar from sewage sludge feedstock (SB). WB was generated through the gasification process of dry wood chips with initially high moisture content around 40-60% wt. on a wet basis. The raw material underwent heating for 6 hours with temperatures ranging from 500 to 600 °C. The gasification process occurred at a fixed-bed multi-stage gasifier (GP750) located in a combined heat and power (CHP) plant (Brynda et al., 2020).

SB was produced through a pyrolysis process using sewage sludge from Trutnov, a city in the northern part of the Czech Republic. The SB producer did not provide more background information about the supplied biochar. The physico-chemical properties as well as nutrient content of both WB and SB can be found in Table 5. Although SB holds large amounts of soil-promoting nutrients, it also contains some contaminants. The analysis of the SB used shows the content of polychlorinated biphenyls (PCBs) to be < 0.01 $mg \cdot kg^{-1}$, the content of polycyclic aromatic hydrocarbons (PAHs) to be <0.5 $mg \cdot kg^{-1}$ and halogenated organic compounds (AOX) to be 105 $mg \cdot kg^{-1}$. However, according to Czech regulations in Table 6, all of these values are below the limit for soil application, hence can be applied to soils.

Table 5 Parameters of the two biochars, used as soil amendments.

Parameters	Sewage Sludge Biochar	Wood Biochar
Bulk Density ($g.dm^{-3}$)[a]	633	160
Total Porosity (%)[a]	55	74
pH (-)	11.7	11.1
Conductivity ($mS.cm^{-1}$)	1.5	0.14
N_{tot} ($g.kg^{-1}$)[c]	14.6	5.8
C_{tot} ($g.kg^{-1}$)[c]	223	868
C/N	18	150
P_{tot} ($g.kg^{-1}$)[d]	40.6	0.89
S_{tot} ($g.kg^{-1}$)[d]	7.03	0.34
Mg_{tot} ($g.kg^{-1}$)[d]	13.5	2.85
Ca_{tot} ($g.kg^{-1}$)[d]	47.4	16.4
K_{tot} ($g.kg^{-1}$)[d]	4.11	3.9

[a]NF EN 13041
[b]Hydrometer method
[c]Elemental analyzer
[d]*Aqua-regia* digestion

Table 6 Amount of elements (metals and contaminants) in experimental sewage sludge biochar (SB) in mg/kg and their limiting values in mg/kg for soil application according to Czech regulations and directives: (a) Decree No. 474/2000 Coll. - Decree of the Ministry of Agriculture on setting requirements for fertilisers, (b) Czech directive 86/278/EEC, (c) Czech regulation No. 257/2009 Sb. and (d) Czech regulation No.437/2016 Sb (Ministerstvo, 1998).

Element	SB mg/kg	Czech regulations for soil mg/kg
As	2.94	30[(a)]
Cd	0.46	5[(a)]
Cu	375	50-140[(b)]
Ni	44.4	30-75[(b)]
Pb	57.2	50-300[(b)]
Zn	1370	150-300[(b)]
Hg	0.003	0.5[(a)]
PCBs	<0.01	0.02[(c)]
PAHs	<0.5	20[(a)]
AOX	105	500[(d)]

5.2 Experimental design

The experimental design consisted of the variation in ratio between the two above mentioned biochars. Percentage of WB to SB was 0%, 5%, 10%, 20%, 30%, 40% (w/w) with five replicates per variant. All the variants were added at 2% total biochar amendment to soil. We expected that this mixture provides soil with large amounts of nutrients from SB and stable organic carbon content and enhanced nutrient sorption ability thanks to WB.

The experiment was an incubation in open bottles. In total, 40 bottles (seven sets each of five replicates) were used, and three samplings were performed. The initial sampling occurred from the 20th to the 21st of October 2023, followed by the second sampling between the 8th and 9th of November 2023, the third and final sampling took place from 14th until 15th of December. The exact amount of soil and amendments per set are described in detail in Table 7. Consequently, the pots were kept in the dark to prevent the development of microalgae and plants. Moisture was maintained throughout the incubation time at 70% water holding capacity.

Table 7 The list of variants describing the content of each amendment, containing different ratios of sewage sludge biochar (SB) and wood biochar (WB).

