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SOIL CHARACTERISTICS AND HEAVY METALS CONCENTRATION IN BAIA MARE POLLUTED SITES

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Abstract. *The aim of this study is to assess the base level of soil pollution in five sites from an urban area affected by interference between natural and anthropogenic sources. The analysis of chemical characteristics of soil, such as pH, humus and heavy metal concentrations (Pb, Cd, Cu, Zn), was performed to identify the contaminated sites and to explore the potential the need for a remediation process. Sampling design was performed for collecting accurate data in assessment of soil quality and heavy metal contamination. Within the five analyzed sites, Craica showed moderate to extreme acid reaction of soil, with a pH that reached 4.19 in soil depth. The recorded percentage of humus varied greatly between sites, with the maximum recorded in Craica site and 2.12 at the Romplumb site. Lead was identified in the range 114-418 in four of the five sites analyzed, while copper was dominant in the fifth site, with more than 120 mg/kg. Zn was found in higher quantities in the depth of soil, in four of the five analyzed sites, which indicates a historical contamination and deposition of this element. Heavy metals were found in all the five sites analyzed, with different combinations of soil pollution, which indicates the need for bioremediation and the extraction of pollutants from soil.*

Keywords*: soil pollution, heavy metals, bioremediation requirement, site assessment*

INTRODUCTION

Soil is an essential natural element for agriculture and represents the main environment for plant nutrition, having an important role in agrochemical, physicochemical, chemical and biological contexts (Yang et al., 2022). It is distinguished by characteristics such as pH, nutrient availability, adsorption capacity and ion exchange, which make it a suitable environment for the application of fertilizers and amendments (Vidican and Sandor, 2015). The most important function of soil is the ecological function that contributes to the cycle of elements. (Vegter et al., 1993). The protection of this substrate aims to maintain or restore its multifunctionality (Onica et al., 2017; Sandor et la., 2016). This concept, multifunctionality of soil, implies preserving its ability to perform various functions, but not indefinitely.

Soil is exposed to pollution and is more difficult to recover than water and air due to slow self-purification processes. Pollution is the result of the presence of chemicals created by human activities or natural soil modifications. Contamination typically occurs from the destruction of underground storage facilities, the use of pesticides, the seepage of polluted water into subsurface layers, the spillage of oil and fuel, the leakage of waste from landfills, or the direct disposal of industrial waste into the soil. (Havugimana et al., 2017). A different perspective on current research highlights the case studies that focus on heavy metals and synthetic organic chemicals as the main soil contaminants. Soil also contains a number of biological contaminants, such as pathogens and parasites, which cause detrimental effects on human health (Burgess et al., 2013). Types of organic pollutants commonly found in soil are polychlorinated biphenyls, polybrominated dibenzofurans, polycyclic aromatic hydrocarbons, organophosphorus and carbamate insecticides, herbicides, and organic fuels, especially gasoline and diesel.

In addition to human factors, natural causes can also contribute to soil pollution, through phenomena such as earthquakes, landslides, hurricanes, floods, acid rain, and deforestation. These natural disasters can cause significant damage to soil composition (Havugimana et al., 2017).

The causes of soil degradation can be directly or indirectly linked to human activities. Soil pollution is considered a consequence of unhygienic habits or inappropriate practices, caused by the chaotic removal and storage of residues from human activities, industrial waste or the inappropriate use of chemicals in agriculture (Ahmed et al., 2022). Rapid urbanization and industrialization in developing countries will bring a large amount of pollutants into the urban environment in the short term. These pollutants include polycyclic aromatic hydrocarbons, phenols, heavy metals, and arsenic compounds. Intensive human activities will contribute significantly to this pollution (Li et al., 2018).

