

## ASSESSING THE SOIL QUALITY OF A FORMER INDUSTRIAL AREA, USING POLLUTION LOAD INDEX AND ENRICHMENT FACTOR

Ana Moldovan<sup>1,2</sup>, Anamaria Iulia Török<sup>1</sup>, Băbălău-Fuss Vanda<sup>1</sup>, Valer Micle<sup>2</sup>

<sup>1</sup> INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath Street, 400293 Cluj-Napoca, Romania;

<sup>2</sup> Technical University, Faculty of Materials and Environmental Engineering, 103-105 Muncii Boulevard, 400641 Cluj-Napoca, Romania  
e-mail: ana.moldovan@icia.ro

### Abstract

Soil degradation involves the decline of soil quality and fertility due to the acidification, salinization or chemical contamination of soils from agricultural or industrial sources. In this study, spatial changes of topsoil quality were investigated in the lower basin of Arieș River, an area with a wide history of industrial activities. A sampling campaign has been done along the lower Arieș catchment, during a rainy season (November 2019). The topsoils pH and metals content were analysed. In order to assess the quality of the soil samples, soil contamination index  $C_d$  and enrichment factor  $EF$  were computed. The results of the present study showed that the topsoil samples from the former industrial sites had a high Cu, Pb and As content. According to the  $C_d$ , one sample presented a level of concern due to high level of heavy metals content, and  $EF$  assigned a considerable degree of soil enrichment - in case of two topsoil samples.

### Introduction

Intensive anthropogenic land use activities have a negative impact on the land ecosystem and can lead to the land degradation. The quality of the soil is given by its capacity to function within land-use and ecosystem boundaries, with a balanced chemical composition (Fusaro et al., 2018, Paz-Kagan et al., 2014). The soil is an environmental segment that can store various pollutants, a witness of the historical anthropogenic activities with negative effects on the quality of the environment. Hence, it is crucial that methodologies assessing impacts caused by historical and actual anthropogenic activities to use related impacts in their frameworks (Turran et al., 2019, Ma et al., 2020). To assess soil quality, indicators have been used, evaluating different soil functions, utilizing chemical, physical, and biological attributes (Chavaz et al., 2017).

The present study aims to establish the current quality of the six topsoils sampled from the lower Arieș River basin. Their quality was assessed with the help of two indices: soil contamination index  $C_d$  (Rehman et al., 2020) and enrichment factor  $EF$  (Siddiqe et al., 2020).

### Experimental

#### 1. Study area

The Arieș River catchment is an area affected by past mining and industrial activities. Although, in the last decade, most of the anthropogenic activities were stopped, the historical pollution is still leaving their mark on the soil quality (Levei et al., 2013, Butiuc-Keul et al., 2012).

The lower basin begins at the border between Cluj and Alba counties and continues until Arieș River joins the Mureș River and overlap entirely to the Transylvanian Depression. The geomorphological substrate of the lower basin is a clay rich area (Costea, 2009).

The history of the studied area is characterized by intense industrial activities, like extractive, chemical (Turda) and metallurgical industries (Câmpia Turzii). In the present, the land use is primarily managed for farming activities in the lower reaches of the Mures river (Frink, 2009).

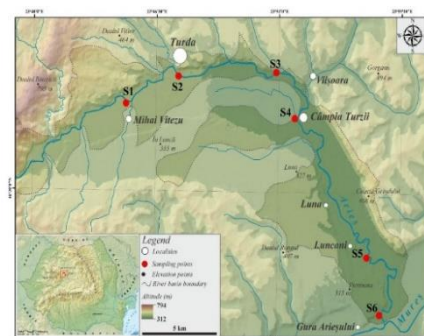


Figure 1. The lower Arieș River basin and sampling points

### 2. Sampling and testing

Soil samples were collected at the 0.10–0.20 m depths, from 6 different areas (Figure 1), in November 2019. Sampling locations were chosen with respect to the history of anthropic activities carried out in the area.

The soil samples were homogenized, dried at 105 °C for 24 h and passed through a 4 mm sieve. To analyze the pH, the samples were dispersed in water with a soil/water ratio of 1:5. The samples pH was determined using a 350I multiparameter (WTW). 3 g of soil samples were digested in a mixture of HCl and HNO<sub>3</sub> (3:1) prior to measure the concentrations of metals. Fe, Ni, Cr, Cu, Zn, Cd, Pb, Na, Mg, K, Ca, Mn, Ba, Al, Sr, P concentrations were measured using Optima 5300 DV Spectrometer (Perkin Elmer), while As concentration was determined by ELAN DRC II Spectrometer (Perkin-Elmer). All chemicals were of analytical grade (Merck).

