Czech University of Life Sciences Prague

Faculty of Environmental Sciences

Department of Environmental Geosciences

Diploma Thesis
Pyrolyzed sewage sludge for sustainable brownfield reclamation

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CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Faculty of Environmental Sciences

DIPLOMA THESIS ASSIGNMENT

Bc. Daniela Casadiego Hernandez

Environmental Geosciences

Thesis title

Pyrolyzed sewage sludge for sustainable brownfield reclamation

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Objectives of thesis

The main aims are as follows:
(i) To verify the extent of potentially toxic elements release from soil samples amended with pyrolyzed sewage sludge ("sludgechar").
(ii) To evaluate the soil quality changes after the addition of sludgechar to a degraded brownfield/contaminated soil.

Methodology

1. Based on recommended literature and other sources found by the student the theoretical part will be elaborated. It will include a short description of the sewage sludge (generation, characteristics, composition, risks) and pyrolysed sewage sludge (properties, composition, benefits, potentials and drawbacks). The general description will be supplemented with suitable examples of sewage sludge utilization for soil remediation and reclamation including related environmental and health risks.

2. The practical part will include (i) basic properties of the studied materials, (ii) incubation of sludgechars in soils, (iii) soil extractions etc. as well as the samples preparation, analytical methods and the laboratory equipment used. Sample preparation and treatment, laboratory experiments, and analytical data treatment will be performed by the student independently under the control of the thesis supervisor and consultant.

3. The results will be presented in written and graphical forms. The discussion will be elaborated carefully based on the main results and with reference to relevant literature. The conclusion will be brief and concise.

The text will be spell-checked and grammar checked before being sent to the supervisor.

The proposed extent of the thesis

50-60 pages

Keywords

wastewater treatment residues; pyrolysis; soil remediation; contamination

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Recommended information sources

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Electronic approval: 28. 3. 2024

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Dean

Prague on 28. 03. 2024

Declaration

I hereby declare that I have independently elaborated the diploma thesis with the topic of " Pyrolyzed sewage sludge for sustainable brownfield reclamation" and that I have cited all the information sources that I used in the thesis and that are also listed at the end of the thesis in the list of used information sources.

I am aware that my diploma/final thesis is subject to Act No. 121/2000 Coll., on copyright, on rights related to copyright and on amendment of some acts, as amended by later regulations, particularly the provisions of Section 35(3) of the act on the use of the thesis.

I am aware that by submitting the diploma thesis I agree with its publication under Act No. 111/1998 Coll., on universities and on the change and amendments of some acts, as amended, regardless of the result of its defence.

With my own signature, I also declare that the electronic version is identical to the printed version and the data stated in the thesis has been processed in relation to the GDPR.

In Prague on March 28th, 2024 _____

Pyrolyzed sewage sludge for sustainable brownfield reclamation

Abstract

The following study investigates the effect of the application of pyrolyzed sewage sludge (PSS) for the sustainable remediation of contaminated soils. The main goal is the assessment of five PSS materials regarding their efficiency for metal and metalloid remediation in soils. The methodology includes laboratory experiments with five contaminated soils from distinct locations in the Czech Republic amended with pyrolyzed sewage sludge. Using standardized leaching in water and other soil extractions the concentrations of toxic metals and metalloids were identified and the immobilization efficiency of PSS was estimated. The results have shown that all the used PSS amendments showed some immobilization efficiency for the toxic metals, As, and Sb. Additionally, the samples with pyrolyzed sewage sludge occasionally showed higher pH values than the control samples which was a secondary positive effect. This study demonstrates the benefits and risks of using different PSS to immobilize toxic metals, As and Sb giving information for future remediation decisions. However, further investigation is needed to reach more conclusive results such as the PSS efficiency for metal(loid) immobilization in the field.

Keywords: Sewage sludge, pyrolyzed sewage sludge, toxic metals, soil remediation.

Pyrolyzované čistírenské kaly pro udržitelnou rekultivaci brownfieldů

Abstrakt

Následující studie zkoumá vliv použití pyrolýzních čistírenských kalů (PSS) na udržitelnou sanaci kontaminovaných půd. Hlavním cílem je posouzení pěti materiálů PSS z hlediska jejich účinnosti při remediaci kovů a metaloidů v půdách. Metodika zahrnuje laboratorní experimenty s pěti kontaminovanými půdami z odlišných lokalit v České republice, které byly doplněny pyrolyzovanými čistírenskými kaly. Pomocí standardizovaného vyluhování ve vodě a dalších půdních extrakcí byly zjištěny koncentrace toxických kovů a metaloidů a odhadnuta imobilizační účinnost PSS. Výsledky ukázaly, že všechny použité úpravy PSS vykazovaly určitou imobilizační účinnost pro toxické kovy, As a Sb. Kromě toho vzorky s pyrolyzovaným čistírenským kalem občas vykazovaly vyšší hodnoty pH než kontrolní vzorky, což byl sekundární pozitivní efekt. Tato studie ukazuje výhody a rizika použití různých PSS k imobilizaci toxických kovů, As a Sb, což poskytuje informace pro budoucí sanační rozhodnutí. K dosažení přesvědčivějších výsledků, jako je účinnost PSS pro imobilizaci kovů(loidů) v terénu, je však zapotřebí dalšího zkoumání.

Klíčová slova: Čistírenské kaly, pyrolyzované čistírenské kaly, toxické kovy, sanace půdy.

1 Introduction

Contemporary environmental management and the need for sustainable solutions for the reclamation of degraded areas bring scientific interest to treatments such as sewage sludge. Sewage sludge is a by-product of wastewater treatment plants requiring considerable effort for appropriate and reliable management for its final disposal (Mannina et al., 2023). Sewage sludge contains a variety of nutrients (e.g. N, P, K, Ca, Mg) but may also include toxic compounds (e.g. potential toxic metal(loid)s) causing serious problems (Liu et al., 2024) due to their environmental effects.

Soil pollution may be described as the contamination or the presence of toxic, harmful, or hazardous materials in the soil. That might be due to geogenic reasons or due to human activity from industrial, agro-based, or waste management operations (Senthilkumar & Naveen Kumar, 2020). Toxic metals and metalloids do not decompose. Thus, contamination raises environmental and economic problems worldwide since contaminated soils represent the heritage of industrial pollution (Ajibade et al., 2021). In the Czech Republic, soil contamination from metals and metalloids is primarily due to its industrial and mining history (Zumr, 2023). Remediation of contaminated soils through sustainable solutions (e.g. pyrolyzed sewage sludge) helps to boost the quality of the environment (Hou et al., 2023).

The current work aimed at researching the possibility of remediating metal(loid) contaminated soil using pyrolyzed sewage sludge (PSS). Pyrolysis can minimize the hazardous effects of the sludge and ensure its safe application in soil. However, a clear understanding is still necessary concerning the behavior of this treated material in remediating contaminated soils.

The thesis structure includes a literature review on soil contamination and mobility of metals and metalloids, pyrolysis of sewage sludge, potential risks, and benefits of PSS followed by the experimental methods used in this work and the obtained results. In turn, the findings are developed further and discussed to form a conclusion that adds knowledge to the existing information on the topic.

Overall, this study attempts to fill a breach in the research regarding the use of pyrolyzed sewage sludge in applications for the remediation of contaminated soils and is geared toward the sustainability of resource management and environmental restoration. It is recommended to test contaminated soil with PSS at different time intervals to find the most efficient period for immobilizing hazardous metal(loid)s in soil with diverse features and pollutants.

2   Objectives

- To verify the extent of potentially toxic elements released from soil samples amended with PSS.
- To evaluate the soil quality changes after the addition of PSS to degraded/contaminated brownfield soils.

3   Literature review

3.1   Soil contamination by metals and metalloids

Soil contamination by metal(loids) is an issue for both researchers and policymakers in determining its implications (Paltseva & Neaman, 2020). Metal(loid) pollutants interfere with the soil-based ecological equilibrium, and this negatively affects microbial communities, inhibits plant growth and reduces diversity (Rashid et al., 2023). Toxic heavy metals like lead, arsenic, cadmium, and mercury have impacts on soil living organisms and plants which results in disturbance of the food chain, thus impairing the functioning of ecosystems (Mitra et al., 2022). The intricate relationship between soil contaminants and their effects on biota necessitates a thorough evaluation of factors such as bioavailability and total elemental concentration in soils (Alengebawy et al., 2021). Thus, the analysis of bioavailability and total concentration is a crucial issue that requires further research and becomes one of the topics discussed in detail below.

3.1.1   Bioavailability and total concentration of metals and metalloids in soils

Bioavailability is the extent to which a material is available so that it can be taken up or utilized by living organisms or their tissues and/or cells (Nikinmaa, 2014). Bioavailability is very important in the context of soils as it determines how much vital nutrients and other chemicals are available to plants, bacteria, and other organisms for absorption and utilization (Kim et al., 2015). Control of bioavailability in soils takes place under the influence of various factors: the physical and chemical soil characteristics, the organic matter content, the pH, and many other interactions with the soil components (Li et al., 2016). The bioavailability of nutrients and potentially toxic metals in the soil is a direct determinant of a plant's health and production capability, as well as other processes that ecosystems run (Alengebawy et al., 2021).

Total concentrations, on the other hand, indicate the complete quantity of a substance without discriminating between the proportion that is readily available for absorption by organisms and the one that is not (Peijnenburg et al., 2007). Total concentrations comprise both soluble and accessible forms as well as those that are attached to soil particles or exist in less accessible chemical forms (J.-X. Wang et al., 2021).

The primary distinction between bioavailability and total concentrations is their relevance to living organisms. Total concentrations provide a broader picture of the chemical's

presence in the environment, whereas bioavailability provides insight into the actual quantity of a material that can be consumed by organisms (EPA, 2007). For example, soil may have a high total concentration of a hazardous metal, but if the metal is mostly in a form that plants cannot readily absorb, it may still be safe for the plants (Kabata-Pendias, 2010).

3.2 Mobility of metals and metalloids in soils

Metals and metalloids are significant natural constituents of all soils and their occurrence in the mineral fraction may include potentially toxic metal species. (Gadd, 2007). Also, metals and metalloids may be involved in several complex chemical and biological interactions. The main chemical interactions are classified as adsorption, desorption, complexation, redox, and ionic exchange (Caporale & Violante, 2016). Biological interactions are categorized as uptake by plants, microbial interactions, metal-microbe interactions, bioaccumulation, and biomagnification (Kabata-Pendias, 2007). The most important parameters governing metal and metalloid mobility are pH, redox potential, and the existence or character and concentration of organic and inorganic ligands (which incorporate humic acids, fulvic acids, root exudates, and nutrients) (Violante et al., 2010).

Anthropogenic activities, especially in agriculture, industry, and mining, bring the source of metals and metalloids into the environment (Edelstein & Ben-Hur, 2018). The activities thus introduce serious environmental pollution by releasing toxic metals and metalloids into soils and sediments (Das et al., 2023). Also, the weathering of the rocks naturally releases metals and metalloids into the surrounding environment (Qu et al., 2020). There is international concern about soils contaminated with toxic metals and metalloids since they directly relate to human health and environmental degradation (Nguyen et al., 2021). The toxic metals and metalloids in the soil can affect the environment and cause toxicity to living organisms, by bioaccumulation, biomagnification, soil/water contamination, ecotoxicity to aquatic life, soil microbial activity, and long-term environmental persistence (Singh et al., 2022).

3.3 Potential hazards of risk metals and metalloids to environment and human health

Regarding Zn, some of the studied soils were higher than the permissible limits described in the section **6.1** and **6.2** even after the PS treatment which can lead to some toxic effects including retardation in growth since Zn can impede the necessary absorption of other minerals (Hamzah Saleem et al., 2022). Also, damages the cell through harm to the cell's membrane and protein (Sinclair & Krämer, 2012). And eventual death, which occurs when the intake of Zn is very high and usually happens to lower organisms (Balafrej et al., 2020). However, Zn is essential for plant growth due to its engagement in various critical metabolic processes and cellular activities (Hussain et al., 2022).

Excessing the Pb permissible limits can lead to being considered a poisonous substance to most plants and animals; hence, greatly reducing the diversity of species within an

ecosystem (Collin et al., 2022). Pb can also be taken into food in the soils where they have been affected by contamination because Pb is taken up by the plant mainly from the roots and hence from the soil solution and, in doing so, may enter the food chain. (A. Kumar et al., 2020).

Cadmium accumulates in soil and can infiltrate water sources, harming aquatic creatures and potentially entering the food chain. In high quantities, it can also be hazardous to plants. It can disrupt metabolic processes, impair food absorption, and damage cell structures, resulting in poor growth and cadmium buildup in plant tissues (Genchi et al., 2020).

Finally, As in large quantities may be hazardous to the environment because it is highly toxic and can cause even death in plants, animals, and microorganisms (WHO, 2022). Also, As can mobilize and accumulate in living organisms because easily interconvertible forms of As in the environment afford it an easy, ready uptake by biota (ATDSR, 2007). This "mobilization" allows As into food chains and its tissue build-up over time (Martins et al., 2019). Arsenic can contaminate huge sources of water, and, overall, cast a poisonous influence on aquatic and terrestrial ecosystems which can reduce biodiversity, disrupt food webs, and alter the environment's health (Ghosh et al., 2022).

3.4 Sewage sludge

Sewage sludge is the residual semi-solid matter remaining following the wastewater treatment process, which separates liquids and solids. The collected solids either go to an aquatic environment and are given additional treatment beforehand or are disposed of. The constituents removed during wastewater treatment include grit, screenings, and sludge (Metcalf & Eddy, 2003).

Usually, two processes produce sewage sludge; sedimentation and separation processes and biological processes. Sedimentation and separation are carried out to remove the suspended solids and other materials from the water during the wastewater treatment and this process results in sludge formation after physical and chemical processes are applied (Tiwari & Awasthi, 2022). To treat the wastewater in the biological processes conducted in wastewater treatment plants, microorganisms are used to degrade the organic content.

The sludge production in the Czech Republic was 197.991 tons/year of dry matter in 2022 (Český statistický úřad, 2023). The sludge stemming from the wastewater treatment process is usually liquid or semisolid liquid; the concentration contains 0.25–12% solids by weight (Metcalf & Eddy, 2003). The solid fraction varies between the above limits due to the different methods of effluent treatment. Normally, sewage sludge has specific characteristics determined from the wastewater source. The typical chemical composition and properties of some parameters and metals are shown in **Table 1.** Additionally, the content of heavy metals, pesticides, and hydrocarbons also needs to be determined when sewage sludge is to be incinerated or landfilled.

Table 1 Typical chemical composition and properties of sludge

Sludge composition	Untreated primary (mg/kg)	
	Range	Medium
Nitrogen (N. % of TS)	1.5 - 4	2.5
Phosphorus (P_2O_5. % of TS)	0.8 - 2.8	1.6
pH	5.0 - 8.0	6.0
Arsenic (As)	1.1 - 230	10
Cadmium (Cd)	1 - 3.410	10
Chromium (Cr)	10 - 99000	500
Cobalt (Co)	11.3 – 2490	30
Copper (Cu)	84 - 17000	800
Iron (Fe)	1,000 - 154000	17000
Lead (Pb)	13 - 26000	500
Manganese (Mg)	32 – 9870	260
Mercury (Hg)	0.6 - 56	6
Zinc (Zn)	101 - 49000	1700

Source of data: (Fericelli, 2011)

Inappropriately managed sludge can cause contamination of soil and water bodies by potentially toxic metals, pathogens, and other pollutants (Agoro et al., 2020). Moreover, some processes involving sludge result in bad odors which are publicly unwanted and indicate health risks since pathogens may be present (Wing et al., 2014). Therefore, since 1998 European legislation (UWWTD) has banned dumping of sewage sludge into the sea as a protection measure for the marine environment. In addition, sludge disposal deposits in landfills are planned to be eliminated in the future (35-45% of the sludge in Europe is currently stored in landfills). Agricultural use has become the principal disposal method for sewage sludge, but the usage differs between EU countries; 89 % of the total dry mass of the sludge produced was being utilized in agriculture in Ireland in 2019, 74% is being composted in Hungary in 2019, 87% is being incinerated in the Netherlands in 2018 and 100% is landfilled in Malta in 2019 (Eurostat, 2022).

Sewage sludge use can have potential risks due to toxic element content (elevated levels of toxic metals such as cadmium, lead, mercury, and chromium), organic contaminant content (persistent organic pollutants (POPs)), pathogens (bacteria, viruses, and parasites), emerging contaminants (pharmaceuticals and personal care products (PPCPs)), airborne contaminant release (dust and aerosols). Thus, the application of raw sewage sludge can result in soil and water contamination (leaching and runoff) and contaminant bioaccumulation in plants and animals (R. P. Singh & Agrawal, 2008).

On the other hand, sludge also contains a high amount of nutrients such as N, P, K, S, Ca, Mg, and more (Christodoulou & Stamatelatou, 2016). The nutrient recovery due to the application of fertilizers in the agriculture fields is among several other benefits of sewage sludge application (Marin & Rusănescu, 2023). Also, regarding the creation of energy,

sludge can be treated by anaerobic digestion processes generating biogas and, consequently, producing heat or electricity (Sevillano et al., 2021).

Treating sewage sludge is therefore crucial for several reasons. To begin with, is to sanitize the sludge since it can contain pathogens and toxins (Mikula et al., 2022). Furthermore, sewage sludge has elements such as nutrients and organic content that can be obtained and used as fertilizers or for generating energy (Rorat et al., 2019). Lastly, sludge treatment reduces the volume of sludge while stabilizing the composition making it more portable and easier to dispose of (Fayssal, 2024).

3.4.1 Pyrolysis and pyrolyzed sewage sludge (PSS)

Due to the richness in nutrients and organic matter sludge can be a beneficial soil amendment if properly treated. The sewage sludge can be treated in several ways, and the most novel of them is pyrolysis. Pyrolysis is the combustion of any organic material (polymers, gaseous hydrocarbons, hydrocarbon-rich oils) in the absence of oxygen (Rangabhashiyam et al., 2022). Pyrolysis results in a much smaller concentration of hazardous substances and lowers the threats to the environment compared to the direct use of sludge (Al-Rumaihi et al., 2022). Also, during pyrolysis, the production of secondary products such as biochar and fuel gases with multiple applications is possible. These sustainable resources introduce new possibilities for sludge management and safe and efficient reuse (de Morais et al., 2023). The field of study on sludge treatment, which is well-considered as a waste management and sustainable agriculture strategy, is undoubtedly a huge turning point (Lamastra et al., 2018).

One of the products of sewage sludge pyrolysis can be PSS which is an option for the treatment and sustainable utilization of waste produced by wastewater treatment plants (WWTP) (Capodaglio & Callegari, 2017). The research on PSS is still on the go, and various technologies and approaches are being investigated, designed to optimize the process, and maximize the efficiency and sustainability of the production of PSS and any other secondary products (Trabelsi et al., 2021). Nevertheless, technical, economic, and environmental issues should be resolved, like the safe management of the products and the long-term assessment of the environmental and economic impacts of PSS use (Teoh & Li, 2020). Overall, PSS offers an opportunity to convert problematic waste into useful resources (Gao et al., 2020). Its successful implementation could contribute significantly to waste management and the transition to a circular, low-carbon economy (Porshnov, 2022).

3.4.2 Uses of pyrolyzed sewage sludge in soils

According to Ghodke et al., 2021, sludge pyrolysis can produce different products with different applications depending on the pyrolysis temperature (**Figure 1**). (Djandja et al., 2020)
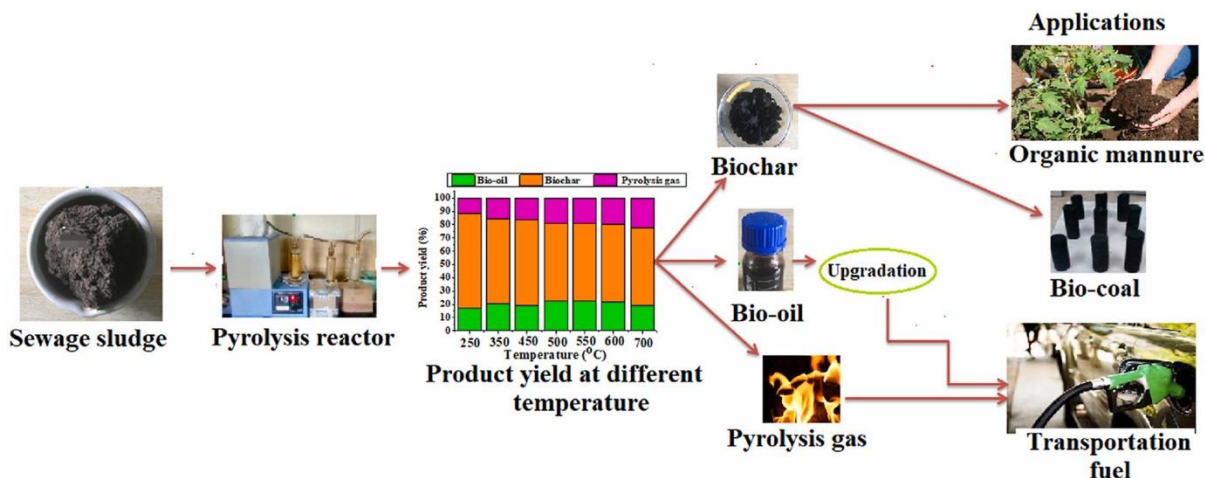
Figure 1 Production and applications of PSS. Reproduced from (Ghodke et al., 2021)

Pyrolyzed sewage sludge can be used as a provision of carbon-based organic material, supply nutrients, and increase of water-holding capacity of the soil (Brewer & Brown, 2012). Pyrolyzed sewage sludge can be a tool in agriculture as it boosts soil fertility, enhances the soil structure, enriches the nutrient level in soils, and reduces the amount of nutrient loss (Allohverdi et al., 2021). The addition of PSS is known to increase the efficiency of nitrogen fertilizers by improving the chemical properties of the soil (Callegari & Capodaglio, 2018). It may also increase the cation exchange capacity (CEC) of the soil by up to 40% and the pH of the soil by up to 1 pH unit. However, though PSS ecological contribution to agriculture is recognized, it has not yet achieved the commercial state therefore further research is needed (Enaime et al., 2023).