Heavy metal pollution is a global environmental problem that threatens food security and the environment. It is caused by the rapid growth of agriculture and industry. The development of new industries and the increase in the number of people have also contributed to the increase in these conditions. The heavy metals that contaminate soils are mercury (Hg), cadmium (Cd), lead (Pb) and chromium (Cr), these toxic substances are retained by the soil and act as a filter for their properties (Pop et al., 2023). This type of pollution and acid deposition have significant negative effects on the soil, including altering the chemical composition by 1-3 units, leaching of exchangeable bases, and mobilizing large amounts of exchangeable Al, which are toxic to plants. It also leads to a decrease in nutrients, especially mobile phosphorus, affecting plant fructification (Bora et al., 2019). In addition, the disruption of microbiological activity, the decrease in bacterial populations and dehydrogenase activity, as well as the increase in the fungal population and the colonization index with these microorganisms, reduce the rate of humification of organic matter. (Bora et al., 2019).

Industrial and agricultural activities have a significant impact on the environment, which can be positive or negative. The impacts vary depending on their nature, duration, magnitude and perception, and can be direct or indirect, reversible or irreversible, and influencing different levels, from local to national. (Mihăiescu, 2019).

The aim of this study was to analyze the presence and the level of heavy metals in urban soil from Baia Mare. The specific objectives were: *i*) to assess the values of Pb, Cd, Cu and Zn in five different sites; *ii*) to determine the necessity for bioremediation based on reference values; *iii*) and to explore the pH and humus percent of soils for the assessment of potential phytoremediation in the research areas.

MATERIAL AND METHODS

The experiment is located on 5 plots of land in Baia Mare, with a total area of 7.3 hectares. The plots analyzed are located in the sites named: Craica (with two plots due to the heterogeneity of area), Colonia Topitorilor, RombPlumb, Ferneziu and Urbis. These lands marks the demarcation line between the residential area and the industrial area that was polluted by anthropogenic mining activities.

For the 5 sites it was considered that soil samples should be collected following a regular grid pattern (which could be a standard square grid or a staggered square grid, known as a skeleton pattern), to provide an adequate representation of the extent and nature of contamination at the site. In the first part of the research, analyses were carried out to determine the pH and humus of polluted soils in Baia Mare, followed by the determination of heavy metals from the same affected areas.

The pH of the soil was determined by the potentiometric method of analysis, which is an electrochemical method based on determining the electromotive force of an electrochemical cell under equilibrium conditions, that is, when the electric current through the cell is practically zero. Potentiometric determination of pH involves the use of electrodes that indicate the concentration of hydronium ions (pH sensors). These sensors are characterized by the fact that, under certain conditions, they present an electrode potential that is linearly correlated with the pH of the solution with which they are in contact.

The humus content of the soil was determined by the WALKLEY-BLACK method. Both the soil pH and the humus content were determined at the Office of Pedological and Agrochemical Studies in Cluj.

Heavy metals in the soil were determined using the Portable XRF Spectrometer (mobile PXRF analyzer). This device provides the quantification of chemical elements from mobile Cl(17) to U(92) in soil samples. It is equipped with an X-ray tube with a thin Rhodium (Rh) window, a locked and completely sealed sampling compartment, without leakage radiation.

RESULTS AND DISCUSSIONS

The way in which these heavy metals accumulate in plant and animal organisms, including the human body, as well as the pathological effects they cause, justify the attention paid to these pollutants (Balali-Mood et al., 2021; Briffa et al., 2020). The lack of an adequate system for monitoring and controlling heavy metals in soils, air and water can represent a real danger to the environment and, in particular, to human health. Heavy metals can be present in the environment either naturally or in excessive concentrations (from artificial sources), mainly originating from mining activities, the non-ferrous metallurgy industry, the combustion of solid and liquid fuels, as well as from vehicle exhaust emissions.

In the area of Baia Mare municipality and its surroundings, the predominant soils are included in the classes of argillovisols (typical brown and clayey alluvial soils, typical brown luvic and pseudogleyed, albic and pseudogleyed luvisols), cambisols (typical brown acid, lithic, andic and cryptospodic soils, brown eumesobasic gleyed and pseudogleyed), and umbrisols (andosols), according to research conducted by ICPA (Research Institute for Pedology and Agrochemistry). All this research has highlighted the pollution of soils in the Baia Mare area, especially with heavy metals, pollution that can be attributed to both industrial activities and mineral resource deposits in this region.