### 3. Soil quality assessment

Two methods to calculate the potential ecological risk were used to evaluate the current quality of the soil samples collected in 2019. To identify the contributions of the heavy metals to soil pollution, soil contamination index  $C_d$  (Eqs. 1-2) and enrichment factor  $EF$  (Eqs. 3-4) were assessed.

$$C_f = \frac{C_{Ai}}{C_{Ni}} - 1 \quad (1)$$

$$C_d = \sum_{i=1}^n (C_f) \quad (2)$$

Where,  $C_{Ai}$  is the value of the concentration of  $i^{\text{th}}$  metal ions in the analyte and  $C_{Ni}$  represents the maximum allowable concentration (MAC) of the elements, according to the national legislation (Law 756/1997).  $C_f$  and  $C_d$  results higher than 1.0 indicate a powerful contamination with metals (Ullah and Muhammad, 2020).

$$EF = \frac{Re_{sa}}{Re_{bk}} \quad (3)$$

$$PER = \sum_{i=1}^n EF \quad (4)$$

where,  $Re_{sa}$  is the value of the concentration of  $i^{\text{th}}$  metal ions in the analyte and  $Re_{bk}$  is the value of the concentration of  $i^{\text{th}}$  metal ions in the background sample (Kabata-Pendias, 2011, Kukdrer et al., 2014).

## Results and discussion

### 1. Descriptive statistics of heavy metal concentrations

Soil screening values for pH and metal content are presented in Table 1. The tested soil samples pH was neutral (in the range of 7.5 to 8.0 pH units). The high exceeding rates of heavy metals comparing with intervention threshold for sensitive soil indicated an obvious accumulation in topsoil, especially for Cu, Pb and As. The concentration of Cu was higher than the intervention concentration in S2 and S3, while the Pb and As admissible concentrations were exceeded in the soils sampled from S2 and S4. All other metals content fall within the permissible guideline values. Romanian environmental legislation has not established limiting values for Fe, Na, Mg, K, Ca and Al to soil quality, due to the natural presence of these elements in soils.

Table 1. The analyzed parameters in the tested soil sample

		<i>S1</i>	<i>S2</i>	<i>S3</i>	<i>S4</i>	<i>S5</i>	<i>S6</i>	<i>ITSS*</i>	<i>BK**</i>
<i>pH</i>	pH units	8.0	8.0	7.5	7.8	7.8	7.7	-	-
<i>Fe</i>		10287	10428	10785	10677	10912	10426	-	-
<i>Ni</i>		31.6	44.8	42.4	38.5	30.8	24.5	100	15–50
<i>Cr</i>		28.4	43.1	37.2	35.8	48.2	26.1	300	42–200
<i>Cu</i>		146	216	204	175	87.3	82.8	200	11–13
<i>Zn</i>		202	305	291	356	104	111	600	31–90
<i>Cd</i>		<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	5.00	-
<i>Pb</i>		22.3	157	58.3	117	16.8	33.2	100	10–35
<i>Na</i>		410	462	517	427	126	123	-	-
<i>Mg</i>	mg/kg	2456	2103	2871	2603	2737	2503	-	-
<i>K</i>		3274	3311	4279	3612	1654	1216	-	-
<i>Ca</i>		10062	1345	17532	12341	4276	5062	-	-
<i>Mn</i>		785	1127	1254	1096	513	349	2500	310–1007
<i>Ba</i>		100	84.7	124	97.2	49.8	49.7	625	315–500
<i>Al</i>		15262	19473	20004	18006	15312	9818	-	-
<i>Sr</i>		44.3	52.4	75.8	61.6	20.8	13.4	-	-
<i>P</i>		325	265	85.6	192	236	174	-	-
<i>As</i>		18.2	25.1	24.5	27.1	17.2	21.1	25	-

\* Intervention threshold for sensitive soils according to Law 756/1997

\*\* Heavy metal concentration (mg/kg) in background soils of the world (Semenkov et al., 2020)

Comparing with the metal concentration background soils of the world, the content of Cu and Zn from all the samples analyzed exceeded, while Pb and Mn were higher than their corresponding background values in the perimeter of the former industrial areas. Ni, Cr and Ba content are similar to the indicated limits for the metals content of the background soils, (Semenkov et al., 2020).