Set	Variant	Description	Mass calculation
1	Control	non-amended soil	200g soil
2	WB0%	soil + 2% (w/w) of sludge biochar	196g soil + 4g SB
3	WB5%	soil + 2% (w/w) of biochar composed of 95% SB and 5% WB	196g soil + 3.8g SB + 0.2g WB
4	WB10%	soil+ 2% (w/w) of biochar composed of 90% SB and 10% WB	196g soil + 3.6g SB + 0.4g WB
5	WB20%	soil + 2% (w/w) of biochar composed of 80% SB and 20% WB	196g soil + 3.2g SB + 0.8g WB
6	WB30%	soil + 2% (w/w) of biochar composed of 70% SB and 30% WB	196g soil + 2.8g SB + 1.2g WB
7	WB40%	soil + 2% (w/w) of biochar composed of 60% SB and 40% WB	196g soil + 2.4g SB + 1.6g WB

5.3 Sampling and analysis

A total of three samplings were carried out. The first one took on day one (T1), the next one after 19 days (T2) and the last one after another 36 days (T3) corresponding to the 55 day difference from T1 to T3. The same procedure was followed in each sampling. Firstly, the soil mass either in isolation or with amendments was placed into individual bottles. The sample was kept moist at 70% water holding capacity, which corresponds to 25 ml of water per bottle. Subsequently, a rhizon (brand EijkelkampAgrisearch equipment, NED) equipped with a probe was introduced into each bottle containing the sample. A syringe needle was affixed to the end of each rhizon, and the bottles were left in darkness overnight. The application of pressure through the syringe facilitated the extraction of moisture from the sample into the syringes. The next day, another 8 ml of water was added into each bottle, which then followed with the transfer of the liquid from the syringes into tubes for subsequent analysis. However, it is noteworthy that not all replicates yielded a different volume of soil solution for analysis.

Initially, the volume of each available sample was recorded, followed by immediate measurements of pH, measured by WTW pH 3310 metre and redox potential (Eh), measured by a WTW Multi-parameter 3420 metre. Subsequently, a portion of each sample was transferred into tubes and diluted with 2% HNO_3 for ICP

(Inductively Coupled Plasma) analysis to determine total elemental composition. In a separate set of tubes, the samples underwent dilution with ultra-pure water for the determination of TOC/TN.

6.Results

6.1 pH and redox potential

Results, depicted in Figure 4, showed that the amendments application increased the pH compared to the Control. In both the first (T1) and the second (T2) sampling the pH was increasing gradually and reached its peak in amendment consisting of 80% SB and 20% WB. Then in both of these samplings the pH decreased slightly for amendment WB30% and WB40%. In the third sampling (T3) the pH seemed to increase gradually the more WB was added into the biochar ratio, reaching the highest levels of pH in amendment WB40%. The time also affected the pH levels, as observed in Figure 4. The pattern of the pH slightly increased after 19 days (during T2 compared to T1) and then dropped significantly after another 36 days (in T3) in the majority of the treatments: in the Control, amendments WB0%, WB5%, WB20% and WB30%. The exceptions of this pattern were found in WB10%, where the pH level decreases gradually with time and in WB40%, where the pH level dropped after 19 days (in T2) and increased after another 36 days.

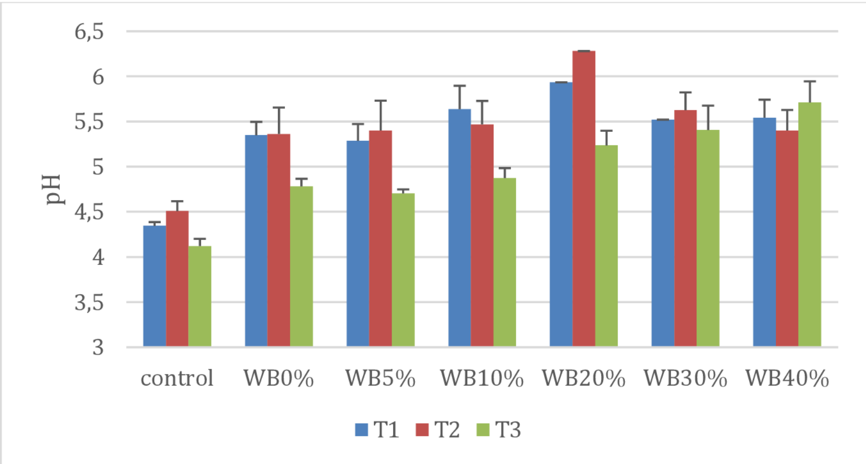

Figure 4 The pH monitored in soil solution of the Zvěřínek soil amended with different ratios of sludge biochar and wood biochar, referred to as WB followed by a percentage indicating the percentage of wood biochar in the biochar mix. Solutions were sampled on day 1 (T1), day 19 (T2) and day 55 (T3).