Soil pH is one of the most important factors influencing the uptake of heavy metals. In fact, their solubility and bioavailability increase as soil pH decreases, leading to greater uptake of metals by plants. The lowest value is recorded in the Craica 2 site, where pH=4.19, being extremely acidic, and the highest value is recorded in URBIS, where pH=7.74, being slightly alkaline. The difference between the lowest and highest pH values is 3.55 units (Table 1.). This suggests a significant diversity of soil characteristics depending on location and depth. They can influence the type of vegetation and the agricultural or industrial activities possible in these areas.

The behavior of metals varies between acidic and alkaline soils. Heavy metals are more soluble and available in acidic soils than in neutral or slightly alkaline soils. Highly acidic soils (with a pH between 4.0 and 5.0) can contain high concentrations of heavy metals, which can become toxic to the growth of certain plants (Naz et al., 2022). Soil pH can also influence plant growth through its impact on the activity of beneficial microorganisms. In highly acidic soils, bacteria that decompose organic matter are inhibited. This prevents the decomposition of organic matter, leading to its accumulation and the binding of nutrients, especially nitrogen, which remain trapped in the organic matter. (Asira et al., 2013).

The difference between the highest and lowest humus values is 3.33%, between 5.45% at Craica 1 and 2.12% at Romplumb (Table 1.). This difference highlights the fact that soil in different locations can vary considerably in its capacity to support plant life, depending on the amount of humus present. Locations with high humus values (Ferneziu 1, Craica 1, Craica 2) are more favorable for agriculture and vegetation, while Romplumb is poorer in organic matter and requires improvements to support plant growth in the long term.

Humus is the basic component of soil, resulting from the action of biocenosis in the process of soil formation. Humus is a widespread component in nature, being a representative of natural organic matter, often called humic acids. It plays an essential role in plant growth, maintaining the stability of the soil structure and transporting heavy metals. Humus can also form relatively insoluble complexes, thus reducing the availability of heavy metals in the soil and inhibiting their migration and absorption through processes such as physical adsorption, chelation, redox reactions, desorption by leaching and activation of antioxidant enzyme systems (Zhao et al., 2022).

Table 1

Soil pH and humus characteristics of the five studied sites

Location	Coordinates	Depth (cm)	pH	Soil reaction	Humus (%)	Supply
Romplumb	N47°41´19.5´´ E23°37´41.6´´	< 20	6.86	Neutral	2.12	Low
		> 20	7.22	Neutral		
Ferneziu	N47°40´34.5´´ E23°37´23.2´´	< 20	6.73	Neutral	5.29	High
		> 20	6.60	Neutral		
Colonia Topitorilor	N47°40´02.6´´ E23°36´21.4´´	< 20	7.55	Slightly alkaline	3.42	Normal
		> 20	7.29	Neutral		
Urbis	N47°39´49.3´´ E23°36´24.5´´	< 20	7.51	Slightly alkaline	4.41	Medium
		> 20	7.74	Slightly alkaline		
Craica 1	N47°38´18.5´´ E23°34´6.6´´	< 20	6.06	Moderately acidic	5.45	High
		> 20	5.95	Moderately acidic		
Craica 2	N47°38´18.6´´ E23°34´12.1´´	< 20	4.35	Extremely acidic	4.51	High
		> 20	4.19	Extremely acidic		

Due to the strong interference between natural and anthropogenic sources, the similarities between pollutants released by different economic agents and the lack of a unified soil quality monitoring system in the area, none of the studies manages to quantify the contribution of each source to soil pollution in the investigated area (Münzel et al., 2022). The severity of the potential consequences for ecosystems and human health is so great that a remediation process is necessary, especially in the case of current or planned use of the area in

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question (Burger, 2007; EPA, 2022; Trușcă et al., 2022; Vâtcă et al., 2022). Remediation or cleaning of contaminated sites can lead to the complete elimination or reduction of the effects of these contaminations.

