METAL CONTENT IN THE SURFACE SOILS OF INDUSTRIAL AREAS IN NOVI SAD

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Abstract

The scope of this study was to investigate the heavy metal content in the industrial soils of Novi Sad, Serbia. A total of twenty topsoil samples (0–10 cm depth) were collected. The chemical properties of soil as well as the particle size distribution of soil (<2 mm fraction) were determined. Pseudo-total concentrations of cadmium, copper, lead, and zinc were measured using the ICP-OES device. Total mercury content in the samples was analysed using a Direct Mercury Analyzer (DMA) 80 Milestone. The results showed that the conc- entrations of Cu and Zn were found to be elevated at two locations. The concentration of Cd was very high at the same locations. Results revealed that no elevated values were detected for Pb at any location; all values were at the level of those in natural, unpolluted soils.

KEY WORDS: pollution, heavy metals, industrial soils

Introduction

Soil pollution by heavy metals is a widespread problem, posing a significant risk to human health or the environment. Rapid industrial growth and urbanisation of society have, in addition to numerous advantages, also resulted in the intensification of pollution of the environment. When compared to rural areas, urban areas have a higher population density, which results in more intense traffic, and are located closer to industrial plants and other sources of anthropogenic pollution [1]. As a result, the soil in urban areas is more susceptible to the negative effects of these factors. Industrial activities have great effects on heavy metal pollution, ecological risks, and health risks [2]. Heavy metals that have contaminated the soil are responsible for the disruption of natural geochemical cycles. Due to the fact that they are not biodegradable and have complex activity in the soil as well as long biological half-lives of elimination from the body, heavy metals are classified as dangerous pollutants. The aim of the study was to determine the concentration of Cd, Cu, Pb, Zn, and Hg in soil near industrial plants in Novi Sad, Serbia.

Of the five examined metals, copper and zinc are essential for organisms. However, if they are found in the soil in high concentrations, they can be toxic. The remaining three metals, cadmium, lead, and mercury, do not have a natural metabolic role in living organisms, but even in small concentrations they can have negative metabolic effects. Therefore, we can call these metals potentially toxic elements (PTE)[3]. In recent decades, there has been a general trend toward an increase in environmental pollution caused by cadmium (Cd). This is a result of its increased use in industry as well as the use of phosphorus fertilisers [4]. Cadmium is quite mobile in soil and therefore more available to plants than other toxic metals including Pb and Cu. Cadmium is an element of high toxicity, several times greater than arsenic.

All three naturally occurring forms of mercury (Hg) (methyl mercury (MeHg), Hg^0 and Hg^{2+}) have a negative impact on the environment and represent a global risk to human health. The main anthropogenic sources of mercury are ore processing and cement production, especially

coal and oil burning and gold production. Because atmospheric deposition is the primary source of mercury soil pollution that has a cumulative effect, it is of the utmost importance to know the background concentrations of mercury in the soil and to establish soil quality monitoring. Because of the high sensitivity of the equipment used for direct mercury determination in this study, the total mercury content (THg) was able to be determined for all of the soil samples. Mercury is a neurotoxin, making it a particularly hazardous substance for living things to be exposed to.
Copper (Cu) is found in the soil associated with organic matter, iron and manganese oxides, soil silicates, clay and other minerals. A characteristic feature of copper is that it is most often specifically adsorbed or "fixed" in the soil and has very low mobility [5]. Copper found in high concentrations in the uppermost layers of the soil is evidence that it was introduced by human activity (metal smelters, application of mineral fertilizers, waste sludge, fungicides and bactericides, organic fertilizers, etc.).
Lead (Pb) is one of the most common pollutants in urban areas. In addition to pollution due to the long-term use of leaded gasoline in the past decades, significant anthropogenic sources of lead are also lead mines and smelters, coal burning, various industrial processes (production of lead batteries), production of some types of rubber and plastic, and others [6].
Zinc (Zn) is an essential trace element for plant and animal organisms as it is a participant in numerous enzymatic reactions. Conversely, excess zinc in the soil is phytotoxic [7]. The content of Zn in the soil is determined by a number of factors, one of which is certainly the parent substrate from which the soil was formed. As a rule, soils with a fine-grained mechanical composition contain more zinc than coarse-grained soils.
The criteria presented in 2005 based on the average values of a large number of data for the concentration of potentially toxic elements in the soils of the Mediterranean, Central Europe, and Eurasia are shown in Table 1. In the Republic of Serbia, the criteria for non-agricultural land are in force according to the Regulation on the programme of systematic monitoring of soil quality, indicators for assessing the risk of soil degradation and the methodology for developing remediation programmes [8]. This regulation defines the limit values (GV) and remediation values (RV) of certain dangerous and harmful substances on non-agricultural land (Table 3).

