30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

Editor
Prof. Dr Snežana Šerbula

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PREFACE

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 kept three areas in focus: ecology, environmental protection and sustainable development. The conference will be held on Mt Stara Planina in hotel Stara Planina, Serbia, 20–23 June 2023. The monograph is published on the occasion of the 30th anniversary of the conference. On behalf of the scientific and organizing committee, it is a great honor and pleasure to wish all the participants a warm welcome to the conference.

The monograph is published on the occasion of the 30th anniversary of the conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These Proceedings 103 papers from the authors coming from the universities, research institutes and industries in 11 countries: Australia, USA, Brazil, Spain, Portugal, Libya, Italy, Bulgaria, Bosnia and Herzegovina, North Macedonia, and Serbia.

As a part of this year's conference, the 5th Student Session – EcoTERS'23 is being held. We appreciate the contribution of the students and their mentors who have also participated in the conference.

The support of the Gold donor and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'23. The organizing committee would like to extend their appreciation and gratitude to the Gold donor of the conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the conference participants for their support to the EcoTER'23. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'23.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

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AVAILABILITY OF TOXIC ELEMENTS IN ROADSIDE SOILS (HIGHWAY 75, VOJVODINA, SERBIA): IS THERE ANY SIGNIFICANT CONTAMINATION RISK?

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Abstract

In this paper we provide the observations of a group of toxic elements Cu, Pb, Cr, Co, Ni, Pb, V, Zn, Sb, and Mo, in the soils that are sampled at the distances of 1 m and 5 m (two layers) from the road (Highway 75, north section). The observation of toxic elements are indicating a level of the existing contamination, availability and ecological risk. The mean values of the content of the elements Cr, Cu, Mo, Pb, Sb and Zn are lower with respect to the reference MAC values, whereas the mean and particular values of the content of Co, V, and Ni are higher. The content of the Sb, Pb, Mo, Cr, Cu, V and Zn reach higher values in the surface layer near to the road – at a distance of 5 m. The particular values of Pb, Zn and Cu only in the surface samples, at both distances, at two sampling localities, are indicating the presence of anomaly. However, the results of the content of the elements in most mobile forms are suggesting a presence of insignificant content of the toxic elements, which can easily become available to the environment and spread by streams or groundwater. The results of the Risk assessment code (RAC) confirms that there is a lower risk of contamination of the near-road environment by these toxic elements.

Key words: roadside soils, toxic elements, mobility, risk assessment.

INTRODUCTION

Traffic at regional highways and roads represents the main anthropogenic activity often inducing soil pollution. Traffic can frequently be a source of a number of toxic- or potentially toxic elements: Cu, Cd, Pb, Cr, Co, Ni, Fe, Mn, Pb, V, Zn, Sb, Hg, Ba, and Mo [1–3]. These elements can be emitted from different sources and traffic-related processes: wearing (tire, asphalt pavements, vehicle, banks, brake system etc.), spilling or combustion of fossil fuels, transportation of different materials, etc. The contamination levels of soils can be influenced by a number of factors such are: traffic frequency, vegetation, terrain configuration, wind direction, age of roads. Additionally, mobility of these elements largely depends on soil properties (granulometric composition, pH, cationic capacity, clay content, carbonates, and

organic matter) or forms in which these elements are released etc. Contamination of the surrounding soil by water is referring to the washing of the pavement accounting for activity of streams, draining, splashing, including the infiltration of these elements into deeper sections or layers of the soil [4]. Consequently, the impact of this source of the pollution increases significantly at different distances from roads and different depths. With an increase in the distance from the edge of the road, the concentrations the elements such as Zn, Cu, Pb and Cd decrease exponentially with the distance, reaching up to a distance of 100 m from the pollution source [5].