Furthermore, PSS can be used in the remediation and restoration of contaminated soils, as it has shown the potential to reduce the diffusion of a variety of organic and inorganic contaminants present in mobile forms in soils. The large surface area and porous shape, which are typical for pyrolyzed organic-based amendments, are responsible for the ability of the PSS to absorb various contaminants that can be found in soils and water (Prakash & S, 2023). When applied to soil that includes toxic metals and metalloids, the PSS works to reduce their availability hence preventing bioaccumulation of these elements by plants and soil organisms (**Figure 2**) (Černe et al., 2021). In addition, the fact that PSS can form stable complexes with these contaminants is beneficial as this helps the in-situ immobilization and limited leaching of the pollutants into groundwater (Li et al., 2021).
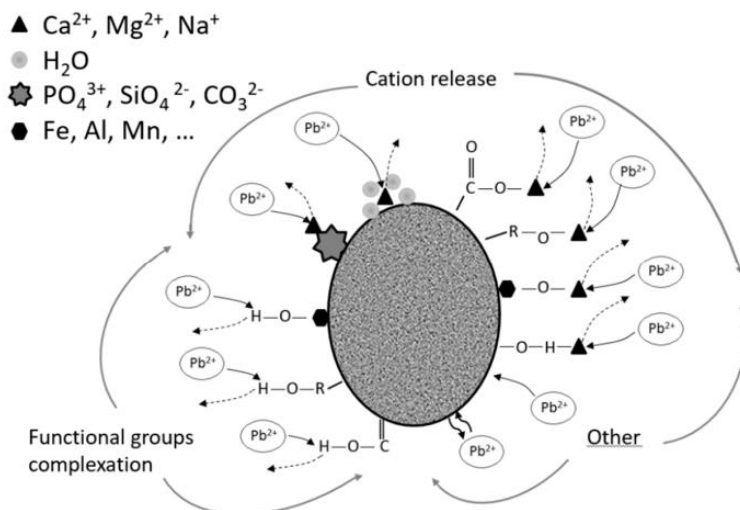
Figure 2 Conceptualization of Pb adsorption mechanisms by biochar. Reproduced from (Callegari & Capodaglio, 2018)

The use of PSS as a strategy for low-cost and efficient mitigation of metal and metalloid contamination is an opportunity among environmental remediation processes (L. Wang et al., 2021). Additionally, some PSS has comparable or even better adsorption properties than commercial activated carbon (Zhang et al., 2013). Nevertheless, comprehensive studies are required for a better understanding of all metal(loid) retention mechanisms as well as the environmental and climatic implications of PSS application (Murtaza et al., 2023).

The PSS can also be used to improve soil properties, promote carbon sequestration, as a secondary feedstock to produce activated carbon, to produce catalysts, as a gas adsorbent, for fuel cell systems, and as a base for supercapacitors (an energy storage device that uses capacitive and electrochemical principles to store electrical charge)(Callegari & Capodaglio, 2018).

3.4. Benefits resulting from the use of PSS in soils

Potential environmental benefits of the use of PSS in soil are (i) remediation of contaminated sites (Gregory et al., 2014), (ii) addition of plant-available nutrients (Oram, et al., 2014), (iii) improving soil pH (Singh, Singh, & Cowie, 2010), (iv) reducing non-CO_2 greenhouse gas emissions (Cayuela et al., 2013), and (v) reducing loss of nutrients through leaching (Ventura et al., 2013).

The remediation of contaminated soil with the use of PSS has been closely considered due to the wide range of advantages (L. Zhao et al., 2023). The PSS is useful for being able to recover land that has been polluted by different contaminating substances (Hoang et al., 2022).

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Additionally, using the PSS is a regenerative, and functional approach to providing plants with nutrients (Di Costanzo et al., 2021). The pyrolysis process, therefore, transforms the sludge into solids of large nutritional value, in nitrogen, phosphorus, and potassium which plants can absorb readily (Racek et al., 2020). On top of that, the environment becomes favorable for root development and beneficial microorganisms in the soil (Xu et al., 2023), finally leading to higher agricultural productivity and quality of the environment (S. Singh et al., 2020).

Also, PSS can be an effective approach to reducing indirect carbon dioxide greenhouse gas emissions (H. Sun et al., 2022). The greenhouse gas that escapes because of anaerobic digestion is benign because the amount that is leaked out is roughly the equivalent of the amount that is released either from landfills or treatment plants (Hu et al., 2022). Furthermore, pyrolysis changes relatively unstable organic pollutants to more stable ones that in turn reduce releases of short-lived greenhouse gases. For example, nitrous oxide and volatile organic compounds, the consequent effect is better air quality and climate change mitigation (Cheng et al., 2022).

3.5. Potential risks resulting from the use of PSS

The use of PSS has disadvantages, and it is imperative to look at them carefully (Gulzar et al., 2022). Environmental problems associated with the application of PSS to land, include the following (Camps Arbestain et al., 2014):

- Unbalanced addition of nutrients to the soil.
- Possible negative effects on the soil biota.
- The expected sorption of herbicide and pesticide residues and the resulting impact on the efficacy of these products.
- Potential input of heavy metals, polycyclic aromatic hydrocarbons (PAHs), and dioxins with the PSS.
- Environmental pollution from dust, erosion, and leaching of biochar particles aerosol emissions from improper pyrolysis.

Additionally, The effects of PSS on soil microbial populations, invertebrates, and other soil species are still unclear (Y. Zhao et al., 2023). To comprehend the possible ecotoxicological consequences, more research is required. Vereš et al., 2014 stated that the use of PSS in contaminated soils must adhere to environmental rules. This includes a proposed amendment to the EC 2003/2003 regulation by the European Commission in 2016, endorsed by the European Sustainable Phosphorus Platform in 2015. In addition, reference is made to regulations such as EC No. 66/2010, related to the EU Ecolabel, and EC No. 1907/2006 on the "Registration, Evaluation, Authorization and Restriction of Chemicals (REACH)" (MEYER et al., 2017). Failure to follow these standards may result in legal and environmental penalties.

4. Methodology

4.1. Soil samples

The soil samples used in this study were obtained from five distinct localities in the Czech Republic which represented different land uses i.e., post-mining areas, brownfields, and a private garden. All studied samples are degraded and/or contaminated soils that would benefit from remediation using pyrolyzed sewage sludge. Details about the soils and the contaminants are presented Table 2. Each soil sample is given a code name representing it. The exact origin cannot be revealed due to confidentiality reasons. In every case, the soil was taken from 0-25cm depth, air-dried, and sieved at < 2mm before further use in experiments (Mitzia et al., 2024).

Table 2. Soil samples characteristics

Soil code-name	Source of contamination	Main contaminants	Contamination total content (mg/kg)
Zn-rich (ZR)	Post mining/smelting	Zn	3000–3600
		Pb	3900–8600
		As	310–390
		Cd	30–50
As-rich (AR)	Natural enrichment	As	~18,000
Brownfield (BF)	Landfill/ coal mining	Pb	70–80
Smelter (SM)	Post smelting area	Zn	3000–3600
		Pb	3900–8600
		As	310–390
		Sb	~230
Garden (GD)	Former landfill	Cd	1–3

Source: (Mitzia et al., 2024)

In the following experiments, five different pyrolyzed sludges were applied in the studied soils to test their efficiency in metal(loid) immobilization and soil improvement. The raw sludges originated from WWTPs from five different locations in the Czech Republic representing large, medium, and small-sized towns. Sludges were obtained from WWTPs where the technologies cover mechanical-biological wastewater treatment with or without tertiary treatment and with or without sludge stabilization. Due to a binding agreement with the WWTPs, further information about the sewage sludge treatment technologies and the exact origin of the raw sludge cannot be revealed. All sludges were pyrolyzed at 600-650° C before further application to soils. In the following sections, the pyrolyzed sludges are denoted as PS1, PS2, PS3, PS4, and PS5.

Table 3. Metals and metalloids concentration in pyrolyzed sludges

Element (mg/kg)	PS1	PS2	PS3	PS4	PS5
Zn	1428±9.78	2155±70.2	1717±115	1732±17.0	1593±48.9
Pb	27.9±3.46	22.3±3.10	20.1±0.57	28.8±12.1	36.2±8.87
Cd	1.66±0.28	1.58±0.14	3.19±0.19	3.06±1.36	2.03±0.18
Cu	332±28.2	190±36.7	1776±229	410±45.5	268±29.2
As	6.51±0.12	7.58±3.36	8.65±5.21	12.5±4.13	10.7±2.32
Sb	2.24±0.65	4.02±0.66	3.09±0.20	4.91±2.08	8.70±2.15

Source: (Mitzia et al., 2024)

4.2. Leaching test on soil amended with pyrolyzed sludges

The standardized leaching test EN 12457 was performed to identify the available nutrients and toxic elements in the five soil samples. For each sample, 4 g of soil was placed in a polyethylene bottle (in triplicates). Then, 40 mL of demineralized water was added to each sample and put in the shaker for 24 hours at 100 rpm. Afterwards, the samples were centrifuged for 10 min at 8000 rpm and filtered with 0.45 µm nitrocellulose filters. The extractants were immediately subjected to measurement of physicochemical parameters i.e., pH, redox potential (Eh), and electric conductivity (EC). Finally, the extractants were diluted with 2% (HNO_3) for inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) analyses and with demineralized water for ionic chromatography (IC) and dissolved organic carbon (DOC) analysis.

4.3. Soil extractions for metals and metalloids

These extractions were performed to determine the amount of exchangeable metals and metalloids in the studied soils. For each sample, 1 g of soil was placed in a polyethylene bottle in duplicates. Then, 40 mL of 0.11 M acetic acid (CH_3COOH) was added, and the sample was put in the shaker for 16 hours at 200 rpm. After 16 hours, the extractants were centrifugated for 10 min at 8000 rpm and filtered with 0.45 µm filters. Then, these extractants were diluted with 2% nitric acid (HNO_3). Finally, the samples were diluted and tested by ICP-OES (if the concentrations were lower than the detention limit of ICP OES, the sample was analyzed with ICP-MS).

Additionally, metalloids (particularly As and Sb) were extracted in the soils using the Wenzel et al., 2001 extraction method. The extraction was performed using each sample, 1 g of soil was placed in a polyethylene bottle in duplicates. Then, 25 mL of 0.2 M ammonium sulfate ((NH_4)$_2SO_4$) was added and put in the shaker for 4 hours at 200 rpm. After 4 hours, the extractants were centrifugated for 10 min at 8000 rpm and filtered with 0.45 µm filters. Then, these extractants were diluted with 2% nitric acid (HNO_3). Finally, the samples were diluted and tested by ICP-OES (if the concentrations were lower than the detention limit of ICP OES, the sample was analyzed with ICP-MS).

Table 4. Equipment and chemicals used in the experiments

Equipment	ICP OES iCAP 7000,Thermo Scientific
	ICP MS iCAP Q .Thermo Scientific
	pH meter 3210 ProfiLine Meter, WTW
	Digital Analytical Scale, Mettler Toledo
	Centrifuge, Thermo Scientific
	IC Dionex ICS-5000+, Thermo Fisher Scientific
	TOC-L CPH, Shimadzu
	0.45 µm nitrocellulose filters
Chemicals	Nitric acid (HNO_3)
	Acetic acid (CH_3COOH) 0.11 M
	Ammonium sulfate (($NH_4)_2SO_4$) 0.2 M
	Demineralized water; IWA 120 iol, WATEK
	pH buffer technical, pH 4,01 ±0,03, WTW
	pH buffer technical, pH 7,00 ±0,03, WTW
	pH buffer technical, pH 10,01 ±0,03, WTW

5. Results

5.1. Leaching of target contaminants in water (EN 12457 method)

This part presents the results of the leaching of contaminants from the soil samples in water, according to the EN 12457 standard. The analysis of leaching in water is essential, as it provides information on the possible release of toxic elements present in the sample being evaluated (in this case, soil treated with waste-derived material), which could represent a hazard to living organisms. The EN 12457 method evaluates the leachability of elements in waste materials. In the following experiments, the most important (in terms of total concentrations in the soils; **Table 2**) toxic metals and metalloids are described such as Zn, Pb, As, Cu, Cd and Sb.

5.1.1. Zinc (Zn)

In this section, the results regarding Zn concentrations in the five distinct studied sites are presented.
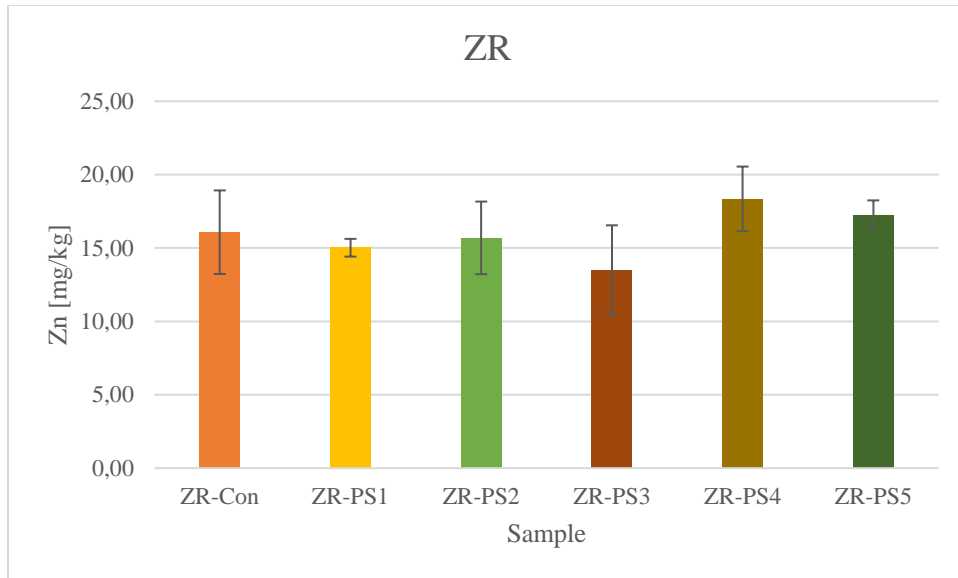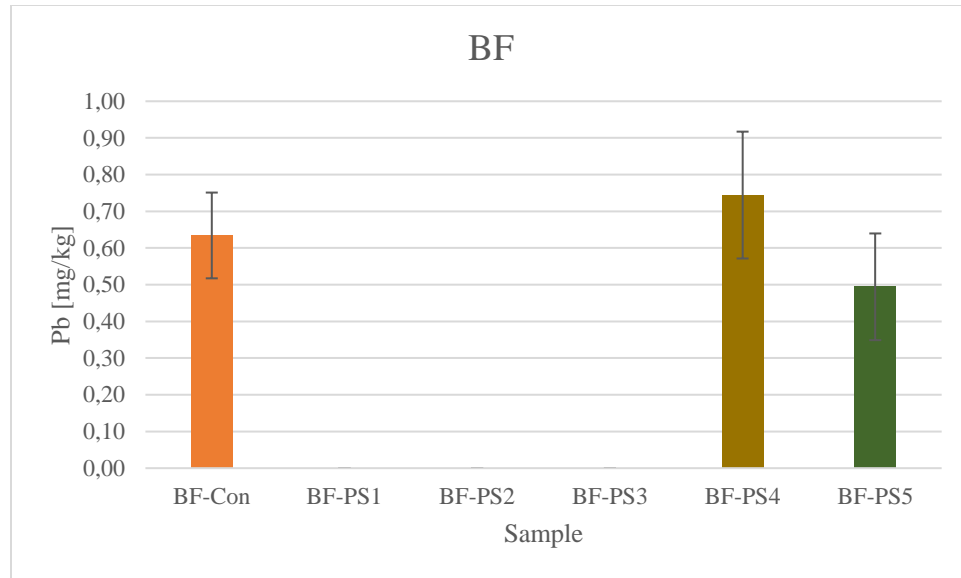
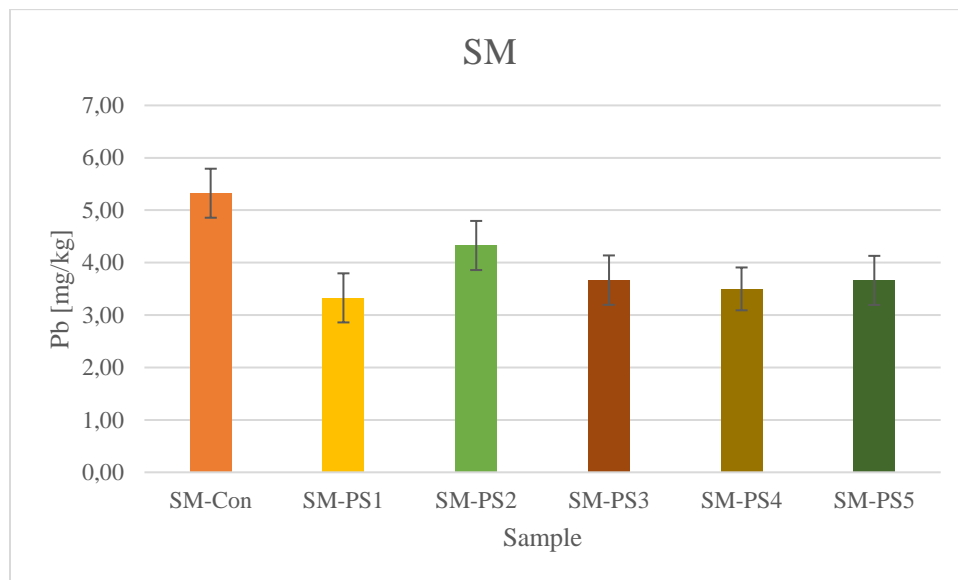**Figure 3 Concentration of Zn based on EN 12457 method in Zn-rich soil.**
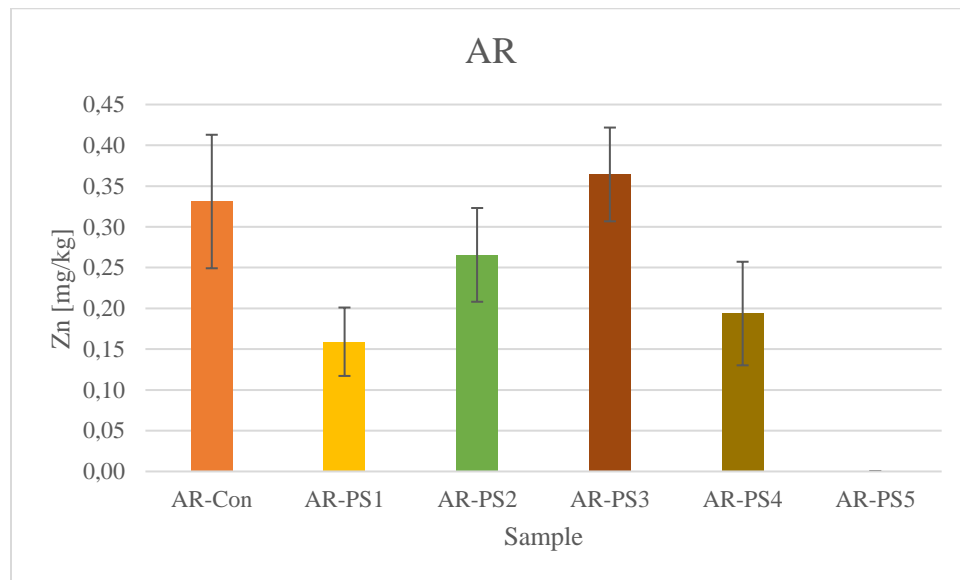
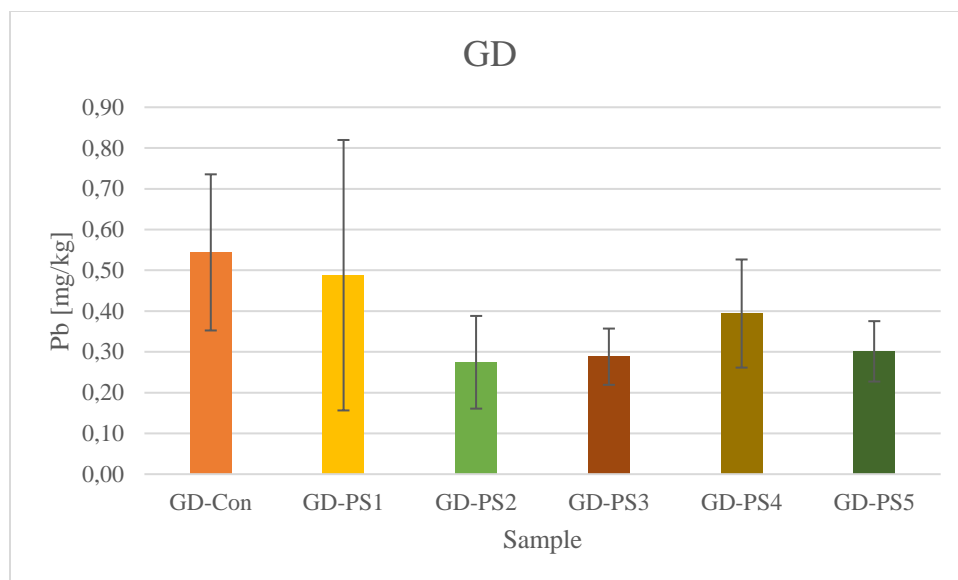**Figure 4 Concentration of Zn based on EN 12457 method in As-rich soil.**
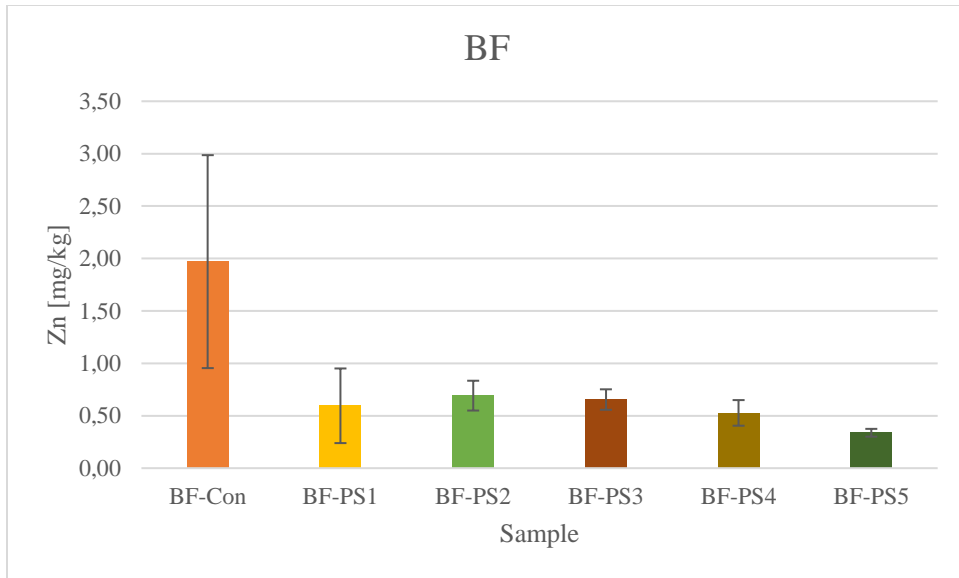
Figure 5 Concentration of Zn based on EN 12457 method in Brownfield soil.
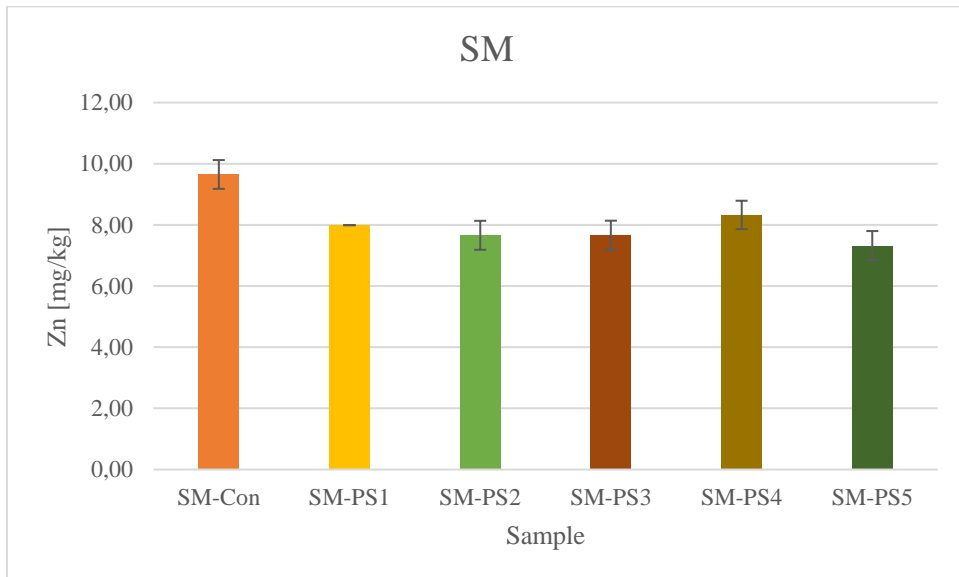
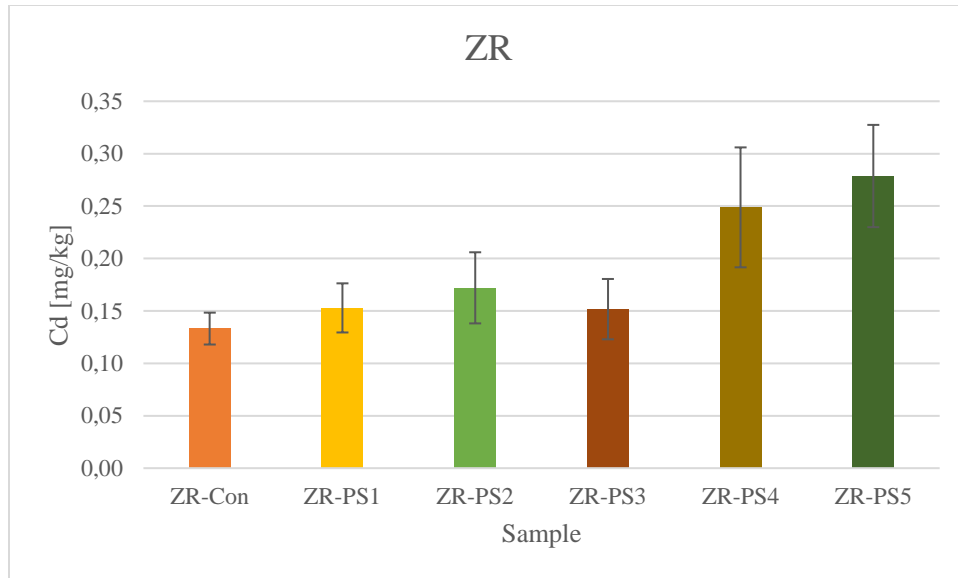**Figure 6 Concentration of Zn based on EN 12457 method in Smelter soil.**
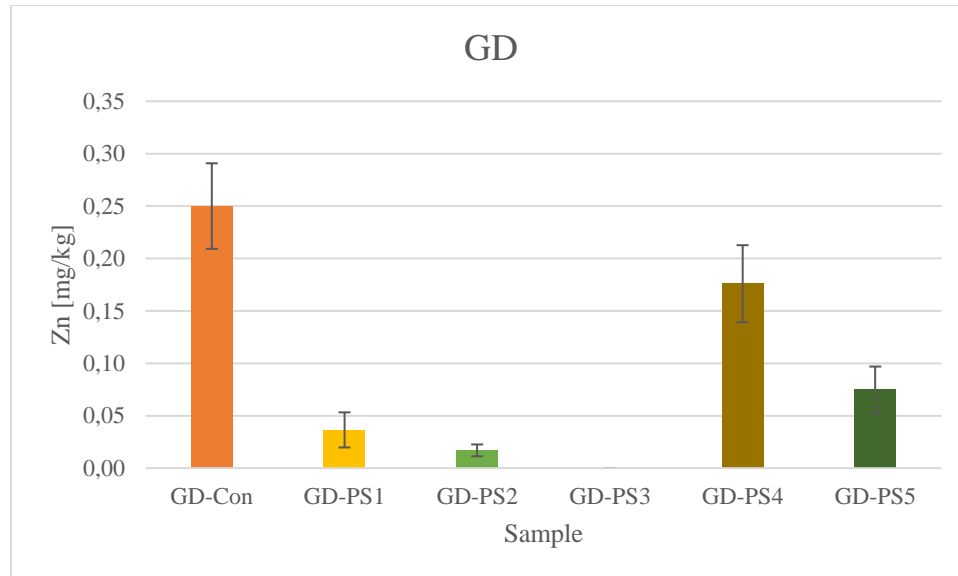
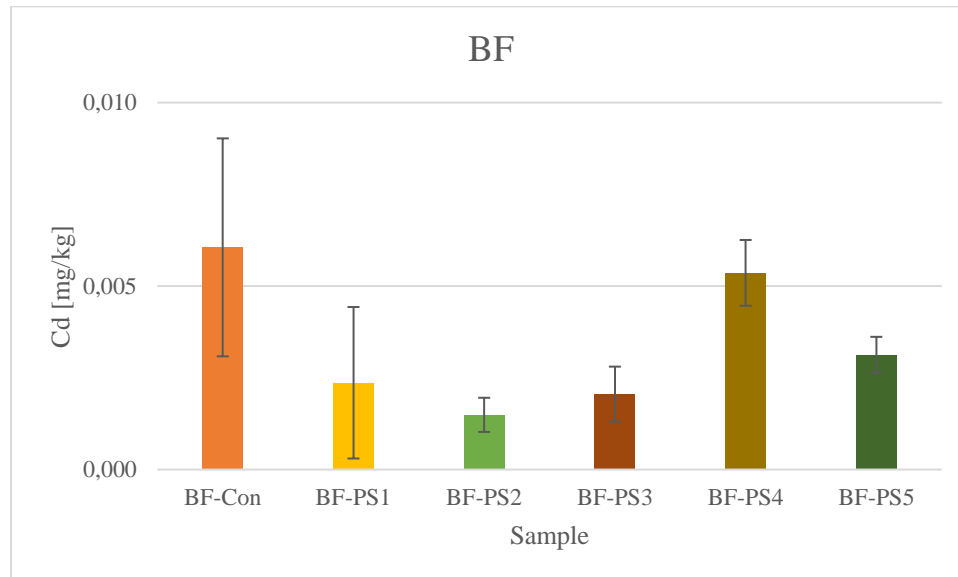**Figure 7 Concentration of Zn based on EN 12457 method in Garden soil.**

