ASSESSMENT OF STRONTIUM, RUBIDIUM AND SCANDIUM STATUS IN SOILS AFFECTED BY SOLID WASTE DEPOSITS

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ABSTRACT

The aim of the study was to assess the level of contamination of soil with strontium, rubidium and scandium in the solid waste deposits. The study was performed on soil samples collected from Moldova Noua, southwest of Romania, an area with historical anthropogenic history. The soil analysis was performed using X-ray fluorescence (XRF). The samples were collected from five collection points using a random pattern from around the illegal waste deposit and all analyses were performed in triplicate. To assess the influence of wastes on the soils concentration levels of strontium (Sr), rubidium (Rb) and scandium (Sc), were calculated contamination factors (CF), and pollution index (PI_L) by reporting the concentration of the investigated elements of the upper earth crust concentrations and geo-accumulation index (I_{geo}) calculated by reporting the elements concentration values to a control sample, used as reference. The reference sample was collected from an area close to the waste deposit but located in a protected green area. The results show that from the investigated elements, scandium is the element of concern, the soil presenting a moderate contamination level with this element.

Keywords: *heavy metals, contamination factors, pollution index, geo-accumulation index*

INTRODUCTION

The rising number of illegal waste dumps represents a global problem and is the result of the increase of waste production correlated with the ever-growing population. Even if official waste disposal sites are available, illegal waste dumps occur everywhere around the world, most commonly on the periphery of colonized areas, forest margins, as well as at other places, contaminating the environment and degrading land [15]. The metal concentration and behavior of metals associated with various industrial, mines or municipal wastes in soil systems is much higher and affects metal mobility, being decidedly dependent on the waste type. The modifications in time of the environmental conditions, such as changes in pH, the

degradation of the organic waste matrix, or soil solution composition, may modify metal mobility [10].

The aim of the study was to assess the level of contamination of soil with strontium, rubidium and scandium on disposed solid wastes. Contaminations are less investigated in rubidium, strontium and scandium soils. Compared to the number of studies related to hazardous heavy metals, strontium occurs in nature, is estimated to approximately 320 ppm in the upper Earth's crust [12]. Rubidium is an alkali metal, almost as abundant as zinc. According to Rudnick et al, in the upper earth crust are approximately 84 ppm rubidium [12]. Rubidium is easily taken up by plants, similar to potassium and generally is concentrated in flowers and young leaves [6]. It is appreciated by a recent study as the best predictor variable for estimating the clay content and salinity of soils [14]. Scandium is a naturally occurring element in the soil and its concentrations vary across geographic regions. In the earth's crust, Sc is varying from 16 ppm [8] to 25 ppm [2]. The soils as well as the natural and/ or mineral water [7] have a specific natural content of metal cations, which depend on the background concentrations specific to the investigated area. The control area was chosen, as it is a protected area and due to its natural potential and ecological value. The Romanian territory shelters a huge variety of habitats, of national as well as European interest.

MATERIALS AND METHODS

Description of the Study Site: The investigated area is located in the southwest of Romania, close to Moldova Noua city and close to the Danube.

The study was conducted on soil samples from an area where an illegal waste deposit was identified and compared to soil samples from a vegetation area, practically a protected area, which is considered as a control area. All samples were collected using a random pattern from around the waste deposit (Figure 1).