In the literature, availability of elements is observed as: 1) mobility – content of the elements available in the soil (in mobile forms); 2) bioavailability – the content available to the extent that it can be adopted by the plants, and 3) toxicity – content that causes a toxic effect in organisms [6]. For that reason, ecological effects of the toxic elements are strongly dependable on the content of the elements in mobile forms, rather than the total content [7]. The sequential extraction (SE) methods can be used to investigate the availability – mobility, bioavailability, as well as the risk assessment of the groundwater contamination (here defined as "geoavailability"). The following study discusses the influence of the traffic and road (Highway 75) as a potential pollution source affecting its roadside soils. We discuss a possible geoavailability, whereby we are assessing the risk of soil contamination with the following chosen elements: Cu, Pb, Cr, Co, Ni, Pb, V, Zn, Sb, and Mo.

MATERIALS AND METHODS

The investigated road samples are collected alongside the northern section of the Corridor "X" (Highway 75, Belgrade–Subotica, northern Serbia). Sampling of the soils was planned for fifteen localities (K1–K15) that are distributed alongside the highway itself. Sampling was performed prior its reconstruction in 2012. The soil samples are collected along a single side of the highway (K1–K10; direction Subotica–Belgrade), collected at a length of 20 km. The sampling across the second side of the highway was at a length of 4 km (K11–K15). Sampling was performed at the distance of 1 and 5 m from the edge of the road at all localities. The sampling at the distance of 5 m (or the place of near-road drainage system) was performed in the two separate layers with different near-subsurface depths: surface layer – T (with depths of 0–10 cm) and a subsurface layer – B (depths of 30–50 cm).

The SE method, which is applied onto 45 roadside soil samples, involves the five phases (F1–F5) [8]. The following study is observing the phases which are targeting the forms of the toxic elements: adsorbed and soluble (F1), included or occluded by Fe/Mn hydro-oxides and carbonates (F2). The concentration of the chosen toxic elements in the investigated soil samples is measured by applying the ICP/OES technique (Inductively Coupled Plasma/Optical Emission Spectrometry – iCAP-6500 Duo, Thermo Scientific, UK). The mineralogical characterization of the samples was performed by using the X-ray powder diffraction (XRPD) analysis (PHILIPS powder automatic X-ray diffractometer, PW-1710). The content of organic matter (%) is measured as a loss of ignition after heating the samples at 600°C, in duration of 4 h. The granulometric analysis subdivided the acquired soils samples

into the three grain fractions [[illegible]]: sandy (0.25–0.063 mm), silty (0.063–0.005 mm) and clayey (<0.005 mm) fraction.

RESULTS AND DISCUSSION

M[illegible]

The most abundant mineral in the soil samples collected out from the surface layer (T) and the subsurface layer (B) is quartz. Across the majority of the samples collected at all distances, the following minerals were detected: Clay-group minerals, Feldspars and carbonates (Dolomite and Calcite). The Clay minerals are mainly comprised of Illite, Sericite and Chlorite. Only in a few samples, Amphibole minerals are detected in the samples at the distance of 1 m (K4, K11 and K12), and 5 m (K7, K8, K10, K12, K13). Granulometric composition slightly changes with the distance and within the layers itself. Namely, the mean content of the sandy and clayey fractions (in %) has a slight decrease, whereas the silty fraction slightly increases. Within the layers the mean content of the silty and sandy fractions varies slightly, however, the presence of the clayey fraction is unchanged.

[illegible]

The results show that the mean values of the following toxic elements Cr, Cu, Mo, Pb, Sb and Zn are lower than the reference values (at the distances of 1 and 5 m from the road; Table 1). The reference values represent the maximum allowed values (MAC) defined by domestic regulative (Official Gazette 88/2010) and modified according to the content of clayey fraction (4.23%) and organic matter (5.1[illegible]%).