It can be concluded that the topsoil samples with high concentration of metals were obtained near from the former industrial areas of „Chemicals“ from Turda and „Wire Industry“ from Câmpia Turzii. In this study, the metal concentrations observed in soils of the studied area corresponded to base values found in the Iron Quadrangle region from Brazil, which is one of the richest mineral-bearing regions in the world (Souza et al., 2015).

## 2. Soil pollution assessment using $C_d$ and $EF$

The indices  $C_f$  and  $EF$  were implemented to evaluate the level of metal pollution in the environment of industrial areas in the lower Arieş River basin. Contamination index  $C_d$  was computed for 8 heavy metals: Ni, Cr, Cu, Zn, Pb, As, Cd, Mn and it is presented in Table 2. For S2,  $C_f$  for Cu, Pb and As were higher than unity, and the value of  $C_d$  (1.53) indicated a powerful contamination with heavy metals.  $C_f$  indicated a high contamination for Pb in the sample S3, however the  $C_d$  was low ( $C_d < 1$ ), which indicates a moderate metal contamination. For S2 and S3,  $C_f$  mean values were observed as  $Pb > Cu > As > Zn > Ni > Mn > Cr > Cd$ .

Table 2. The contamination index computed for soil sampled from the lower Arieş River basin

	$C_f - Ni$	$C_f - Cr$	$C_f - Cu$	$C_d - Zn$	$C_f - Pb$	$C_f - As$	$C_f - Cd$	$C_f - Mn$	$C_d$
S1	-0.579	-0.716	0.460	-0.327	-0.554	0.213	-1.00	-0.686	-5.90
S2	-0.324	-0.547	1.12	0.214	1.48	1.07	-1.00	-0.476	1.53
S3	-0.487	-0.642	0.750	0.187	1.340	0.807	-1.00	-0.562	-1.70
S4	-0.435	-0.628	1.040	-0.030	0.166	0.633	-1.00	-0.498	-3.45
S5	-0.589	-0.518	-0.127	-0.653	-0.664	0.147	-1.00	-0.795	-6.65
S6	-0.673	-0.739	-0.172	-0.630	-0.336	0.407	-1.00	-0.860	-6.60

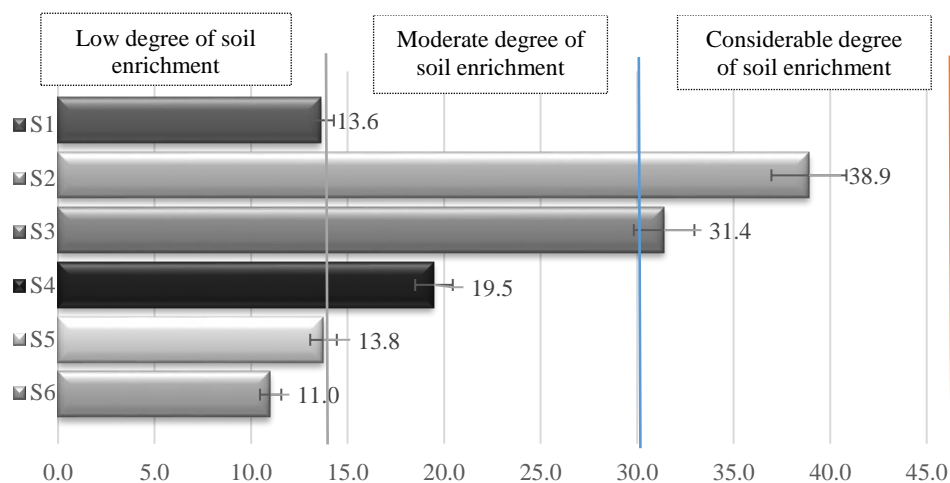


Figure 2. The enrichment factor  $EF$  computed for the soil samples

Enrichment factor ( $EF$ ) is usually employed for differentiating metals originating from natural weathering from parent materials or human-induced processes (Kabala et al., 2020). Figure 2 showed that the values of  $EF$  were very high and varied greatly across different sites. According to Hossain Bhuiyan (2020), S1, S5 and S6 have a low degree of enrichment, S4, a medium degree, S2 and S3, a considerable degree of metal enrichment. The sequence of heavy metals as regards to calculated mean  $EF$  values was  $Cr > Pb > Ni > As > Zn > Cu > Cd$ .  $EF$  was an effective tool in proving the initial hypothesis: that the historical pollution is still very present in the topsoil of the studied area. Ciarkowska and Gambus (2020) suggested a high ecological risk in an industrial area from Nowa Huta district of Krakow, generated by the soil accumulation of Cr and Pb. In addition, a change in the management strategies applied to the sites is recommended by the authors.