Figure 5 shows a change in redox potential (Eh) in the amended soil samples. The results indicated a decrease in Eh after biochar application. The most significant decrease seemed to happen in the amendment with the ratio of 80% SB and 20% WB, especially during the second sampling.

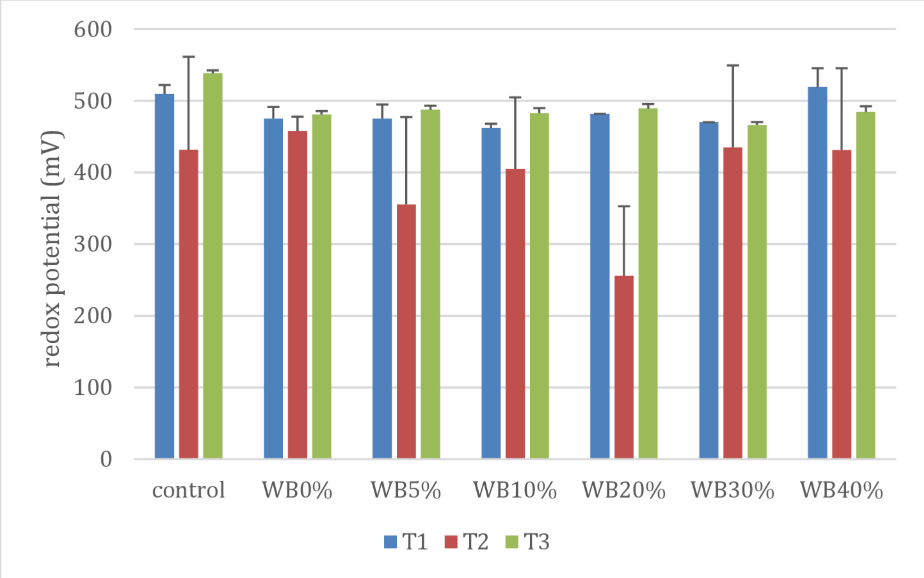

Figure 5 The redox potential (Eh) (mV) measured in the soil solutions sampled in an agriculture soil amended with varying ratios of SB and WB. Each amendment shows the measured redox potential levels for all three samplings; on day 1 (T1), day 19 (T2) and day 55 (T3).

6.2 Dissolved organic carbon and nitrogen contents in soil solution

Dissolved organic carbon (DOC) content varied in the two samplings, as displayed in Figure 6. In the first sampling the DOC increased by 24%, in comparison to the Control only with the amendment of SB without any WB. The addition of WB decreased the DOC content in a dose dependent manner. On the contrary, in the second sampling, the DOC content decreased with the amendment of only SB (WB0%) compared to the Control and then started to increase gradually. The highest content of DOC in the second sampling was reached at the ratio of 70% SB and 30% WB, the increase was by 115%. However, upon addition of 10% more of WB, at WB40%, the DOC content drops rapidly again.

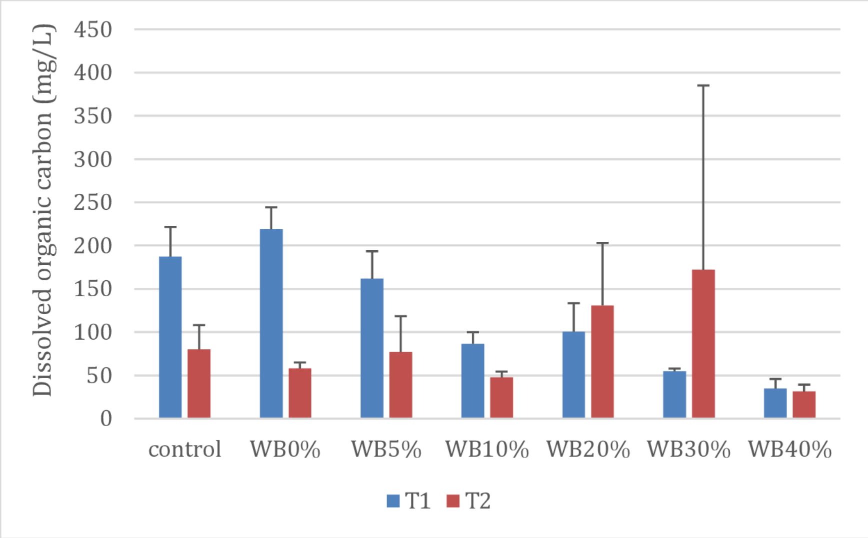

Figure 6 Measured Dissolved Organic Carbon (DOC) content in soil compared to soil amended with biochar at different rations of SB and WB. In total two samplings were carried out, the first sampling (T1) and after 19 days followed by the second sampling (T2).