Table 1 *The mean $C_{average}$ and most available content $C_{(F1+F2)}$ of the toxic elements in the samples (at the distances of 1 and 5 m)*

D[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	N[illegible]	[illegible]	[illegible]	S[illegible]	M[illegible]
	$C_{average}$	24.0	50.0	66.3	32.2	27.8	[illegible]11	27.2	0.47	0.51
1m	St dev	13.4	68.4	42.6	17.[illegible]	13.3	2.14	8.08	0.48	0.20
	$C_{(F1+F2)}$	0.0[illegible]	0.27	3.04	<0.01	0.26	0.13	0.46	<0.05	<0.02
	$C_{average}$	20.[illegible]	27.3	56.7	24.[illegible]	27.4	7.04	2[illegible]7	0.86	0.52
5m (T)	St dev	[illegible].[illegible]7	26.3	32.5	7.7[illegible]	10.5	2.22	7.5[illegible]	0.35	0.21
	$C_{(F1+F2)}$	0.06	0.08	0.[illegible]7	<0.01	0.26	0.15	0.35	<0.05	<0.02
5m (B)	$C_{(F1+F2)}$	<0.02	<0.03	<0.01	<0.01	0.84	0.63	0.3[illegible]	<0.05	<0.02
	MAC*	20.7	5[illegible]5	70.7	58.6	14.3	3.21	17.2	3.00**	3.00**

*MAC – modified maximum allowed contents; **unmodified values.

The mean and particular values of the content of Co, V, and Ni suggest the presence of the contamination in the roadside soils both at surface and subsurface layer. However, some previous research of the agricultural soils in the area of Vojvodina, indicated an anomaly in the content of the toxic elements such are Co, Ni, and Cr. Especially at the localities that are near the Fruška Gora Mt. complex [10]. The maximum values above the MAC of Cu are registered in the samples K3, K14, K15 (1 m), K12, K14, K15 (5 m T)/K12, K15 (5 m B). The Pb and Zn content values overcome the MAC and are registered in K13, K14, K15 (1 m)

and K14, and K15 (5 m T). Nevertheless, the content of these elements in subsurface layer does not exceeds MAC values. Content of Cr exceeds MAC only in the sample K2 at a distance of 1m away from the road, whereas content of the Sb and Mo does not exceed MAC in any sample. Summary, the most contaminated localities K14 and K15 are placed near the Fruška Gora Mt. complex (exposed bedrock assembly). The localities are labeled as the points with extremely high concentrations in the surface samples of Pb (at the distance of 1 m – 218 and 214 $mgkg^{-1}$), Zn (179 and 135 $mgkg^{-1}$), including elevated values at the distance of 5 m Pb (57.3 and 113 $mgkg^{-1}$) and Zn (124 and 136 $mgkg^{-1}$). The values of Cu content are higher reaching 20.7 $mgkg^{-1}$(1 m – 57.1 and 48.7; 5 m – 40.9 and 41.5 $mgkg^{-1}$).The content of the elements Zn, Cu, Cr, Co in the surface layer are slightly decreasing with the sampling distances. In fact, the content of Pb decreases significantly, suggesting the presence of anthropogenic source, which is almost certainly the road activities itself. On the other hand, the mean content values of Mo, V, Ni are unchanged, being undependable of the distance. Thus, the influence of the road as their source of contamination is ruled out.

As the measure of the geoavailability we have taken into account the sum of the content of the elements occurring in the first two phases (F1+F2, Table 1). According to the results, it can be concluded that an insignificant content of the toxic element can become mobile and available to the environment, likely spreading by local streams or groundwater. That refers, in particular, for the most contaminated localities K14 and K15 (Pb_{F1+F2} 0.70 – 2.98 $mgkg^{-1}$; $Zn_{(F1+F2)}$ 6.87 – 30.2 $mgkg^{-1}$).

