

## MOBILITY OF LEAD IN SOILS POLLUTED BY NON-FERROUS METALLURGICAL PLANT IN NORTHWESTERN ROMANIA

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### **Abstract**

*The soil contamination with Pb and the Pb mobility in soils near a non-ferrous metallurgical plant in Baia-Mare town, a well-known region for its high level of environmental pollution, were studied using the Community Bureau of References (BCR) Sequential Extraction Procedure. The results indicated a high concentration of the total Pb content, which exceeded the alert thresholds in all samples and the intervention thresholds in more than a half of the samples, according to the Romanian legislation for less sensitive soil uses. About 24% of the total Pb content was found to be in mobile forms and about 48% in mobilizable forms, indicating that, despite the suspending of ore processing activities, a significant soil contamination with mobile Pb fractions still exists. These mobile and mobilizable fractions represent a potential threat to the environment and to human population living around the plant. About 11% of the total Pb content was found in the residual fraction, considered to be immobile and not posing significant risk for the environment.*

**Keywords:** BCR sequential extraction procedure, Pb mobility in soil, soil contamination.

### **INTRODUCTION**

Metals in soil are associated with different soil components and according to their mobility, are divided into exchangeable, reducible, oxidizable and residual forms (Tack et al., 1995). In order to accomplish a comprehensive risk assessment of soil pollution with metals, along the total metal content, the identification of the metals mobility in soil is also necessary. The most used methods to determine the metal fraction in soils are the Tessier (Tessier et al., 1979) and the BCR schemes (Quevauviller, 1998).

Usually, metals extracted in the first three steps of a BCR procedure are related with anthropogenic contamination and the metals found in the residual fraction are linked to natural occurrence in the parent rock (Ratuzny et al., 2009).

The town of Baia-Mare, located in the North Western part of Romania, was one of the main mining and ore processing centre during the late 19<sup>th</sup> and early 20<sup>th</sup> Century. Mining exploitations and non-ferrous ore processing plants functioned in the town and around the

town for a long period of time, but currently, all these facilities are either decommissioned or in the preservation process.

The environmental components in this area have been contaminated for years with metals, due to dust emission, mining and metallurgical wastes (Frentiu et al., 2008a; Frentiu et al. 2008b; Senila et al., 2001). Recently, the area recorded a downward trend of pollution as a positive consequence of measures to limit environmental pollution from industrial activities (Levei et al., 2009; Miclean et al., 2008). Also, in the last years, the metallurgical non-ferrous plants had changed their technological processes and had tried to use cleaner technologies to reduce the environmental pollution in the area (Modoi et. al., 2013; Bird et. al., 2009).

Since the end of 2012, the Pb metallurgical non-ferrous plant situated in the proximity of the studied area is in a preserving stage.

In order to understand the possible Pb effects that could be generated on the soil component, the Pb fractions were evaluated using BCR sequential extraction procedure (Zimmerman and Weindorf, 2010). This method has a large

application in the assessment of soil contamination with heavy metals and allows the prediction of metal mobility in soil (Frentiu et al., 2009).

## MATERIALS AND METHODS

### Sampling

A number of 15 soil samples (S1-S15) were collected near the Pb metallurgical non-ferrous plant, from a hill, covering almost 11,800 m<sup>2</sup>. On the top of the investigated hill a smokestack existed, but in the present it is decommissioned (Figure 1). All soil samples were taken from a 30 cm depth using a stainless steel shovel.

