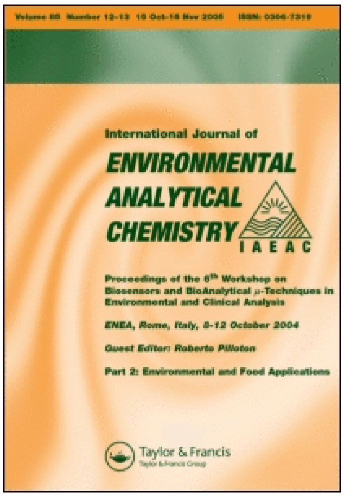

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Characterisation of soil quality and mobility of Cd, Cu, Pb and Zn in the Baia Mare area Northwest Romania following the historical pollution

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Characterisation of soil quality and mobility of Cd, Cu, Pb and Zn in the Baia Mare area Northwest Romania following the historical pollution

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The paper presents a characterisation of the soil quality and mobility of Cd, Cu, Pb and Zn in the Baia Mare city, northwest Romania, historically polluted with airborne particulate matter resulted from non-ferrous ores processing. Although the impact of the ores smelters on the environment is relatively limited today, Baia Mare is still a highly polluted site with Cd, Pb, Cu and Zn. The concentration ranges of metals in soil were (mg kg^{-1}): 1.9-25.4 Cd, 87.7-9880 Pb, 78.3-962 Cu, 109-11500 Zn, of which in (%): 1.3-80; 2.2-40; 2.0-34 and 0.3-21 as mobile species in 0.005 mol L^{-1} diethylenetriaminepentaacetic acid (DTPA). Baia Mare is more polluted with Cu, Pb and Zn than Copsa Mica and Cu, Pb than Zlatna, other smelter centres in Romania. Also, pollution is higher compared to similar centres in Europe. Cd, Pb and Cu are the most severe contaminants as available species for plants and should be considered in the soil remediation strategy. The PCA on metal contents following aqua regia mineralisation and DTPA extraction allowed the identification of anthropogenic origin from three sources associated with the Flotation Station (residual species), Cuprom plant (Cu, Cd and Zn mobile species) and Romplumb plant (Pb mobile species). The car traffic as anthropogenic source does not modify the pollution pattern caused by industrial activity since no association between Pb and Zn was found. On the other hand, an affinity between Cd and Zn as well as between Cu and Pb were also identified. A particular case is that of Cu, for which the PCA revealed an interference of polluters. Statistics are in agreement with the distribution maps of contaminants.

Keywords: soil contamination; historical pollution; heavy metals; DTPA extractable metals, PCA

1. Introduction

Soil pollution with heavy metals is a major environmental problem due to their high toxicity, low biodegradability, and cumulative nature and represents a serious threat to human health by entering into food chain or by leaching into groundwater [1–3]. Mining and the related operations are the most important anthropogenic sources of heavy metals in the environment [4]. Metals are partitioned between the liquid and solid phase of soil.

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In soil solution metals are present as free ions or inorganic and organic soluble complexes, while in the solid phase as labile adsorbed ions and immobilised in secondary and primary minerals [5,6]. It has been reported that the total trace metal concentration in soil is a poor indication of plant availability, since the free metal ions are in general the most bioavailable and toxic form [6–8]. Generally poor correlations were found between total metal content and plant phytoavailability [7].

Determination of aqua regia extractable metal fraction often referred as total content of metals is a necessary step in estimating the overall metal pollution of soil but provides no information regarding chemical nature or mobility of metals [9,10]. To assess the metal mobility in soils both the single or sequential extraction schemes can be performed. The Tessier's five-step sequential extraction procedure [11–15] and the original three-step extraction procedure proposed by the European Community Bureau of Reference (BCR) [16,17] or the modified four-step BCR method [18–22] used to fractionate heavy metals in soil/sediment/sludge samples are relatively complicated and time consuming. In exchange the single extraction approach is simpler and offers in shorter time information about metal mobility in the environment. A variety of neutral salt extractants have been used as well as extractants using organic ligands capable of forming a strong complex with metals such as EDTA (ethylenediamminotetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid) [7,23–28]. The single extraction using DTPA was initially designed to predict micronutrient deficiencies (Zn, Cu, Fe, Mn) in neutral to calcareous soils [29], but is also employed for the estimation of non-essential or toxic metal (Cd, Cr, Ni, Pb) availability for plants. DTPA can release the soluble, exchangeable, adsorbed and organically bound metals, and possibly some of the metals fixed on oxides [7,28,30–36].

