

SOIL POLLUTION ASSESSMENT IN THE BAIJA MARE AREA AFTER PARTIAL CLOSURE OF ORE PROCESSING ACTIVITIES

¹Levei Erika, ¹Roman Cecilia, ¹Roman Marius,
²Ponta Michaela, ²Frentiu Tiberiu

¹INCDO-INOE 2000 - Research Institute for Analytical Instrumentation, 67 Donath, 400293 Cluj-Napoca, Romania, email: erika.levai@icia.ro

²Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos, 400028, Cluj-Napoca, Romania, email: ftibi@chem.ubbcluj.ro

ABSTRACT

The paper presents the assessment of the soil pollution with Cu, Pb and Zn in the Baia Mare area, historically polluted with metals resulted from mining and processing of non-ferrous ores. Despite the closure of mines and reducing the activity related to ore processing, Baia Mare is still a highly polluted site with Pb, Cu and Zn. The Tessier extraction scheme carried out on soil samples recently collected revealed the residual fraction as dominant for all three metals, followed by the reducible fraction bound to Fe and Mn oxides. The exchangeable fraction, considered as the most mobile fraction and that bound to carbonates, which can be mobilized under acidic conditions, were lower. The presence of the oxidisable metal fraction was also observed.

INTRODUCTION

Soil pollution with heavy metals is a major environmental problem due to their high toxicity, low biodegradability and cumulative nature. Moreover it represents a serious threat to human health by entering into food chain or by leaching into groundwater (Schulin et al., 2007; Wu et al., 2008; Frentiu et al., 2008). Metals can be distributed among the soil components and associated with them in different ways: ion-exchange, adsorption, precipitation, complexation. Thus, the composition and properties of soil have a wide influence on the mobility, bioavailability and toxicity of metals.

Baia Mare was the main mining and ore processing centre in NW Romania, recognized as a "hot spot" in Europe with respect to metal pollution (Cordos et al., 1995; Frentiu et al., 2009; Levei et al., 2009). The main industry of the area developed more than one century ago was based on the processing of non-ferrous ores containing Cu, Pb and Zn. The extracted ores were concentrated at the Flotation Station and processed within the Romplumb and Cuprom plants to produce sulphuric acid and different Cu and Pb products. Currently, the Romplumb lead smelter is operating at reduced capacity, focused on the recovery and refinement of Pb from wastes, while the Flotation plant and Cuprom smelter have been closed since December 2007 and January 2009, respectively.

The objective of this study was to assess the soil pollution with Cu, Pb and Zn after the closure of mines and cutback of the ore processing activities, using the Tessier sequential extraction scheme, which offers data about the partitioning of metals on five fractions: exchangeable (EXCH), bound to carbonates (CARB), reducible (RED), oxidisable (OX) and residual (RES).

MATERIALS and METHODS

Sampling

In 2010 a number of 30 soil samples were collected from 0–20 cm depth in the vicinity of the Flotation Station (9 samples), Cuprom (9 samples) and Romplumb (12 samples) plants Baia Mare town, NW Romania. The soils were air-dried at room temperature, ground to a fine powder in a tungsten-carbide swing mill and sieved to <90 μm .

Sample preparation and chemical analysis

Total metal contents in soil were obtained following the mineralisation of 1.0 g soil sample with 10 ml *aqua regia*. Sequential extraction according to the Tessier scheme was carried out using 2.5 g soil, in order to separate the following five fractions (Tessier et al., 1979). The soluble and exchangeable fraction (EXCH) was extracted with 20 ml of 1M MgCl_2 (pH=7.0) for 1h. The carbonates (CARB) were extracted by leaching with 20 ml 1M NaAc (pH=5) for 4h. Metals bound to iron and manganese oxides, representing the reducible fraction (RED) were extracted with 50 ml of 0.04M $\text{NH}_2\text{OH HCl}$ in 25%HOAC (pH=2) at 96 °C for 5.5h. Metals bound to organic matter, representing the oxidisable fraction (OX) were extracted with 12.5 ml of 3.2M NH_4Ac for 0.5h, after oxidation with 0.02M HNO_3 and 30% H_2O_2 (pH=2.0) at 85 °C for 2 h. The residual fraction (RES) was dissolved in *aqua regia* using 7 ml of 10M HCl and 2.3 ml of 15.8M HNO_3 on a hot plate for 2 h. All solid/liquid separations were performed by centrifugation at 5000 rpm for 15 min. The supernatant was removed and analysed for metals. For each fraction a blank was subjected to the same procedure. The inductively coupled plasma scanning spectrometer SPECTRO CIROS^{CCD} (Spectro Analytical Instruments Kleve, Germany) was used for the determination of metal contents. The soil pH was determined in a suspension of 1:5 (v/v) soil in 1M KCl. The organic carbon content (OC) was determined 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 0.2M Mohr salt solution in the presence of diphenylamine as indicator.

RESULTS

Values of pH, organic matter and total Cu, Pb, Zn contents are presented in Table 1. Concentrations of metals in the analysed samples varied in a large range. The concentrations of Cu and Pb were the highest in the soil samples from Romplumb, while that of Zn near the Flotation Station. Moreover, the contents of Cu and Pb exceeded the alert levels (AL) for less sensitive soil in all samples, while the median value exceeded the corresponding intervention level (IL) set by the Romanian legislation (MO, 1997).

