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ASSESSMENT OF HEAVY METALS CONTENT IN THE PROXIMITY OF A CONTAMINATED SITE FROM CLUJ-NAPOCA (ROMANIA)

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ABSTRACT. The present study was conducted in the proximity of a contaminated site from Cluj-Napoca city (Cluj County, Romania), where metal processing activities have been carried out for decades. Metal content and physico-chemical parameters were analyzed in soil, water and sediment samples, while organic matter (OM) and total organic carbon (TOC) was additionally analyzed for the soil samples. The sources of heavy metals were evaluated based on multivariate statistical analysis, while the soil and sediment contamination degree was assessed based on specific pollution indices. The calculated indices indicated a significant pollution with Cd and Pb, which may represent a risk if the area would become a residential area.

Key words: *heavy metals, contaminated site, soil pollution indices, multivariate statistical analysis, Cluj-Napoca*

INTRODUCTION

Large areas with variable metal concentrations are distributed in different regions in Romania. In most cases, these metal accumulations in soil represent the negative consequences of anthropic activity, such as mining activities, operating metallurgical plants, fuel stations and depots, waste disposal etc. (Li et al., 2013; Comm (2006) 231). According to the Romanian legislation (Law 74/2019), when the metal concentrations exceed the intervention thresholds, these areas are classified as contaminated sites. Metal polluted sites are difficult to remediate because these contaminants cannot be biologically degraded, but can become bioavailable for the microorganisms and plants developing in those soils (Jézéquel and Lebeau, 2008). The bioavailability of metals is directly linked to solubility of the solid-phase form into a solution phase. Soil microorganisms and root exudates can increase the solubility rate and act as metal sorbents (Traina and Laperche, 1999; Majewska et al., 2007). Some organisms can develop metal tolerance, while others cannot cope with the ecotoxicological effects. Thus, heavy metals (HMs) can pose a risk to human health by passing into the food chain and generate imbalances in the natural ecosystems.

Following the previous European demarches for creating a Soil Directive, each member state of the EU had to identify the contaminated sites present at national level. In 2015, nine potentially contaminated sites and 19 contaminated sites were reported for Cluj County (Romania) based on the national environmental legislation (HG 683/2015). According to the public information provided by the Environmental Protection Agency of Cluj, eight contaminated sites are found in the administrative territory of Cluj-Napoca (Annex no 8). The contamination of these areas was mainly generated by landfill activities, fuel supply and depots, metal processing and galvanizing activities, where heavy metals (HMs) and petroleum hydrocarbon (PHC) were identified as the main pollutants found in soil.

In Romania, various studies were conducted in different areas identified as contaminated sites, in order to assess HMs effects on soil quality, vegetation development, microbiota diversity or human health (Damian et al., 2019; Mihăileanu et al., 2018; Rogozan et al., 2016). Dispersion into the environmental factors needs to be evaluated in order to link the negative effects with the real sources of HMs. Pollutants tend to exceed the initial surface, considered to be polluted, due to their propagation from an environmental factor to another, thus generating a spread environmental impact (Bizo et al., 2015; Muntean et al., 2015).

The present study was conducted in the industrial area of Cluj-Napoca city (Cluj County, Romania), in the proximity of a contaminated site where, for decades, metal processing activities took place. Since the municipality plans to redevelop this industrial part of the city in terms of a residential area with neighborhoods and playgrounds for the inhabitants, it is necessary to perform a study focused on the possibility of HMs spreading in the surrounding environment. Metal content and physico-chemical parameters were analyzed in soil, water and sediment samples, while organic matter (OM) and total organic carbon (TOC) was additionally analyzed for the soil samples. The sources of heavy metals were evaluated based on multivariate statistical analysis. Additionally, the contamination degree was assessed based on specific pollution indices.

MATERIALS AND METHODS

Study area, samples collection, processing and analyzing

The study area is located in Cluj-Napoca city (Romania), near a contaminated site situated on the eastern side of Someșul Mic River (figure 1). In the proximity of the site are Feroviarilor Park, Central Railway station of Cluj-Napoca and Nadăș River. The activity that generated the contaminated site was based on metal processing and has been in operation for decades (Annex no 8).

A total of nine water (A), sediment (B) and soil (C) samples were collected downstream (sampling point 1), in the proximity (point 2) and upstream (point 3) from the contaminated site, along the Nadăş River. Supplementary, a soil sample was collected from a park (point 4) located in the proximity of the contaminated site (figure 1).

The water was sampled in 250 ml sterile bottles, by immersion under the surface water, according to ISO 5667-3:2018 and ISO 5667-1:2006. Approximately 500 g of sediment samples were collected in sterile polyethylene bags, with a clean stainless steel hand auger. In the case of soil sampling, the surface vegetation was first removed and then 500 g of soil were collected from the surface (0 – 10 cm in depth) by a stainless steel hand auger and transferred to polyethylene bags, according to Order 184/1997. All the samples were transported to laboratory in cold (4ºC) and dark conditions.