The objective of this study was to characterise the soil quality in the Baia Mare city northwest Romania, historically polluted with airborne particulate matter and fine-grained sediments containing Cd, Cu, Pb and Zn resulting from non-ferrous ores processing. The standard comparison of registered heavy metal concentration with accepted hazardous threshold values achieved in previous studies [3,12,37–40] does not provide sufficient information about the multivariate pollution process existing in the area. The principal component analysis (PCA) on contents of Cd, Cu, Pb and Zn in soil extracted in aqua regia and DTPA carried out in this study allowed the association between the anthropogenic origin of metals and the existing pollution sources. The influence of soil properties (pH and organic matter content) in the behaviour of these elements based on the Pearson's correlation matrix is also discussed.

2. Experimental

2.1 *Site description and sampling*

The city of Baia Mare with 150,000 inhabitants is located in the Maramures County northwest Romania, in a depression, at an altitude of 228 m from the level of the sea, between 47°39′–47°48′ N latitude and 23°10′–23°30′ E longitude. The hills (350–800 m height) and mountains (1200–1500 m height) bordering the city in the north-east side determine an E-W wind orientation. The depression shows long periods of still atmosphere with a negative impact on the pollution level. The city is crossed from east to west by two rivers, Sasar and Firiza. The territory surface together with the periurban area is 235.7 km^2, of which 31.7 km^2 agricultural fields for vegetables and traditional cereals. The leaf-bearing wood is about 80% of the surrounding surface and the chestnut tree area is the biggest in Romania. The main industry of the city developed more than one century ago is based on the processing of non-ferrous ores containing Cu, Pb and Zn. At the end of the 19th century and beginning of the 20th there were established the Flotation Station, a Cu smelter (Cuprom plant) and a Pb smelter (Romplumb) that are currently active. Non-ferrous ores are concentrated at the Flotation Station and processed within the two other plants to produce sulphuric acid and different Cu and Pb products. The soil has been contaminated for years by waste and dust emission from the Cu and Pb smelters and tailings deposited around the Flotation Station [3,12,37–40]. The emission of airborne particulate matter in the atmosphere caused a diffuse pollution of soils with Cd, Cu, Pb, Zn, As on an area of ~900 km^2 largely exceeding the city surface. This type of pollution decreased after 1990 due to recent progress of production technologies and equipment as well after building of a high chimney (351.5 m) by Cuprom Company to evacuate residual gases. Although the environmental effects of the smelters are relatively limited today, intensive ore processing together with a poor environmental management in the past transformed Baia Mare into one of the most polluted industrial centres in Europe.

In 2007 a total of 31 single soil samples were randomly collected from the Baia Mare city over a surface of 18 km^2 on the west side from the pollution sources and considering the preferential E-W wind direction. The zone includes residential areas, public parks, roadsides and small private allotments used for growing vegetables. Sampling was performed from 0–20 cm depth using a stainless steel shovel. The coordinates of sampling points recorded with a 310 Magellan GPS are presented in Figure 1. The locations in km are related to the geographical coordinates 47°38′24″ N latitude and 23°32′11″ E longitude

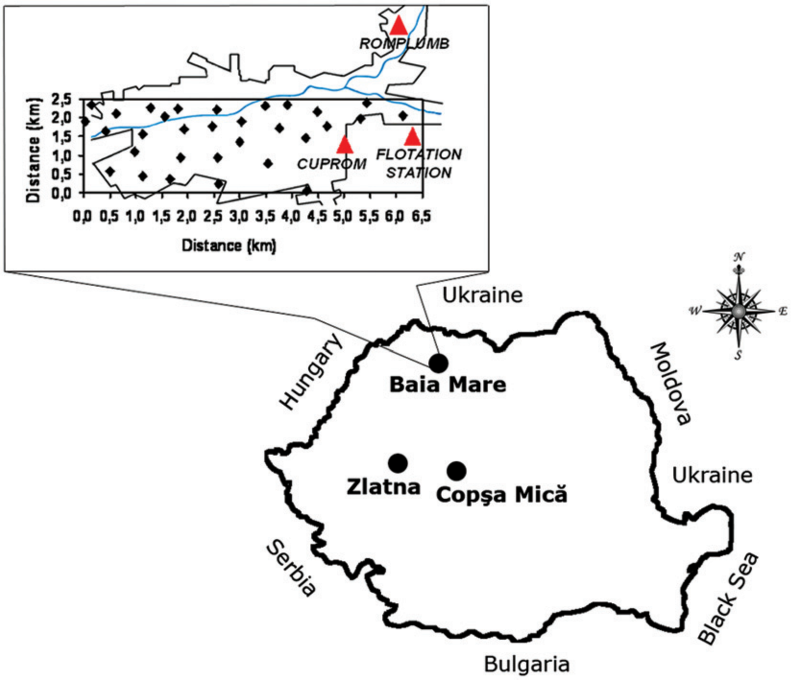

Figure 1. Location map of Baia Mare with the sampling points and the main polluters along with other two Romanian non-ferrous smelting centres.

taken as reference (0; 0 km). The coordinates were calculated by transforming the distance from the reference in centigrade and multiplying with 0.01875 for latitude and 0.0128 for longitude. The position corresponding to the pollution sources are also indicated. The spatial distribution maps were drawn using Origin Lab (OriginLab Corporation, Northampton, USA). Prior to create the 3D contour graphs data were converted to random XYZ matrix using the correlation gridding tool. Thus a continuous surface based on the discrete 3D XYZ triplets resulted. The correlation method computes a new value for each cell in the regular matrix from the values of the points in the adjoining cells in the matrix that are included within the search radius [41].

