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EcoTER'22

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Prof. Dr Snežana Šerbula

21-24 June 2022, Hotel Sunce, Sokobanja, Serbia

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ENVIRONMENTAL RISK ASSESSMENT OF PTES IN AGRICULTURAL SOILS AFFECTED BY INDUSTRIAL ACTIVITIES IN BELGRADE

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Abstract

This study investigated the effects of proximity to different contamination sources, such as a coal mine, thermal power plants and fly ash disposal sites, in three Belgrade municipalities (Obrenovac, Lazarevac and Surčin) on agricultural soil contamination with As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn. Concentrations of As, Cr, Cu, Ni, Pb and Zn were within the reference range for European soils and did not exceed the limit thresholds set by national legislation, except for Cr in Lazarevac and Ni at all the examined sites. The highest concentrations of As, Cr, Cu and Ni were measured in soil from Lazarevac, with the largest differences determined for As, Cr, and particularly Ni. The high Ni content in soil samples in Lazarevac indicates potential risk from the toxic effects of this element in the soil, close to the mine, the Kolubara-A thermal power plant and the ash dump. However, overall, values obtained for ecological risk indices were low, meaning that there is negligible enrichment and contamination of soil with the tested elements at the study sites and, therefore, no potential ecological risk to the environment or agricultural crop production.

Keywords: industrial pollution, potentially toxic elements, agricultural soils, pollution indices

INTRODUCTION

Soil contamination is one of the greatest issues in terms of threats to soil resources both in Europe and globally [1]. Although the distribution of contamination sources varies from country to country, industrial activities are responsible for the contamination of more than 60% of European soils and, in terms of contamination from local sources, data from the European Environment Agency indicate that today there are more than 650,000 registered sites where polluting activities occur in national and regional inventories [2]. In Serbia, the latest update to the Cadastre database shows that 709 contaminated sites have been recorded [3].

Anthropogenic activities, such as mineral resource exploitation, energy production, metal processing and smelting, and industrial waste disposal, have been proven to be the primary sources of pollution from potentially toxic elements (PTEs) [4,5]. These activities contribute considerably to polluting metal levels in soils, in particular agricultural soils in the vicinity of industrial facilities, resulting in contamination and a decrease in soil quality [6]. Pollution from PTEs has become a critical issue as they can accumulate and be retained in soils for a long time. Once the content of elements exceeds environmental quality standards, they pose potential ecotoxic risks [7]. Hence, soil pollution indices can provide information on soil quality and degree of contamination for each soil sample, based on individual PTE levels [8–10].

Previous research indicates the geochemical origin of PTEs in Serbian soils [11], as is the case with most soils in the world [7]. However, soil contamination with PTEs is becoming more serious and widespread, particularly in industrial centres. In Belgrade, the problem of pollution is mainly related to anthropogenic activities. Namely, on the territory of the City of Belgrade, there are three thermal power plants (‘Nikola Tesla-A’ and ‘Nikola Tesla-B’ in Obrenovac and ‘Kolubara-A’ in Lazarevac), opencast coal mines, and large areas of ash deposit sites, which pose a risk to the environment, food production, and the health of residents.

This study aimed to quantify As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn concentrations in agricultural soils and to estimate the potential environmental risks from soil pollution in three Belgrade municipalities. Contamination levels and the potential ecological risk to the environment were assessed using the contamination factor (Cf), degree of contamination (Cdeg), potential ecological risk (Er^i), and the potential ecological risk index (RI).

MATERIALS AND METHODS

Site description and soil sampling

Soil sampling was conducted in three Belgrade municipalities: in fields close to the fly ash disposal site at the ‘Nikola Tesla-A’ thermal power plant, located in the municipality of Obrenovac (Krtinska village, 44030 ’N, 19058’ E; average altitude 80 m), in the municipality of Lazarevac (Sokolovo village 20019’7’’ E, 44028’32’’ N, average altitude 93 m), and in the municipality of Surčin (Jakovo village, 20015’45’’ E, 44044’35’’ N, average altitude 75 m). Soil at each sampling site was sampled from six individual sampling points from a depth of 0-10 cm. The samples were dried to a constant weight, ground, and sieved through a 2 mm sieve.