The pH, redox potential (E_h), electrical conductivity (EC), total dissolved solids (TDS) and salinity of water samples were measured *in situ* by using a portable multiparameter (WTW Multi 350i, Germany). In the case of soil and sediment samples, these parameters were measured in the aqueous extract of soil/sediment (5:1 ratio), using the national protocol SR 7184-13/2001 (Ispas et al., 2020).

Fig. 1. *Study area with the sampling points*

In order to perform the heavy metals analyses on soil and sediments samples, the samples were previously air dried, grounded, sieved through a 250 μm sieve, mineralised with *aqua regia*, filtered and diluted with HNO_3 (0.5 M) to a final volume of 100 ml, according to ISO 11466:1995 protocol (Roba et al., 2015). The water samples were previously filtered and acidified to a pH of 2 with HNO_3 (63%). The analyses were performed by using an atomic absorption spectrometer (AAS, Analytik Jena ZEEnit 700, Germany) equipied with an air-acetylene flame and a graphite furnace.

The total organic carbon and organic matter was determined through Walkley and Black's (1934) method.

The grain-size analysis (sedimentation and sift method) was done according to national and international protocols (SR EN 14688-2: 2005; SR ISO 11465:1998).

Determination of pollution indices and multivariate data analysis

A variety of evaluation indices such as Geo-accumulation index (I_{geo}) (Muller, 1969), Contamination factor (CF) (Loska et al., 1997), Pollution load index (PLI) (Tomlinson et al., 1980) and Enrichment factor (EF) (Islam et al., 2018) were used to quantify the degree of metal contamination in both soil and sediment samples (table 1).

Table 1. *Pollution indices*

Indices formulae	**Quality class**
$I_{geo} = log_2 \frac{C_n}{1.5 \cdot B_n}$ *C_n* – concentration of metal *n* in soil or sediment; *B_n* – geochemical background; 1.5 – correction factor for background values	unpolluted (I_{geo}≤0); unpolluted to moderately polluted (0<I_{geo}<1); moderately polluted (1<I_{geo}<2); moderately to strongly polluted (2<I_{geo}<3); strongly polluted (3<I_{geo}<4); strongly to extremely polluted (4<I_{geo}<5); extremely polluted (I_{geo}≥5) (Muller, 1969)
$CF = \frac{C_n}{B_n}$ *C_n* – concentration of metal *n* in soil or sediment; *B_n* – geochemical background	low contamination factor (CF<1); moderate contamination factor (1≤CF<3); considerable contamination factor (3≤CF<6); very high contamination factor (CF≥6) (Loska et al., 1997)
$PLI = (CF_1 \cdot CF_2 \cdot \ldots \cdot CF_n)^{1/n}$ *CF* – contamination factor for metal *n*	unpolluted (PLI<1) and polluted (PLI>1) (Tomlinson et al., 1980)

Indices formulae	Quality class
$EF = \frac{C_n / C_{Fe}}{B_n / B_{Fe}}$ *C* – concentration of metal *n* and reference metal (Fe) in soil or sediment; B_n – geochemical background *for metal n* and reference metal (Fe)	deficiency to minimal enrichment (EF<2); moderate enrichment (2<EF<5); significant enrichment (5<EF<20); very high enrichment (20<EF<40); extremely high enrichment (EF>40) (Islam et al., 2018)

Multivariate data analysis – hierarchical clustering and principal component analysis (PCA) – was performed on all three types of samples to determine groups and the main elements of groups in order to identify the sources of provenance for the analyzed metals. The data analyses were performed using Past version 3.26b.

RESULTS AND DISCUSSION

Physico-chemical parameters

The soil and sediment samples proved to have a predominantly sandy texture (table 2), the highest value of sand being registered in sample B2 (75.18%) and the lowest in sample C2 (45.01%). Regarding the clay content, the highest value was identified in sample C2 (21.36%) and the lowest in sample B2 (7.61%). The presence of coarse particles may influence the heavy metals accumulation through sedimentation rather than their accumulation by adsorption processes.