In the statistical treatment of our data we used XLStat as a Microsoft Excel plug-in (Addinsoft).

2.2 *Instrumentation*

The inductively coupled plasma scanning spectrometer SPECTROFLAME (Spectro Analytical Instruments Kleve, Germany) ICP-AES was used for the determination of metal contents extracted in aqua regia. A Perkin-Elemer Sciex ICP-MS (Model ELAN DRC II, Toronto, Canada) was used for the determination of metals available in DTPA. Operating parameters of ICP-MS are summarised in reference [42]. Polyatomic interferences of the analyte isotopes were reduced by applying the dynamic reaction cell technology (DRC) with methane as reaction gas.

To characterise the mineral composition of the soil samples the X-ray diffraction patterns were recorded with a Dron 3 diffractometer (Scientific Industrial Union, Sankt Petersburg, Russia).

2.3 *Reagents, standard solutions and CRMs*

Concentrated nitric acid 65% (w/w) and hydrochloric acid 37% (w/w) were employed in the digestion of soil samples with aqua regia. The DTPA extraction solution was prepared to contain 0.005 mol L^{-1} DTPA, 0.01 mol L^{-1} $CaCl_2$, 0.1 mol L^{-1} triethanolamine (TEA) and adjusted to pH 7.3 with 1 mol L^{-1} HCl solution. The following solutions were prepared for the determination of the organic matter in soil: 1.6% (w/v) CrO_3 in 96% (w/w) H_2SO_4; 0.2 mol L^{-1} Fe $(NH_4)_2$ $(SO_4)_2$ $6H_2O$ in 0.5% (w/v) H_2SO_4 and 1% (w/v) diphenylamine as indicator. The solution of 1 mol L^{-1} KCl was used as buffer to measure the soil pH.

The CRM 025-050-RTC-Laramie New York, USA purchased from LGC PromoChem GmbH (Wessel, Germany) was analysed within the quality control of determinations.

2.4 *Sample preparation and chemical analysis*

Total metal contents in soil were obtained following the mineralisation of 1.0000 g soil sample ($n = 3$) with 10 ml aqua regia using the microwave digestion in closed vessels [43]. The available Cd, Cu, Pb and Zn contents were determined by leaching 3 replicates of 10 g soil (<2 mm) with DTPA solution under continuously shaking for 2 h at 20 ± 2°C [44]. Metal concentrations in solutions were determined by ICP-AES [45] and DRC-ICP-MS [46]. The digestion programme for soil samples together with the instrumental detection limits of elements (3σ criteria) in ICP-AES and DRC-ICP-MS are presented in Table 1.

Table 1. Operating conditions for the microwave digestion system and instrumental detection limits (LOD) in ICP-AES and DRC-ICP-MS.

Digestion method					
Stage		1	2	3	4
Temperature/°C		180	100	100	100
Ramp time/min		5	1	1	1
Hold time/min		25	10	1	1
Power/%[a]		60	20	10	10
Detection limits		Cd	Cu	Pb	Zn
ICP-AES	λ/nm	214.438	324.754	220.351	213.856
	LOD[b]/mg kg^{-1}	0.2	0.2	1.0	0.1
DRC-ICP-MS	Isotope	^{114}Cd	^{63}Cu	^{208}Pb	^{64}Zn
	LOD[b]/mg kg^{-1}	0.003	0.07	0.003	0.25

Notes: [a]100% power corresponds to 1450 W.
[b]LOD calculated according to 3σ criteria.

Table 2. Found values, standard deviation of reproducibility and limit of reproducibility for Cd, Cu, Pb and Zn by ICP-AES in CRM 025–050 ($n = 6$) compared to certified values.

Element	Certified value mean ± U[a] (mg kg^{-1})	Found value mean ± U[a] (mg kg^{-1})	Standard deviation of reproducibility, s_R (%)	Limit of reproducibility, R[b] (%)
Cd	369 ± 46.3	365 ± 18.6	2.6	7.2
Cu	7.76 ± 1.68	8.18 ± 0.82	5.0	14.0
Pb	1447 ± 203	1523 ± 118	4.0	11.2
Zn	51.8 ± 8.29	49.1 ± 5.09	5.2	14.5

Notes: [a]expanded uncertainty $k = 2$ for 95% confidence interval.
[b]$R = 2.8$x s_R, 95% confidence interval.