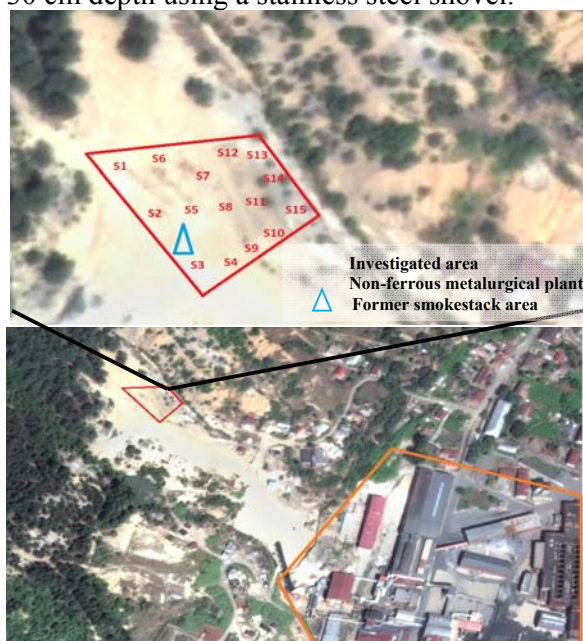


Figure 1. Sampling site

### Sample preparation and analysis

The soil samples were dried at 105°C for 24 h, crushed and sieved through a 2 mm diameter sieve. The fraction below 2 mm was collected, homogenized and stored in polyethylene bags until analysis.

To determine the Pb mobility in soil, the BCR sequential extraction procedure was performed according to Zimmerman and Weindorf (2010). An amount of 1 g of soil sample was weighed into a 50 ml centrifuge tube and sequentially exposed to different reagents.

The acid-extractable Pb fraction (F1) was extracted in 40 ml of 0.11 M CH<sub>3</sub>COOH for 16 h at 20±5°C, under continuous shaking (15 rpm). The extract was centrifuged at 4,500 rpm

for 10 minutes. The supernatant was filtered in 50 ml tubes.

To determine the reducible Pb fraction (F2), the residue from F1 was subjected to extraction in 40 ml of 0.1 M NH<sub>2</sub>OH·HCl (pH=2 with HNO<sub>3</sub>) for 16 h under continuous shaking at 20±5°C.

For the oxidizable Pb fraction (F3) 10 ml 8.8 M H<sub>2</sub>O<sub>2</sub> were added to the residue from F2, and shaken for 1 h at room temperature. Then another 10 ml H<sub>2</sub>O<sub>2</sub> (pH=2) were added in each tube and heated to 85°C in a water bath, until the sample volume was reduced to approximately 1 ml. After cooling, 50 ml of 1 M NH<sub>4</sub>OAc (pH=2 with HNO<sub>3</sub>) were added and shaken for 16 h at 20±5°C.

For determining the residual fraction (F4), the residue from F3 was dried and collected into 100 ml reaction flask. A volume of 28 ml aqua regia (21 ml of 12 M HCl and 7 ml of 15.8 M HNO<sub>3</sub>) was added and maintained at room temperature for 16 h. The mixture was then heated under reflux conditions for 2 h. The solution was filtered and diluted to 50 ml with 0.5 M HNO<sub>3</sub>.

To determine the total Pb concentration, an amount of 1 g soil sample was weighed, introduced into the reaction flask and extracted in 28 ml aqua regia.

The Pb concentration from the extracts was determined by inductively coupled plasma optical emission spectrometry using an OPTIMA 3500 DV spectrometer.

The pH of soils was measured in a suspension 1/5 (m/v) soil to water extract with the 350i multiparameter (WTW, Wilhelm, Germany).

## RESULTS AND DISCUSSIONS

The results indicated a high variability of Pb compounds in the studied area. The total concentration of Pb compared with the alert thresholds and the intervention thresholds for less sensitive soils are presented in Figure 2.

Total Pb concentration ranged between 300-25,000 mg/kg and exceeded the alert thresholds (250 mg/kg) in all samples, while in 68% of the analyzed samples it exceeded the intervention threshold (1,000 mg/kg) for less sensitive use, set by the Romanian legislation (Law 756/1997).