Table 2. *Grain-size composition of sediment (B) and soil (C) samples*

Sample	Texture	Clay (%)	Silt (%)	Sand (%)	Gravel (%)
B1	Clayey sand	8.25	17.59	74.16	0
B2	Sand	7.61	3.75	75.18	13.47
B3	Clayey sand	15.99	11.35	72.66	0
C1	Clayey sand	11.77	13.53	58.99	15.72
C2	Sandy clay	21.36	20.05	45.01	13.58
C3	Clayey sand	15.60	18.95	65.23	0.20

The values of physico-chemical parameters for the investigated samples can be seen in table 3. All the samples exhibit a neutral to slightly alkaline pH. All the water samples had the pH within the limits (6.5 – 8.5) imposed by national legislation (Order 161/2006). Furthermore, a correlation can be observed between pH and Eh. The negative values indicate a reducing environment. The analyzed soils and sediments have a neutral to slightly alkaline pH, which does not favor the mobilization of heavy metals like in the case of a strong acidic pH (Frențiu et al., 2009).

Table 3. *The physico-chemical parameters of water (A), sediment (B) and soil (C) samples*

Parameters	A1	A2	A3	B1	B2	B3	C1	C2	C3	C4
pH	7.7	7.7	7.7	7.6	7.4	7.5	7.5	7.5	7.7	7.7
Eh (mV)	-61.0	-58.0	-61.7	-52.7	-44.9	-49.5	-51.3	-53.1	-63.0	-60.9
TDS (mg/l)	522	528	532	568	681	581	110	209	113	109
EC (µS/cm)	822	824	832	885	1210	903	171	328	176	169.8
Sal (‰)	0.3	0.3	0.3	0.4	0.4	0.4	0.0	0.0	0.0	0.0

The lowest values of TDS were identified in aqueous soil solution and the highest one in the aqueous sediment solution (table 3). It is important to mention that the soil and sediment samples collected near the contaminated site (B2 and C2) recorded higher values for TDS and EC, which may be correlated with the anthropogenic activities from the area. Salinity registered constant values for each investigated component (table 3).

Heavy metal content in water samples

The metal content in Nadăș River was correlated with the environmental regulations for surface water quality (Order 161/2006), in order to establish the ecological status of the water bodies (table 4). Based on Zn, Cu, Fe, Mn and Cd level, the analyzed samples belong to 1st water quality class (very good ecological status) (Order 161/2006). It was observed that the Zn and Cd concentrations decrease from upstream to downstream, while Cu concentrations increase from downstream to upstream. Since these differences are not significant, the presence of these heavy metals in water cannot be correlated with the proximity of the contaminated site.

Table 4. *Heavy metals concentration in water samples*

Heavy metal	Water sample (μg/l)			Quality class (Order 161/2006) (μg/l)				
	A1	**A2**	**A3**	**I**	**II**	**III**	**IV**	**V**
Zn	23	24	24	**100**	**200**	**500**	**1000**	**>1000**
Cu	19	18	15	**20**	**30**	**50**	**100**	**>100**
Pb	32	21	21	**5**	**10**	**25**	**50**	**>50**
Ni	28	28	30	**10**	**25**	**50**	**100**	**>100**
Fe	43	54	20	**300**	**500**	**1000**	**2000**	**>2000**
Mn	ND*	ND	ND	**50**	**100**	**300**	**1000**	**>1000**
Cd	ND	0.31	0.38	**0.5**	**1**	**2**	**5**	**>5**
Cr	45	9	18	**25**	**50**	**100**	**250**	**>250**

**ND – not detected*

The Pb concentrations from samples A2 and A3 correspond to 3rd water quality class (moderate ecological status), while the Pb level from A1 belongs to 4rd water quality class (low ecological status). The content of lead increases from upstream to downstream, so the contaminated site may have an impact on the river water quality. Considering the content of Ni and Cr, the sample A1 belongs to 2nd quality class (good ecological status). Since there is no upward trend for metal concentration, either downstream or upstream, the presence of Cr cannot be correlated with the anthropic activities from the contaminated site, but rather with different sources.

For better understanding of possible metal sources, multivariate hierrarchical clustering and principal component analysis was used. Based on statistical analysis, two clusters and two sub-clusters were differentiated (figure 2A). Cluster 1 grouped five elements (Pb, Cu, Ni, Zn, Fe), where Pb, Cu, Ni and Zn formed sub-cluster 1a, and Fe formed sub-cluster 1b. The arrangement from sub-cluster 1a indicates that Pb and Cu have a different source than Ni and Zn. The position of Fe in PCA, clearly separated by other elements may indicate a different source of provenance, probably a natural one (figure 2). Cluster 2 grouped two elements (Cd and Mn), clearly separated from other metals. Considering that the presence of Cd is often associated with industrial activities, this may suggest another anthropogenic source for these two elements.