The soil pH was determined in a suspension 1 : 5 (v/v) soil to 1 mol L^{-1} KCl by stirring for 5 min as indicated in [47]. The organic carbon (OC) content was determined using the Schollenberger method by oxidising the organic matter from 0.2 g soil with 5–10 ml of 1.6% (w/v) sulfochromic mixture on a hot plate for 20 min. The excess of chromic acid was titrated with 0.2 mol L^{-1} Mohr salt solution in the presence of diphenylamine as indicator [48].

2.5 *Quality control of analysis*

The accuracy and precision in ICP-AES was checked by the determination of metals in the CRM of soil mineralised with aqua regia and results are presented in Table 2.

Recovery degrees (%) were 99 ± 6 (Cd), 105 ± 10 (Cu), 105 ± 8 (Pb) and 95 ± 10 (Zn) for 95% confidence interval. The relative standard deviation of reproducibility s_R and limit of reproducibility R (2.8xs_R) were in the range of 2.6–5.2% and 7.2–14.5%, respectively.

The relative standard deviation of reproducibility and limit of reproducibility in DRC-ICP-MS for a concentration of 5 $\mu g\,L^{-1}$ elements were in the range of 0.5–3.2% and 1.4–9.0%, respectively.

3. Results and discussion

3.1 *Soil characteristics*

The identified major minerals (20–50%) were quartz, silicates (feldspar plagioclase), and sulphates (gypsum). Minor identified minerals (5–20%) were silicates (K-feldspar, muscovite, illite, chlorite), hydroxide (goethite), carbonate (calcite), sulphate (jarosite), sulphide (chalcopyrite). Trace identified minerals (<5%) were silicates (sepiolite, illite-montmorillonite, vermiculite), carbonate (dolomite). Primary minerals contained in the local ores such as sulphides (pyrite, galena, sphalerite) and compounds resulted from the oxidation of non-ferrous sulphides (Cu, Pb and Zn sulphates) were also found in traces.

The descriptive statistics for total element contents along with normal/alert/intervention level according to Romanian legislation [49], the pH values and OC (%) are presented in Table 3. Results revealed the high variability of metal contents and a non-normal distribution as indicated by skewness and kurtosis.

The comparison of soil metal contents with the Romanian legislated levels for sensitive soils showed that Pb exceeded the alert level (50 $mg\,kg^{-1}$) in all samples and the intervention limit (100 $mg\,kg^{-1}$) in all but one sample. The concentrations of total Cd, Cu and Zn were over the corresponding alert levels (3; 100; 300 $mg\,kg^{-1}$) in 61%, 77% and 90% of the total samples and exceeded the intervention levels in 29%, 45% and 51% of cases, respectively.

Along with our results, literature data about contents of heavy metals in soil in other non-ferrous ores processing centres in Romania are presented in Table 4. Compared with Copsa Mica, another Cd, Pb and Zn processing centre in Romania, the level of pollution is higher in Baia Mare excepting Cd [50,51]. Pb and Zn contents in soil have comparable intervals for Baia Mare and Zlatna, a former Cu and H_2SO_4 production centre, while Cu and Cd are higher in Zlatna [50,52].

A summary of the soil DTPA extraction results in Baia Mare compared with other studies in Europe is shown in Table 5. The comparative mobility of the studied metals as a percentage of DTPA extractable content with respect to total content was: Cd (1.3–80%) > Cu (2.2–40%) > Pb (2.0–34%) > Zn (0.3–21%).

Considering the total metal content, Baia Mare has a higher level of soil contamination with Cu and Zn than Pribram (Pb smelting) in Czech Republic [53] and Cu, Pb and Zn than Nord-Pas-de-Calais (Pb and Zn smelting) in France [54]. The DTPA extractable content of Cd in soil from Baia Mare is of the same magnitude, while Cu is higher and Pb lower than in the previous two centres. In case of Zn, the concentration extracted in DTPA is four times higher compared to Pribram site and five times lower than in Nord-Pas-de-Calais. In terms of the DTPA extraction degrees, results are similar for all three sites. On the other side, Papafilippaki reported lower contents and DTPA extraction degrees of metals in soils of agricultural use [55]. It is obvious the anthropogenic input of metals around the smelting centres and the relation with the nature of the contamination source. Based on the total content of metals in soil and extractability in DTPA, Cu and Zn should be considered together with Pb and Cd, much more toxic, in the soil remediation strategy in the Baia Mare city.

Table 3. Descriptive statistics for total metal contents in soil (mg kg^{-1}) in the Baia Mare city ($n = 31$) compared to normal/alert/intervention values for sensitive soils according to Romanian legislation, pH and OC (%).