Most of the treatments minimized the Zn concentrations in BF, SM and GD but in ZR and AR were the opposite by approximately 2,3 times. The highest immobilization of Zn was observed in the treatment PS5 in the BF soil (**Figure 5**) and the lowest in the treatment PS4 in the ZR soil (**Figure 3**). In the rest of the soils, Zn was slightly immobilized by all the PS treatments. In particular, the leachability of Zn increased after treatment with PS4 in the soil ZR (**Figure 3**) and treatment with PS3 in the soil AR (**Figure 5**). In soil GD, a total decrease of Zn was observed in the PS3 treatment. The most effective treatments for Zn immobilization were PS3 and PS5 for most of the samples except ZR and AR soil (**Figure 3** and **Figure 4**). Treatment PS5 decreased Zn concentrations by approximately 66 % in the studied soils (**Figure 4**, **Figure 5**, **Figure 6** and **Figure 7**) but also increased the Zn concentrations by approximately 7% in the ZR soil (**Figure 3**).

5.1.2. Lead (Pb)

This part of the thesis shows the results of the Pb concentration levels at the five soils that were studied.

17
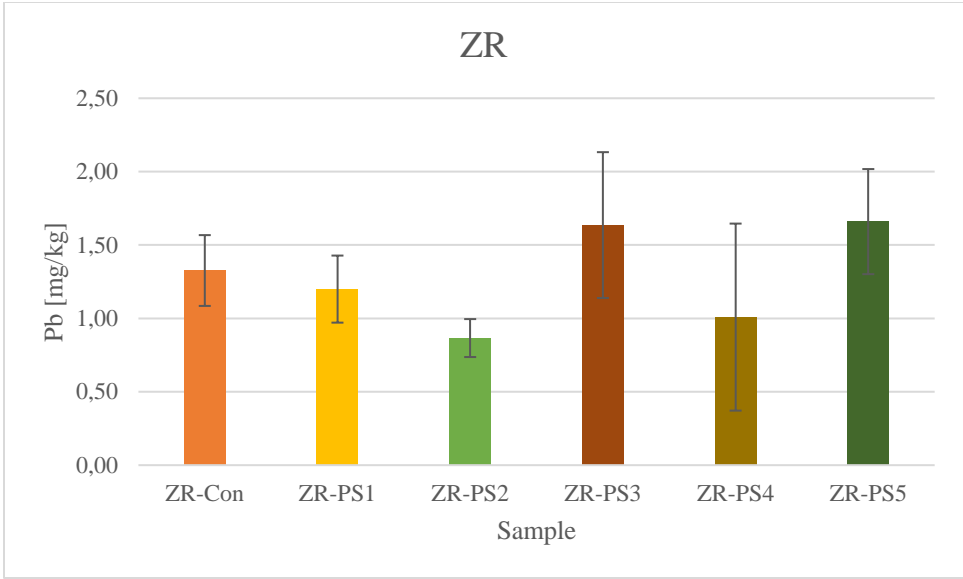
Figure 8 Concentration of Pb based on EN 12457 method in Zn-rich soil.
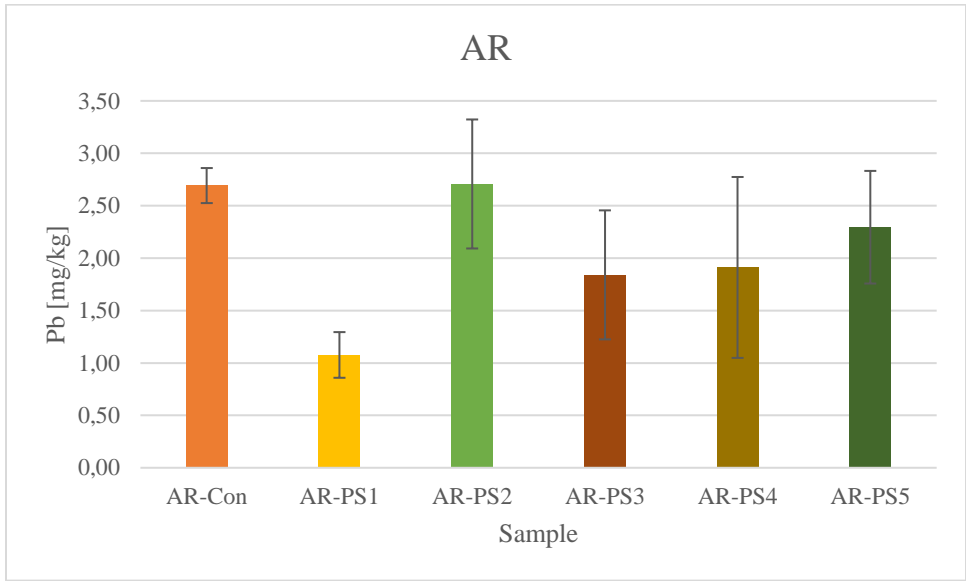
Figure 9 Concentration of Pb based on EN 12457 method in As-rich soil.

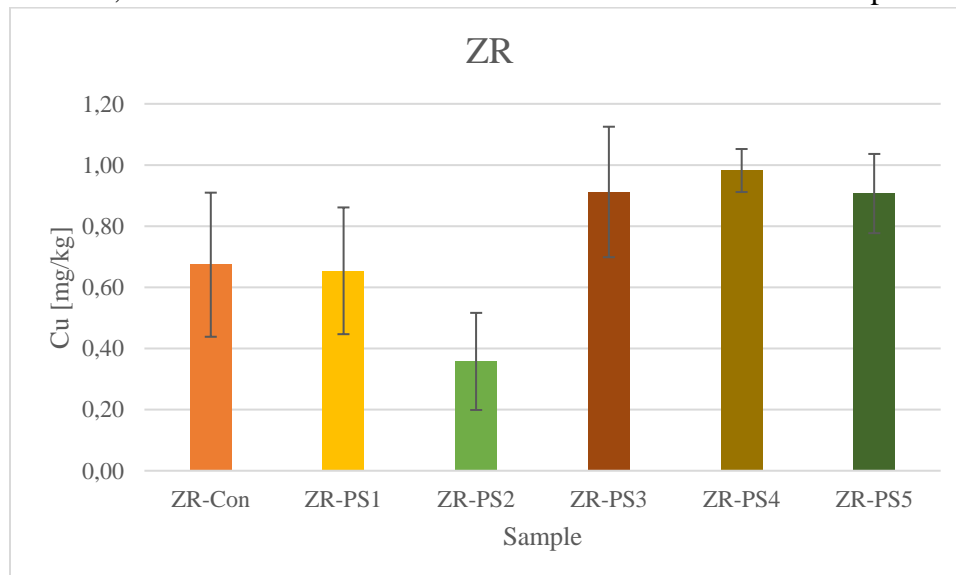**Figure 10 Concentration of Pb based on EN 12457 method in Brownfield soil.**

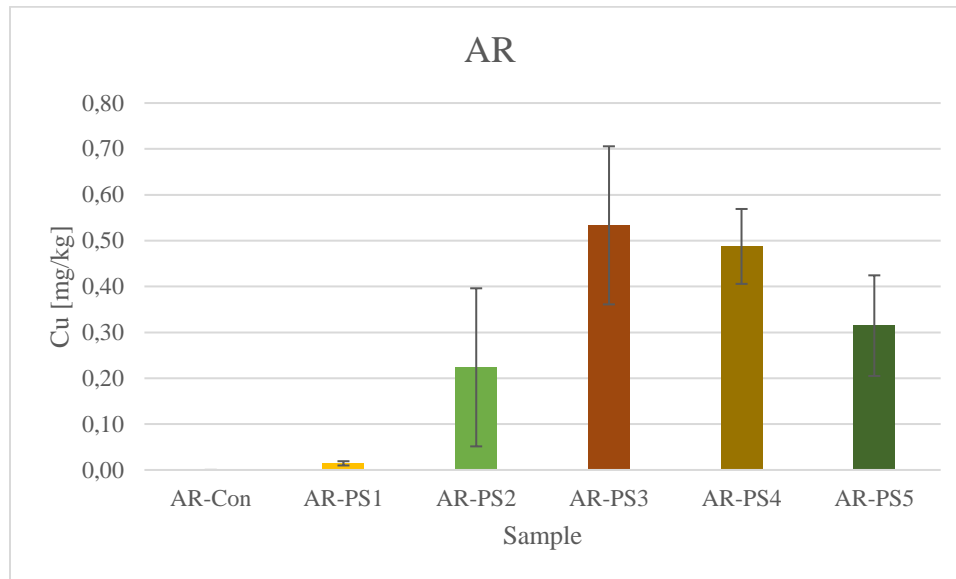**Figure 11 Concentration of Pb based on EN 12457 method in Smelter soil.**

Figure 12 Concentration of Pb based on EN 12457 method in Garden soil.

Most of the treatments minimized the Pb concentrations in AR, SM, and GD soils but in ZR and BF, Pb increased by approximately 20 units. The major immobilization of Pb was observed in the treatments PS1 and PS3 in the AR soil (**Figure 9**) and the lowest in the treatment PS4 in the BF soil (**Figure 9**). In the rest of the soils, Pb was slightly immobilized by all the PS treatments. In particular, the leachability of Pb increased after treatment with PS3 in the soil ZR (**Figure 8**). In soil SM, a decrease of Pb was observed in the PS1 treatment. The most effective treatment for Pb immobilization was PS1 for all the samples. Treatment PS1 decreased Pb concentrations by approximately 48 % in the studied soils (**Figure 8, Figure 9, Figure 10, Figure 11** and **Figure 12**).

5.1.3. Cadmium (Cd)

In this section, the findings on Cd concentration in soils from the five studied locations are presented. However, the results for the AR and SM soils are not included because the concentration recorded was below the detection limit of the used device.
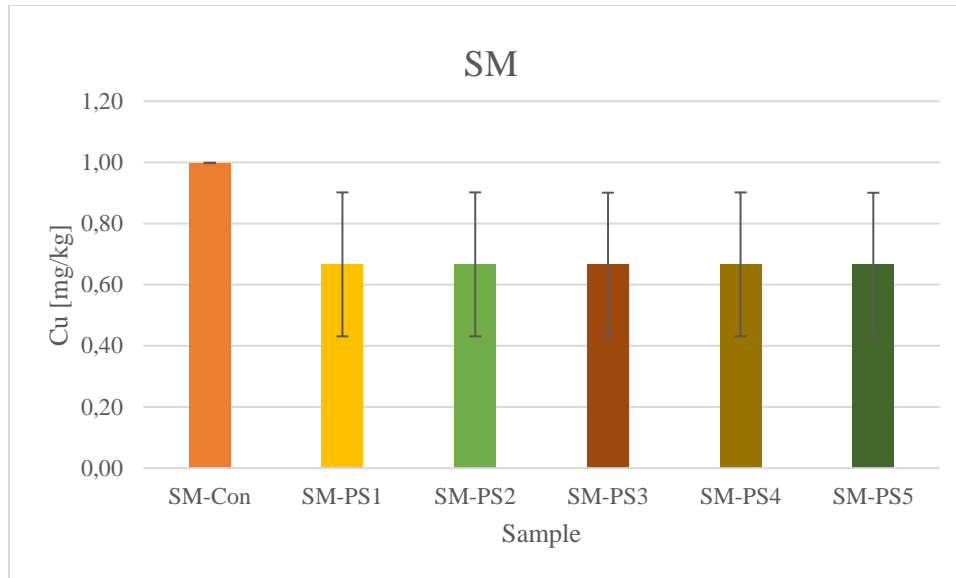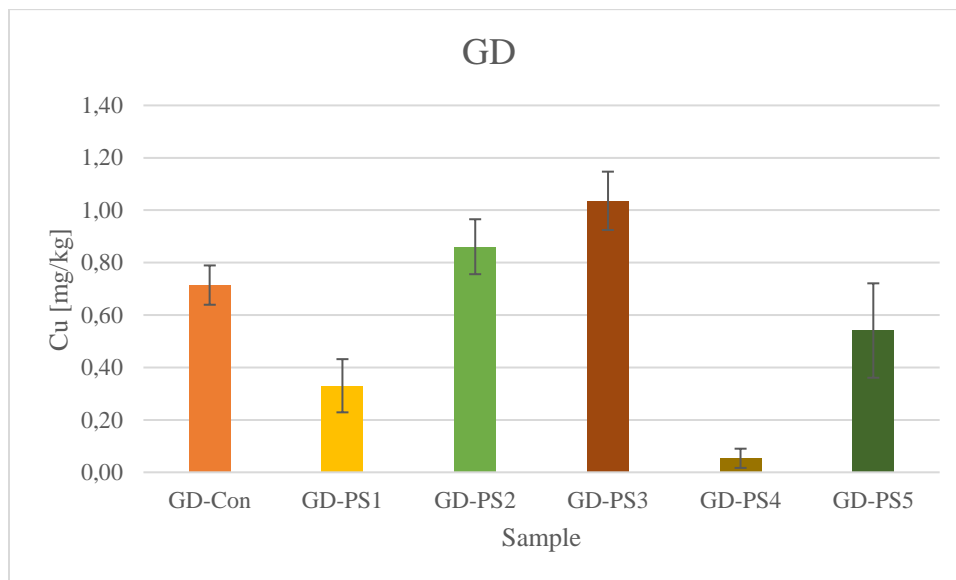
Figure 13 Concentration of Cd based on EN 12457 method in Zn-rich soil.