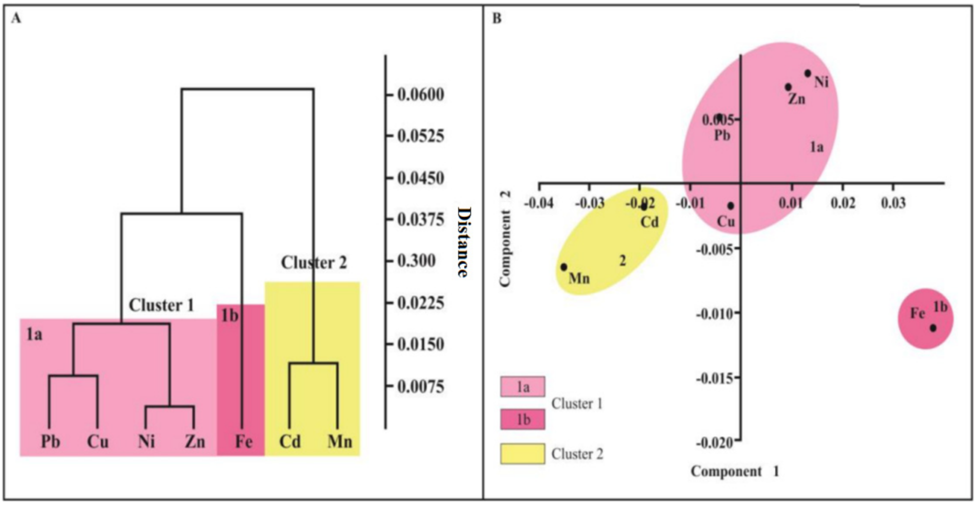

Fig. 2. *Distribution of the chemical elements on clusters (A) and principal component analysis (B) in water samples*

Principal Component Analysis revealed two main principal components (figure 2B). Principal component 1 (PC1) retains 89.24% of the variance and groups only the samples with positive values (> 0.70 correlation) for all the investigated elements. Principal component 2 (PC2) retains 8.87% of the variance and groups the elements with positive values (Ni) (>0.60 correlation), which was negatively correlated with all the other elements. In conclusion, based on statistical analysis a certain increase of concentration for Ni, Zn and Pb can be outlined, probably due to the anthropogenic activities in the investigated area.

Heavy metal contamination in sediment

The content of metals in the sediment from Nadăș River was evaluated according to national legislation (Order 161/2006) (table 5). Zn and Cr have been identified in the accepted limits by the environmental legislation. Even though Fe and Mn indicate elevated concentrations, they cannot be assessed in terms of ecological status because there are no listed national limits for these metals in sediments (Order 161/2006). Their occurrence might be correlated with the natural background of the area, but other studies should be performed or confronted.

Table 5. *Heavy metals concentration in sediment samples*

Heavy metal	**Sediment sample (mg/kg)**			***Regulation limit (*Ord. 161/2006*) (mg/kg)**
	B1	**B2**	**B3**	
Zn	88	49	93	150
Cu	39	28	47	40
Pb	28	102	31	85
Ni	38	9	30	35
Fe	20452	10121	10554	-
Mn	334	212	494	-
Cd	2	1.47	1.88	0.8
Cr	48	17	37	100

Cadmium exceeds the maximum allowed limits in all the samples (table 5), recording the highest concentration downstream, while near the contaminated site was identified the lowest concentration. A downstream Cd accumulation can be supposed, but the source of contamination can be disputed because a descending trend from upstream is not observed in the analyzed samples. Lead was found with the highest concentration near the contaminated site (B2). Considering the sand texture of this sample (table 2), sedimentation followed by accumulation in the sediment layer is expected to be favored for heavy metals (Salomons and Stigliani, 1995). Thus, the contaminated site might represent the source of pollution with Pb in the area, this element being present in high concentration in the water sample too. Copper exceeded the limits in the upstream sample (B3), while the lowest concentration was identified near the contaminated site (B2). These results indicate that Cu might have another contamination source than the evaluated site, considering that a lower content was registered downstream. Nickel exceeded the limit in the downstream sample (B1), but the lowest concentration was again near the contaminated site (B2). Comparing the sediment texture (table 2) with the heavy metals content it was observed that upstream and downstream samples are both containing a higher percentage of clay, thus might have led to higher metal adsorption rates.

Because it is hard to predict the source of contaminations, multivariate hierarchical clustering and PCA were used for a better understanding. The multivariate clustering analysis generated two main clusters and two sub-clusters (figure 3A). Cluster 1 comprises six elements (Pb, Zn, Ni, Cu, Cd, Mn) which are divided in sub-cluster 1a with five elements (Pb, Zn, Ni, Cu, Cd) and sub-cluster 1b with one element (Mn). Given this grouping, is considered that there exist two different sources for the analyzed metals, corresponding to each sub-cluster. Cluster 2 is also formed by a single element (Fe), located far from other metals, so it is believed to correspond to a third source of provenance, a natural one as in the case of water samples. Being known the close connection between water and sediment as environmental components is assumed that the presence of Pb, Zn, Ni, Cu, Cd and Mn can be correlated with anthropogenic sources.