Total nitrogen (TN) content varied in the two samplings, as displayed in **Error! Reference source not found.**. In the first sampling the TN content was reduced upon biochar addition in comparison to the Control, apart from the biochar amendment at a ratio of 80% SB and 20% WB, when the TN content increased by 55%. Interestingly, in the second sampling the TN content was the lowest at a ratio of 80% SB and 20% WB, declining by 87%. The highest content of TN in the second sampling was recorded after an amendment at a ratio of 90% SB and 10% WB, the increase in comparison to Control was by 14%.

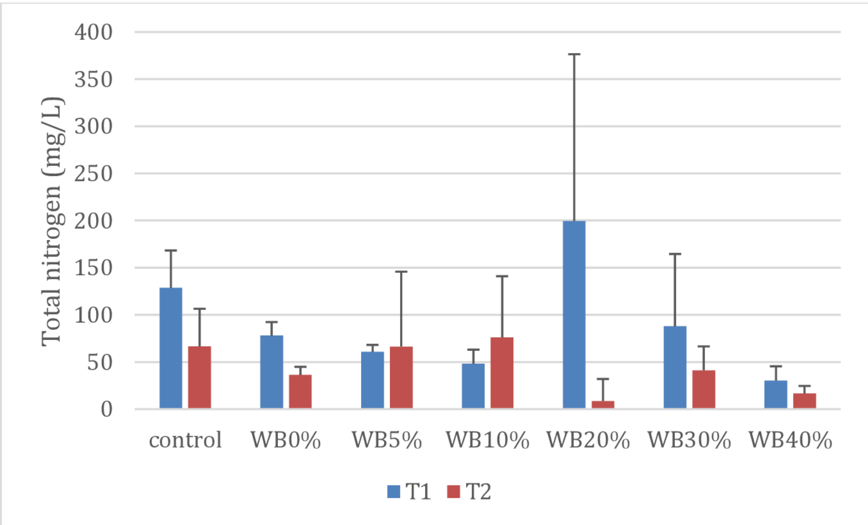

Figure 7 Measured Total Nitrogen (TN) content in soil compared to soil amended with biochar at different rations of SB and WB. In total two samplings were carried out, the first sampling (T1) and after 19 days followed by the second sampling (T2).

6.3 The composition of macronutrients

The total concentrations of nutrients, including phosphorus (P), potassium (K), magnesium (Mg) and sodium (Na) were measured in all three samplings and the results are shown in Figure 8. The concentrations of P, which reached the highest concentration during the second sampling, amended with 20% WB, followed by the second highest in WB30%. The lowest concentration of P was measured for all three samplings in WB10%. The highest concentration of K was observed in the treatment WB30% during the second sampling, however, the same amendment displayed the lowest concentration of K during the first sampling. The resulting Mg concentrations seemed to increase upon any biochar amendment addition, since the lowest concentrations were observed in the Control. The highest concentrations of Mg were found in amendment WB5%. For the Na content, the more WB was added the higher the concentration of Na was observed, the highest concentrations showcased in WB40%.