Figure 14 Concentration of Cd based on EN 12457 method in Brownfield soil.
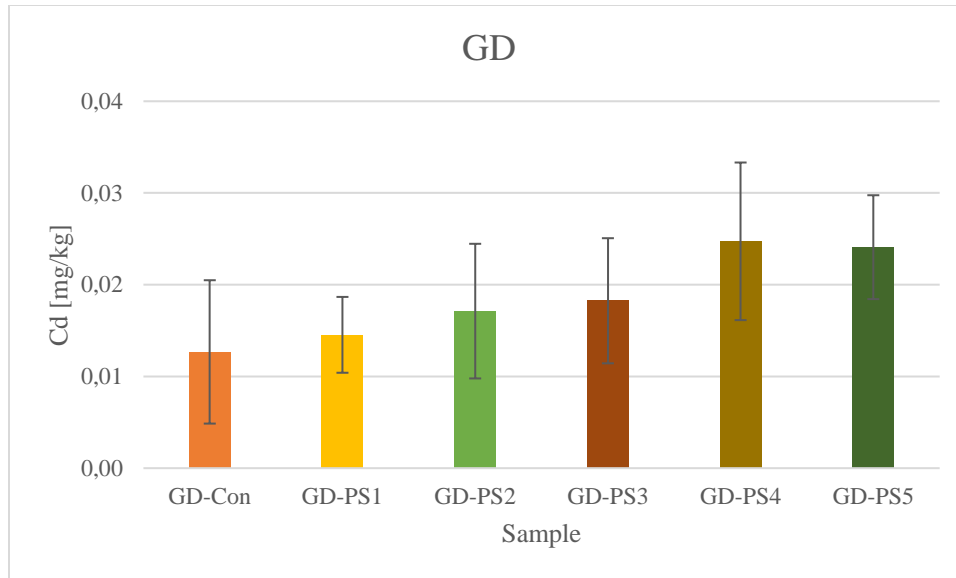
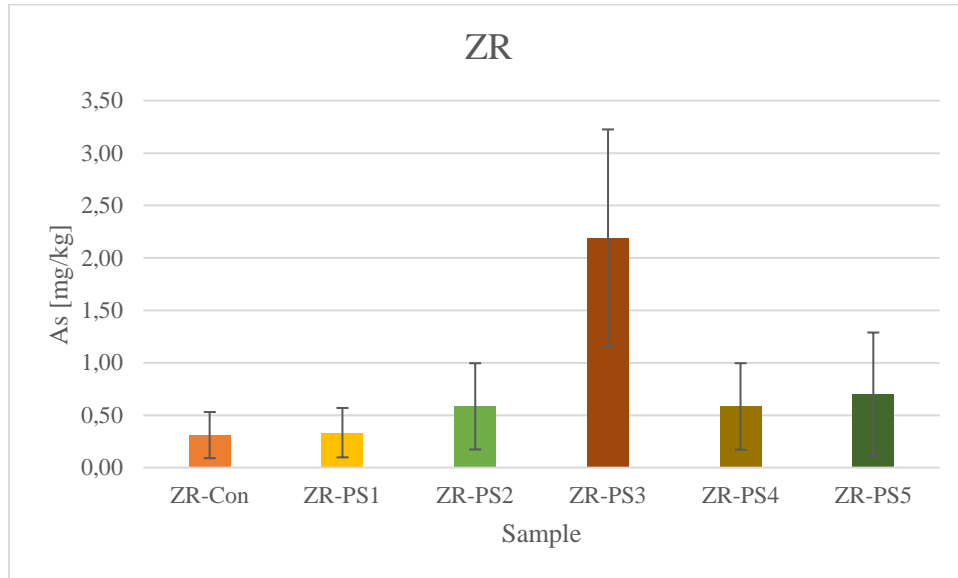**Figure 15 Concentration of Cd based on EN 12457 method in Garden soil.**

Only in the BF soil were minimized Cd concentrations, but in ZR soil and GD soil were the opposite by approximately 0,1 units (**Figure 13** and **Figure 15**). The major immobilization of Cd was presented in the treatment PS2 in the BF soil (**Figure 14**) and the lowest in the treatment PS5 in the ZR soil (**Figure 13**). The leachability of Cd increased after treatment with PS4 in the soil ZR and GD (**Figure 13** and **Figure 15**). In soil BF, a decrease of Cd was observed in the PS2 treatment by approximately 98 % but increased the Cd concentrations by approximately 32% in the ZR and GD soil (**Figure 13** and **Figure 15**).

5.1.4. Copper (Cu)

In this section, results related to Cu concentration in the studied soils are presented.

Figure 16 Concentration of Cu based on EN 12457 method in Zn-rich soil.

Figure 17 Concentration of Cu based on EN 12457 method in As-rich soil.
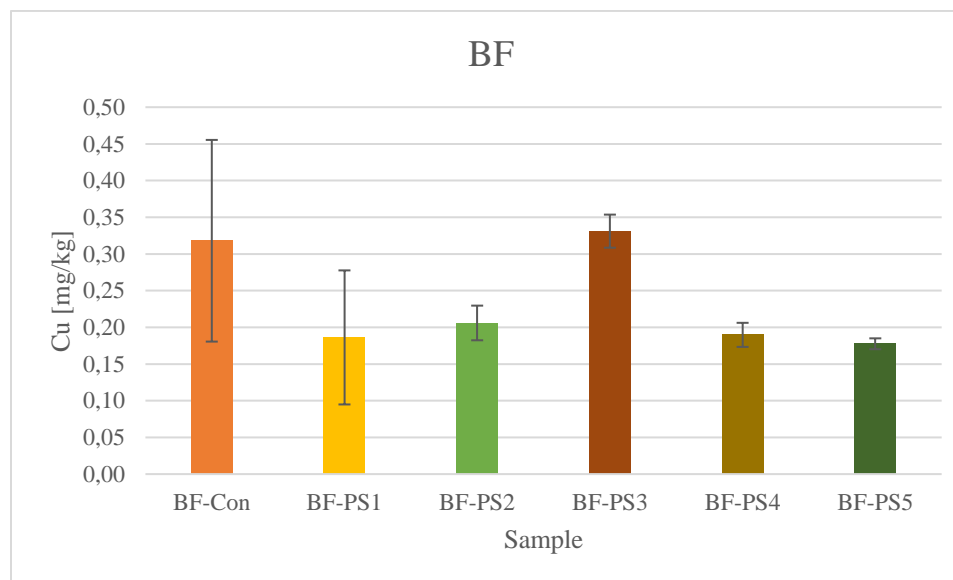
Figure 18 Concentration of Cu based on EN 12457 method in Brownfield soil.

Figure 19 Concentration of Cu based on EN 12457 method in Smelter soil.

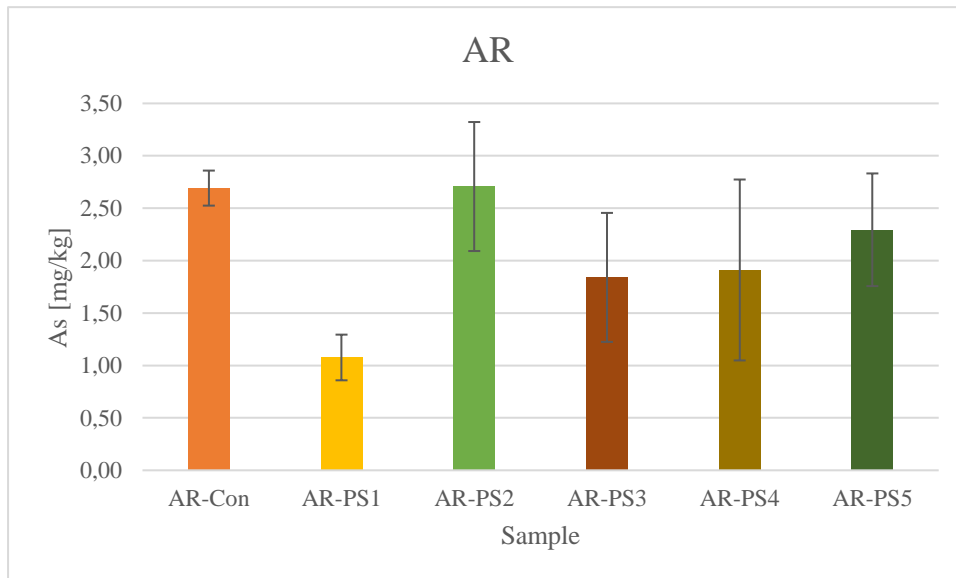**Figure 20 Concentration of Cu based on EN 12457 method in Garden soil.**

Cu concentrations were significantly reduced only in the SM soil but for the rest of the soils, they increased by approximately 0,3 times (**Figure 16**, **Figure 17**, **Figure 18** and **Figure 20**). The highest immobilization of Cu was observed in the treatment PS4 in the GD soil and the lowest in the treatment PS3 in the same soil (**Figure 20**). The leachability of Cu increased after treatment with PS4 in the soil ZR (**Figure 16**). In soil GD, a decrease of Cu was observed in the PS2 treatment (**Figure 20**). The most effective treatments for Cu immobilization were PS1 for most of the samples except AR soil (**Figure 17**). PS1 decreased Cu concentrations by approximately 32 % in the studied soils but also increased Cu concentrations by approximately 28% in the AR soil (**Figure 17**).

5.1.5. Arsenic (As)

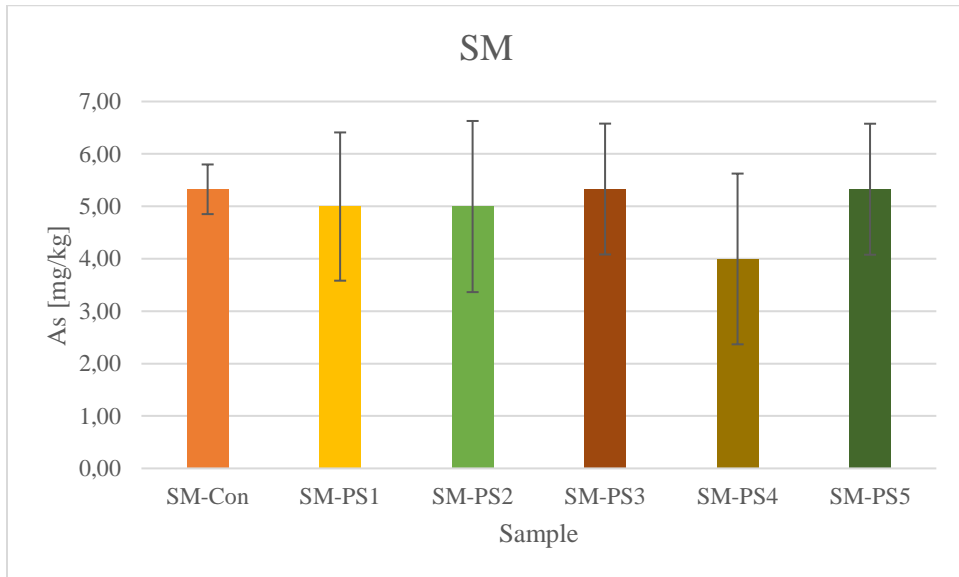This section presents the results of As concentration in the studied soils.

Figure 21 Concentration of As based on EN 12457 method in Zn-rich soil.

Figure 22 Concentration of As based on EN 12457 method in As-rich soil.
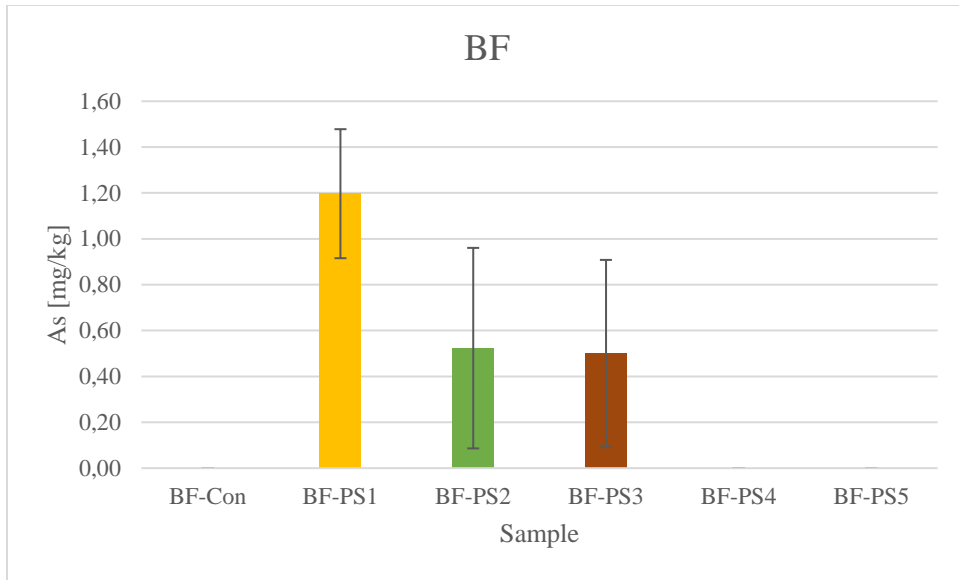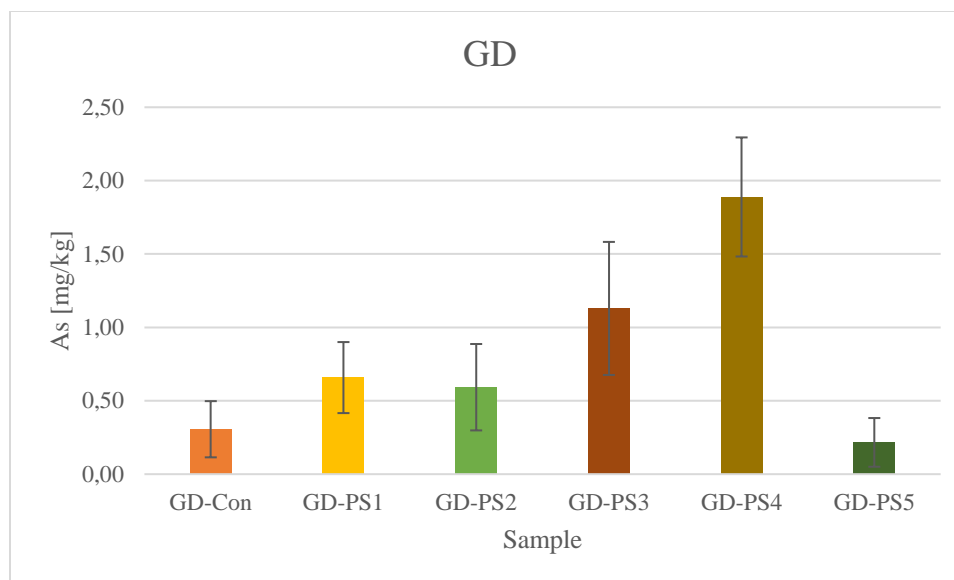
Figure 23 Concentration of As based on EN 12457 method in Brownfield soil.

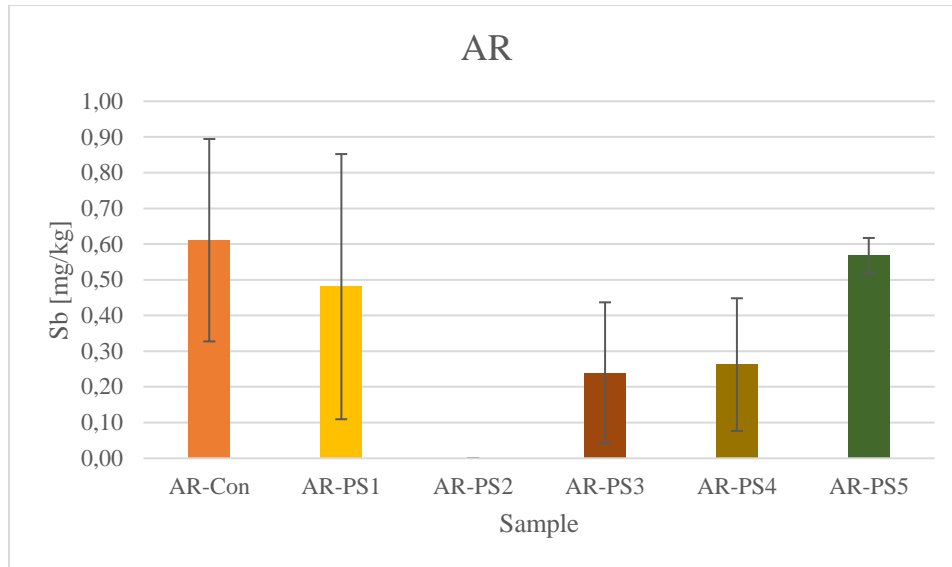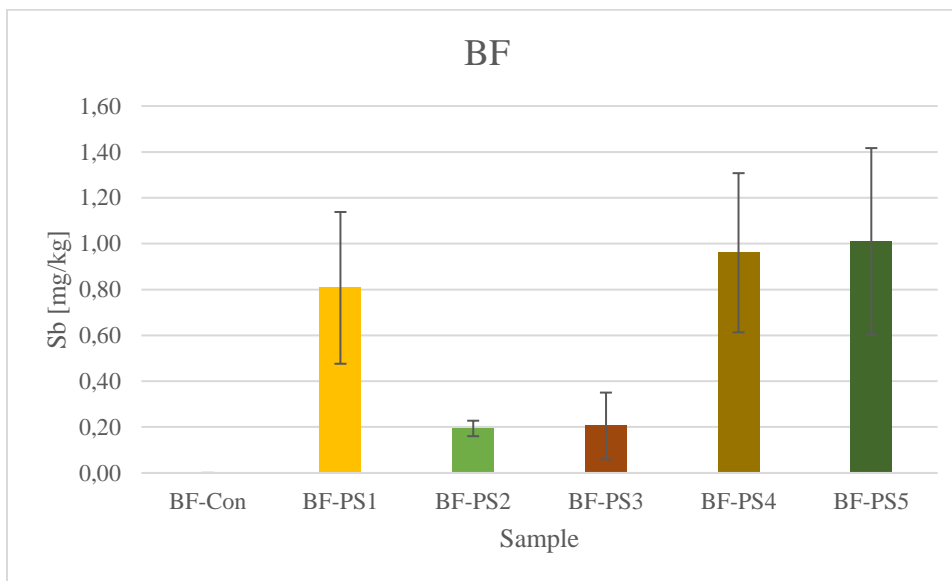**Figure 24 Concentration of As based on EN 12457 method in smelter soil.**

Figure 25 Concentration of As based on EN 12457 method in Garden soil.

The concentrations of As were significantly reduced only in the SM soil but for the rest soils they increased by approximately 12 times. The highest immobilization of As was observed in the treatment PS1 in the AR soil (**Figure 22**) and PS5 in the GD soil (**Figure 25)** and the lowest in the treatment PS4 in the GD soil (**Figure 25**). The leachability of As increased after treatment with PS1, PS2 and PS3 in the soil BF (**Figure 23**). In contrast, in soil GD, a decrease of As was observed in the PS5 treatment (**Figure 25**). The most effective treatment for As immobilization was PS1 for AR soil (**Figure 22**) and SM soil (**Figure 24**). PS1 decreased As concentrations by approximately 32 % in AR soil (**Figure 22**) and SM soil (**Figure 24**) but also increased As concentrations by approximately 38% in the ZR and GD soil (**Figure 21** and **Figure 25**).

5.1.6. Antimony (Sb)

In this section, the soil samples are analyzed for Sb concentration. The results for ZR and SM showed concentrations below the detection limit of the used devices and are consequently omitted from this section.

Figure 26 Concentration of Sb based on EN 12457 method in As-rich soil.

Figure 27 Concentration of Sb based on EN 12457 method in Brownfield soil.
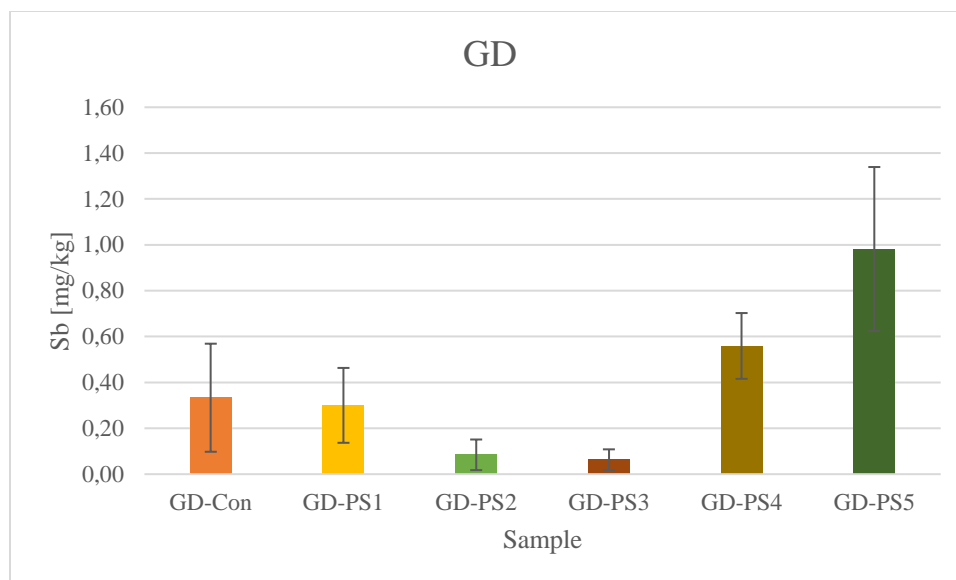
**Figure 28 Concentration of Sb based on EN 12457 method in Garden soil.**

The concentrations of Sb were significantly reduced only in the AR soil but for the rest of the soils, they increased by approximately 1 unit. The highest immobilization of Sb was observed in the treatment PS2 in the AR soil (**Figure 26**) and the lowest in the treatment PS5 in the BF soil (**Figure 27**). In the rest of the soils, Sb was slightly immobilized by most of the PS treatments. In GD, a decrease of Sb was observed in the PS2 treatment (**Figure 28**). The most effective treatments for Sb immobilization were PS2 for most of the samples except BF soil (**Figure 27**). Treatment PS2 decreased Sb concentrations by approximately 83 % in the GD soil (Figure 28) but also increased Sb concentrations by approximately 0,08% in the BF soil (**Figure 27**). The leachability of Sb increased after treatment with PS5 in the soil GD (**Figure 28**).