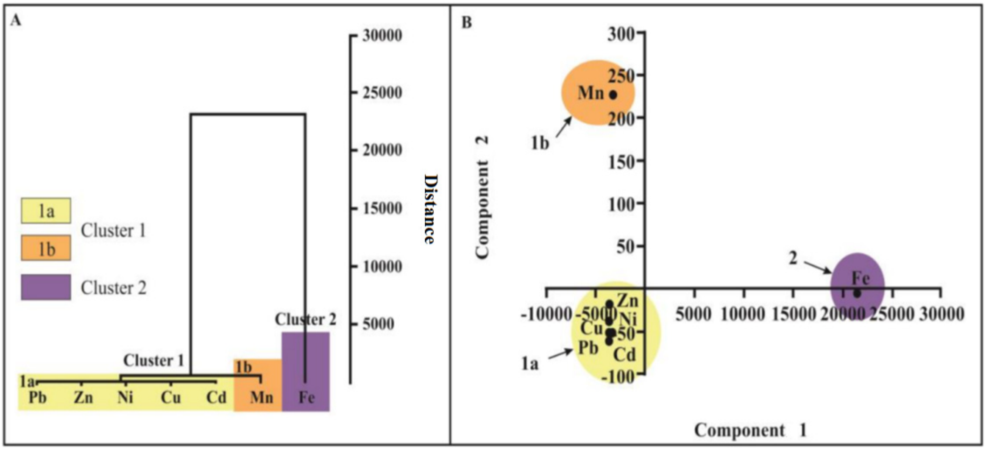

Fig. 3. *Distribution of the chemical elements on clusters (A) and principal component analysis (B) in sediment samples*

Principal component analysis (figure 3B) confirms the cluster division, with a clear differentiation of chemical elements. PC1 retains 99.98% of the variance and groups all the elements with positive values (>0.9 correlation), and PC2 retains only 0.01% of the variance, including only one element (Mn) with positive values (>0.020 correlation) which negatively correlates with all other elements. Thus, a certain increase in Mn content in sediments can be assigned to anthropogenic activities.

Heavy metal contamination in soil

The metal concentration in soil was correlated with the environmental thresholds set for less sensitive use of soil (table 6) because the investigated area is found in the proximity of a contaminated site. Mn and Cr concentrations were found under the normal threshold, so the surface of the investigated area was not contaminated with these metals. Fe indicated elevated concentrations, but compared with the control sample (C4), located approximately 1 km further, is noted that the highest concentration of Fe was in the control area.

Table 6. *Heavy metal concentration in soil samples*

Heavy metal	Soil samples (mg/kg)				*Pollution thresholds (mg/kg)		
	C1	**C2**	**C3**	**C4**	**Normal**	**Alert**	**Intervention**
Zn	131	127	59	118	100	700	1500
Cu	107	59	25	47	20	250	500
Pb	63	87	24	98	20	250	1000
Ni	29	23	25	19	20	200	500
Fe	20452	20230	10554	20844	-	-	-
Mn	537	444	340	503	900	2000	4000
Cd	1.96	1.97	1.63	1.59	1	5	10
Cr	29	28	23	22	30	300	600

**According to Ord. 756/1997 approving the Regulation regarding the assessment of environmental pollution, for less sensitive uses of soil*

Based on these results, is clear that Fe has a natural occurrence in the environment, as it was assumed for Fe content in sediments. The Fe contents in soil and sediment are comparable, so it can be assumed that Fe is present in the natural background. The low Fe concentrations in water samples strengthen this assumption, because the Fe fraction found in the background is not water soluble (Zimmerman and Weindorf, 2010).

The other analyzed metals, Zn, Cu, Pb, Ni and Cd, exceed only the normal thresholds for less sensitive use of soil in all samples, but this is already an indicator for contamination. Comparing with the thresholds for sensitive use, Pb would exceed the alert threshold (50 mg/kg) and would be very close to exceed even the intervention threshold (100 mg/kg). Is known that an area can be framed as potentially contaminated site when the alert thresholds are exceeded and becomes a contaminated site when the intervention thresholds are overpassed (HG 683/2015). Considering that in the surroundings of the contaminated site are living or working buildings of Cluj inhabitants, is difficult to establish a clear demarcation between less sensitive and sensitive use of soil. Therefore, special measurements should be considered regarding remediation of the area, starting with the decontamination of the investigated site, which can be considered the main source of metal dispersion. Another argument for this recommendation is given by the increased content of Zn, Cu, Pb, Ni and Cd also in the control sample (C4), exceeding the normal thresholds. The control sample was collected from Feroviarilor Park, an area considered to be unpolluted, and where redevelopment plans are being considered. Especially Pb is critically close to reach the intervention threshold (100 mg/kg) for sensitive type of soil. This might be an indicator that the contamination is more expanded than initially thought.