Parameter	Unit	Min.	Max.	Median	Mean	Std. dev.	Skewness	Kurtosis	Normal value[a]	Alert value[b]	Intervention value[c]
Cu	mg kg^{-1}	78.3	962	168	280	240	1.42	1.13	20	100	200
Pb	mg kg^{-1}	87.7	9880	479	1056	1736	4.66	23.9	20	50	100
Zn	mg kg^{-1}	109	11500	652	1685	2454	2.73	8.25	100	300	600
Cd	mg kg^{-1}	1.90	25.4	3.35	6.65	6.28	1.79	2.69	1	3	5
pH		4.30	7.83	6.98	6.80	0.89	−1.03	0.70	–	–	–
C org	mg kg^{-1}	0.20	4.39	2.33	2.31	0.97	−0.03	0.51	–	–	–

Notes: [a]Normal value refers to concentration for which the site is considered clean with no eco-toxicological risk.
[b]Alert value is the concentration above which the contaminant should generally be regarded as undesirable and possibly unacceptable and some form of remedial action may be necessary.
[c]Intervention value indicates the contaminant concentration above which it is considered as posing an environmental risk and clean-up is necessary.

Table 4. Contents of Cd, Cu, Pb and Zn in soil in other non-ferrous ores processing centres in Romania.

Site	Element	Range ($mg\,kg^{-1}$)	Mean ($mg\,kg^{-1}$)	Median ($mg\,kg^{-1}$)	Reference
Copsa Mica (Cd, Pb and Zn smelting)	Cu	29.6–150	57.0	71.1	[50]
	Pb	28.6–761	250	292	
	Cd	–	9.9	–	[51]
	Cu	–	61.0	–	
	Pb	–	338	–	
	Zn	–	547	–	
Zlatna (Cu smelting and H_2SO_4 production; stopped activity)	Cd	< LOD–330	3.35	–	[52]
	Cu	41.0–12000	863	–	
	Pb	32.0–7860	740	–	
	Zn	89.0–15600	920	–	
Baia Mare (Cu, Pb and Zn smelting, H_2SO_4 production)	Cd	1.9–25.4	6.65	3.35	Present study
	Cu	78.3–962	280	168	
	Pb	87.7–9880	1056	479	
	Zn	109–11500	1685	652	

The great potential for chemical remobilisation of Cd and Cu in the Baia Mare soil in neutral reagents (1 mol L^{-1} $MgCl_2$) or weakly acid (0.11 mol L^{-1} HOAc) was previously remarked when performing the Tessier's and BCR partitioning schemes on soil samples collected in the vicinity of the Baia Mare city [3,12]. These partitioning approaches showed also the tendency of Zn and Pb to be immobilised in soil as residual or reducible species on Fe-Mn oxides. Our results were similar to those reported by Kashem *et al.* [27] who found that most Cd was associated in the mobile fraction, while Pb and Zn in the reducible and residual ones.

3.2 *Distribution maps of pH, OC and Cd, Cu, Pb and Zn on top soil*

The spatial distribution of pH, OC (%) and metal contents extracted in aqua regia and DTPA in soil on 0–20 cm horizon are presented in Figure 2.

According to the distribution map, the OC was below 1.2% in the proximity of the Flotation Station, where soil was found to have low acidic reaction, with pH values in the range of 4.3–5.0. With increasing distance from this polluter, as the soil pH turned to neutral and slightly alkaline, the OC values were higher, up to 4.4%. However, these values were one order of magnitude below those reported in Nord-Pas-de-Calais in France [54] as a result of a more marked deterioration of soil quality.

The distribution maps revealed the anthropogenic origin of metals and led to the following statements. Although the maximum of the total content for all four metals was registered around the Flotation Station, the contamination with mobile metal species from deposited tailings is less important compared to the area in the proximity of the Cuprom plant. The distributions of the residual species (Cu_{REZ}, Zn_{REZ}, Cd_{REZ}, Pb_{REZ}) calculated as difference between the total and extractable content in DTPA were similar to those of the total metal contents and were no more drawn. The maximum of the DTPA extractable metals was identified 2–3 km far from the Cuprom plant where deposition of airborne particulate matter occurred. This pollution pathway was emphasised by the high

Table 5. Descriptive statistics for DTPA-extractable metal contents in soil (mg kg^{-1}) in the Baia Mare city ($n = 31$) compared with other studies in Europe.