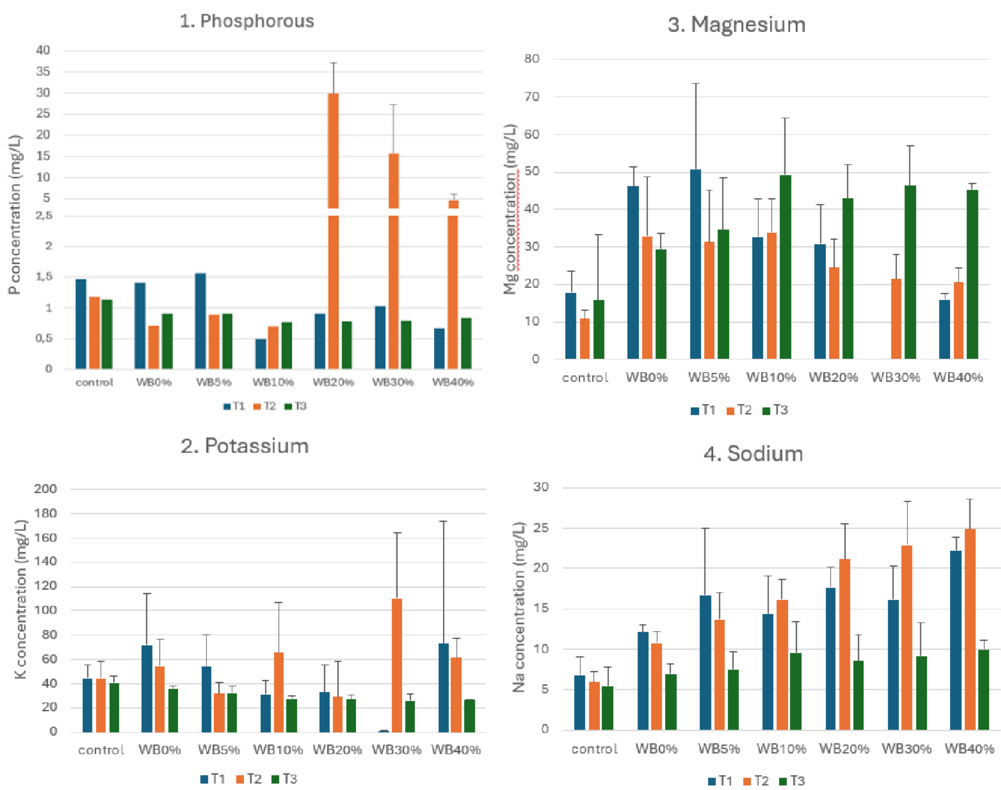

Figure 8 The concentrations in mg/L of phosphorus (1.), potassium (2.), magnesium (3.) and sodium (4.) in soil compared to the soil amended with biochar at different rations of SB and WB. In total three samplings were carried out (T1, T2, T3).

6.4 The composition of metals and metalloids in the soil solution

The total concentrations of elements, including arsenic (As), cadmium (Ca), copper (Cu), nickel (Ni) and lead (Pb), were measured in all three samplings and the results are shown in **Error! Reference source not found.**. The general trend of our experiment's data indicates that the leached metal concentration gradually decreases with time, and it appears that this decline was directly related to the amount of WB supplied. Even though there are some exceptions to this pattern. According to the results the concentration of As decreased as more WB was added. Upon addition of WB40% the As content decreased by 62% in comparison to the Control. The results for Cd exhibited a gradual decrease in concentration with more WB added. Cd leachate reached the highest concentrations during T1 in all the treatments, in comparison with T2 and T3, during which the concentrations decreased significantly even in the Control. The drop in Cd concentration is the most significant in WB40% in all three samplings (T1, T2 and T3). The same trend is presented in Cu, apart from an anomaly observed in WB30% after 36 days (T3) , when the concentration reached 86 mg/L, which is a 95% increase compared to the Control. The leaching of Ni appeared to be reversed, contrary to the trend observed in other metals. During the initial sampling (T1), no Ni was detected to have leached in the Control. Nickel began to leach at amendment WB10% and then increased as more WB was applied. The Ni concentration in the untreated soil reached 37 mg/L after 19 days, during the second sampling (T2), and increased to 49 mg/L after another 36 days, during the third measurement (T3). In the results for Pb, a progressive decrease in concentration manifested in the first and third sampling. The Pb concentration in the untreated soil dropped from 174 mg/L to 25 mg/L after 19 days (compared from T1 to T2), although it had risen to 59 mg/L after another 36 days (in T3). The Pb concentrations subsequently decrease regardless of time upon amending with WB0%. However, the Pb starts to increase upon any WB added after 19 days (in T2). Pb leachate reached the highest concentration in the amendment of 20% WB and 80% SB.