Statistical analysis differentiated two main clusters and two sub-clusters (figure 4A). Cluster 1 includes five elements (Pb, Cu, Zn, Cd, Ni) grouped as following: Pb+Cu+Zn and Cd+Ni. This distribution suggests distinct source for each group. Since Zn is mentioned as a pollutant in the contaminated site (Annex no. 8, PUG 2014), is assumed that Pb and Cu are generated from the same anthropogenic source. The elements order in soil was the same with the one in sediment samples. Cluster 2 clearly separated Fe and Mn in two sub-clusters, thus indicating different source of provenance. Sub-cluster 2a comprises Fe and was considered to have a natural source as previously discussed, while sub-cluster 2b is formed by Mn, its source being pointed out by the further discussed PCA.

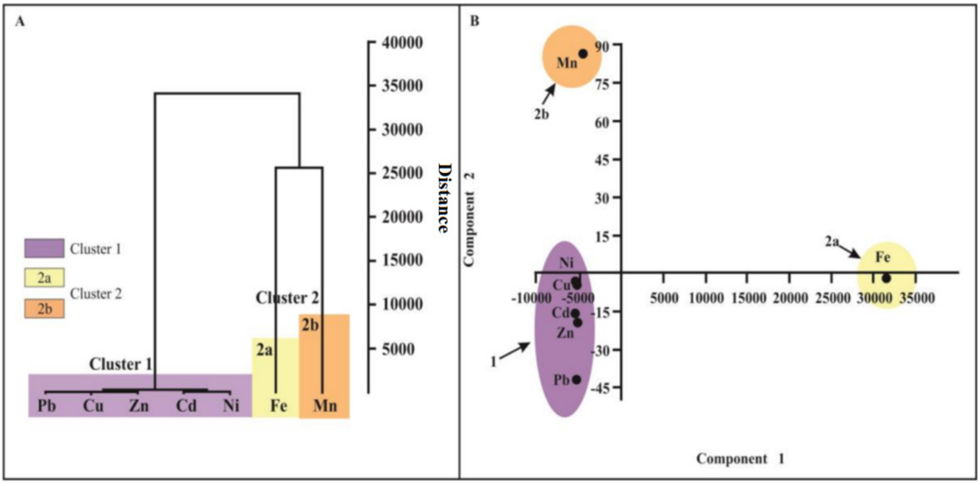

Fig. 4. *Distribution of the chemical elements on clusters (A) and principal component analysis (B) in soil samples*

Cluster separation is outlined by principal component analysis too (figure 4B). PC1 retained 99.99% of the variance and groups the elements with positive values (> 0.9 correlation). PC2 retained only 0.0009% of the variance and groups the positive values of Mn which negatively correlates with Pb. Thus, a certain increase in Mn can be assigned to anthropogenic activities.

Total organic carbon (TOC) and organic matter (OM) in soil

Heavy metals mobility in soil can be influenced by different factors, like the pH and total organic carbon (Walker et al., 2004; Zeng et al., 2011; Bian et al., 2014; Khan et al., 2014; Khadar et al., 2020; Zhong et al., 2020). Organic matter contains several active groups influencing the adsorption of heavy metals and preventing their desorption (Zhang et al., 2020). In the investigated area, TOC ranged from 0.18% (C3) to 0.95% (C1), recording lower concentrations than the soil from the park (C4) (1.73%) (figure 5). Similar variation was observed for OM, ranging between 0.5% (C3) and 2.8% (C1) in the study area, compared to 5.1% in control sample (C4) (figure 5). The lower levels of TOC and OM, registered in the proximity of the contaminated site, comparing to the sample collected from the park, can indicate that the identified metal contamination generated a degradation of soil quality in the proximity of the contaminated site. The affinity of heavy metals to organic matter was lower for Zn, Ni, Cu and Cd, these metals being negatively correlated with soil organic carbon, and higher for Pb which is positively correlated with soil organic carbon. Other studies have reported that Cu and Pb were strongly retained in the soils with higher concentrations of organic matter or Fe/Mn oxides than Zn and Cd (Martínez and McBride, 1999).