Site	Parameter	Unit	Min.	Max.	Median	Mean	Std. dev.	Skewness	Kurtosis	Reference
Baia Mare, Romania (Cu, Pb and Zn smelting, H_2SO_4 production)	Cu_{DTPA}	mg kg^{-1}	18.0	190	40.0	59.0	47.4	1.57	1.79	Present study
	Pb_{DTPA}	mg kg^{-1}	20.0	290	87.0	112	68.4	1.10	0.95	
	Zn_{DTPA}	mg kg^{-1}	21.0	338	71.0	86.0	73.7	2.38	6.06	
	Cd_{DTPA}	mg kg^{-1}	0.28	6.50	1.50	2.00	1.33	1.87	3.80	
Pribram, Czech Republic (Pb smelting and mining)	Cu_{DTPA}	mg kg^{-1}	–	–	–	6.70	–	–	–	[53]
	Pb_{DTPA}	mg kg^{-1}	–	–	–	257	–	–	–	
	Zn_{DTPA}	mg kg^{-1}	–	–	–	21.2	–	–	–	
	Cd_{DTPA}	mg kg^{-1}	–	–	–	2.30	–	–	–	
Nord-Pas-de-Calais, France (Pb and Zn smelting)	Cu_{DTPA}	mg kg^{-1}	–	–	–	23.2	–	–	–	[54]
	Pb_{DTPA}	mg kg^{-1}	–	–	–	150	–	–	–	
	Zn_{DTPA}	mg kg^{-1}	–	–	–	455	–	–	–	
	Cd_{DTPA}	mg kg^{-1}	–	–	–	1.4	–	–	–	
Crete, Greece (agrochemical contamination)	Cu_{DTPA}	mg kg^{-1}	1.55	15.9	3.19	4.86	–	–	–	[55]
	Pb_{DTPA}	mg kg^{-1}	0.97	3.98	2.36	2.28	–	–	–	
	Zn_{DTPA}	mg kg^{-1}	1.31	3.26	1.82	2.09	–	–	–	

Subscript index DTPA stand for content of metal extracted in DTPA.

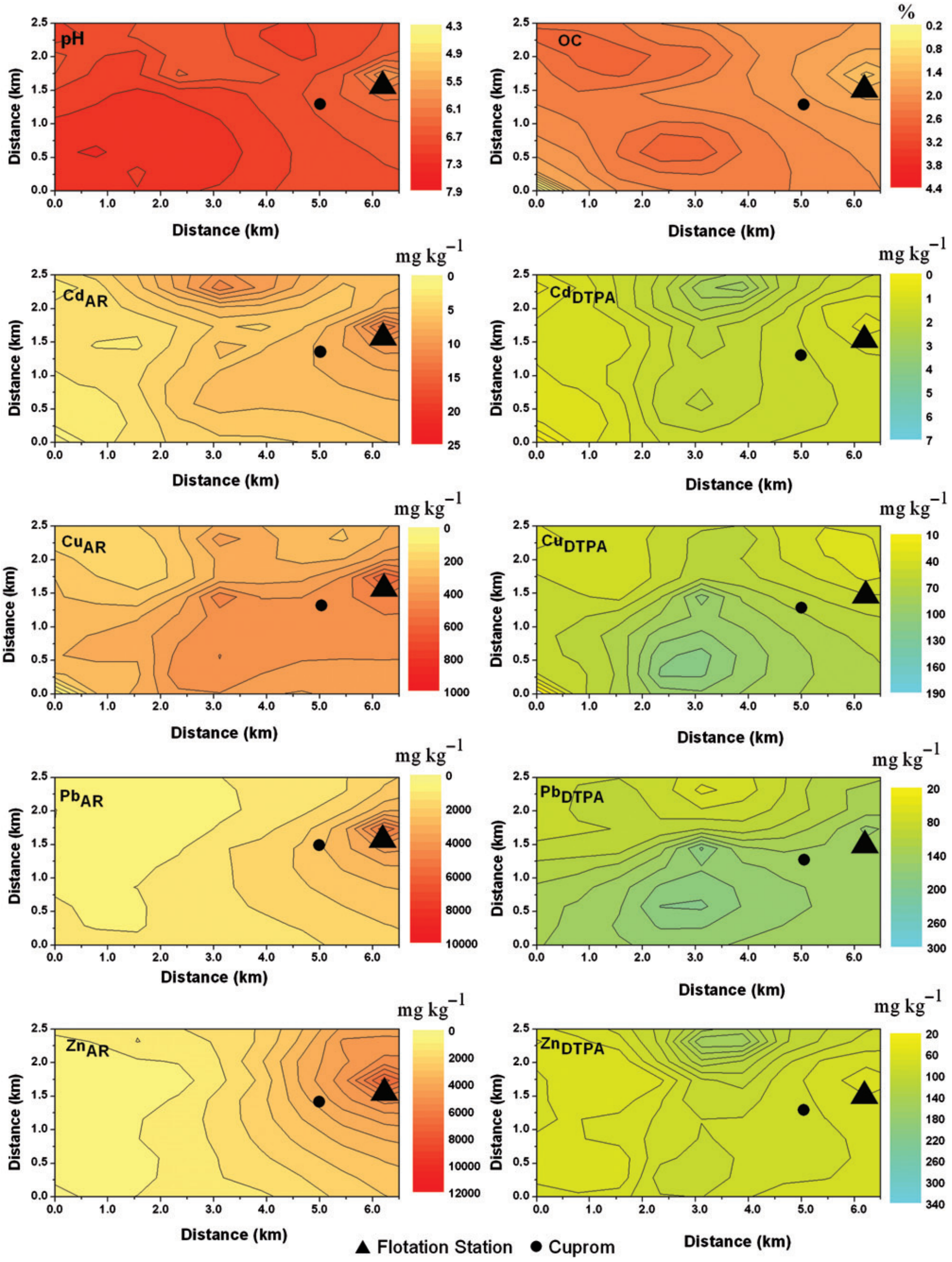

Figure 2. Spatial distribution of soil pH, OC (%), total content of metals extracted in aqua regia (Cu_{AR}, Zn_{AR}, Cd_{AR}, Pb_{AR}) and content of mobile metals extracted in DTPA (Cu_{DTPA}, Zn_{DTPA}, Cd_{DTPA}, Pb_{DTPA}).