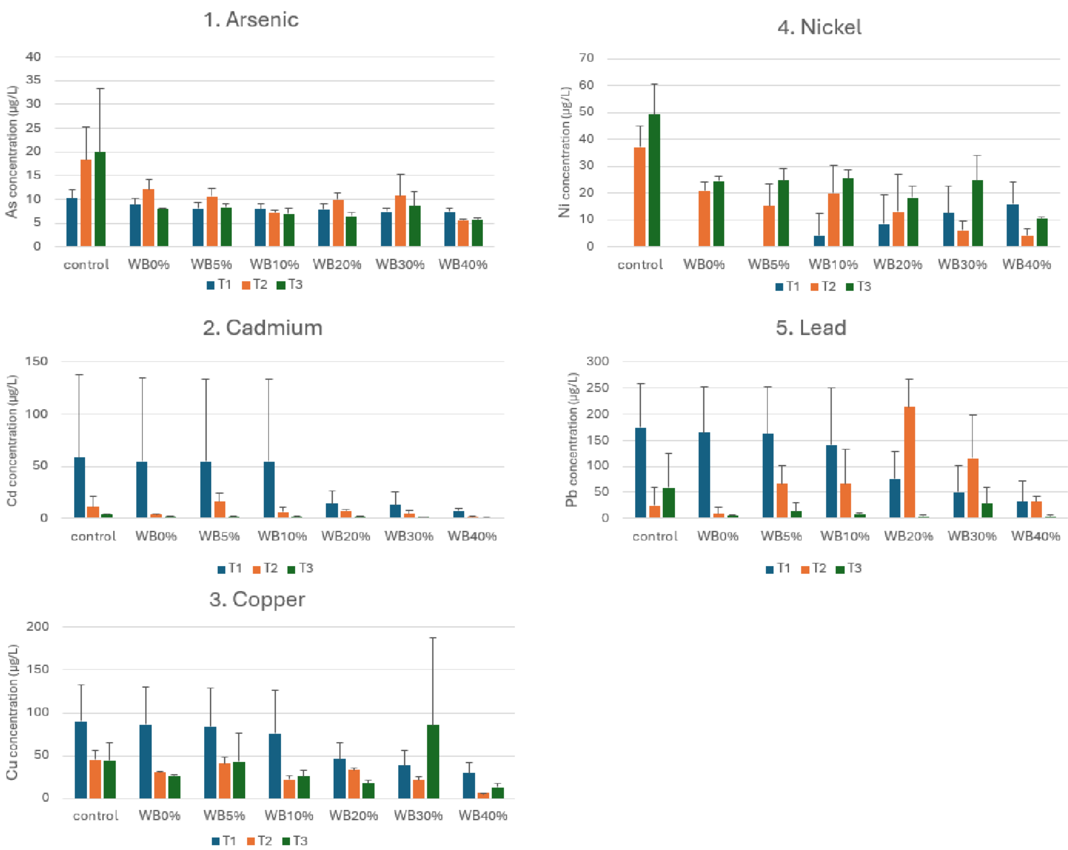

Figure 9 The concentrations in µg/L of arsenic (1.), cadmium (2.), copper (3.), nickel (4.) and lead (5.) in soil compared to the soil amended with biochar at different rations of SB and WB. In total three samplings were carried out (T1, T2, T3).

7. Discussion

7.1 Impact of biochar application on pH

All amendments increased the pH values of the sample by around one pH unit as compared to the Control. The largest increase was observed at WB20%, by 1.8 unit. The first explanation is that both biochars have a higher pH than the soil, specifically SB (11.7) and WB (11.1). Secondly, the functional groups in biochar interact with hydrogen ions in soil, lowering their concentration and increasing soil pH. Carbonates, bicarbonates, and silicates in biochar react with H+ ions, neutralizing soil pH (European Commission. Joint Research Centre. Institute for Environment and Sustainability., 2010; Yaashikaa et al., 2020). PH is an important factor, influencing nutrient availability, microbial activity and soil structure (Y. Ding et al., 2016).

In this instance, the alkaline pH resulting from the biochar amendments led to a soil pH above 5 in all treatments, which according to (Hazelton, P., & Murphy, B., 2017) is promoting the availability of essential nutrients such as P, N, K, S, Ca, and Mg. Even though the alkalinity of biochar increases the bioavailability of nutrients, it contributes to the decrease in bioavailability of metals. According to a meta-analysis (Chen et al., 2018) 78 studies showed that increasing pH can cause metal precipitation, decreased their solubility and increased their adsorption. The desired elemental composition in soils due to the alkaline pH can enhance plant growth and overall soil health (Hazelton, P., & Murphy, B., 2017).

7.2 Impact of biochar application on DOC and macronutrients

Nutrients play a crucial role in supporting plant growth. For instance, nitrogen and potassium aids in the overall development of crops and phosphorus promotes root growth, thereby enhancing water and nutrient utilisation efficiency (Velli et al., 2021). Previous biochar experiments suggested that carbon content in soil would likely increase with biochar addition. In a study (Velli et al., 2021) the soil treated with biochar showed an increase in total organic carbon (TOC) for all the biochar amendments. Upon reviewing the work of (Khanmohammadi et al., 2017) the application of sewage sludge biochar led to a notable rise in soil TOC compared to the untreated soil. Their experiments used two types of soils, from Falavarjan and Ziar regions, with both of them showing an increase in TOC by 1.4 g/kg and 1 g/kg, respectively. In our experiment the rise in the soil TOC content was expected particularly in treatments with higher WB ratios, as WB alone had high carbon content. The amount of DOC in the soil solution decreased gradually as more wood biochar was added. The biochar addition introduced higher levels of carbon into the soil, and the decrease in the soil solution suggests that the carbon is being conserved within the soil. The decrease in DOC was the most significant for both samplings (T1 and T2) in WB40%. These results suggest that the most effective ratio for maintaining C in the soil is 40% WB and 60% SB. This indicates that the WB application may lead to an effective C conservation within the soil.