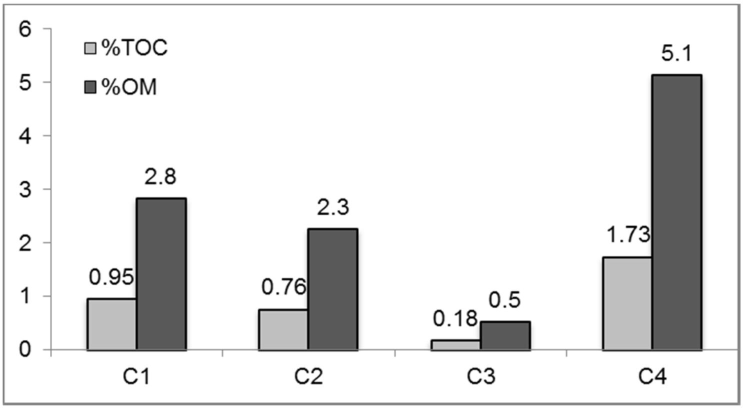

Fig. 5. *Total organic carbon (TOC) and organic matter (OM) content in soil samples*

Soil quality indicators

Based on the previous analyses, various levels of metal contamination with different sources of propagation were identified. For a better understanding upon the involved processes in metal occurrence in soil and sediment samples, several soil quality indicators were calculated.

Considering the values obtained for the geo-accumulation index (I_{geo}), Cd indicated an intense process of accumulation in soil (C1, C2) and sediment (B1) samples (figure 6), corresponding to an extremely high level of contamination (quality class 6). The sediment located near the contaminated site (B2) can be considered heavily contaminated with Cd (quality class 4).

It is important to mention that the soil sampled from the park (C4) corresponds to a heavily to extremely contaminated soil with Cd (quality class 5). Except for Fe, which confirmed the assumption of natural occurrence related to background because no contamination can be assumed in this case (quality class 0), the content of Zn, Cu, Pb, Ni and Mn corresponds to unpolluted to moderately polluted soil and sediments (quality class 1).

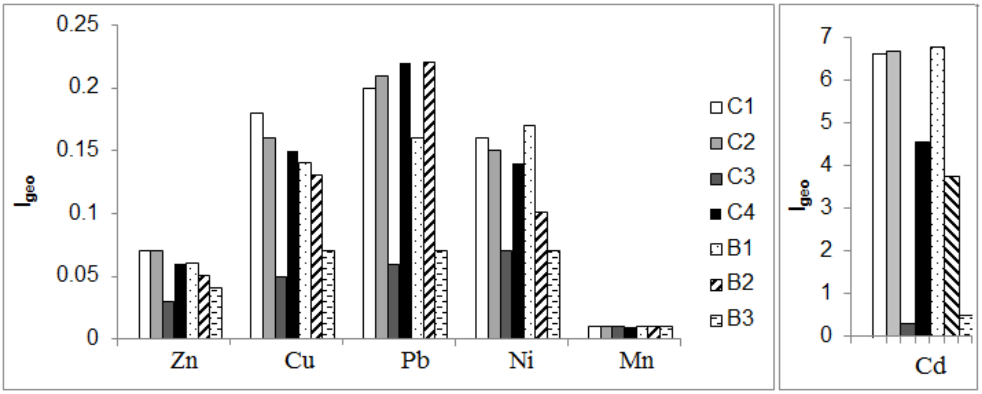

Fig. 6. *Geo-accumulation index for soil (C1 – C4) and sediments (B1 – B3)*

Another indicator used in the assessment was the contamination factor (CF). Based on the Cf values for Zn, Cu (excepting sample C1), Ni, Fe, Mn and Cr, the soil and sediments samples correspond to low and moderately contamination factor (figure 7). Samples C1, C2, C4 and B2, registered a considerable contamination factor for Pb. There is only one metal (Cd), which exhibits a very high contamination factor for all the investigated soil and sediments samples.

Pollution load index assesses the overall soil quality in regard to accumulation of several metals, not just one individual metal (Tomlinson et al., 1980). PLI ranged between 1.03 (B2) and 2.05 (C1), indicating the fact that the analyzed soil and sediments can be considerate polluted with heavy metals (especially with Cd). This is a consequence of the high values obtained for CF_Cd, this metal exceeding the normal threshold in soil and the maximum limit in sediments (Ord. 756/1997; Ord. 161/2006).