fraction of mobile species (80–90%) in 1 mol L^{-1} $MgCl_2$ in the dust evacuated through the chimney [12].

3.3 *Pearson's correlation matrix and PCA results*

In polluted areas the study on distribution and correlation of metal mobility related to the polluting sources, which could modify the natural distribution of metals in soil is not possible without considering a statistical approach. The Pearson's matrix (Table 6) indicates a significant positive correlation among aqua regia extractable metal contents as well as among the residual species. A significant positive correlation between the DTPA extractable fraction and total element content is observed only for Cu. Also there is a good correlation among DTPA extractable contents of Cu, Cd, Zn, while Pb is correlated with total Cu and that extracted in DTPA. This correlation shows an affinity between Cd and Zn, and Cu and Pb, respectively.

In agreement with similar chemistry of Cd and Zn with respect to ionic structures, electronegativities and ionisation energies [56], the affinity between these metals was found in previous studies [3,22] on soils and river sediments collected in the Baia Mare zone. The positive correlation between Cu and Zn extractable in DTPA is due to the presence of their water soluble sulphates, while that between Cu and Pb to their carbonates and possible organic complexes. Results confirm previous observation of Cordos *et al.* [38], who found Cu as sulphate and carbonate, Zn as sulphate and Pb as carbonate in the Baia Mare soil. The role played by the organic matter in the bioavailability and mobility of metals in soil has been reported [7,55,57]. Organic matter could be a reliable indicator of the bioavailable and mobile metal content in soil shown by the negative correlation of metals extracted in aqua regia and residual species related to OC. However, considering the slight positive correlation between DTPA extractable contents and OC, the complexation of metals in soil appears less important in the studied area. This is also a result of a low OC in soil. Thus, soluble species originate mainly in airborne particulate matter and result less from complexation processes. Species susceptible to pH changes, which are potentially phytoavailable, could be attributed to carbonates but the slight correlation between DTPA extractable species and soil pH suggests that the retention of metals as carbonate is not dominant. Therefore the pH and OC associated with DTPA extractant is a poor representation regarding metal mobility in polluted soils in the studied area.

The PCA on contents of Cd, Cu, Pb and Zn in soil extracted in aqua regia and DTPA was carried out in order to identify the anthropogenic origin of metals related to the existing pollution sources. The applicability of the PCA method in such studies has been demonstrated [58–62]. In Table 7 the Varimax rotated factor loadings are presented.

It was found that three PC described 78.3% of the total variance of the system including 31 objects and 14 experimental variables. The first latent factor PC1, which explains 41.8% of the total variance, could be named 'ore enrichment' and is associated with aqua regia extractable metal contents and residual species. It expresses pollution with residual species caused by the ore processing at the Flotation Station as shown by metal distributions around this polluter. The PC2 latent factor named 'Cu ore roasting' describing 23.4% of the total variance is associated with Cu, Zn and Cd extractable in DTPA and can be attributed to pollution caused by the Cuprom plant with easily soluble species. The PC3 latent factor explaining 13.1% of the total variance includes

Table 6. Pearson's correlation matrix.