Soil sample preparation and measurement

To determine total PTE content, soil samples were digested in a microwave oven (CEM, 39 MDS-2000), using the USEPA 3052 method [12]. PTE concentrations in soil were measured using optical emission spectrometry for simultaneous multi-element analysis (ICP - OES, Spectro Genesis). The content of chemical elements was expressed in mg kg^{-1} of the dry sample. The analytical procedure was validated using standard reference material (Loam soil - ERM - CC141), which underwent standard digestion procedures to control the quality of the laboratory protocol, and an accuracy of 100±15% was achieved. All samples were prepared in three repetitions and standard deviation was less than 10%. The detection limits were: As-0.007, Cd-0.001, Cr-0.001, Cu-0.014, Fe-0.018, Hg-0.002, Mn-0.009, Ni-0.018, Pb-0.004, and Zn-0.001.

Contamination and ecological risk assessment

Contamination factor (Cf)

An assessment of soil contamination can be conducted using the contamination factor (Cf). Cf is the ratio of the concentrations of the tested element (C_i) and its pre-industrial values, i.e., background (C_b). Background values of PTEs in the study area were proposed by Mrvić *et al*. [11,13] and Knežević [14]. Cf is calculated using Equation (2):

$$Cf = C_i/C_b \tag{2}$$

Degree of contamination (Cdeg)

The degree of contamination (Cdeg) represents the sum of the contamination factors and is calculated using Equation (3):

$$C_{deg} = \sum_{i=1}^{n} Cf \tag{3}$$

Potential ecological risk (E_r^i)

The potential ecological risk (E_r^i) of a particular PTE is the product of the Cf and the toxic response factor (T_r^i) of a particular PTE and is calculated using Equation (4):

$$E_r^i = T_r^i \times Cf \tag{4}$$

T_r^i reflects the level of toxicity and biological sensitivity to contamination with a particular element. T_r^i values are as follows: As-10, Cr-2, Cu-5, Pb-5, Ni-5, and Zn-1 [15].

Potential Ecological Risk Index (RI)

The Potential Ecological Risk Index (RI) represents the sum of E_r^i and is calculated using Equation (5):

$$RI = \sum_{i=1}^{n} E_r^i \tag{5}$$

The recommended classifications for all factors and indices are described in Pavlović *et al.* [10].

RESULTS AND DISCUSSION

The combustion of coal in power plants results in the emission of a wide range of pollutants including PTEs, which, once released, reach the surrounding soil, where they are deposited and remain for years [5,16,17]. The results of this study showed that Cd and Hg content in the studied soils were below the detection limit. The highest average concentrations of the tested PTEs were measured in soil from Lazarevac, with the largest differences determined for As and Cr, and in particular Ni. Concentrations of As, Cu, Pb and Zn, were at background levels for European soils [18] and did not exceed maximum allowable concentrations (MAC) as set by national legislation [19] (Table 1). Somewhat higher concentrations of Cr were measured in soil from Lazarevac, where the content was above background and MAC values (Table 1). These elevated Cr concentrations may be due to the thermal power plant, i.e., the dispersion of ash particles from ash dumps to agricultural fields, with this ash characterized by increased levels of various PTEs [20]. A similar study in

Kostolac (Serbia) also revealed Ni, Cu and Cr concentrations above the prescribed limits [17]. It was further found that average Ni concentrations at all the sites exceeded background values for European soils and MAC, with concentrations of this element in soil from Lazarevac significantly higher (up to 134.82 mg kg^{-1}), which indicates a potential risk from the toxic effects of this element. However, such high Ni concentrations do not necessarily indicate that it is of predominantly anthropogenic origin. Namely, previous studies by Mrvić *et al.* [11,13] have shown that Ni and Cr in Serbian soils are mainly of geochemical origin, i.e., they are naturally found in these soils in elevated concentrations. Numerous soil surveys conducted in central parts of Serbia, including Belgrade, have concluded that the origin of Ni and Cr in soil is determined to a great extent by the geological substrate [21–23]. However, the proximity of open pit mines, coal combustion plants, and ash deposit sites can also contribute significantly to an increase in Ni content in surrounding agricultural soils. Since Pb and Zn content in the tested soil samples was uniform and did not exceed the MAC, it can be concluded that these elements do not represent a limiting factor for the cultivation of agricultural crops on the examined soils.

The results show that there is generally no risk in terms of elevated PTE concentrations, except for Ni. In this sense, potential risk occurs in soils in the municipality of Lazarevac, where, due to the proximity of the mine, ash deposit site and 'Kolubara-A' thermal power plant, there is a risk of the accumulation of PTEs in surrounding agricultural soils.