Table 1. The content of metals in the soils of Europe (The European Soil Databasee, version V2.0, EUR 19945 EN) [9]

Element mg/kg	Background - Natural Values	Slightly Higher Values	Contamination	High Contamination
Cu	< 36	36 – 100	100 – 500	> 500
Zn	< 140	140 – 500	500 – 3000	> 3000
Cd	< 0,8	0,8 – 5,0	5 – 20	> 20
Pb	< 85	85 – 150	150 – 600	> 600

Experimental

All laboratory analyses were performed at the Laboratory for Soil and Agroecology of the Institute of Field and Vegetable Crops, Novi Sad, accredited according to the standard ISO/IEC 17025 (2005). The surface soil samples from 10 cm depth were collected in industrial zones of the city of Novi Sad, according to the methodology of the reference sample (circle method). One sample represents the average value of several individual soil samples, which were taken in concentric circles around one central point. The soil samples were air-dried at room temperature and milled to a particle size of < 2 mm. Particle size distribution was determined by the internationally recognised pipette method. The size fractions were defined as follows:

coarse sand (2 - 0.2 mm), fine sand (0.2 - 0.02 mm), silt (0.02 - 0.002 mm) and clay (< 0.002 mm). Chemical properties were obtained following standard procedures. The pH value in a 1:5 (V/V) suspension of soil in 1 mol/L KCl was determined using a glass electrode according to ISO 10390 (2010). The free $CaCO_3$ content was determined according to ISO 10693 (1995) by the volumetric method. Oxidation using the sulphochromic oxidation method specified in ISO 14235 was used to determine the amount of organic matter present.

The samples were analysed for pseudo-total contents of Cd, Cu, Pb, and Zn after digesting the soil in concentrated HNO_3 and H_2O_2 (5 HNO_3:1 H_2O_2, and a 1:12 solid:solution ratio) by stepwise heating up to 180 °C using a Milestone Vario EL III for 55 min. The concentration of metals was determined by ICP-OES (Vista Pro-Axial, Varian) in accordance with US EPA method 200.7:2001. The samples were analysed for total mercury content using the Direct Mercury Analyzer DMA 80 Milestone, which combines techniques of thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry (λ = 253.65 nm) in solid soil samples. The detection limits for the metals studied were: 1.5 mg/kg (Cd), 5 mg/kg (Cu), 5 mg/kg (Pb), 5 mg/kg (Zn), and 0.0033 mg/kg for total Hg content.

Results and discussion

Table 2 shows the results of grain size analysis and basic chemical properties of the soil in industrial zones of the city of Novi Sad. The largest part of the examined soil samples corresponds to the mechanical composition of fine sand, 43.5%, while 13.7% of the examined soils have a clayey mechanical composition. The organic matter (OM) content in the soils varies from 0.22% to 4.70%, and the pH in KCl ranges from 7.07 to 8.46. The pH value and OM content have a significant influence on the accessibility of harmful and dangerous substances in the soil. The content of free $CaCO_3$ in the soil of the investigated localities is in a relatively wide range of classes, from weakly carbonated to highly carbonated soil.

Table 2. Physical and chemical properties of the soil in industrial zones of the city of Novi Sad, (n=20)

	Coarse sand %	Fine sand %	Silt %	Clay %	pH- KCl	$CaCO_3$ %	OM %
Mean	22.18	43.50	20.64	13.69	7.60	10.21	2.33
Median	13.95	40.39	17.70	13.02	7.59	9.97	2.47
Min	1.90	25.34	1.80	1.48	7.07	0.59	0.22
Max	71.10	68.68	35.80	27.20	8.46	28.85	4.70
SD	21.79	12.79	10.01	8.79	0.38	6.95	1.02

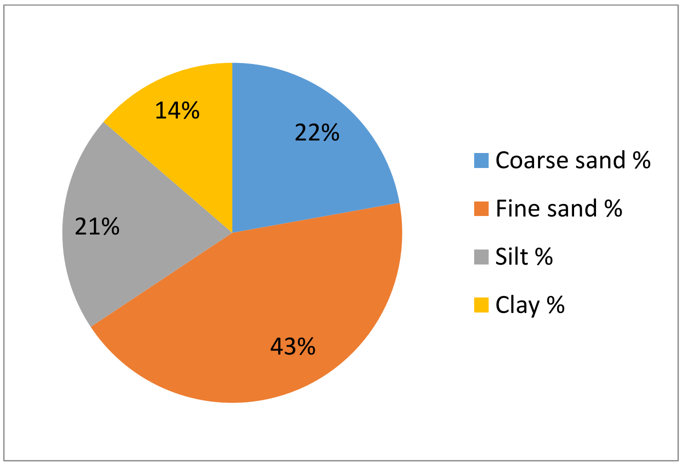

Figure 2. Particle size distribution in the soil of industrial zones in the city of Novi Sad

Statistical descriptions of metal concentrations (mg/kg) in the industrial soils of Novi Sad are shown in Table 3. Cadmium was detected at two locations in this research. Elevated concentrations of cadmium content were found in these samples, with concentrations of 4.54 mg/kg and 17.6 mg/kg, respectively. According to the criteria listed in Table 1, the soil from this locality belongs to contaminated soils.