In this experiment, the used sewage sludge biochar (SB), with a nitrogen content of 14.6 g/kg, provided a great nitrogen supply to the soil. After evaluating the results, it is clear that the TN in the soil solution decreases with increasing WB and with time. TN content increased only in WB10% during the second sampling (T2) and WB20% during the first sampling (T1). However, in treatment WB20% the decline in TN content decreased by 87% in T2. Utilizing biochar lowers N leaching, according to earlier research (Xu et al., 2016), where treatments with 2%, 4%, and 8% of biochar decreased total nitrogen leaching by 18%, 20%, and 20%, respectively, when compared to the Control. The results of our experiment confirm this pattern of TN leaching decline alongside biochar addition, particularly WB. This effect propounds three hypotheses. It might mean that the N is fixed on the biochar surface (Yaashikaa et al., 2020). N could also be fixed by microorganisms whose activity is boosted by the presence of biochar (Nguyen et al., 2017). The decrease in N leaching as time progresses may also imply nitrogen fixation by soil. According to the aforementioned study (Xu et al., 2016), the biochar's capacity to improve the soil's cation and anion exchange capabilities is what presumably caused the decrease in TN leaching.

The experimental soil Zvěřínek contained 410 mg/kg of phosphorus, 8,490 mg/kg of potassium and 220 mg/kg of magnesium. Although the total concentration of these nutrients appears to be sufficient under Czech legislation for arable land (Ministerstvo, 1998), as seen in Table 8, it does not show the degree of availability of these nutrients. Nutrient availability is a crucial factor for determining if the soil needs additional fertilisation to ensure optimal plant growth. The nutrient availability for plants to uptake is dependent on many factors, including soil's pH, content of organic matter, cation exchange capacity and also leaching provides information on nutrient mobility (Abd El-Mageed et al., 2021). According to (Zemanová et al., 2017) research, there was an increase in all of the available nutrients that were tested—K, Mg, Na, and P—when biochar was added. It is consistent with our experiment's findings as well, which indicated that adding biochar gradually increased the amount of P, K, Mg, and Na in the soil solution.

*Table 8 Czech legislation limits for **arable land** for chosen elements: phosphorous (P), potassium (K) and magnesium (Mg) in mg/kg, defined by ICP-OES method (Mehlich III) (Ministerstvo, 1998).*

Content	P mg/kg	K mg/kg	Mg mg/kg
Low	<55	<105	<105
Sufficient	56-85	106-170	106-160
Good	86-125	171-310	161-265
High	126-200	311-420	266-330
Very high	200<	420<	330<

For P, the highest increase was observed in WB5% during T1 and T2 in WB20%. A slight decline of P leaching was observed over time. The concentration of K in the soil solution increased upon introducing the amendments, apart from during the third sampling (T3). The leaching of K was the least significant and the most stable during T3, suggesting stabilisation of the nutrient in soil over time. Mg concentrations rose in all three samplings (T1, T2 and T3) upon SB addition. However, the more WB was added the less Mg leached into the soil solution. Thus indicating that the ratio of 40% WB and 60% makes Mg more conserved within the soil. The Na content was the lowest in T3 in all the amendments, proving that Na leaching decreases with time. Na concentration per amendment was the highest during T1 until the addition of 10% of WB, followed by the highest concentration observed in T2 for WB20%, WB30% and WB40%. Therefore the Na leaching increases upon WB addition and decreases over time.

7.3 Immobilisation of metals and metalloids upon biochar application

Soil contamination by heavy metals negatively impacts soil characteristics and limits productivity and environmental functions. Heavy metals impair the activity of soil microorganisms, leading to slower growth and reproduction of plants (Chen et al., 2018). In immobilised forms, heavy metals can persist for extended periods before becoming available again to living organisms, including plants (Friedlová, 2010). The pattern of our experiment's data indicates that the leached metal concentration gradually decreased with time, and it appears that this decline was directly related to the amount of WB supplied. This suggests that leached metal concentrations can be gradually reduced by incorporating WB into the soil and could be attributable to metal fixation on the WB surface, as generally biochar has a large surface area. Thus could lead to better soil quality, increased agricultural growth, and a lower environmental effect from metal leaching.