***Table 1** Average content of PTEs (mg kg^{-1} d.w.) in agricultural soils in the municipalities of Obrenovac, Lazarevac and Surčin. Values are presented as mean and standard deviation*

Locality/PTEs	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Surčin - Jakovo	7.093 (1.140)	68.278 (0.776)	34.106 (0.514)	47933.117 (617.654)	711.979 (14.924)	96.050 (4.465)	59.691 (2.637)	85.019 (3.080)
Lazarevac - Sokolovo	13.370 (0.903)	107.011 (17.517)	36.312 (1.251)	46526.27 (5362.197)	613.031 (44.228)	134.827 (7.643)	57.673 (12.557)	84.337 (5.512)
Obrenovac - Krtinska	5.264 (0.928)	61.932 (2.388)	31.743 (0.478)	42006.42 (573.636)	470.323 (5.606)	98.716 (1.071)	52.957 (1.762)	80.543 (4.222)
Background values in European soils[a]	/	75–100	50–100	/	/	50–70	70–100	150–200
MAC[b]	25	100	100	/	/	50	100	300
Background[c] values	10.4	61	30	24771	489.29	72	37	68

[a]Background values in European soils [20]; [b]Maximum allowable concentrations of PTEs [21]; [c]Background values of PTEs in the studied soils (method: Median + 2MAD) [12,14,15].

Contamination levels and ecological risk assessment

PTE pollution is a notable threat to agricultural production and, in soils, can cause potential ecological risks [24]. The results of Cf and Cdeg (Figure 1) indicate a low degree of contamination in the soils from Surčin and Lazarevac, although the potential risk from contamination is more pronounced in Lazarevac. Categorized according to E_r^i and RI, soils in the examined localities can be classified as soils with low potential ecological risk.

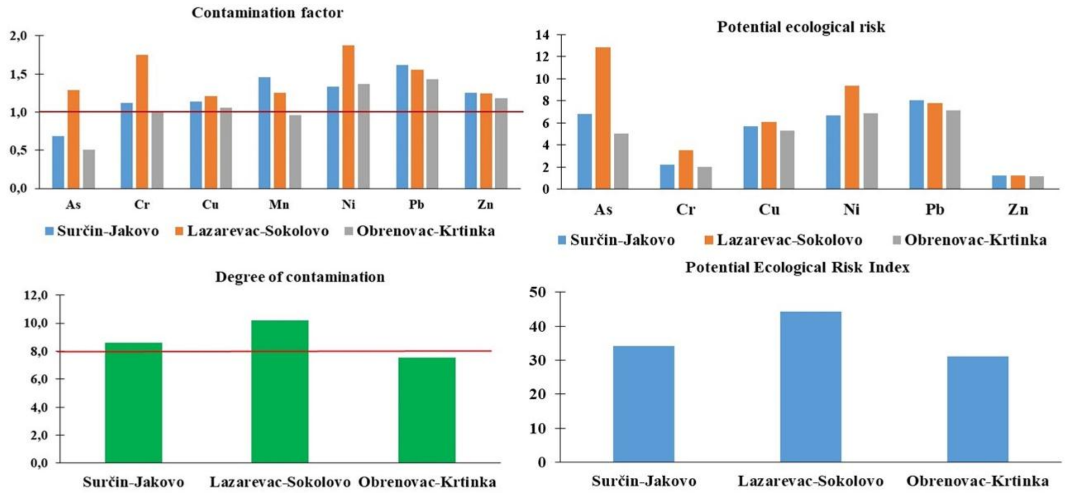

Figure 1 *Contamination level and ecological risk assessment of PTEs in the examined soils using the contamination factor (Cf), degree of contamination (Cdeg), ecological risk index (E_r^i), and potential ecological risk (RI)*

CONCLUSION

Concentrations of all the tested PTEs were within the range of background values for European soils and did not exceed the MAC set by national legislation, except Cr in Lazarevac and Ni at all the localities. In terms of localities, the highest As, Cr, Cu and Ni concentrations were measured in soil from Lazarevac, with the largest differences determined for As, Cr, and particularly Ni.

The elevated Ni content in all the tested samples, but particularly in Lazarevac, indicates the potential risk from the toxic effects of this element in soil, in the vicinity of the mine, the 'Kolubara-A' thermal power plant, and the ash deposit site in the municipality of Lazarevac. However, overall, the values obtained for ecological risk indices were low, meaning that there is negligible enrichment and contamination of soil with the tested elements at the study sites and, therefore, no potential ecological risk to the environment or agricultural crop production.

This study could contribute to knowledge on the accumulation of PTEs in soil, especially in agricultural soil. In the vicinity of industrial facilities in large urban and industrial areas, which require safe agricultural products, it is necessary to assess the environmental risk and form strategies for dealing with this risk.

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