Regarding the lead (Pb) content in the soil, levels were recorded that ranged between 43.69 mg/kg dw (Site Craica 1 < 20 cm) and 417.97 mg/kg dw (Site Urbis > 20 cm). It is observed that the lead levels in the soil exceeded the normal value of 20 mg/kg dw (Table 2). The alert threshold for sensitive soil (50 mg/kg dw) was exceeded in all sites, except for the Craica 1 pilot site. The alert threshold for less sensitive soil (250 mg/kg dw) was exceeded in the Ferneziu pilot site > 20 cm and in the Urbis. Cadmium (Cd) in the soil had levels ranging from 0.24 mg/kg d.w. (Site Romplumb < 20 cm) to 1.25 mg/kg d.w. (Site Craica 1 > 20 cm). Compared to the threshold value, it can be seen that the Cd levels in the soil did not exceed the permissible limit

Table 2

Soil Pb and Cd levels in the five studied sites

Location	Coordinates	Depth (cm)	Pb mg/kg	Cd mg/kg	Reference values mg/kg	Pb	Cd
Romplumb	N47°41´19.5´´ E23°37´41.6´´	< 20	117.32	0.24	Normal values	20	1
		> 20	172.39	0.27			
Ferneziu	N47°40´34.5´´ E23°37´23.2´´	< 20	119.77	0.33	Sensitive *Alert threshold*	50	3
		> 20	288.05	1.22			
Colonia Topitorilor	N47°40´02.6´´ E23°36´21.4´´	< 20	114.92	0.99	Less sensitive *Alert treshold*	250	5
		> 20	123.81	1.17			
Urbis	N47°39´49.3´´ E23°36´24.5´´	< 20	342.98	0.46	Sensitive *Intervention threshold*	100	5
		> 20	417.97	0.51			
Craica 1	N47°38´18.5´´ E23°34´6.6´´	< 20	43.69	0.80	Less sensitive *Intervention treshold*	1000	10
		> 20	46.36	1.25			
Craica 2	N47°38´18.6´´ E23°34´12.1´´	< 20	50.59	1.10			
		> 20	52.42	0.43			

Lead (Pb) is one of the most widespread heavy metal contaminants in soil and poses a significant threat to plants. Although lead does not play a biological role in plants, it can cause significant morphological, physiological, and biochemical problems. (Zeng et al., 2007). However, the magnitude of these effects varies depending on concentration, age and affected organs. However, plants have internal detoxification mechanisms, which include selective metal uptake and excretion. Plant responses to lead exposure are often used as tools (bioindicators) for assessing environmental quality (Flora et al., 2012). Cadmiu (Cd) is a heavy metal toxic, non-essential heavy metal that affects plant morphology and physiology by inducing oxidative stress, generated by oxygen free radicals and lipid peroxidation in cell membranes. Exposure to cadmium in soil induces osmotic stress in plants by significantly reducing relative leaf water content, stomatal conductance, and transpiration (Xie et al., 2015).

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Copper (Cu) in the soil recorded levels that varied greatly (Table 3) between 21.13 mg/kg dW (Site Romplumb < 20 cm) and 128.96 mg/kg dW (Site Craica 2 > 20 cm). It was observed that the copper levels in the soil exceeded the normal value of 20 mg/kg at all sampling points. The alert threshold for sensitive soil (100 mg/kg) was exceeded only at the Pilot Sites Craica 1 and Craica 2. The levels of zinc (Zn) in the soil ranged between 62.85 mg/kg (Site Craica 2 > 20 cm) and 385.22 mg/kg dw (Site Craica 1 > 20 cm). It was seen that the levels of zinc identified in the soil exceeded the normal value of 100 mg/kg dW in most of the sampling points.