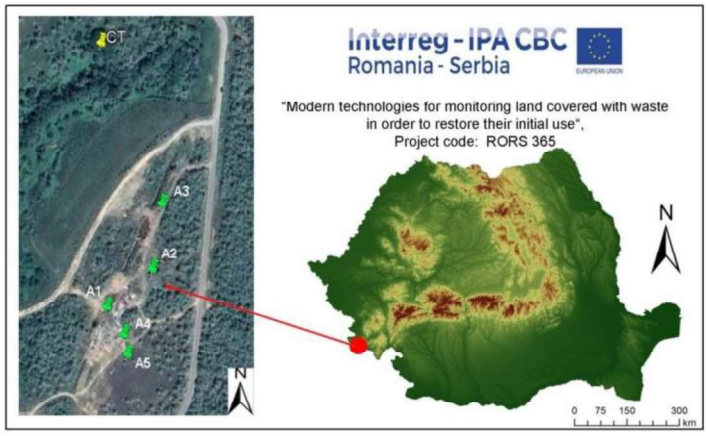

Fig. 1. *Map of the investigated experimental area [4], [5]*

Legend: A1, A2, A3, A4, A5 - Soil sampling collection points, CT – Soil sampling control point

The soil samples was collected from the topsoil (0-20 cm depth) using a standard auger. For evaluating the soil status of the experimental area (Table 1) were established five collection areas (A1, A2, A3, A4, and A5). From each collection area were sampled three replicates, which were thoroughly mixed to obtain a homogenous soil mixture.

Preparation of soil samples for analysis

For the accuracy of the analysis results, the fragments of leaves and small stones were removed and the soil samples were dried until the water content became less than 10%, and ground into a fine powder (~ 100μm). For XRF analysis, the soil sample is analyzed in a sample cup with a thin built-in polypropylene film.

Table 1. *GPS Stereo coordinates of the soil samples collection points*

Samples Area	Sample code	x	y
Illegal waste deposit	A1	362637.919	234144.254
	A2	362679.914	234201.804
	A3	362754.786	234216.725
	A4	362605.614	234163.640
	A5	362582.523	234167.162
Control sample, area with vegetation	CT	362947,015	234151,003

Legend: A1, A2, A3, A4, A5 - Soil sampling collection points, CT – Soil sampling control point

Soil analysis

The analysis of the soil samples were performed using X-MET8000 - X-Ray Fluorescence Analyzer. The apparatus is factory calibrated. All analysis were done in triplicate and result were shown as average ± SD

Contamination indices

Soil contamination with strontium, rubidium and scandium, was evaluated using pollution indices (contamination factor, pollution index of soil loadings (PI_L) and geo-accumulation index (I_{geo})) presented in Table 2. Soil Contamination Factor (CF) represents a quantification of the contamination level relative to upper earth crust composition of the investigated metals as shown in Table 2.

In this paper, we used separately, both, the concentration of elements in the Earth's crust as well as concentration of the control samples as reference values. The concentration of elements in the Earth's crust are presented in Table 3 [1], [13].

The Geo-Accumulation Index (I_{geo}) of a sample site was calculated according to the relation shown in Table 2 [9]. The classifications of contamination level based on CF, PI_L and I_{geo} are presented also, in Table 2.

Statistical Analysis

The experimental data were statistically evaluated using Excel 2007, PAST Version 2.17c and Statistica 13.5.0.17 Tibco Software Inc.

Table 2. *The classification of pollution level based on soil pollution indices*

Crt. No	Pollution index and classification of pollution level	Formula	Parameters
1	Soil Contamination Factor (CF) [3]: • CF < 1, low pollution; • 1<CF<3, moderate pollution; • 3<CF<6, high pollution; • CF>6, very high pollution [1]	$CF^i = \frac{C^i_{0-1}}{C^i_n}$	C^i_{0-1} = the mean content of investigated metals from three to five sampling sites C^i_n = the concentration level of the individual metal before depositing waste, practically the concentration of elements in the Upper Earth's crust
2	Pollution Index of Soil Loadings (PIL) [13] • PI_L< 1 no contamination with the studied metals; • PI_L= 1, baseline levels of pollutants are present • PI_L>1 metal concentrations are above the permissible level, which is producing a deterioration of the soil quality	$PI_L = (CF_1 \cdot CF_2 \cdot \ldots \cdot CF_n)^{1}$	n = the number of studied metals (three in this study) and CF is the contamination factor calculated as described $CF_1, CF_2, \ldots, CF_n$ are the contamination factors calculated as described before
3	The Geo-Accumulation Index (I_{geo}) [9] • $I_{geo} \leq 0$ no contamination with the studied metals; • $0 < I_{geo} \leq 1$ mild to moderate contamination • $1 < I_{geo} \leq 2$ moderate contamination • $2 < I_{geo} \leq 3$ moderate to high contamination • $3 < I_{geo} \leq 5$ high contamination • $I_{geo} \geq 5$ exceptionally high contamination	$I_{geo} = \log_2 \frac{c^i_n}{k \cdot c^i_{ref}} = \log$	c^i_n = the measured concentration of heavy metals in the soil (mg/kg), c^i_{ref} = The background concentration of the metals, specific to the studied area Constant k = 1.5 is a correction coefficient that specifies the influence of natural fluctuations and of anthropic sources.