## 5.2. Availability of risk metal and metalloids in the soil extracts

The results of exchangeable concentrations of 1) risk metals and 2) risk metalloids in soil extracts of CH3COOH and (NH4)2SO4 respectively are presented below. The findings are of great importance in assessing the possibility of environmental damage and the feasibility of remediation of contaminated soil.
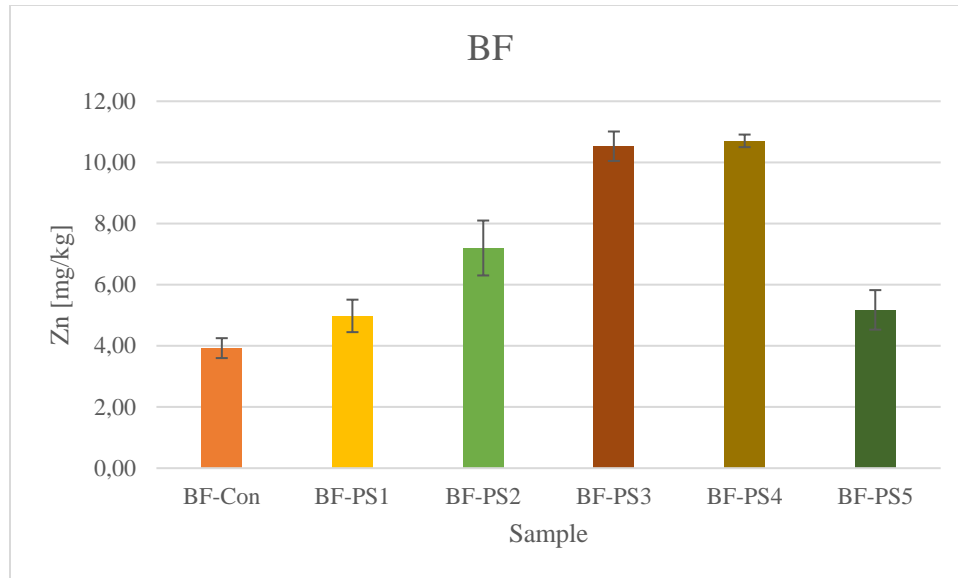
5.2.1. Zinc (Zn)

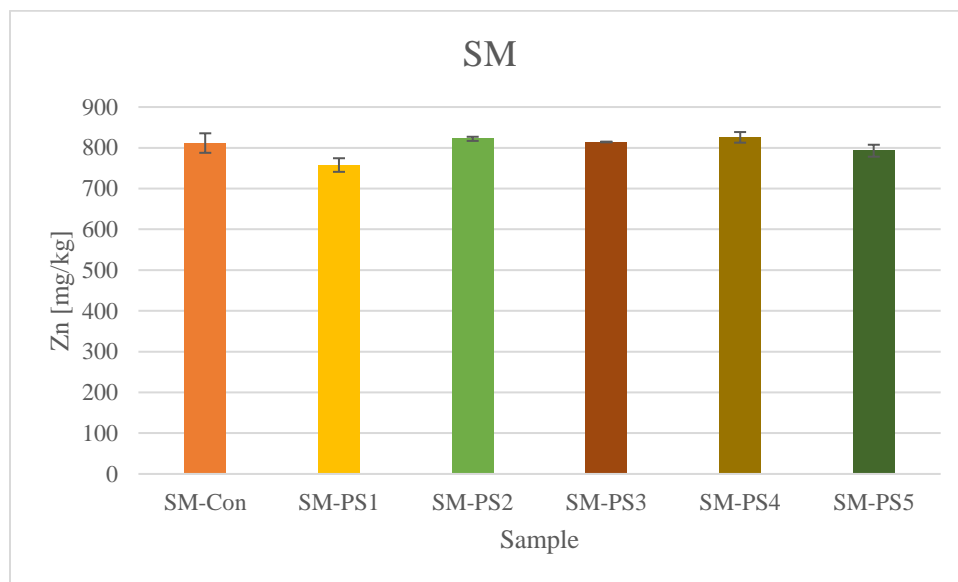This section examines the concentration of available Zn in soil extracts.
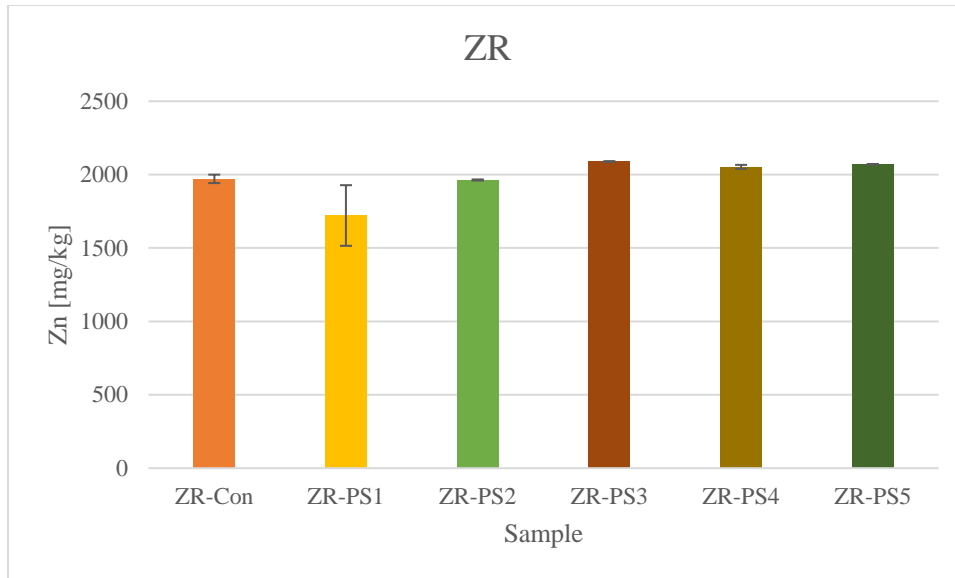
Figure 29 Concentration of Zn in soil extracts in Zn-rich soil.
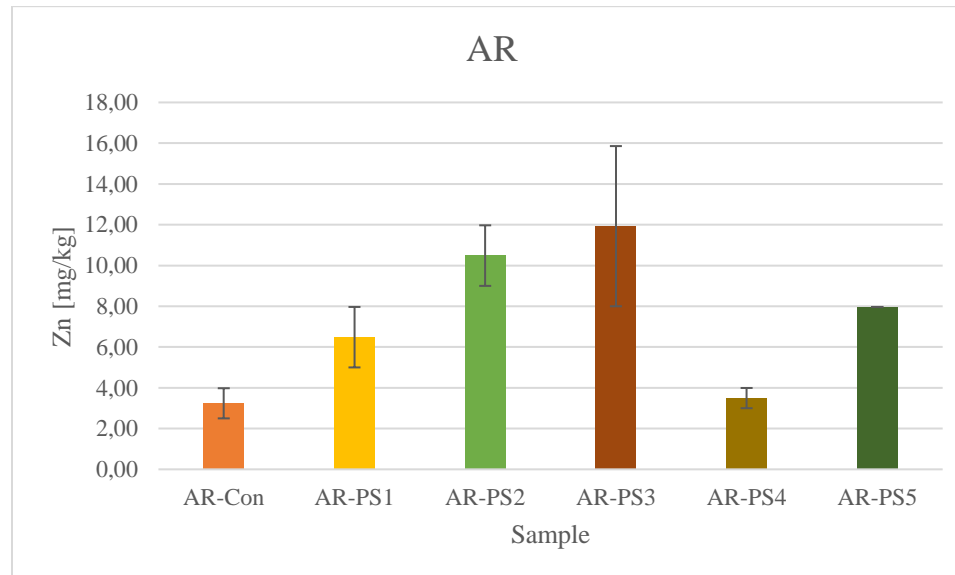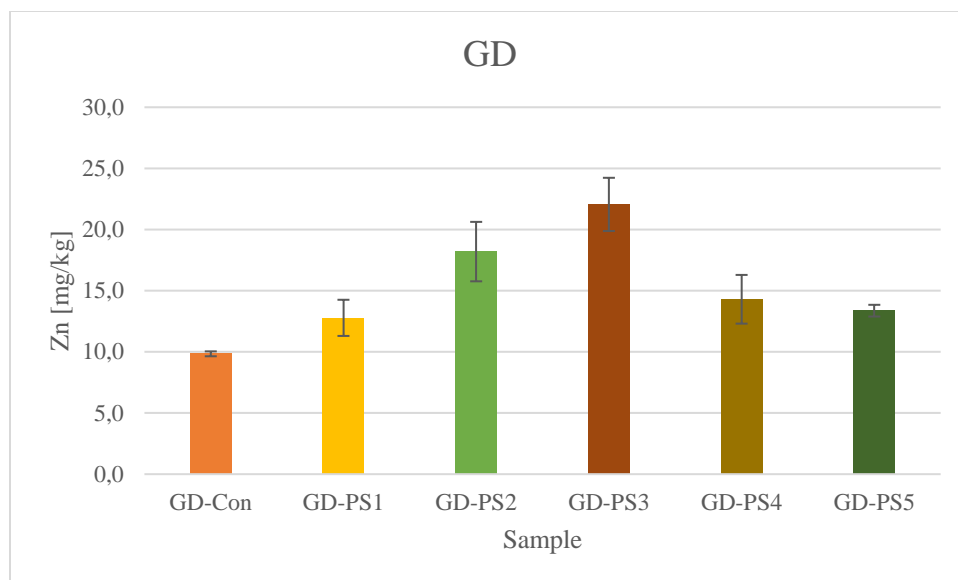

Figure 30 Concentration of Zn in soil extracts in As-rich soil.

Figure 31 Concentration of Zn in soil extracts in Brownfield soil.

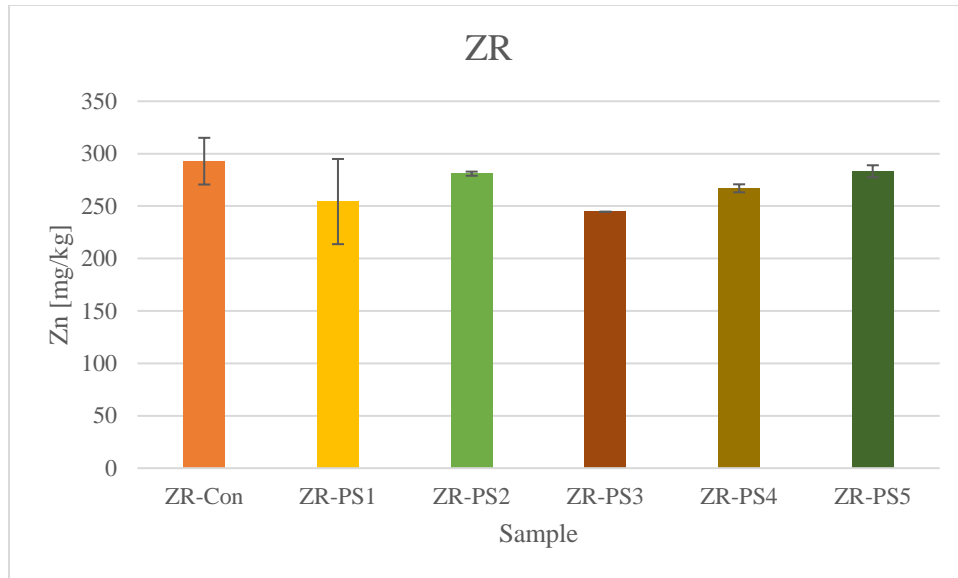**Figure 32 Concentration of Zn in soil extracts in Smelter soil.**

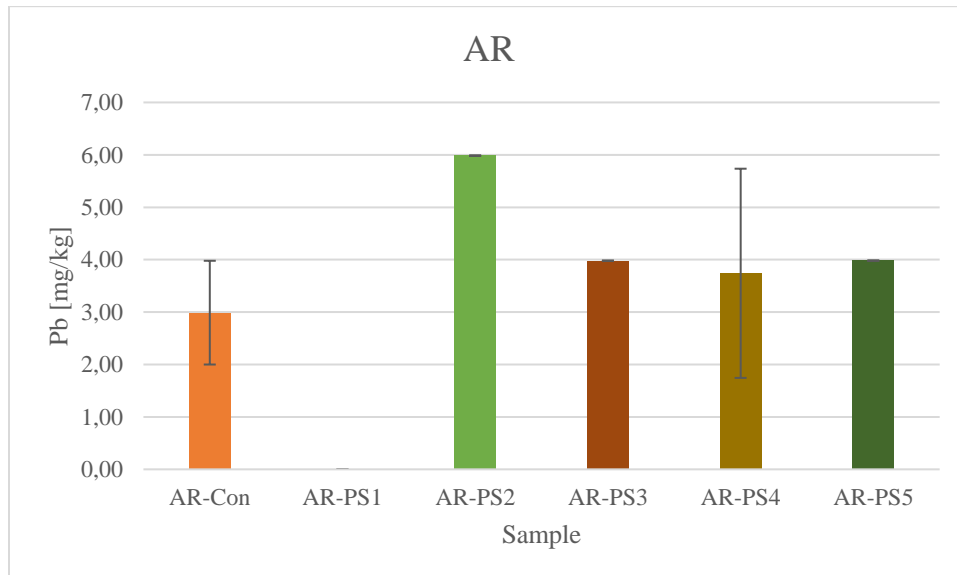**Figure 33 Concentration of Zn in soil extracts in Garden soil.**

Zn concentrations were significantly increased by most of the treatments. The highest immobilization of Zn was observed in the treatment PS1 in the ZR soil (**Figure 29**) and the lowest in the treatment PS3 in the ZR, BF and GD soils (**Figure 29**, **Figure 31** and **Figure 33**). In the rest of the soils, Zn was not immobilized by most of the PS treatments. In particular, the availability of Zn increased after treatment with PS3 in the soil BF (**Figure 31**). PS1 treatment showed the lowest concentrations of Zn in the most highly contaminated soils (ZR and SM) (**Figure 29** and **Figure 32**) although it increased Zn in moderately contaminated soils (AR, BF, GD) (**Figure 30, Figure 31** and **Figure 33**). In particular, PS1 decreased Zn concentrations by approximately 10 % in the ZR and SM soils (**Figure 29** and **Figure 32**) but also increased Zn concentrations by approximately 52% in the AR, BF and GD soil (**Figure 30, Figure 31** and **Figure 33**).
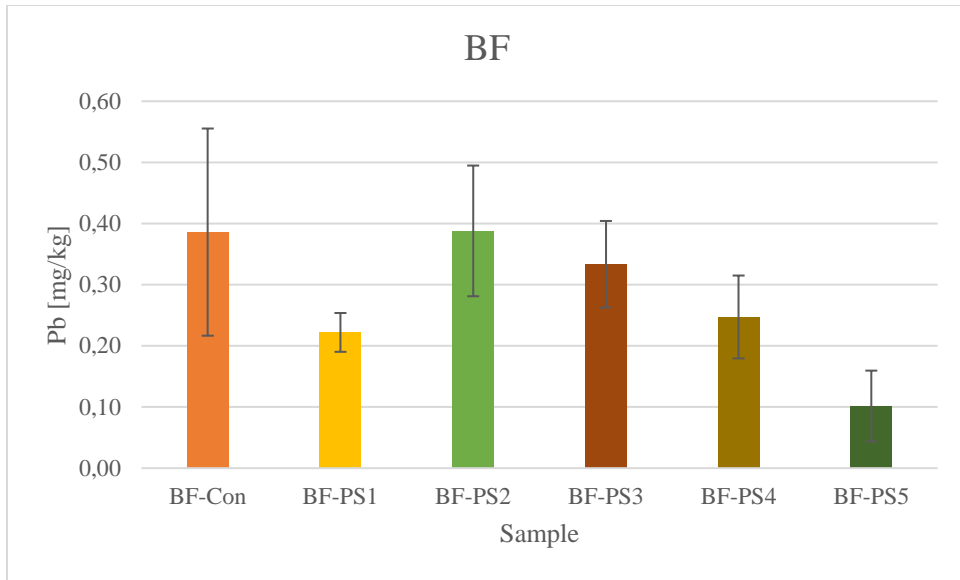
5.2.2. Lead (Pb)

This section provides the results of the soil samples regarding the availability of Pb.
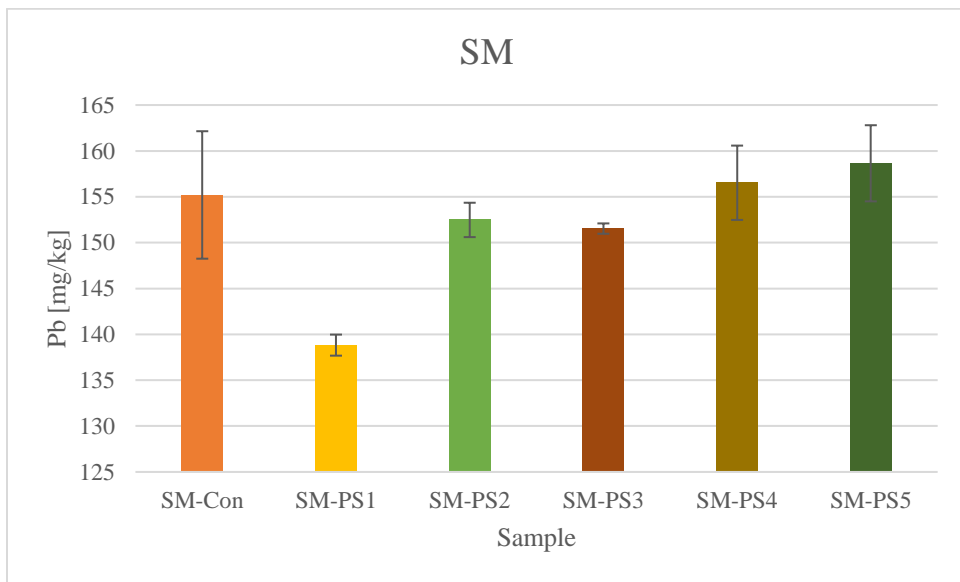
Figure 34 Concentration of Pb in soil extracts in Zn-rich soil.

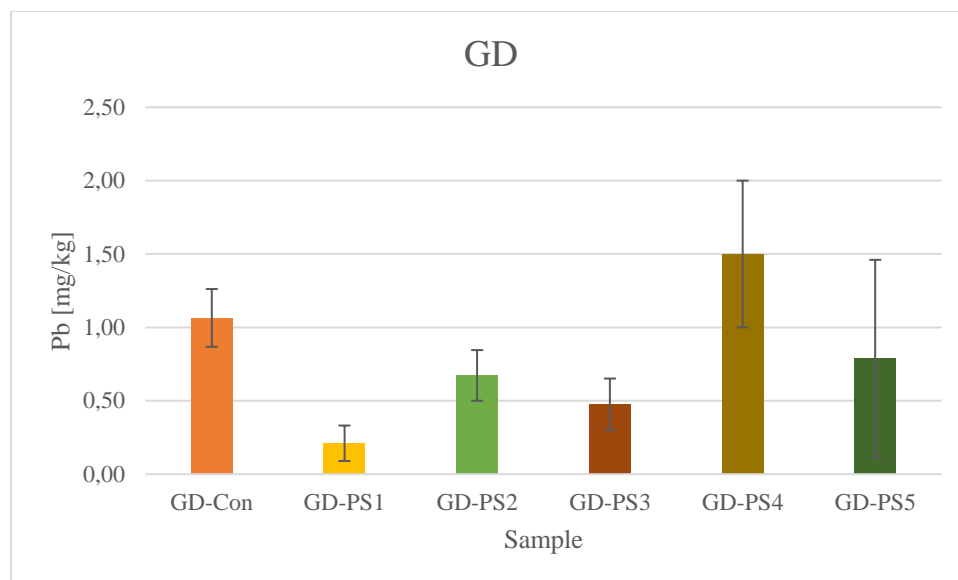**Figure 35 Concentration of Pb in soil extracts in As-rich soil.**

Figure 36 Concentration of Pb in soil extracts in Brownfield soil.