Table 3

Soil Pb and Cd levels in the five studied sites

Location	Coordinates	Depth (cm)	Cu mg/kg	Zn mg/kg	Reference values mg/kg	Cu	Zn
Romplumb	N47°41´19.5´´ E23°37´41.6´´	< 20	21.13	84.57	Normal values	20	100
		> 20	27.00	113.88			
Ferneziu	N47°40´34.5´´ E23°37´23.2´´	< 20	25.45	105.20	Sensitive *Alert threshold*	100	300
		> 20	38.82	152.67			
Colonia Topitorilor	N47°40´02.6´´ E23°36´21.4´´	< 20	32.27	125.69	Less sensitive *Alert treshold*	250	700
		> 20	64.44	160.57			
Urbis	N47°39´49.3´´ E23°36´24.5´´	< 20	22.45	88.43	Sensitive *Intervention threshold*	200	600
		> 20	24.06	115.68			
Craica 1	N47°38´18.5´´ E23°34´6.6´´	< 20	86.33	270.09	Less sensitive *Intervention treshold*	500	1500
		> 20	128.78	385.22			
Craica 2	N47°38´18.6´´ E23°34´12.1´´	< 20	124.31	349.86			
		> 20	128.96	62.85			

Copper (Cu) is an essential micronutrient abundant in various rocks and minerals, being required for multiple metabolic processes in both prokaryotes and eukaryotes. However, excess copper can disrupt normal plant development by negatively influencing biochemical reactions and physiological processes. (Ameen et al., 2023). Soil contamination with copper (Cu) comes from several sources, such as industrial and agricultural activities. Mining deposits and atmospheric deposition can increase the concentration of Cu in soil, exceeding the natural geochemical background, and agricultural practices, such as the use of Cu-based fungicides or the application of Cu-enriched manure or sewage sludge, also contribute to this problem. Due to the negative charge of soil organic matter, Cu, as a cation, binds more easily than other metal cations, leading to its accumulation in the upper soil layers, where the concentration of organic matter is higher (Rodríguez-Eugenio et al., 2018).

Zinc (Zn) acts as an essential nutrient for plants, but at higher concentrations it can become toxic. Being rapidly assimilated by plants, zinc can be extremely phytotoxic. Growth inhibition is a common phenomenon associated with the toxicity of this metal. Zinc plays an important role in the regulation of nitrogen metabolism, cell proliferation, photosynthesis and auxin synthesis in plants. It is also involved in the synthesis of DNA, proteins and facilitates the use of phosphorus and nitrogen in the germination process. Zinc toxicity is manifested by stunted shoot growth, curling and rolling of young leaves, death of leaf tips and chlorosis. Shier, 1994).

Soil pollution, caused by industrial emissions loaded with heavy metals, fluorine, sulfur oxides, nitrogen oxides and other substances, affects an area of over 900,000 hectares. Heavy metals in soils are found in various forms, such as soluble, exchangeable, organically bound, precipitated with carbonates, bound to iron and manganese oxides, precipitated with sulfides or as a residual fraction. Their concentrations vary considerably depending on the extract used (Li et al., 2018). Heavy metals are recognized for their ability to decrease or inhibit the functioning of soil enzymes, disrupt the transformation of carbon, nitrogen and organic matter, and diminish both the biodiversity and biomass of soil microorganisms (Giller et al., 2009).

CONCLUSIONS

The study of soil characteristics in different pilot sites in Baia Mare revealed a significant variation in soil characteristics, which influence the potential installation of vegetation in the area.

The pH differences between locations, ranging from extremely acidic values (pH=4.19 at Craica 2) to slightly alkaline values (pH=7.74 at Urbis), suggested an important variation in soil types and how they can support plants. Also, the differences in humus content, from 2.12% at Romplumb to 5.45% at Craica 1, highlight the variability of soil fertility, with a direct impact on the capacity to support vegetation.

Regarding heavy metal pollution, lead (Pb) levels exceed the normal value of 20 mg/kg in most sites, and the alert threshold of 50 mg/kg is exceeded in all sites except Craica 1. This indicated the presence of soil pollutants, which could affect the health of the ecosystem and plants.

The solution for remediation and management of these contaminated sites is essential for protecting the environment and ensuring healthy soil for agricultural activities and vegetation development for long term

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