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ORIGINAL ARTICLE

Zinc and Lead Content and Availability in Brazilian Soil Contaminated with Residue of a Secondary Smelting Lead Recycling Plant

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ABSTRACT

The sequential extraction procedure of Zinc and lead performed in a Brazilian soil showed that it presents high pollution potential once over 90% of total lead is present in fractions where the metals can be easily mobilized. The fraction contents are as follow: F1 = 174 and 15 mg kg^{-1}; F2 = 3155 and 9.7 mg kg^{-1}; F3 = 99 and 1.6 mg kg^{-1}; Residual fraction = 38 and 5.5 mg kg^{-1} for lead and zinc, respectively. The comparison with non contaminated soil only Pb^{2+} concentration is above its intervention reference concentration, 900 mg kg^{-1}.

Keywords: *BCR sequential extraction; soil contamination, metal ions*

1. INTRODUCTION

The rapid population growth associated with the increasing needs of human beings has been a direct reflection on the industrialization process, which has happened in an uncontrolled way and, in most cases, unsustainably. The consequence of this behavior is the contamination of compartments, such as atmosphere, hydrosphere [1,2] and geosphere, [3] which are the final destiny of all pollutants emitted in the Earth. [4]

Among several anthropogenic substances that reach the environment, the metals, especially those which are able to cause adverse health effects over living organisms even in low concentration, has attracted the attention of several researches in environmental area. [1,5,6] According to them, metal species can enter the environment through several routes such as air deposition after waste incineration [7], mining activities [8], fuel burning [9], industrial activities [10], the use of land for sewage disposal [11], pesticides and herbicides application [12] and others sources.

Soil compartment is formed by several types of substances such as minerals, organic matter, water, air,

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[♠]Corresponding author, e-mail castrogr@ibb.unesp.br living organisms and due to this complex structure metal species are able to participate in a great number of reactions become relatively immobile in subsurface soil environments. [13] Its organic matter is formed mainly by dead and decaying materials and this process may cause the formation of humic substances which have many adsorption sites to interact with metal species. [14,15] The mineral soil fraction is constituted by clay (oxides, carbonates, sulphates) and it can interact with metal species through the process of adsorption/desorption and because of this play key roles in soil fertility, chemical speciation and transport of nutrients and pollutants. [13]

As metal species are distributed in soil matrix associated with different substances the determination of total concentration of given specie does not provide environmental information about its potential of pollution. Numerous methods of fractionation and/or speciation have been developed to differentiate labile and inert metals in solid matrix such as soil and sediment. [16-19] Recently, the method developed by the Community Bureau of Reference [20] has been largely adopted once this kind of method is based on leaching or extraction procedures, which allow for the measurement of a wider range of forms or phases (elements that are bioavailable or not). [19, 21]

1.1. Implications of lead contamination in the city

The soil contamination with lead in a neighborhood of a battery factory in Bauru city was detected in 2002 and since then several cases of deleterious effects on human health due to lead exposure have been documented. Authors studied lead exposure in different population area, with and without contamination history, and found that in Bauru city the lead concentration in children may be above the action limit established by the World Health Organization, 10 µg/dL. [22-24] Lead concentration in children presented relationship with the distance from the source, the farther the lower the concentration, suggesting that secondary lead sources such as drinking water, food, soil and indoor dust also contributed to the overall contamination. [22]

Taking into account the non-degradability of metal species the aim of the present work was to evaluate soil potential of pollution after it was discontinued the inadequate disposal of waste. The availability of zinc and lead was investigated through sequential extraction procedure, BCR and the results were compared with normal values and maximum permissible limits for lead and zinc and the individual contamination factor of each specie was calculated.

2. EXPERIMENTAL

2.1. Soil Sampling

The soil samples were collected in an area of 100 m^2 near to the factory that was used in past to the disposal of waste from the battery process production. The soil samples was collected in the first 10 cm layer with a small shovel and was stored in polyethylene bottles until the analysis. A composite soil sample was used in the experiments. The Figure 1 shows the contaminated area in Bauru City, São Paulo State, Brazil.