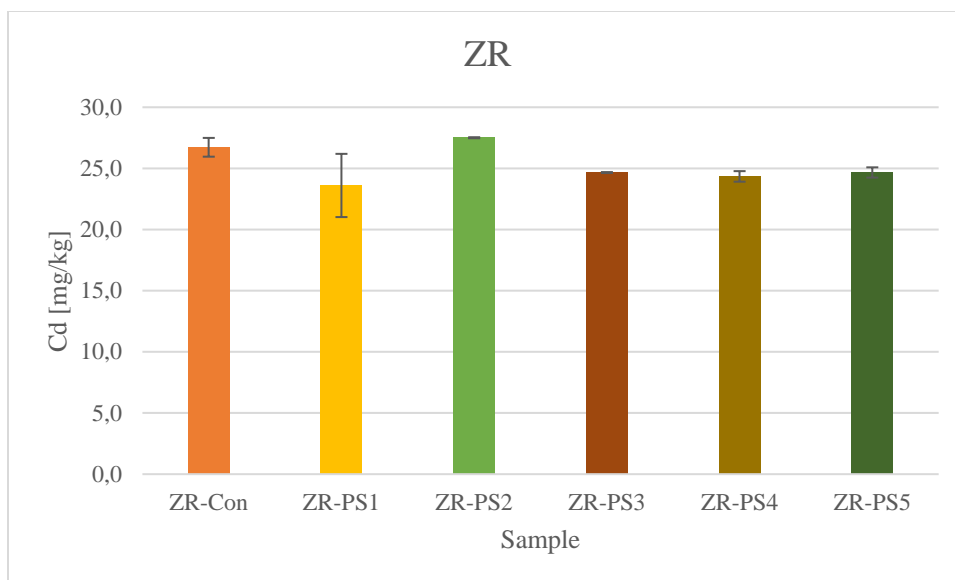**Figure 37 Concentration of Pb in soil extracts in Smelter soil.**

Figure 38 Concentration of Pb in soil extracts in Garden soil.

Pb availability was significantly decreased for most of the soils but for AR, SM and GD soils were the opposite. The highest immobilization of Pb was observed in the treatment PS1 in the AR soil and the lowest in the treatment PS2 in the same soil (**Figure 35**). In the rest of the soils, Pb was immobilized by most of the PS treatments. In particular, the availability of Pb decreases after treatment with PS1 in the soil AR (**Figure 35**). The most effective treatment for Pb immobilization was PS1 for all the samples which decreased Pb concentrations by approximately 49 % in the studied soil (**Figure 34, Figure 35, Figure 36, Figure 37** and **Figure 38**).

5.2.3. Cadmium (Cd)

The results of this section consider the availability of Cd in the studied soils. The results suggested a null concentration for AR, BF, and GD soils and are not discussed further in this part of the analysis.

Figure 39 Concentration of Cd in soil extracts in Zn-rich soil.
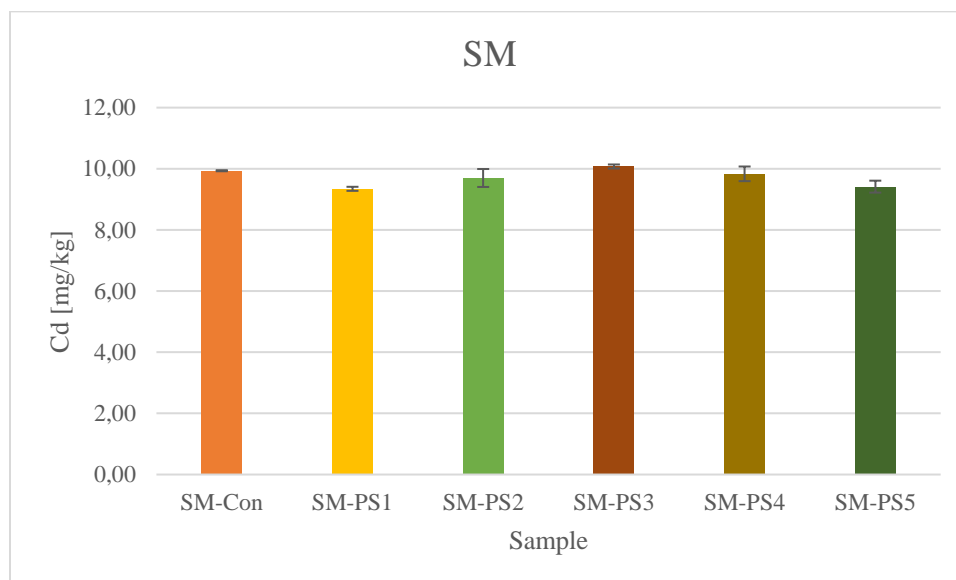
Figure 40 Concentration of Cd in soil extracts in Smelter soil.

Cd concentrations were significantly increased for most of the treatments. However, immobilization of Cd was observed in the treatment PS1 in both ZR and SM soils (**Figure 39** and **Figure 40**). The lowest Cd immobilization observed was in the treatment PS5 in the ZR soil (**Figure 39).** However, the availability of Cd increased after treatment with PS3 in the soil SM (**Figure 40**). The most effective treatment for Cd immobilization was PS1 for both of the samples managing to decrease Cd concentrations by approximately 9 % in the studied soils (**Figure 39** and **Figure 40**).

5.2.4. Copper (Cu)

Within this segment, the focus lies on the Cu availability in the studied soils.

Figure 41 Concentration of Cu in soil extracts in Zn-rich soil.

Figure 42 Concentration of Cu in soil extracts in As-rich soil.
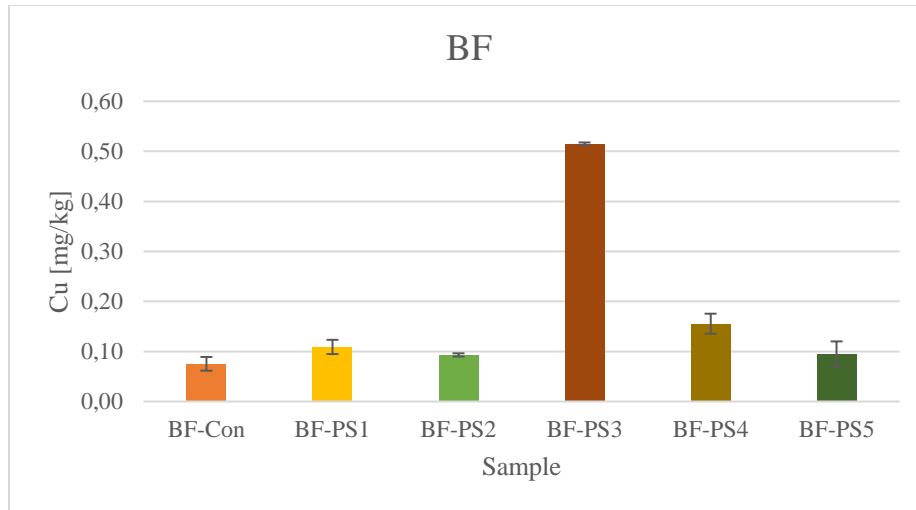
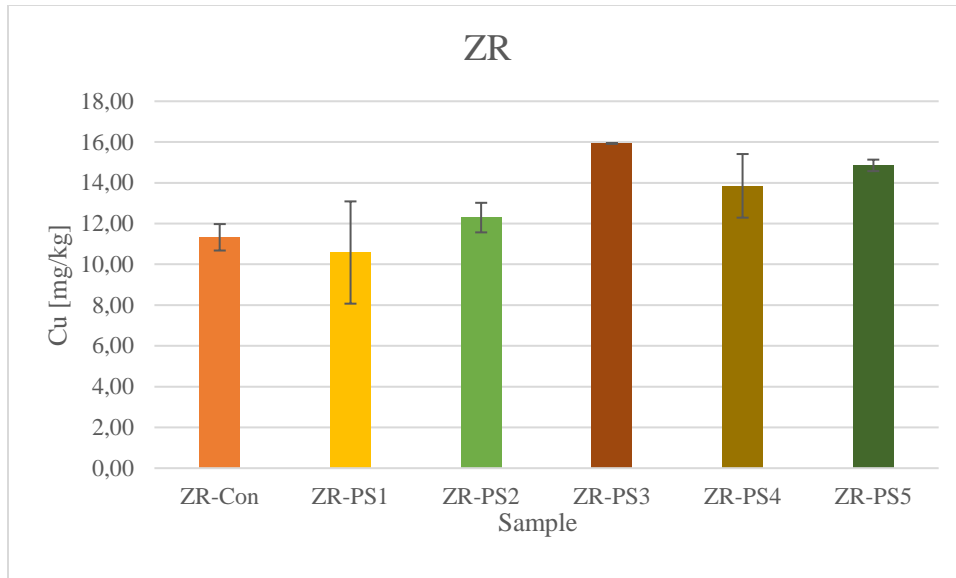**Figure 43 Concentration of Cu in soil extracts in Brownfield soil.**

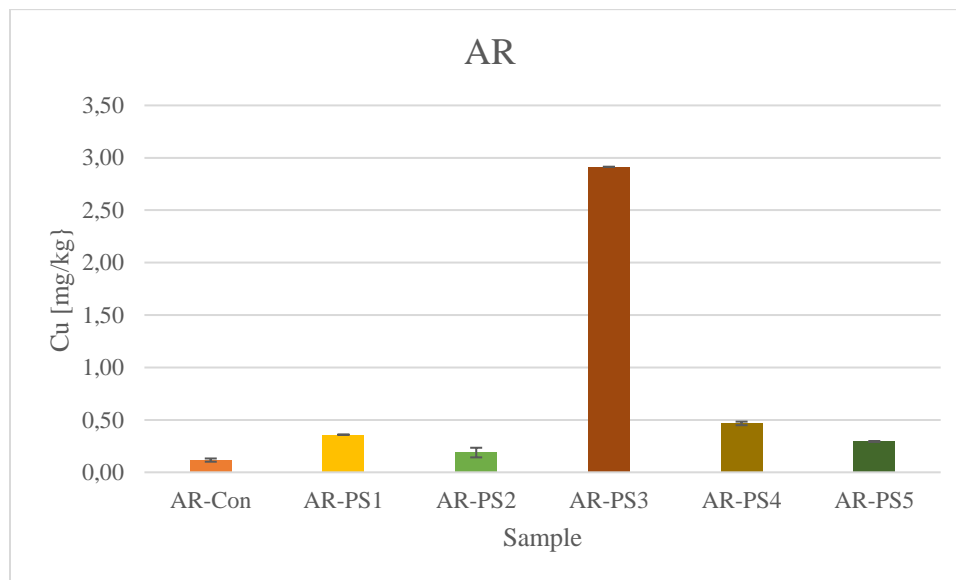**Figure 44 Concentration of Cu in soil extracts in Smelter soil.**

Copper concentrations were significantly decreased by most of the treatments. The highest immobilization of Cu was observed in the treatment PS1 in the ZR soil (**Figure 41**) and the lowest in the treatment PS3 in the BF soil (**Figure 43**). In the rest of the soils, Cu was immobilized by some of the PS treatments. The most effective treatment for Cu immobilization was PS1 for most of the samples except AR and BF soils (**Figure 42** and **Figure 43**). Treatment PS1 decreased Cu concentrations by approximately 8 % in the studied soils but also increased Cu concentrations by approximately 100% in the AR and BF soil (**Figure 42** and **Figure 43**).

5.2.5. Arsenic (As)

The determination of the available level of As in the studied soil samples is presented below.
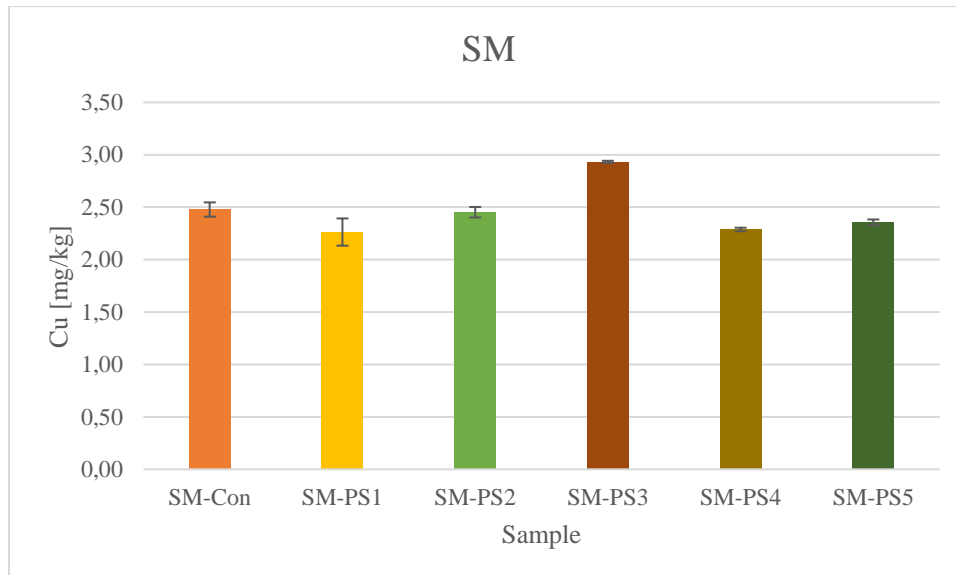

Figure 45 Concentration of As in soil extracts in Zn-rich soil.

Figure 46 Concentration of As in soil extracts in As-rich soil.
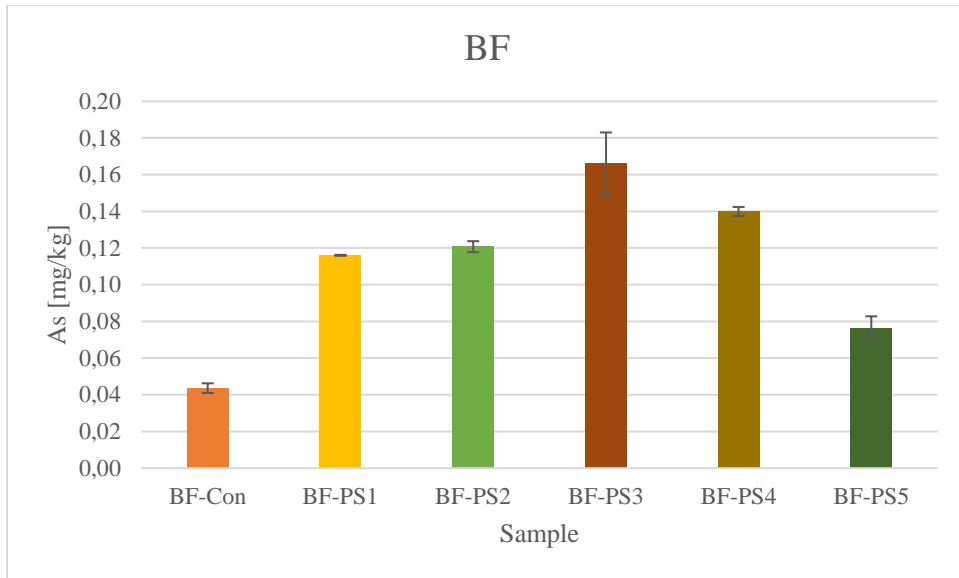
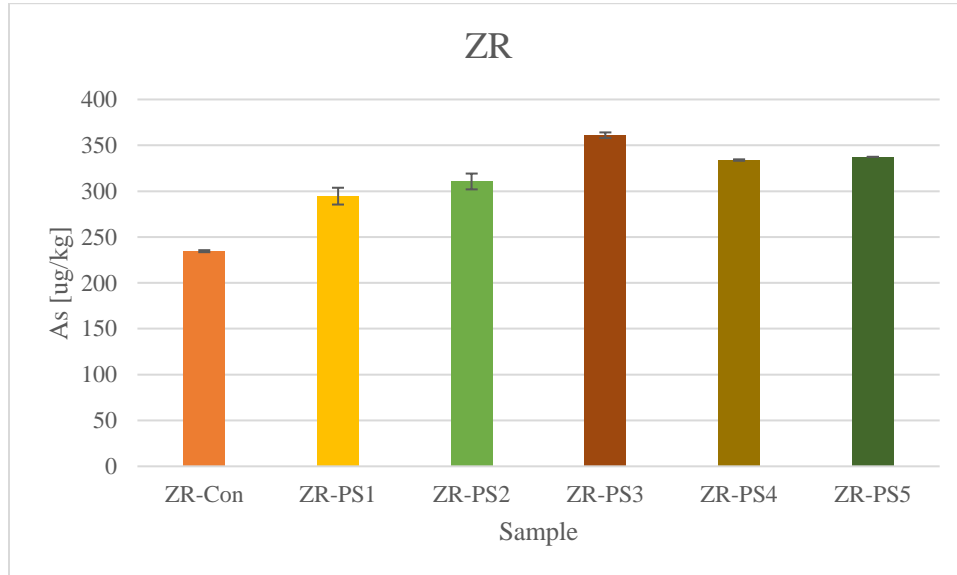**Figure 47 Concentration of As in soil extracts in Brownfield soil.**

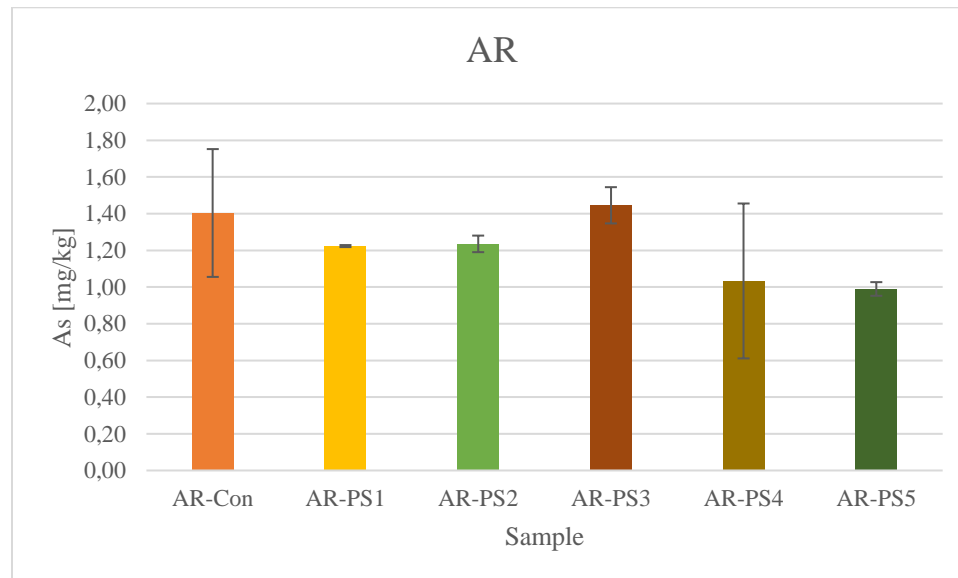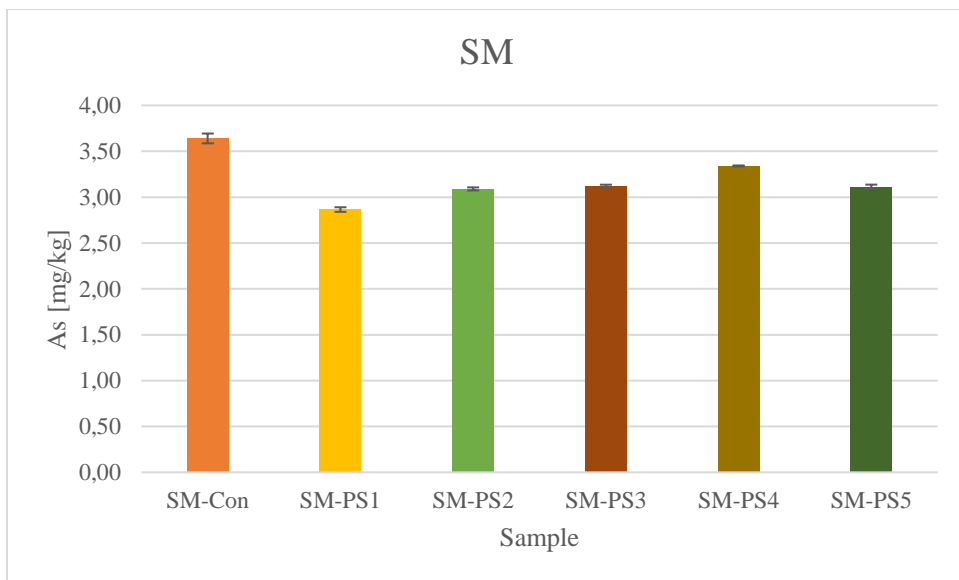**Figure 48 Concentration of As in soil extracts in Smelter soil.**
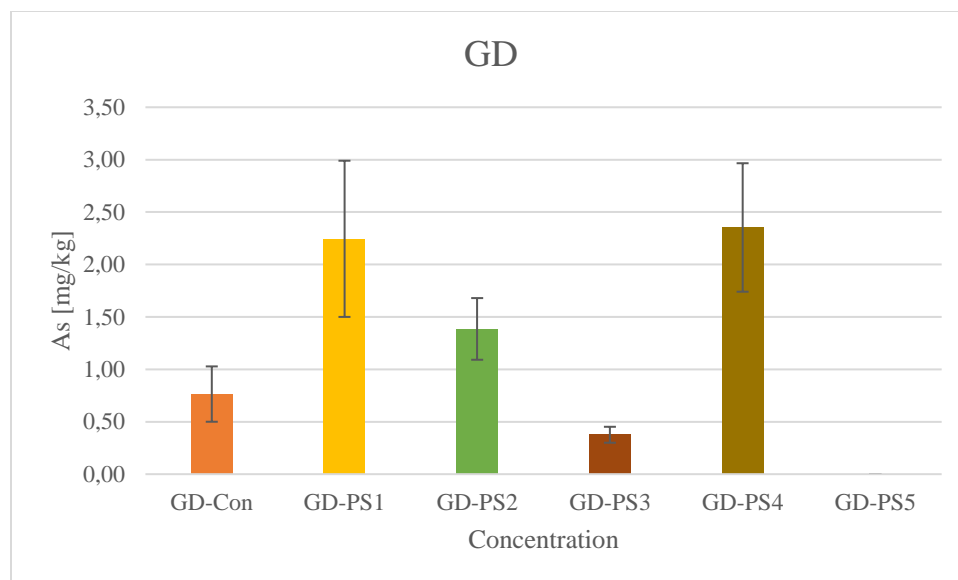
Figure 49 Concentration of As in soil extracts in Garden soil.