Table 3. *Concentration of elements in the earth's crust [12]*

Sample site	Symbol	Heavy metals concentration (ppm)		
		Sr	Rb	Sc
Upper Earth Crust	UEC	370	90	22

RESULTS AND DISCUSSIONS

The level of concentrations of the investigated soil samples are presented in Figure 2. The concentrations of Sr, Rb and Sc in the upper earth crust are appreciated in accordance with Rudnick and Gao, 2003 [12]. As we can observe Rb content is much higher in the upper earth crust and slightly higher in the control sample, which was sampled from an area with vegetation, registered as protected area. The samples with the codes A1-A5 are soil samples collected from an area where illegal wastes are deposited. Comparing the obtained heavy metals concentration values, it is visible that the highest scandium content (202 ppm) is shown by soil sample A2, while for strontium (370 ppm) and rubidium (90 ppm), the highest concentration values mentioned, are those in the upper earth crust [12]. The transfer factors for the evaluated heavy metals for all sampling areas are presented in Table 4.

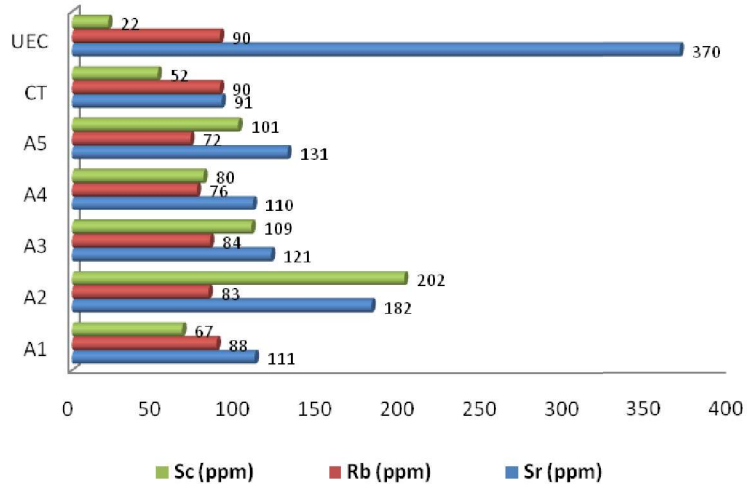

Fig. 2. *Mean values of the concentration of Sr, Rb and Sc in soil samples*

Legend: A1-A5 and CT, soil sample codes, CT – soil control sample, UEC – upper earth crust concentration values.

Table 4. *Individual Transfer Factors (CF) and Pollution Index of Soil Loadings (PI_L) for Sr, Rb and Sc in soil*

Sample code	CF_E (Sr)	CF_T (Sr)	CF_E (Rb)	CF_T (Rb)	CF_E (Sc)	CF_T (Sc)	PI_L
A1	0.35	1.22	1.05	0.98	4.79	1.29	1.209
A2	0.57	2	0.99	0.92	14.43	3.89	2.01
A3	0.38	1.33	1	0.93	7.79	2.10	1.43
A4	0.34	1.21	0.90	0.84	5.71	1.54	1.21
A5	0.41	1.44	0.86	0.8	7.21	1.94	1.36
CT	0.28	1	1.07	1	3.71	1	1.04
UEC	1	-	1	-	1	-	-