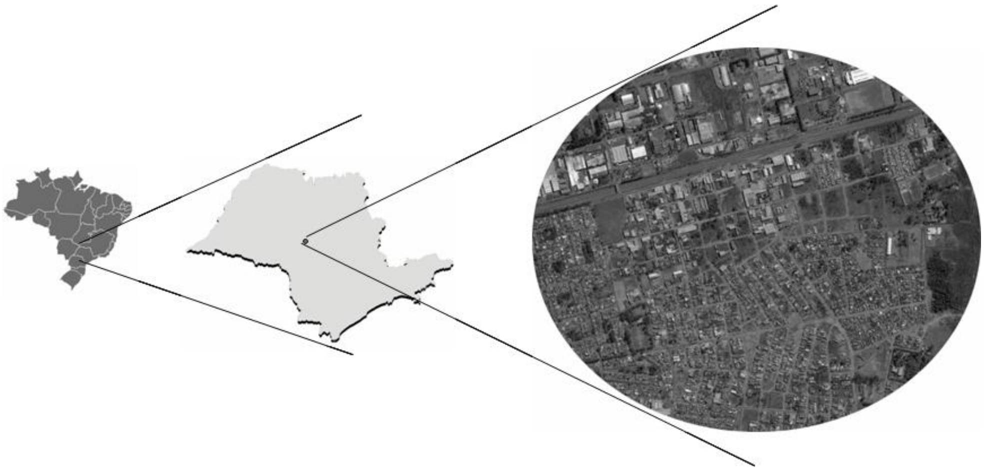

Figure 1. Contaminated area location at Bauru City, São Paulo State, Brazil

2.2. Equipments, reagents and solutions

All glassware and flasks used in this work were previously washed through nitric acid (10% v:v) immersion bath for 24 hours. Elapsed time the material was rinsed with distilled and deionized water (Millipore System, Direct-Q). All reagents used were of analytical grade, zinc and lead standards (J.T. Baker) were prepared after stepwise dilution of 1000 mg L^{-1} stock solution. Ammonium acetate and hydroxylamine hydrochloride were also purchased from J.T. Baker. The acids used were purchased from Synth (Brazil) and distilled in a sub-boiling system (Marconi Instruments, Brazil) before use. Quantitative analysis of zinc and lead were performed with a Shimadzu AA-6800 atomic absorption spectrometer (Tokyo, Japan) and a centrifuge (FANEN, model Excelsa II) was used in the separation process. TGA and DTA curves were obtained using a TA Instruments Model SDT 2960 analyzer with an alumina pan, a sample mass of 8.00 mg, an atmosphere of synthetic air (80% N_2 and 20%

O_2) at a flow rate of 100 mL min^{-1} and a heating rate of 10 °C min^{-1}.

2.3. BCR extraction procedure

The soil sample used was dried until it reached a constant mass and then sieved to obtain a fraction with a <1.0 mm. The BCR sequential extraction procedure consisted of the following steps:

Step 1: 1.0 g of soil and 20 mL of 0.11 mol L^{-1} of acetic acid solution was placed in a 50 mL centrifuge tube. The mixture was shaken for 16 h and then centrifuged to separate the extract from the residue. The remaining solid was washed with deionized water and the washings were discarded.

Step 2: 20 mL of 0.5 mol L^{-1} of hydroxylammonium chloride were added to the residue from step 1, the pH was adjusted to 1.5 with nitric acid, and the extraction was per-formed as described above.

Step 3: The residue from step 2 was treated with two 5.0 mL aliquots of hydrogen peroxide (30% m:m) and evaporated near to dryness. An aliquot of 25 mL of ammonium acetate, pH 2 (adjusted with nitric acid), was then added and the extraction was performed as above.

Residual fraction: The residue from step 3 was digested with 15 mL of aqua regia solution ($HCl:HNO_3$, 3:1 (v:v)).