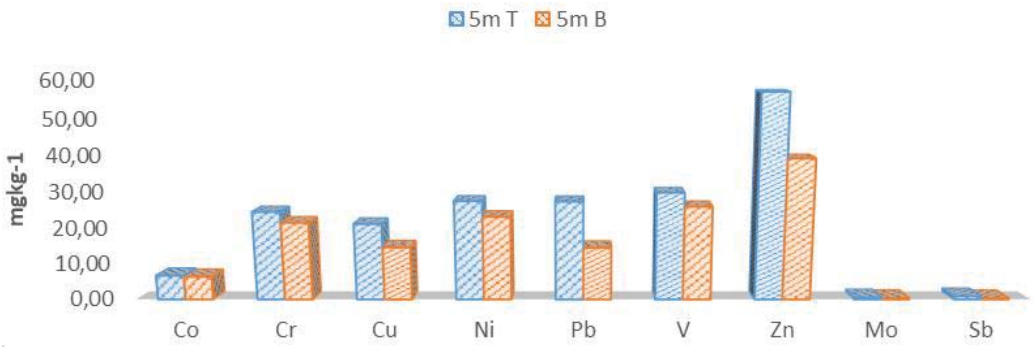

Figure 1 *Distribution of the mean content values of the toxic elements in surface soils (T) and subsurface (B) at the distance of 5 m*

The content of the toxic elements in the soils, at the distance of 5m from the road (Figure 1), shows that the availability and distribution can be observed in the following two aspects: (i) soil profile – due to a possibility of infiltration of contaminant in deeper strata (by rain and stream) and (ii) distribution between the mobile and the immobile forms within strata. The soil profile process is strongly influenced by the following conditions: granulometric composition and presence of components, such are clay minerals or content of organic matter. The granulometric composition, i.e. higher content of sand and larger grains, and lower clay fractions, or more precisely clay minerals, can produce a better permeability of water that is

drained from the highway and is infiltrating into deeper layers (in this case at a distance of 5 m).

The results of the mean values of the toxic elements (Figure 1) may indicate a different distribution of the content of the elements between the two layers. The values of the content of Sb and Pb in the surface layer have three- and two-times higher values. The □ilcoxon (□two-tail□) test is confirming that there is a significant difference between the values of Sb and Pb, as well as Mo, Cr, Cu, V and Zn. That further implies the enrichment is more pronounced in the surface layer of the soil, at a distance of 5 m from the road. One of the reasons can be a higher content of the organic matter, and a lower content of the sand, as well as the presence of clayey fraction in the surface samples. □specially it is referring to the sample K15, wherein the content of the clayey fraction reaches 8.0 □; sandy fraction 16.3□ and 9.86 □ of organic matter in the T layer. The values in the □ layer are: 9.50□ of clayey fraction; 4.84□ of sandy fraction; 5.11□ of organic matter. Thus, the values of Pb (24.3 $mgkg^{-1}$) and Zn content are much lower (51.5 $mgkg^{-1}$), by comparing those one in T layer, named above. □ith regards to the fact that the content of the toxic elements in the subsurface soil samples (T) are lower than in the subsurface (□), it is to expect that the values of the content of available□mobile forms of the elements have a lower amount as well. This hypothesis can be confirmed by the results of their content (F1+F2) (Table 1) in the soils of the □ layer. □rgo, in the most contaminated samples K14 and K15 in the subsurface the content values are: for Pb – 0.08 and 0.83 $mgkg^{-1}$; Zn – 7.48 and 6.87 $mgkg^{-1}$; Cu – 0.38 and 0.19 $mgkg^{-1}$, respectively. Additionally, these values are much lower than the MAC reference values.

Contamination risk assessment – Risk assessment code (RAC)

A degree of the potential mobility or availability of toxic elements, and risk of contamination in the investigated soil is represented by the RAC indices, calculated by the following formula:

$$RAC = \frac{C(F1+F2)}{C(F1+F2+F3+F4+F5)} x100 \quad (1)$$

In this equation, $C_{(F1+F2)}$ represents the sum of the contents in the phases F1 and F2 and $C_{(F1+F2+F3+F4+F5)}$, yielding the already observed total content of the elements.