Table 1. Contents of total Cu, Pb, Zn, organic carbon and pH values in soil

Parameter	Sampling site	Range	Average	Median	AL	IL
pH	Flotation (n=9)	4.1-8.3	6.3	5.7	-	-
	Cuprom (n=12)	3.6-8.7	5.1	4.6		
	Romplumb (n=9)	5.9-7.5	6.7	6.6		
OC (%)	Flotation (n=9)	0.46-6.6	3.6	2.9	-	-
	Cuprom (n=12)	0.6-4.7	2.5	1.7		
	Romplumb (n=9)	1.1-5.3	3.4	3.8		
Cu (mg/kg)	Flotation (n=9)	250-21600	9700	9300	250	500
	Cuprom (n=12)	330-31200	5300	720		
	Romplumb (n=9)	4200-23100	13400	12300		
Pb (mg/kg)	Flotation (n=9)	1100-36000	13900	10500	250	1000
	Cuprom (n=12)	320-12800	3000	1200		
	Romplumb (n=9)	17100-99400	45700	36700		
Zn (mg/kg)	Flotation (n=9)	145-58000	25400	15100	700	1500
	Cuprom (n=12)	280-11600	2000	540		
	Romplumb (n=9)	4400-32700	15500	14700		

According to figure 1, the residual fraction (RES) was dominant for all three metals, followed by the reducible fraction bound to Fe and Mn oxides (RED). The exchangeable fraction (EXCH) of metals, considered to be the most mobile fraction and that bound to carbonate fraction (CARB), which can be mobilized under acidic conditions, were found in lower percentages. The presence of the oxidisable (OX) metal fraction was also observed.

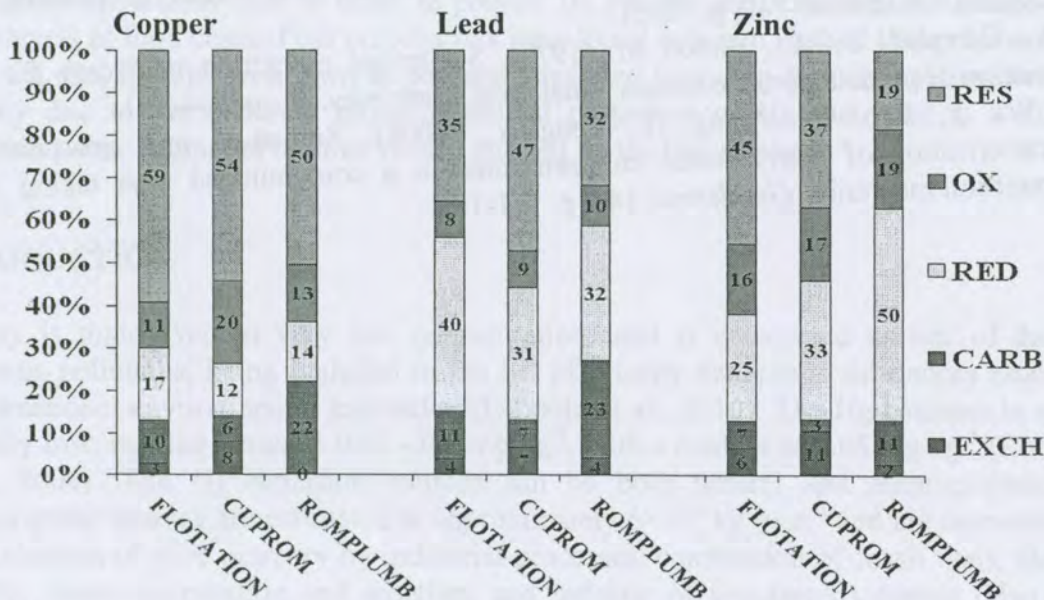


Figure 1. Partitioning of Cu, Pb and Zn in soils as determined by the Tessier scheme

CONCLUSIONS

The results showed that the pollution of soil persists even after the partial closure of the ore processing activities and under severe environmental conditions the remobilisation of metals retained as carbonates, reducible and oxidisable fractions could occur.

LIST OF REFERENCES

- Cordos E.A., Frentiu T., Rusu A., Vatca G. (1995). Elemental speciation of lead, zinc and copper in sedimented dust and soil using a capacitively coupled plasma atomic emission spectrometer as detector. *Analyst*. 120, p. 725-731.
- Frentiu T., Ponta M., Levei E., Cordos E. (2009). Study of partitioning and dynamics of metals in contaminated soil using modified four-step BCR extraction procedure. *Chemical Papers*. 63, p. 239-248.
- Frentiu T., Ponta M., Levei E., Gheorghiu E., Kasler I., Cordos E.A. (2008). Validation of the Tessier scheme for speciation of metals in soil using the Bland and Altman test. *Chemical Papers*. 62, p. 114-122.
- Levei E., Frentiu T., Ponta M., Senila M., Miclean M., Roman C., Cordos E. (2009). Characterisation of soil quality and mobility of Cd, Cu, Pb and Zn in the Baia Mare area Northwest Romania following the historical pollution. *International Journal of Environmental Analytical Chemistry*. 89, p. 635-649.
- MO, 1997. Ministerial Order 956:1997, Official Gazette of Romania, 303/bis/06.11.1997
- Schulin R., Curchod F., Mondeshka M., Daskalova A., Keller A. (2007). Heavy metal contamination along a soil transect in the vicinity of the iron smelter of Kremikovtzi (Bulgaria). *Geoderma*. 140, p. 52-61.
- Tessier A., Campbell P.G.C., Bisson M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*. 51, p. 844-851.
- Wu C., Wu J., Luo Y., Zhang H., Teng Y. (2008). Statistical and geostatistical characterization of heavy metal concentrations in a contaminated area taking into account soil map units. *Geoderma*. 144, p. 171-179.