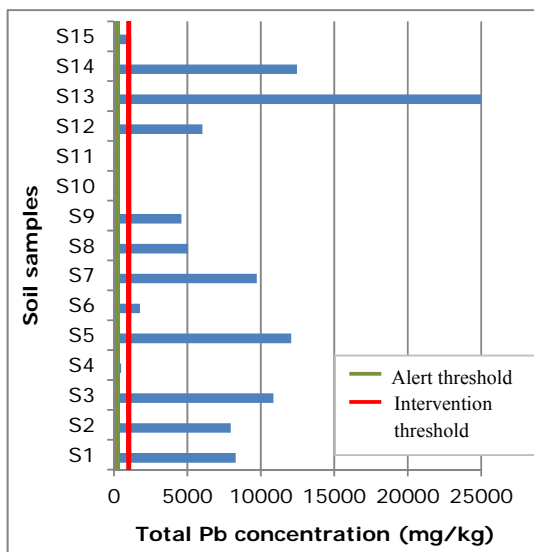


Figure 2. Total concentration of Pb in soil

The highest concentrations of Pb were found in samples situated at about 500 m distance from the metallurgical plant (S13 and S14), prevalent on the East side of the investigated field. This situation could be explained by the W to E predominant wind directions in the area that may favored the particulate Pb dispersion. The pH of soils was acidic, ranging between 3.6 and 5.5 with an average value of 4.8. The results showed that the fractionation of Pb varied from sample to sample, indicating a high variability of the Pb mobility in soil. The distribution of Pb fractions, according to the BCR sequential extraction procedure, is presented in Figure 3.

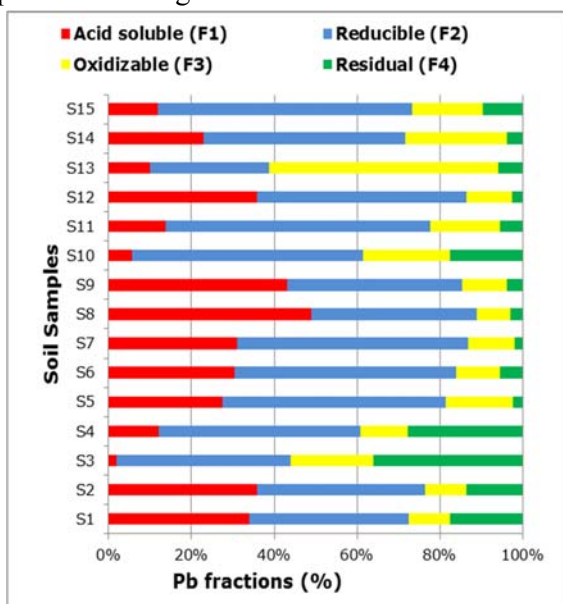


Figure 3. Distribution of Pb fractions in soils

The acid soluble fraction is considered the most mobile fraction of Pb and ranged between 2-49%, with an average of 24%, indicating that significant amounts of Pb can be released into the environment in acidic conditions. Generally, this Pb fraction is absorbed by plants and through the food-chain it can pose significant health risks (Gleyzes et al., 2002). The highest percent of mobile Pb content (>40%) was found in samples S8 and S9, where the soil was the most acidic (pH<4.2), as a consequence of the release of adsorbed and weekly bounded Pb from soil.

Despite the role of pH in determining the metals mobility, only the variation of soil pH cannot explain the high variation of the mobile Pb fraction. This variation could be a consequence of the overlapping pollution with Pb originating from several pollution sources. The multiple sources of pollution are suggested also by the fact that the points with the highest total Pb concentration are not overlapping with the points with the highest mobile Pb fractions. It is considered that the reducible metal fractions have moderate mobility and mobilizable fractions can migrate under extreme environmental conditions. The reducible fraction is formed by Pb compounds bounded to Fe and Mn oxides and the fraction ranged between 29 and 64%, with an average of 48% of the total concentration of Pb. The use of 0.1 M hydroxylamine as a reagent releases metal mostly from amorphous manganese oxide phases and in a lesser extent from iron oxide phase (Schuman, 1983; Vodyanitskii, 2006).

The oxidizable fraction ranged between 8-55%, with an average of 17% and contains the Pb bounded to organic matter and sulphides. It is considered to be less mobile than the previous two fractions. This assumption may be explained by the fact that the Pb organic fraction is supposed to be associated with humic substances which release small amounts of Pb metals in a slow manner, due to their stable molecular weight (Filgueiras et al., 2002). Even though this organic fraction is not bioavailable, it could be mobilized in oxidizing conditions.

immobile and does not represent potential threat to the environment.

## CONCLUSIONS

Generally, Pb was found predominately in reducible fraction, followed by the acid soluble, oxidizable and residual fractions.

The high percentage of Pb found in mobile and mobilizable fractions indicates that the metallurgical non-ferrous plant determined a more extensive pollution than initially considered. Therefore, future studies are needed to be conducted and the development of decontamination methods are taken into account for future researches.

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