Table 3. Metal concentrations (mg/kg) in industrial soils of Novi Sad (n = 20)

	Cu	Pb	Zn	Hg
Number of samples	20	20	20	20
Mean	59.12	19.41	111.26	0.086
Median	**29.20**	**14.65**	**75.35**	**0.052**
Min	5.50	3.20	24.80	0.009
Max	368.60	51.00	413.70	0.664
SD	88.62	12.22	102.60	0.141
Limited value	**36.00**	**85.00**	**140.00**	**0.30**
Remediation value	**190.00**	**530.00**	**720.00**	**10.00**

The obtained values of total mercury content (THg) vary in a wide range from 0.009 to 0.664 mg/kg, which is comparable to the Hg concentrations (0.01-1 mg/kg) of unpolluted soils. One sample exceeded the prescribed limit value for mercury concentration of 0.3 mg/kg. The prescribed limit value for copper, which is 36 mg/kg, is exceeded by the values of copper content in soil samples from five locations. Soil from two locations belongs to soils with slightly elevated values (44.0 and 43.6 mg/kg), and at three locations belongs to contaminated soils with concentrations of 368.6 mg/kg, 221.2 mg/kg, and 144 mg/kg, based on the criteria given in Table 1. It was found that samples with high levels of copper also had high levels of cadmium.
In all investigated locations, the lead content was at the level of background concentrations in the soil (Table 2), with the highest measured concentration being 51.0 mg/kg. In previous research [10], significantly elevated values (about 300 mg/kg) of total lead were detected in the vicinity of the traffic crossroads of Novi Sad as a result of the long-term use of leaded gasoline.
As already stated, four of the soil samples in this research exceed the prescribed limit value for zinc (140 mg/kg). These concentrations are slightly higher in comparison to soils in Europe (Table 1). The two samples represent soils that are already contaminated with high levels of cadmium and copper, as previously described. In these two samples, the concentrations of zinc were 368.6 and 413.7 mg/kg, respectively.

Conclusion

Based on the investigations carried out in 20 locations within the industrial zones of the city of Novi Sad, the following conclusions were made:
- The largest part of the examined soil samples (about 43%) has a mechanical composition of fine sand and the smallest part (14%) of clay.
- The largest parts of the investigated soils are weakly to moderately fortified with organic matter. The samples that were tested had a lot of $CaCO_3$, and most of them belonged to the slightly alkaline soil class based on their pH values.
- According to the content of investigated metals in relation to the criteria from the Regulation for non-agricultural soil, Cd exceeds the threshold value in two locations, Cu in five locations, Zn in four tested samples, and Hg in one location. At one of the investigated sites, the cadmium

concentration is higher than the remediation value, while copper concentrations are higher at two of the sites.

- In this research, extremely high concentrations of cadmium and high concentrations of copper and zinc were detected at two locations. These two relatively small areas under the lawn have a higher proportion of sand and are porous, hence the leaching of cadmium through the soil profile over a longer period of time can potentially pollute a larger area. This can take place over a longer period of time.
- The removal and proper disposal of contaminated soil in this area should be the focus of additional research on these locations, and it should be done with the goal of finding a long-term solution to the problem.

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References

[17] G. Shi, Z. Chen, S. Xu, J. Zhang, L. Wang, C. Bi, J. Teng, Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China, Environmental Pollution 156 (2008) 251-260.

[18] Z. Long, Y. Huang, W. Zhang, Z. Shi, D. Yu, Y Chen, C. Liu, R. Wang, Effect of different industrial activities on soil heavy metal pollution, ecological risk, and health risk. Environ Monit Assess. 193(1) (2021).

[19] J. Briffa, E. Sinagra, R. Blundell, Heavy metal pollution in the environment and their toxicological effects on humans, Heliyon, 6(9) 2020.

[20] A. Kabata- Pendias, H. Pendias, Trace elements in soils and plants, 3rd ed., CRC Press, USA. 2001

[21] K.T. Semple, K.J. Doick,K.C. Jones, P. Burauel, A. Craven, H. Harms, Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. Environ Sci Technol, 38(12) (2004) 228A-231A.

[22] B.E. Davies, Lead, in: Alloway, B.J. (Ed.), Heavy Metals in Soils. Blackie and Son Ltd., 1995

[23] A. Vanek,L. Boruvka, O. Drabek, M. Mihaljevič,M. Komarek, Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry, Plant Soil and Environment 51(7) (2005) 316-321.

[24] "Official Gazette of RS", no. 88/2010 of November 23, 2010

[25] B. Houskova, L. Montanarella, Parent material as a source of natural background values in soils. European Commission-Joint Research Centre, 2005

[10] A. Mihailović, Lj. Budinski-Petković, S. Popov, J. Ninkov, J. Vasin, N.M. Ralević, M. Vučinić Vasić, Spatial distribution of metals in urban soil of Novi Sad, Serbia: GIS based approach, Journal of Geochemical Exploration, 150 (2015) 104-114.