Legend: A1-A5 and CT, soil sample codes, CT – soil control sample, UEC –upper earth crust, CF_T= CF of the metal reported to the background value, CF_E = CF of metal reported to the earth crust value

The transfer factors of the individual metals were calculated both in respect to control (CF_T) as well as to the concentration of elements in the Upper Earth's crust (CF_E). In both situations, the soil samples prove to be contaminated with scandium. The contamination factors for Sr, Rb and Sc were calculated by reporting the individual concentration media for each area to two reference concentration values (CT and UEC) in order to identify the historic pollution due to mining activities of Moldova Noua area and the new pollution area created by depositing the solid wastes. The mines present in Moldova Noua area have a long history of (the Stratigraphic age of Late Cretaceous–Paleocene) Porphyry copper deposits [11].

Based on the recommendations of Ahamad et al, 2020 (Table 2), CF_E (Sc) shows high ($3<CF<6$) and very high pollution ($CF>6$), while CF_T(Sc) shows moderate ($1<CF<3$) to high pollution ($3<CF<6$). CF_E (Sr) shows low pollution ($CF < 1$) while CF_T(Sr) shows moderate pollution, which might confirm that strontium is less in the soil of Moldova Noua area compared to the concentration specific to the upper earth crust. CF_E(Rb) and CF_T(Rb) are similar. Irrespective of the concentration values used to calculate CF, the pollution level of Scandium is high.

PI_L for Sr, Rb and Sc in soil was calculated only for CFT (Figure 3), in order to evaluate the pollution level created as a result of solid waste deposits.

Fig. 3. *Graphical representation of Pollution Index of Soil Loadings (PI_L) for Sr, Rb and Sc*

Legend: A1-A5 and CT, soil sample codes, CT – soil control sample, PI_L - Pollution Index of Soil Loadings

PI_L shows that the entire investigated area poses a high level of pollution (PI_L > 1), even for the control area, due to the elevated level of scandium in the soil, which is causing deterioration of the soil quality.

The geo-accumulation index shows moderate contamination ($1 < I_{geo} \leq 2$) for scandium and zero contamination for strontium and rubidium (Table 5).

Table 5. *Geoaccumulation indices of Sr, Rb and Sc, for the collected soil samples*

Sample code	Igeo(Sr)	Igeo(Rb)	Igeo(Sc)
A1	-0.2983	-0.6174	-0.2193
A2	0.4150	-0.7018	1.3728
A3	-0.1739	-0.6845	0.4828
A4	-0.3114	-0.8289	0.0365
A5	-0.0593	-0.9069	0.3728
CT	-0.5850	-0.5850	-0.5850

Legend: A1-A5 and CT, soil sample codes, CT – soil control sample, Igeo – Geo-Accumulation Index of soil

CONCLUSION

The investigated soil samples, collected from the area with solid waste deposits shows a lower content of rubidium and strontium compared to the normal concentrations of these metals in the upper earth crust, but comparable with the control samples. On the other hand, scandium is present in big quantities in the soil covered by wastes, and less in the control samples. The pollution indices, CF, PI_L and Igeo demonstrate that the pollution with scandium is degrading the soil quality and is a cause for concern.

ACKNOWLEDGEMENTS

All authors are principal authors and have contributed evenly to this paper. Corresponding author: despinabordean@usab-tm.ro.

Interreg - IPA CBC Romania - Serbia

This research paper was funded by Interreg–IPA Cross–border Cooperation Romania-Serbia Programme - financed by the European Union under the Instrument for Pre-accession Assistance (IPA II) and co-financed by the partner states in the Programme, through the project "Modern technologies for monitoring land covered with waste in order to restore their initial use", 2019–2021, code e-MS: RORS 365.

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