Arsenic concentrations were significantly decreased by most of the treatments but in different soils. The highest immobilization of As was observed in the treatment PS5 in the GD soil and the lowest in the treatment PS4 in the same soil (**Figure 49**). On the contrary, the availability of As increased by all treatments and especially by PS3 in the ZR soil (**Figure 45**). The most effective treatment for As immobilization was PS5 for most of the samples (AR; **Figure 46**, BF; **Figure 47**, SM; **Figure 48** and GD soils; **Figure 49**) except ZR soil (**Figure 45**).

5.3. pH

In this section, results obtained from the soil pH measured in water leachates are presented. This analysis provides detailed insight into variations in soil acidity or alkalinity of the different soils. Understanding these differences is critical for determining soil health as well as for evaluating the possible relationship between pH and metal/metalloid immobilization.
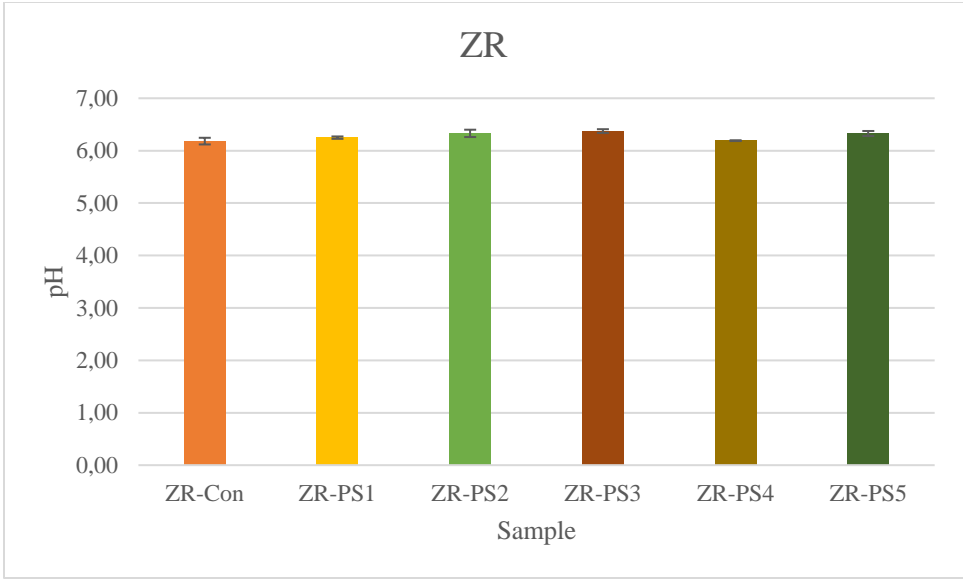
Figure 50 pH measured in water leachates in Zn-rich soil.
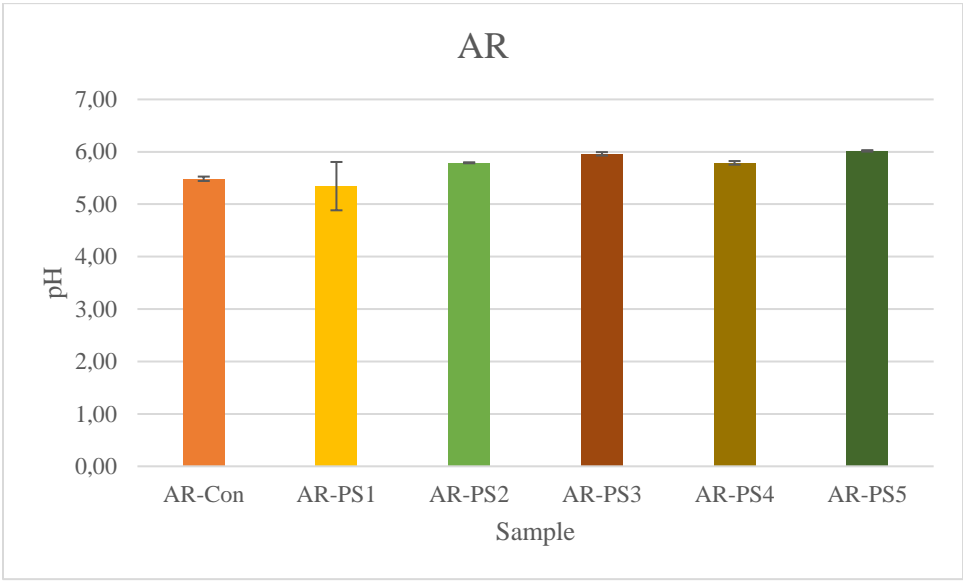
Figure 51 pH measured in water leachates in As-rich soil.
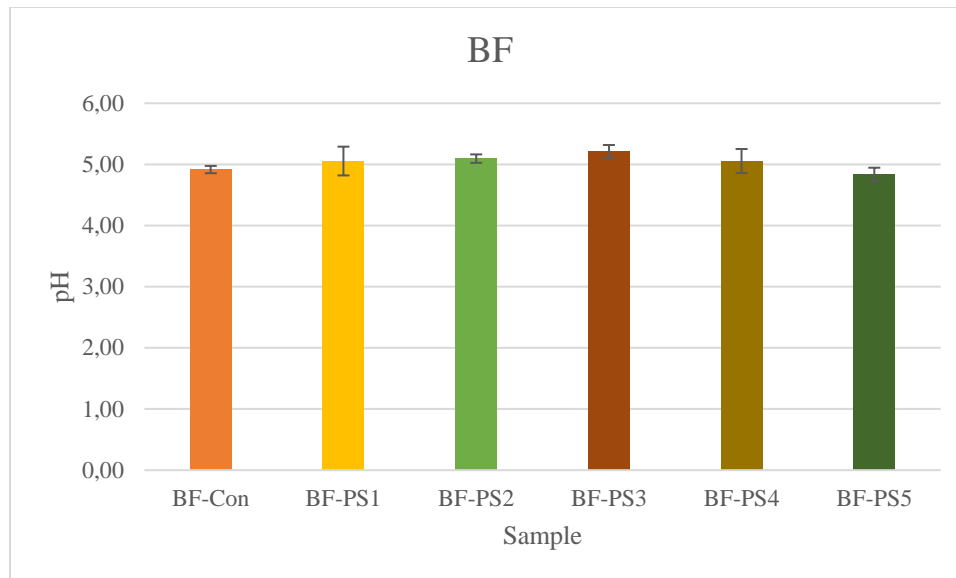
Figure 52 pH measured in water leachates in Brownfield soil.
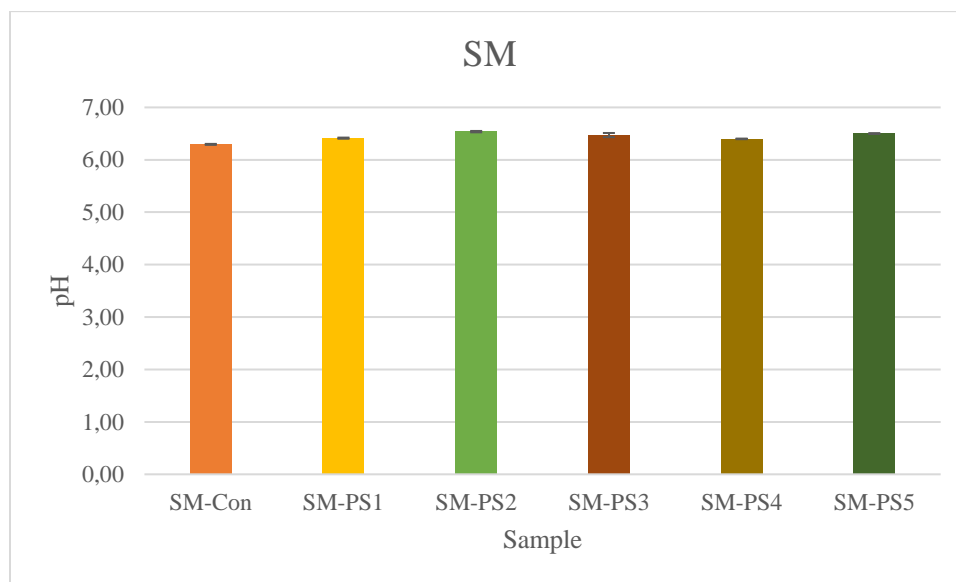
Figure 53 pH measured in water leachates in Smelter soil.
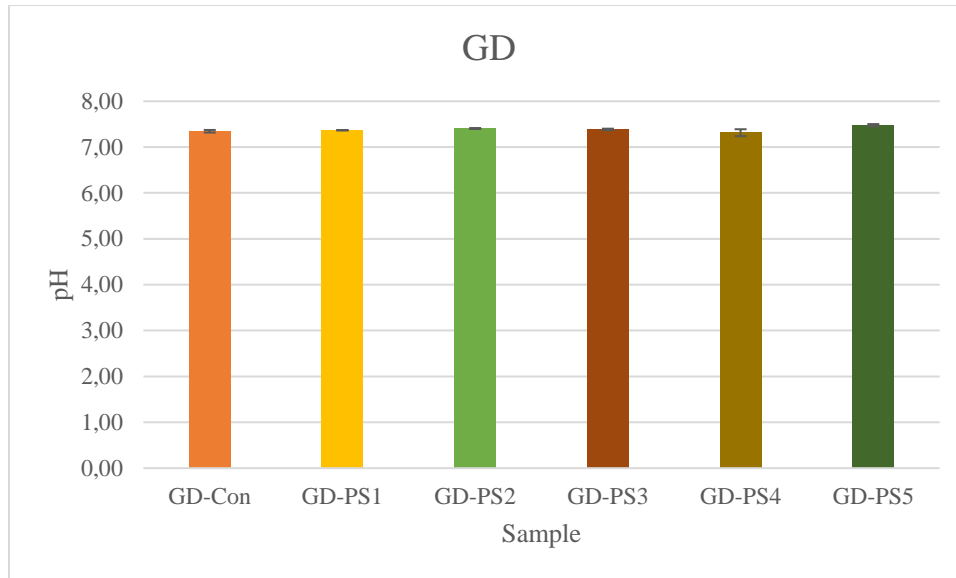
Figure 54 pH measured in water leachates in Garden soil.

Only GD soil had a pH close to 7 (**Figure 54**) but ZR, AR, BF, and SM were less than pH 7 for approximately 0,3 pH units on average (**Figure 50**, **Figure 51**, **Figure 52** and **Figure 53**). For most of the soils, the pH value didn't vary between treatments and control. The soil with the highest pH is GD at approximately 7,38 (**Figure 54**) and the soil with the most acidic pH is BF by approximately 5 (**Figure 52**). For all the soils, the pH was slightly increased by all the PS treatments. In particular, the highest pH increase was in the PS5 at the AR soil (**Figure 51**).

5.4. Oxidation-reduction potential (Eh values)

The importance of redox in the soil shall not be undermined since its influence is mostly on element transformation processes and availability to plants (Considine & Foyer, 2014). redox predominantly governs the conditions in the soils, affecting the mobility and toxicity of elements (Bandara et al., 2020). Finally, the redox balance in the soil also influences mechanisms that accelerate soil health and fertility by reducing organic matter and the activity of many microorganisms (Nivetha et al., 2023). In this part, the results of the five different soils focusing on Eh in soils are presented.

Figure 55 Eh measured in water leachates in Zn-rich soil.

Figure 56 Eh measured in water leachates in As-rich soil.
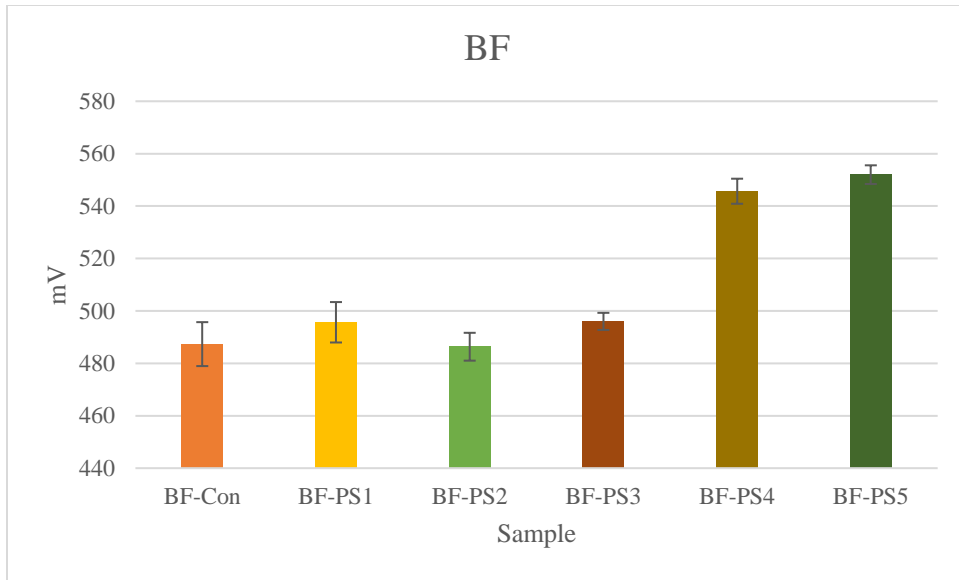
Figure 57 Eh measured in water leachates in Brownfield soil.
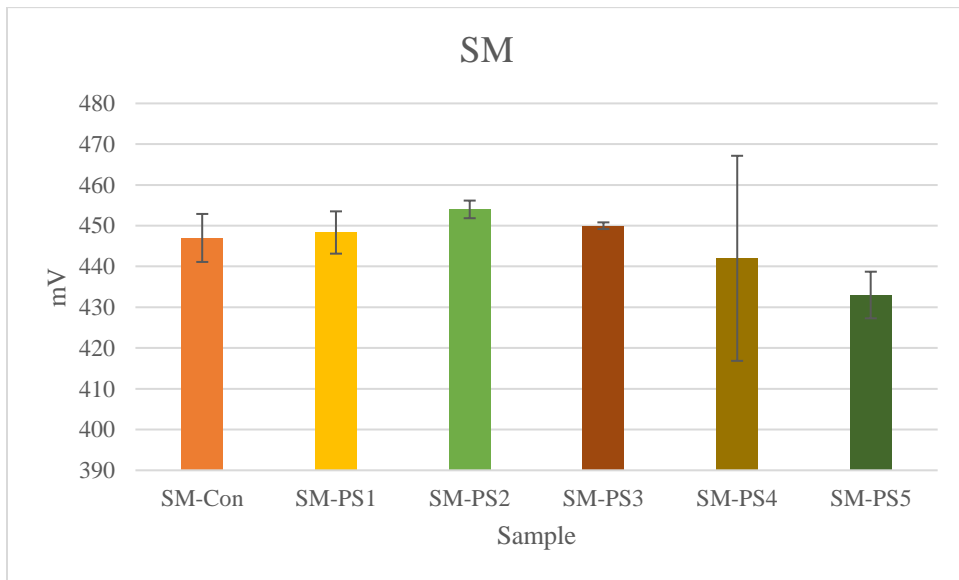
Figure 58 Eh measured in water leachates in Smelter soil.
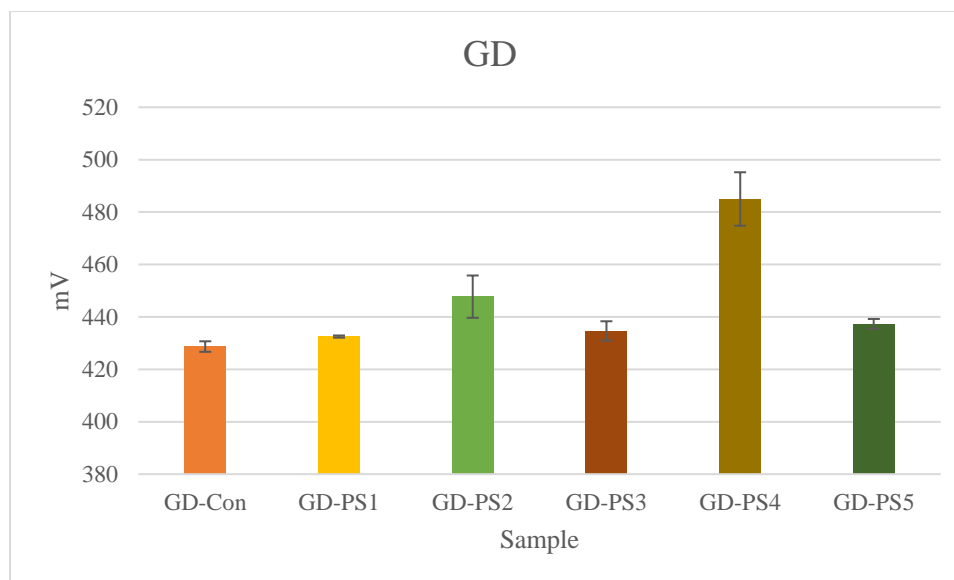
Figure 59 Eh measured in water leachates in Garden soil.

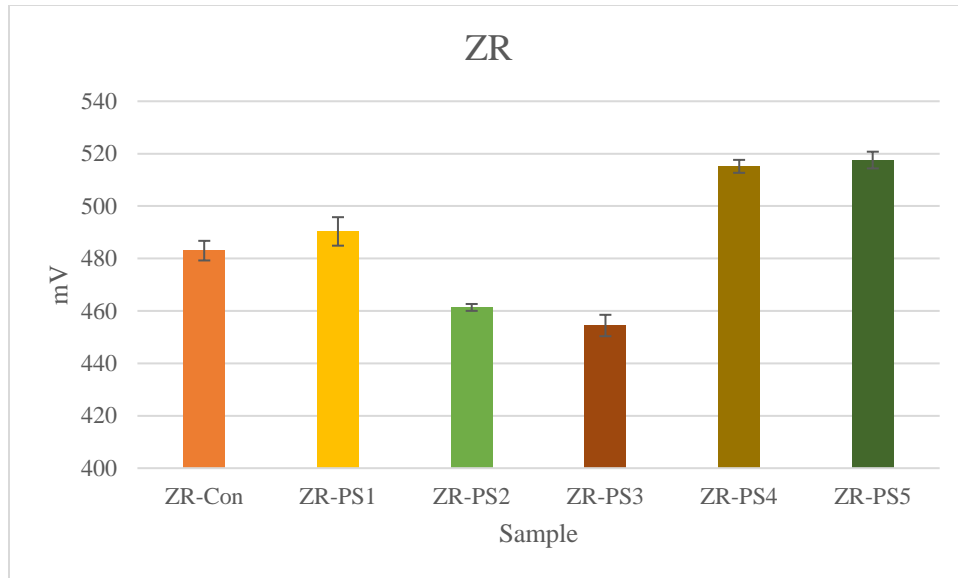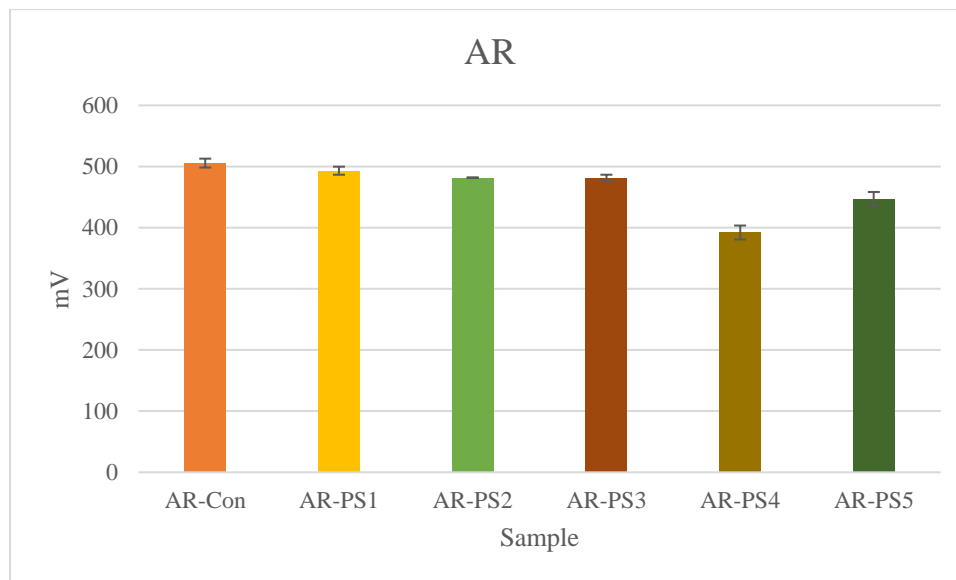Most of the Eh values are in the range of 400 to 500 mV. The maximum Eh value (518 mV) is present in ZR in the treatment PS5 (**Figure 55**) and the minimum Eh value (392 mV) is in the AR in the sample PS4 (**Figure 56**). Treatments PS2 and PS3 often decreased the Eh values in different soils (**Figure 55, Figure 56** and **Figure 57**) while PS4 mostly increased the Eh in ZR (**Figure 55**), BF (**Figure 57**) and GD soils (**Figure 59**).

6. Discussion

6.1.Leaching of risk metal and metalloids in water (EN 12457 method)

In the case of Zn, the highest immobilization was achieved by PS5 treatment in the AR soil with 100% (**Figure 4**) but Zn is essential for the plants to grow so immobilizing Zn completely is not a benefit because it can lead to Zn deficiency (Rudani et al., 2018). Yu et al., 2019 mentioned that plant development may be unaffected when cultivated in a nutrient solution containing less than 5,0 mg/kg of Zn which happens in ZR soil (**Figure 3**). The most efficient treatment was PS5 (See section **5.1.1**) for the soils AR (**Figure 4**), BF (**Figure 5**), and SM (**Figure 6**), while the opposite is the case for ZR (**Figure 3**) and GD soils (**Figure 7**). The ZR soil in the treatment PS4 and PS5 (**Figure 3**), the AR soil in the treatment PS1 to PS3 (**Figure 4**), and the GD soil in the treatment PS2 (**Figure 7**) yielded higher concentrations compared to control samples. The increase of Zn in the samples is probably related to the acidic soil characteristics because the acid pH (**Figure 50**, **Figure 51** and **Figure 54**) can provoke Zn mobility. This means that Zn does not adhere as strongly to soil particles and is more susceptible to being leached into groundwater (Yu et al., 2023). Concentrations higher than 400 mg/kg can be toxic, and detrimental to the metabolic processes in the plants (Kaur & Garg, 2021) which is not the case in the results described about Zn concentration (Section **5.1.1**).