Variables	$\mathrm{Cu}_{\mathrm{AR}}$	$\mathrm{Cu}_{\mathrm{DTPA}}$	$\mathrm{Cu}_{\mathrm{REZ}}$	$\mathrm{Zn}_{\mathrm{AR}}$	$\mathrm{Zn}_{\mathrm{DTPA}}$	$\mathrm{Zn}_{\mathrm{REZ}}$	$\mathrm{Cd}_{\mathrm{AR}}$	$\mathrm{Cd}_{\mathrm{DTPA}}$	$\mathrm{Cd}_{\mathrm{REZ}}$	$\mathrm{Pb}_{\mathrm{AR}}$	$\mathrm{Pb}_{\mathrm{DTPA}}$	$\mathrm{Pb}_{\mathrm{REZ}}$	pH	OC
$\mathrm{Cu}_{\mathrm{AR}}$	**1**	**0.673**	**0.986**	**0.429**	**0.493**	**0.414**	**0.545**	**0.399**	**0.470**	**0.683**	**0.448**	**0.673**	−0.098	−0.170
$\mathrm{Cu}_{\mathrm{DTPA}}$		**1**	**0.541**	−0.122	**0.602**	−0.140	0.134	0.624	−0.016	0.060	0.530	0.039	0.305	0.273
$\mathrm{Cu}_{\mathrm{REZ}}$			**1**	**0.516**	**0.425**	**0.503**	**0.590**	0.313	**0.538**	**0.764**	**0.391**	**0.757**	−0.181	−0.255
$\mathrm{Zn}_{\mathrm{AR}}$				**1**	0.003	**1.000**	**0.443**	−0.047	**0.475**	**0.712**	0.205	**0.712**	−0.273	**−0.421**
$\mathrm{Zn}_{\mathrm{DTPA}}$					**1**	−0.027	0.215	**0.891**	0.002	0.018	−0.070	0.021	0.198	0.231
$\mathrm{Zn}_{\mathrm{REZ}}$						**1**	**0.437**	−0.074	**0.475**	**0.711**	0.208	**0.711**	−0.279	**−0.428**
$\mathrm{Cd}_{\mathrm{AR}}$							**1**	0.298	**0.971**	**0.558**	0.011	**0.564**	**−0.396**	**−0.442**
$\mathrm{Cd}_{\mathrm{DTPA}}$								**1**	0.061	−0.030	0.048	−0.033	0.168	0.267
$\mathrm{Cd}_{\mathrm{REZ}}$									**1**	**0.591**	0.000	**0.597**	**−0.456**	**−0.529**
$\mathrm{Pb}_{\mathrm{AR}}$										**1**	0.310	**0.999**	**−0.539**	**−0.454**
$\mathrm{Pb}_{\mathrm{DTPA}}$											**1**	0.274	0.161	0.092
$\mathrm{Pb}_{\mathrm{REZ}}$												**1**	**−0.551**	**−0.463**
pH													**1**	0.350
OC														**1**

Subscript index AR, DTPA and REZ stand for content of metal extracted in aqua regia, content of metal extracted in DTPA and content of residual species (calculated as difference between the total and DTPA extractable contents), respectively.

Table 7. Varimax rotated factor loadings.

Variable	PC1	PC2	PC3
Cd_{AR}	**0.650**	0.338	−0.545
Cu_{AR}	**0.711**	0.615	0.192
Pb_{AR}	**0.945**	0.012	−0.009
Zn_{AR}	**0.831**	−0.132	0.015
Cd_{DTPA}	−0.056	**0.904**	−0.110
Cu_{DTPA}	0.084	**0.817**	0.436
Pb_{DTPA}	0.376	0.135	**0.769**
Zn_{DTPA}	−0.020	**0.903**	−0.092
Cd_{REZ}	**0.694**	0.127	−0.542
Cu_{REZ}	**0.790**	0.515	0.120
Pb_{REZ}	**0.941**	0.007	−0.040
Zn_{REZ}	**0.831**	−0.159	0.018
pH	−0.466	0.242	0.485
OC	−0.543	0.287	0.388
Explained variance (%)	41.8	23.4	13.1

Subscript index AR, DTPA and REZ stand for content of metal extracted in aqua regia, content of metal extracted in DTPA and content of residual species (calculated as difference between the total and DTPA extractable contents), respectively. The highest loadings are shown in bold face.

DTPA extractable Pb and in some extent DTPA extractable Cu, reflecting pollution from 'Pb ore roasting' in the Romplumb plant.

Generally, the car traffic is a common anthropogenic source of Pb as fuel additive and Zn present in car tyres. In our case, the lack of association between these two elements in the late two latent factors confirms that the car traffic is a pollution source of low importance compared to the industrial activity in the area. These findings are also confirmed by the lack of correlation between the mobile species of these two elements. The presence of the experimental variables for Cu in all three latent factors shows that a net discrimination among pollution sources is rather difficult. This is the result of the relative neighbourhood of Cuprom and Flotation Station and the consequently overlap of pollution effects.

4. Conclusions

The paper demonstrates the high level of pollution with Cd, Cu, Pb and Zn based on the total and DTPA extractable contents in soil in the Baia Mare city compared to other smelters in Romania and Europe. The effect of historical pollution with metals on soil quality is obvious and remediation measures would be necessary. The PCA revealed three anthropogenic origins of contaminants associated with the polluters in the city. The soil contamination with mobile species is maximum in the proximity of pyrometallurgical centres for ore roasting, the main polluters with airborne particulate matter. Around the Flotation Station the total content of metals is maximum and the pollution induced by residual species from deposited tailings is dominant. Statistics revealed that the influence of traffic is insignificant compared to the industrial contamination. In the case of Cu, there is an overlapping of the pollution coming from two main sources. The Pearson's correlation matrix revealed that the retention of metals in soil as organic complexes and carbonates is not dominant and soil OC and pH are poor indicators to predict the mobility of the studied metals. An affinity between Cd and Zn as well as between Cu and Pb were also identified.

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