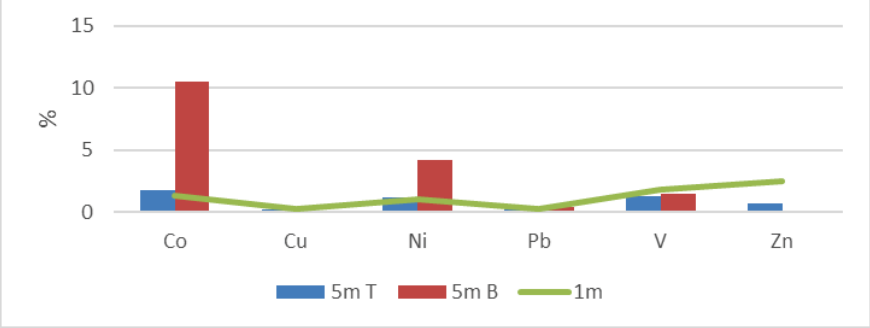

Figure 2 *Mean RAC values of the samples in surface layer (1m and 5m T) and subsurface layer (B)*

According to the results of the average RAC values of Pb, Zn, Cu (Figure 2), these elements are belonging to the group of contaminants having a lower risk of the contamination (RAC< 1). However, in the one of the most contaminated samples K14 (at the distance of 1 m) RAC values of Pb and Cu are indicating a moderate risk level (1.37 and 1.10). The RAC value of Zn, Cu and Pb at the distance of 5 m (T) evaluating a moderate risk level in the samples K14 (6.01) and K15 (5.06). In the case of Cu K14 (1.42) are the lower values for Pb in K15 (0.74). In the subsurface layer, elements like Zn and Pb were not detected in mobile forms, and a lower Cu was calculated at the locality K3 (0.60). A group with the moderate mobility level and ecological risk (1 < RAC< 10) includes the elements: As, Cd, Co, Ni, Zn and V (Figure 2). However, in this case, the content of the elements of the most mobile forms has significantly lower value than MAC. It should be noted here that the highest mean RAC value and mobility of Co and Ni was calculated in the samples collected out from the subsurface layer located at a distance of 5 m (Figure 2).

CONCLUSION

Traffic at regional highways and roads can be the principal source of a number of toxic elements or potentially toxic elements. These elements can often be spread in different manner within soils that is in the vicinity of the roads. These include deeper soil layers. In this paper, we provide the observations of a group of toxic elements in the soils that are sampled at the distances of 1m and 5m from the road, indicating the level of the existing contamination and ecological risk. The mean values of the toxic elements Cr, Cu, Mo, Pb, Sb and Zn have lower values relative to the reference MAC values. These include the particular values of Pb, Zn and Cu that are higher than the MAC in the surface samples. The most contaminated localities by these elements are K14 and K15, with extremely high values of Pb, and Zn. However, observing the results of the content of the elements in most mobile forms, at all localities, the conclusion is that insignificant content of the toxic element can become available to the environment and spread by streams or groundwater. The results of the mean content values of Mo, Cr, Cu, V and Zn; in particular Sb and Pb, indicate its different distribution between two layers. One of the reason can be the conditions – higher contents of the organic matter, a lower content of the sand, and the presence of clayey fraction in the surface samples. In the samples of the subsurface layers, the elements (except Ni and Co) are not detected in the mobile forms or the contents are much lower than MAC. At last, study shows that there is no risk or there is a low risk of the contamination of the environment with Pb, Zn, Cu in soils at the investigated surface and the subsurface roadside soils. This goes even in the localities with a highest content of these elements. The RAC values indicate a moderate ecological risk of the contamination of the soils by As, Cd, Co, Ni, Zn and V. Having said that, the content of the elements of the most mobile forms are significantly lower than MAC, making the risk assessment grouping debatable.

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