In this experiment, the general trend of heavy metal concentration in leachate was a progressive reduction over time. However, there are some exceptions to this pattern. Arsenic and nickel concentrations in untreated soil increased gradually over time, which indicates a progressive increase in Ni leaching over time. The experiment also found that the leaching of As was minimal compared to Ni, with concentrations remaining relatively stable over time. Biochar's effectiveness in immobilising As may increase with higher initial As concentrations, indicating varying behaviour of metals in soil. The Cd content was the lowest at WB40% in all three samplings, which suggests that the ratio of 40% WB to 60% SB is the most efficient at lessening Cd leaching in the soil. Cd leaching has decreased over time, which could be attributed to soil binding mechanism. Cu follows a similar trend to Cd, decreasing with time and WB addition. Apart from a sudden peak in Cu leaching observed in sampling T3 in amendment WB30%, which may be attributed to specific conditions present in the WB30% sample at that particular time point. Further investigation is needed to determine the cause of this anomaly and its implications for overall leaching behaviour.

An encouraging discovery by (Khanmohammadi et al., 2017) demonstrated a decrease in the tested plant's heavy metal uptake following biochar treatment when compared to the Control. This effect was especially substantial for Pb, highlighting the importance of biochar in reducing plant Pb uptake. The variation of Pb leaching over time reveals that adding WB to the soil enhances Pb leaching after 19 days, even when the concentration reduces after another 36 days (T3). This shows that WB's impact on Pb leaching in soil is not consistent over time. Interestingly, a link in the leaching pattern between Pb and DOC was detected throughout this experiment. This finding aligns with the discovery made by (Houben et al., 2012) who explained that fulvic acids, which are essential components of DOC, form stronger complexes with Pb, thereby enhancing its mobility in high DOC concentrations. Hence, the concentration of DOC plays a significant role in the Pb response to treatments, with organic anions having a major influence on Pb mobilization.

It is important to note that the effects of biochar on plant heavy metal uptake are also largely dependent on soil pH. As biochar's alkaline nature helps raising soil pH, it leads to metal precipitation and decreased metal solubility (Chen et al., 2018). Nonetheless, biochar is one of the most effective amendment for lowering heavy metal bioavailability, which has been consistently proven by a meta-analysis of 78 studies (Chen et al., 2018), where biochar-amended soils resulted in lowering mean amounts of Cd, Pb and Cu in plant tissues by 38%, 39%, and 25%, respectively.

8. Conclusion

Firstly, the application of biochar led to a significant increase in soil pH across all treatments, with the highest increase observed in the WB20% treatment. This alkaline pH resulting from biochar addition has several implications, including improved nutrient availability for essential elements such as P, N, K, Ca and Mg. Moreover, the elevated pH levels in soil also contribute to the decrease in bioavailability of metals, as indicated by the decline in leaching concentrations of metals over time.

Secondly, the addition of WB40% showed the highest conservation of C within the soil. The study also demonstrated the effectiveness of biochar in providing

N supply to the soil, with the most significant decline in TN leaching observed in WB40%. This reduction in N leaching can be attributed to various factors such as nitrogen fixation on the biochar surface, microbial activity enhancement, and improved soil cation and anion exchange capabilities.

Furthermore, the addition of biochar led to an increase in the availability of macronutrients - P, K, Mg and Na - in the soil solution. P seemed to be the most available in ratio WB5% and WB20%. Our findings for K and Mg leaching suggested stabilisation of the nutrient in soil over time and reaching the highest concentrations upon higher WB addition. The results for Na showed increased leaching overtime and decreased leaching upon WB addition. These findings suggest that biochar application, especially at higher WB ratios, can enhance nutrient availability for plant uptake, which is crucial for optimizing agricultural productivity.

The overall effect of biochar on concentration in soil solution of the evaluated metals - As, Cd, Cu, Ni and Pb – showed that the amendment WB40% was the most effective in reducing the leached metal concentration. This indicates the potential of this specific ratio of 60% SB and 40% WB to immobilize heavy metals in soil. This immobilization effect can lead to improved soil quality, increased agricultural growth, and reduced environmental impacts from metal leaching. Since 40% WB represented the highest proportion of WB to SB in this study, it would be interesting to conduct another experiment with an even higher WB to SB ratio. This is particularly intriguing given the observed trends, which suggested a gradual decrease in certain parameters as more WB was added.

In summary, this research contributes to addressing the challenges faced in modern agriculture by providing insights into optimising biochar amendments to enhance nutrient content and reduce heavy metal inputs from SB. The optimum ratio for enhancing nutrient availability whilst immobilising metals was WB40%. Understanding these dynamics upon amendment made up of 60% SB and 40% WB is beneficial to make informed decisions to improve soil fertility, crop productivity and the overall agricultural system.

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