## Conclusion

In the lower basin Arieş River, the geographic position and history of industrial activities carried out in the area had a major impact on the soil quality. The aim of the present study was to assess the current quality state of 6 topsoils sampled of different point from lower Arieş River

basin. Although the neutral pH, the soil samples from S2 and S3 Cu, Pb and As content was higher than the intervention threshold for sensitive soils. Furthermore, some metals content such as Cu, Zn, Pb and Mn, was higher than their corresponding background values. According to *Ca*, S2 presented a high level of metal contamination, with a computed value of 1.53. *EF* divided the 6 topsoil samples into three different enrichment categories: low degree (S1, S5, S6), medium degree (S4) and a considerable degree of soil enrichment (S2, S3). In the mentioned pollution index context, the sequence pollution state of the topsoil tested was  $S2 > S3 > S4 > S5 > S1 > S6$ .

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### References

- [1] S. Fusaro, F. Gavinelli, F. Lazzarini, M.G., Paoletti, *Ecol. Indic.* 93 (2018), pp. 1276 – 1292.
- [2] T. Paz-Kagan, M. Shachak, E. Zaassy, A. Karnieli, *Geoderma* 230 – 231 (2014), 171 – 184.
- [3] I.D. Turam., O. Dengiz, B., Ozkan, *Comput. Electron. Agric.* 164 (2019), 104933.
- [4] L. Ma., T. Xiao, Z. Ning, Y. Liu, H. Chen, J. Peng, *Sci. Total Environ.* 724 (2020), 138176.
- [5] H.M.L. Chaves, C.M.C. Lozada, R.O. Gaspar, *Geoderma Reg.* 10 (2017), pp. 18 – 190.
- [6] I. Rehman, M. Ishaq, S. Muhammad, I.U. Din, S. Khan, M. Yaseen, *Environ. Technol. Innov.* 20 (2020), 101155.
- [7] A.B. Siddique, K. Alam., S. Ilam, T.M. Digata, A. Akbor, U.H. Bithi, A.I. Chowdhury, A.K.M.A. Ullah, *Environ. Nanotechnol. Monit. Manag.* 14 (2020), 100366.
- [8] E. Levei, T. Frențiu, M. Ponta, C. Tănăselia, G. Borodi, *Chem. Cent. J.* 7 (2013), 5.
- [9] A. Butiuc-Keul, L. Momeu, C. Craciunas, C. Dobrota, S. Cuna, G. Balas, *J. Environ. Manage.* 12 (2012), S3 – S8.
- [10] M. Costea, *Transylv. Rev. Syst. Ecol. Res.* 7, (2009), pp. 1 – 10.
- [11] J.P. Frink, *Rev. Syst. Ecol. Res.* 7, (2009), pp. 29 – 40.
- [12] R. Ullah and S. Muhammad, *Environ. Technol. Innov.* 19 (020), 100931.
- [13] ORDER no. 756 / 1997 for the approval of the Regulation on the assessment of environmental pollution
- [14] A. Kabata-Pendias, 10.1201/b10158 (2010).
- [15] S. Kükreer, S. Şeker, Z.T: Abacı, B. Kutlu, *Environ. Monit. Assess.* 186 (2014), pp. 3847 – 3857.
- [16] I. Semenkov and T. Koroleva, *Geoderma Reg.* 21 (2020), e00283.
- [17] J.J.L. Leal de Souza, W.A.P. Abrahao, J. da Silva, L.M. da Costa, T.S. de Oliveira, *Sci. Total Environ.* 505 (2015), pp. 338 – 349.
- [18] C. Kabala, B. Galka, P. Jezierski, *Sci. Total Environ.* 738 (2020), 139918.
- [19] M.A. Hossain Bhuiyan, S.C. Karmaker, M. Bodrud-Doza, A. Rakid, B.B. Saha, *Chemosphere* 263 (2020), 128339.
- [20] K. Ciarkowska and F. Gambus, *Sci. Total Environ.* 740 (2020), 140161.