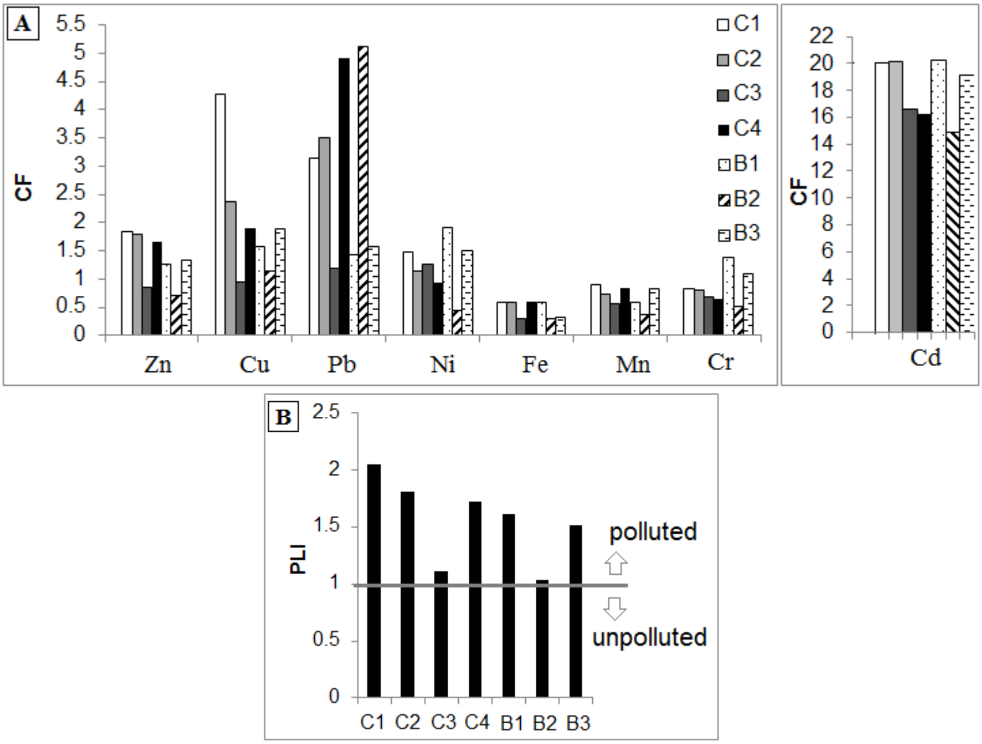

Fig. 7. *Contamination factor (A) and pollution load index (B) in soil (C1 – C4) and sediments (B1 – B3)*

The last indicator used in the assessment was the enrichment factor (EF), whose results are presented in figure 8. Cadmium indicated a very high (C1, C2, C4 and B1) and extremely high (C3, B2 and B3) enrichment, followed by Cu and Pb with a moderate to significant enrichment (figure 8). For Ni, Zn, Mn and Cr, the value of EF corresponded to deficiency to moderate enrichment. If the EF values are higher than 10, it is considered that those metals do not have a crustal sources, but they have an anthropogenic origin (Daskalakis and O’Connor 1995). In the present study the EF_Pb exceeded 10 value only in on sample, while EF_Cd exceeded this level in all the samples. Based on multivariate statistical analyses, not only Cd and Pb can have an anthropogenic source, but some other metals too.

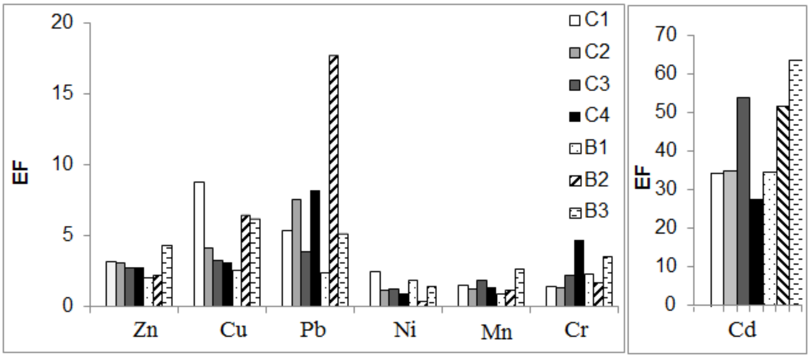

Fig. 8. *Enrichment factor in soil (C1 – C4) and sediments (B1 – B3)*

Cadmium content in sediments exceeded the limit imposed by national legislation, while in soil samples exceeded the normal value, being within the alert threshold. However, the values of the pollution indices indicated a significant contamination with cadmium in the investigated area. In literature, the reference values used for calculating the specific pollution indices may vary greatly. The indices are calculated based on the pre-industrial reference level, the average crust level, background level, or the average content of shale heavy metals (Yahaya et al., 2021). This may lead to a discrepancy in pollution assessment of highly toxic metals, like cadmium.

CONCLUSION

The principal component analysis confirmed the natural source for Fe, related to the abundance in parent material, while the other metals originated from anthropogenic sources. The data may suggest that the presence of Cd and Pb can be associated with the anthropic activities from the contaminated site, while the other metals may have other distinct sources.

Based on the calculated pollution indices, the present study could bring more arguments regarding the impact of the anthropogenic activities on the soil and sediment quality in the proximity of the contaminated site. The indices indicated a significant pollution with Cd and Pb, which may represent a risk if the area would become a residential one. In order to have more comprehensive understanding upon the studied contamination, a much more complex study should be performed in the area.

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Annex no. 8 - https://files.primariaclujnapoca.ro/1.png

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