The highest value of Pb was observed in SM (**Figure 11**) soil in the control sample (5.32 mg/kg) which is probably related to the slightly more acidic pH (**Figure 53)** of the control sample compared to the treated samples. Pyrolyzed sludge application slightly increased the pH which made Pb less mobile because an increase in pH can lead to the formation of less soluble Pb compounds or complexes, reducing the availability of Pb for mobility in the soil (Houben et al., 2013). Treatment PS3 showed the highest immobilization efficiency for Pb in soil BF yielding a concentration of 0 mg/kg (**Figure 10**). However, the overall concentration of Pb in this soil was low (from 0 to 5,32 mg/kg). Additionally, soil ZR in the treatments PS3 and PS5 (**Figure 8**), AR soil in the treatment PS2, and BF soil in the treatment PS4 (**Figure 10**) were higher than the control probably because the soil's pH is acidic and the PSS maintained the soil pH as acid (**Figure 50** and **Figure 52**) (Król et al., 2020).

Criteria and procedures have been established for accepting waste in landfills by EU Directive 1999/31/EC (2003), which includes limit values for Cd in leachate as 0.04 mg/kg for hazardous waste. According to this limit, results obtained from ZR soil (up to 0.28 mg/kg) in the PS5 treatment (**Figure 13**) are higher meaning this soil cannot be kept in landfills. For the rest treatments, the Cd concentration is lower than 0,04 mg/kg. The highest immobilization was observed in the BF soil in the PS2 treatment (**Figure 14**). Besides, the concentration of Cd is much higher in the treated samples than in the control sample in the results of BF soil (**Figure 13**) and GD soil (**Figure 15**). This is because in some cases the PSS may liberate the adsorbed Cd again, raising the concentration of the metal in the environment and therefore in the analyzed samples (Sylwan et al., 2023).

Cooper permissible limit in leachate in water is established as 10 mg/kg for hazardous waste (Alvarenga et al., 2007) which is higher than the results of all the treatments (see section **5.1.4**). Therefore, Cu concentrations does not present a hazard in this case. Moreover, in the results of AR soil in all the treatments except PS2 (**Figure 17**) and in GD soil treated by PS2 and PS3 (**Figure 20**) Cu was higher in control samples rather than treated. Some of the soil microorganisms might interact with the PSS, being in a way favorable for the release of Cu in the soil, hence affecting the concentration of Cu in the samples (Medeiros, 2019). This can be dangerous because it increases plant uptake (V. Kumar et al., 2021). Additionally, Cu mobilization by PSS can be caused due to some factors like soil acidification (L. Chen et al., 2022) as in the AR soil (See **Figure 51**) where all the samples have an acidic pH.

Limit values for As in leachate are set as 0,5 mg/kg for hazardous waste (EPA US, 2002). In this study, all the locations had higher As concentrations than 0,5 mg/kg (Section **5.1.5**). The highest immobilization was observed in the PS1 treatment in AR (**Figure 22**) samples with 60% lower As than the control sample. The ZR soil in the PS3 treatment (**Figure 21**), AR soil in the PS2 treatment (**Figure 22**), the BF soil in all the treatments (**Figure 23**), the SM soil in the PS4 treatment (**Figure 24**), and the GD soil in the PS1, PS2, PS3 and PS5 treatments (**Figure 25**) yielded higher As than the control sample because the addition of pyrolyzed materials typically increases the availability of As (Zoroufchi Benis et al., 2020).

The pyrolyzed materials may greatly increase ion exchange in soil, hence affecting arsenic availability (Palansooriya et al., 2020). In most instances, cations within pyrolyzed materials compete with As for exchange sites on the surface of the soil (Shen et al., 2017), and later release arsenic, hence increasing its availability (Y. Sun et al., 2022).

Finally, Tejnecký, 2007 found that in contaminated soils at Příbram (an area affected by mining and metallurgical activity in the Czech Republic), Sb concentrations in the leachate were in the range of 0,03 to 0,002 mg/kg. The studied soils have higher values (Section **5.1.6**) than the values found in Tejnecký, 2007 implying severe contamination in this case. The highest immobilization was 100% in the AR soil with PS2 treatment (**Figure 26**). The GD soil treated with PS1, PS4 and PS5 treatments (**Figure 28**) showed higher Sb than the control sample because have been reported that Sb pore water concentrations greatly increase under alkaline conditions, which is attributed to the predominant presence of Sb as an oxyanion in aqueous solutions (Hockmann et al., 2015).

6.2. Availability of risk metal and metalloids in the soil extracts

In the Zn case, the highest concentration was 826 mg/kg in sample SM-PS4 (**Figure 32**) and the highest Zn immobilization was 12,7% in the ZR soil at PS1 treatment (**Figure 29**). Most of the samples with PSS have higher amounts of available Zn than the control samples. In particular, in AR (**Figure 30**), BF (**Figure 31**) and GD (**Figure 33**) soils none of the treatments are effective in reducing the availability of Zn. In the case of AR and BF soils it can be related to the acidic soil pH (**Figure 51** and **Figure 52**) because the availability of Zn can be increased when the soil pH becomes more acidic (Desta et al., 2021). In the case of GD soil, higher Zn availability can be related to organics that could have the chemical ability to chelate with Zn ions (S. J. S. Flora & Pachauri, 2010). Chelating agents are generally more soluble than most inorganic ions and, as such, enable the bound metal to be more available to plants or other organisms (G. Flora et al., 2015). The PSS decreases Zn availability for the plants and organisms in the soil (Latini et al., 2019), but in this case, PSS increases Zn availability and can harm the plants because it can affect their growth and development (Balafrej et al., 2020).

Decree 153/2016 Coll. from the Czech Republic established the value Pb in soils as 60 mg/kg (Ministerstvo životního prostředí, 2016) and the highest Pb availability was 283,23 mg/kg in ZR soil with PS5 treatment (**Figure 34**) exceeding this limit. Additionally, AR soil at the PS2 to PS5 treatments (**Figure 35**), BF soil at PS2 treatment (**Figure 36**), and SM soil at PS4 and PS5 treatments(**Figure 37**) have a higher availability of Pb in the soil with PSS than the control samples. Shahzad et al., 2023 indicated considerable increases in Pb content by 94.57%, 190.09%, and 453.55% compared to control samples because acidified PSS might increase the Zn availability as possesses the ability to release protons. These protons can then interact with Pb ions, leading to the formation of complexes which in the early stages can increase Zn availability and then, over time, reduce mobility and availability for the uptake by plant roots (Shahzad et al., 2023). In this study, the AR (**Figure 51**), BF (**Figure 52**) and SM (**Figure 53**) soil pH were acidic and stayed acidic

between the treatments which can explain the increase in Pb availability because the PSS addition didn't increase the pH to the alkaline pH levels. The most effective immobilization of Pb was in the AR soil with PS1 treatment (**Figure 35**). The most effective treatment against all test treatments in all soil types was the treatment with PS1, which reduced the Pb availability significantly. This is probably because it can work under all different soil conditions and its specific composition immobilizes Pb.

Cadmium was present in high concentrations (up to 9,34 mg/kg) in ZR soil (**Figure 39**). Treatment with PS1 was effective in Cd immobilization and lowered the availability to 23,6 mg/kg in the ZR soil. However, PS2 yielded higher Cd concentrations than control. This could be explained because PSS materials may form a complex with Cd immediately after application and the newly formed organic matter may be in complex with the Cd (J. Sun et al., 2020). Such complexes could raise the mobility of Cd in the soil structure and make it more available (Haider et al., 2021).

The limit value for the levels of Cu in agricultural soil is established as 60 mg/kg (Ministerstvo životního prostředí, 2016) and none of the treatments exceed the limit. Therefore, Cu is not considered a contaminant in most cases. However, Cu is an essential element for plants and is involved in photosynthesis, cellular respiration, nitrogen metabolism, etc... (G. Chen et al., 2022). Its deficiency can cause various symptoms such as chlorosis, stunted growth, leaf deformation, and tip dieback (Jeyakumar & Balamohan, 2020). Some samples yielded higher concentrations than the control samples (Section **5.2.4**) probably because other contaminants, for instance, either Zn or Pb, present in the PSS, may cause competition for the sorption sites (X. Chen et al., 2011). An increased concentration from such mechanisms can lead to a higher concentration of cadmium in the solution and, therefore, the PSS samples.

Finally, in the SM soil (**Figure 48**), a high concentration of As (up to 26.5 mg/kg) is observed while the Czech legislation set a limit of 20 mg/kg (Ministerstvo životního prostředí, 2016). However, PS1 showed efficiency, managing to bring the availability of As in the soil down to 0 mg/kg in the ZR soil (**Figure 45**). On the other hand, in ZR soil, the availability of As in samples treated by PS2 − PS5 (**Figure 45**) was increased. This may be due to the changes in the soil chemistry, such as speciation and fractionation of the varying As species in the soil which may result in mobility, bioavailability, fate, and transport changes in the presence of organic-based amendments (Vithanage, 2016).

7. Conclusion

The study objective is to immobilize toxic metals to decrease their availability in the soil. The PSS was used over the soils which are contaminated with hazardous metals to immobilize them. To test the efficiency, various types of PSS were applied to the contaminated soils and investigated if 1) PSS could immobilize toxic metal(loid)s in soils and 2) toxic contaminants from the PSS could be released into the soil.

According to the results, the used PSS (PS1, PS2, PS3, PS4 and PS5) could immobilize different metals in some studied soils (ZR, AR, BF, SM and GD). Not all PSS could immobilize all metals and metalloids or in all tested soils. For each of the five soils, the variability among treatments was investigated. Treatment PS1 immobilized Zn in all the soil water leachates but not in the soil extracts. Treatment PS4 immobilized Pb in the ZR, AR, SM and GD soils, but not in BF soil. Additionally, treatment PS1 immobilized Cd in soil BF, but it was unsuccessful in ZR and GD soil in the water leachates. Also, PS1 immobilized Cd for all the soils in the soil extracts results. Copper was immobilized in the ZR, BF and SM soil by the PS2 treatment but failed in AR soil in the water leachates. PS2 was efficient in lowering the availability of Cu in the soil extract, however for ZR, BF and SM soil failed. Arsenic was immobilized by the treatment PS5 in the soils AR and GD but not in ZR and SM soil. In the soil extracts case, As were successfully immobilized for AR, SM and GD soils but not in ZR and BF soil. Finally, Sb was immobilized by PS2 in the soil AR and GD, but not in BF soil.

The maximum decrease in Pb availability in water leachates was found to be in soil BF by PS1, PS2 and PS3 treatments. In the soil extracts, the maximum efficiency for Pb immobilization was found to be in soil AR by PS1 treatment. The highest Zn immobilization was achieved by treatment PS5 in soil AR and the PS3 in the GD soil in the water leachates. For Cd by PS2 treatment yielded the lowest concentrations in the water leachates in soil BF. Arsenic was immobilized by PS1 in AR soil for the water leachates. In the case of soil extract, the PS5 treatment in the GD soil had the highest immobilization of As. For Cu, the maximum immobilization was PS4 in the GD soil for the water leachates. Finally, the maximum Sb immobilization was from the treatment PS3 in soil AR for the water leachates.

In general, the metal and metalloid immobilization works for some soils and PSS treatments but varies between the soils. There wasn't a PSS treatment that predominantly immobilized all the elements studied in this thesis so it's not possible to affirm that one treatment was successful for all the soils. Maybe extended research should be performed to find more conclusive evidence.

Finally, it can be advisable to test maintaining the soil with the PSS at different time intervals to determine the most effective time for immobilization of toxic metals in soil with different characteristics and contaminants. Also, it is recommended to keep working on PSS in different soils and conduct field experiments monitoring different parameters daily as pH and redox.

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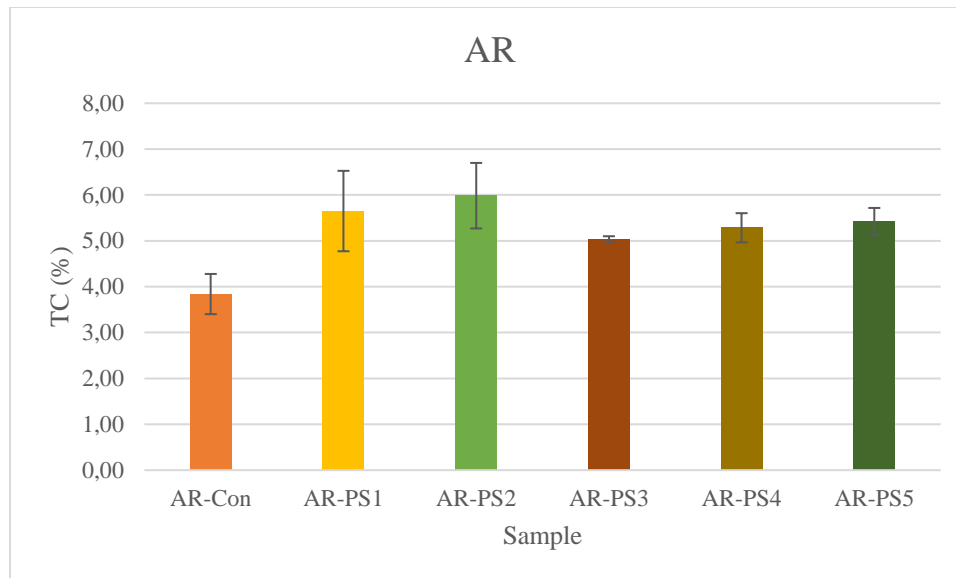
9. Appendix
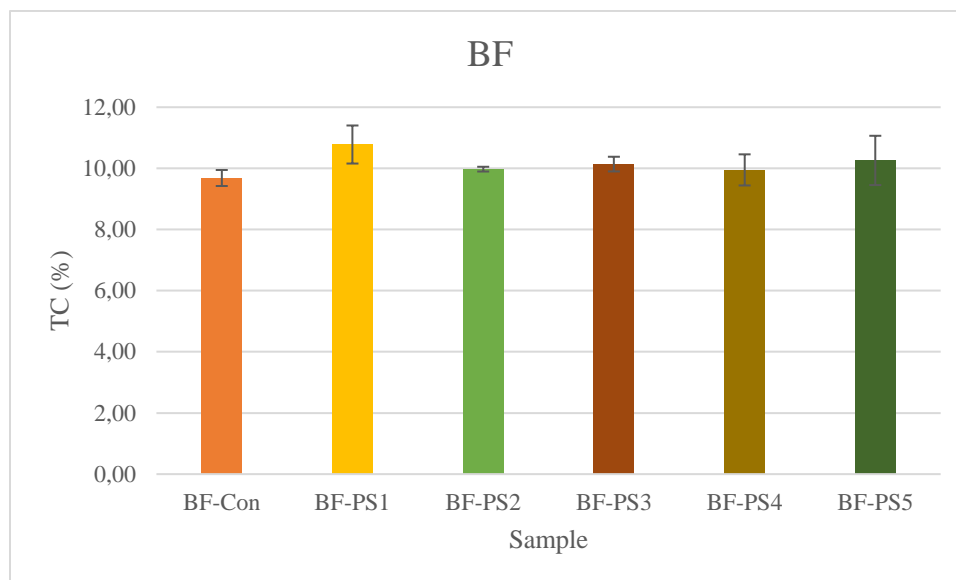
9.1. Total carbon (TC)

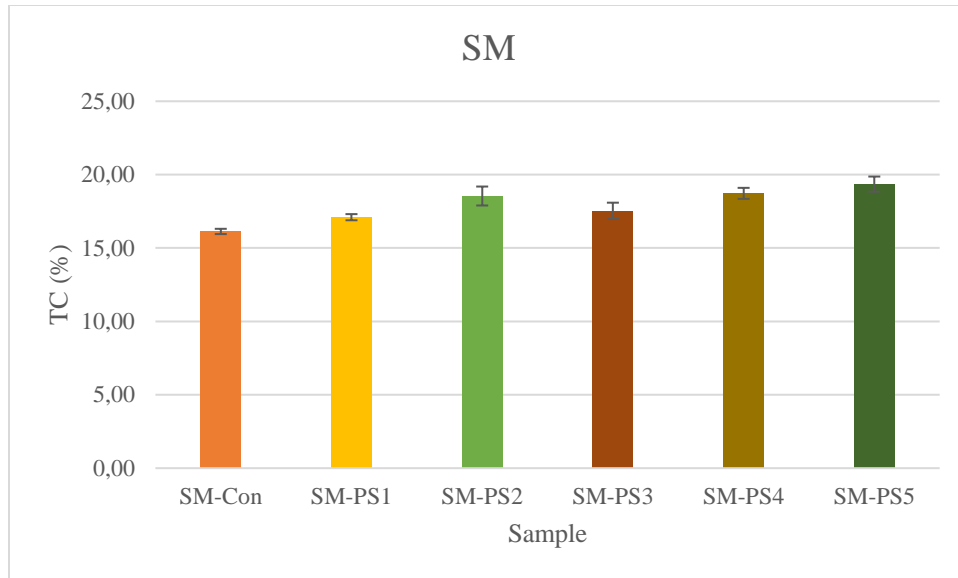In this part, the results of five different locations focus on TC in soils.
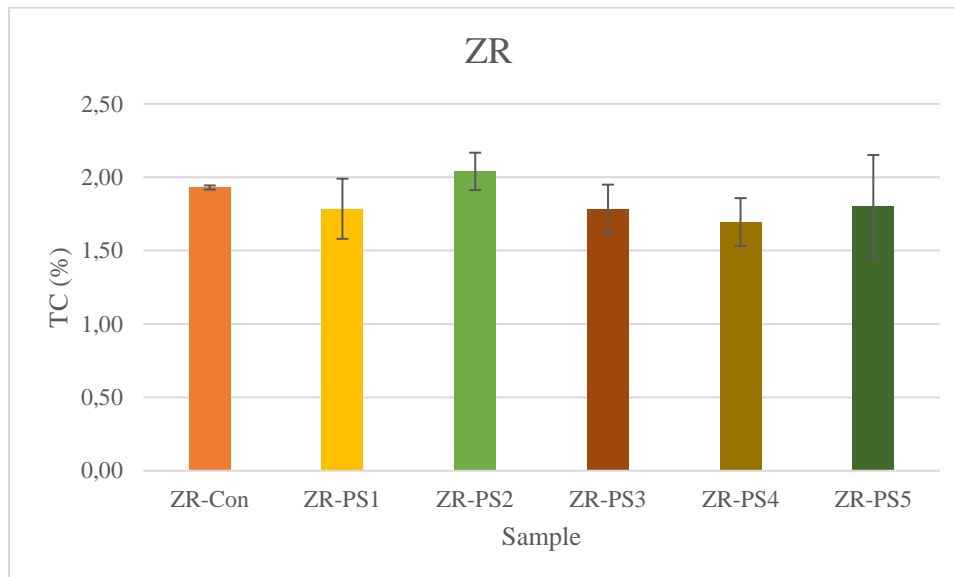
Figure 60 TC measured in water leachates in Zn-rich soil.
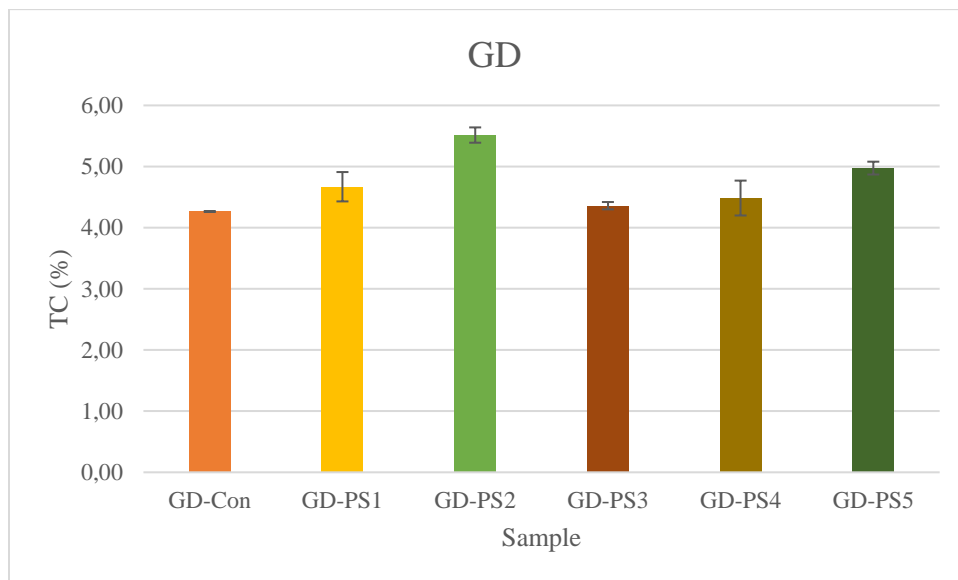
Figure 61 TC measured in water leachates in As-rich soil.

Figure 62 TC measured in water leachates in Brownfield soil.

Figure 63 EC measured in water leachates in Smelter soil.

Figure 64 measured in water leachates in Garden soil.

The higher TC value is present in ZR soil in the PS2 treatment, and the lower TC value is present in the ZR soil in the PS1 treatment. Most of the treatments didn't vary the TC between samples. As-rich treatment increases the TC values in all the samples in comparison to the control sample (AR-Con).