The sum of each metal obtained in all steps was compared with the results obtained through direct sample mineralization using the USEPA 3050B open digestion procedure. [25]

3. RESULTS AND DISCUSSION

3.1. The application of BCR sequential extraction procedure

1.0 g of soil sample was subjected to the BCR sequential extraction procedure and the first step extraction was performed with 0.11 mol L^{-1} of acetic acid solution. After extraction procedure an aliquot of extractant solution was subjected to Flame Atomic Absorption analysis and the metals partioning are represented in Figure 2.

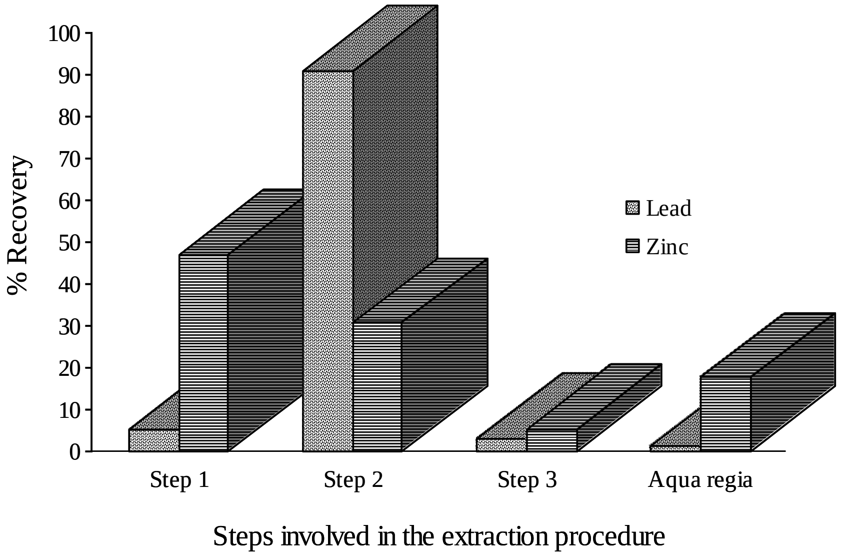

Figure 2. Zinc and lead partioning in contaminated Bauru city soil.

According to Figure 2, the metals extracted in the first stage represent 5.0 and 47 % of total lead and zinc, respectively. This acid-soluble fraction is responsible to the extraction of those metals that are weakly associated with the soil matrix and present in the carbonate fraction, susceptible to changes in pH.

And in this context the rain may play an important role, since its natural pH is slightly acidic due to dissolution of CO_2 existing in air, resulting in the formation of carbonic acid. In industrial sites may be the formation of strong acids in the atmosphere due to the presence of nitrogen and sulfur oxides, which with the precipitation can contribute to the mobilization and transport of metal species to deeper horizons and aquifers.

The second fraction (Figure 2), reducible one, is related with metals that are associated with iron and manganese oxides and was found that 92 and 31 % of the total lead and zinc content are present in this fraction. The oxides can exist in its hydrated form, and this way its surfaces are covered with hydroxyl groups, which can coordinate metal species in soil solution. Similarly to the metals in first fraction, the concentration of H^+ species influences the metal behavior, once a slight decrease in pH values can protonate the coordination sites and mobilize the metals. And in the same way the rain play an import role in the metal mobilization and transport through the soil horizons.

The oxidizable fraction (Figure 2) comprises those metals that are associated with sulfides and organic matter. In general, organic matters in soil are composed by humic substances that are a complex aggregate of brown dark colored organic amorphous substances originated during the decomposition of plants and animals. [14] In this fraction was found 3 and 5 % of the total content of lead and zinc, respectively, which are associated with nitrogen and sulfur atoms and with oxygenated groups, such as carboxylic and phenolic. As the interaction of metal species with organic matter is stronger than those related to carbonates and oxides, the metals in this fraction is considered less labile.

The low metal content found in this fraction is in agreement with the results obtained by thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis, shown in Figure 3.

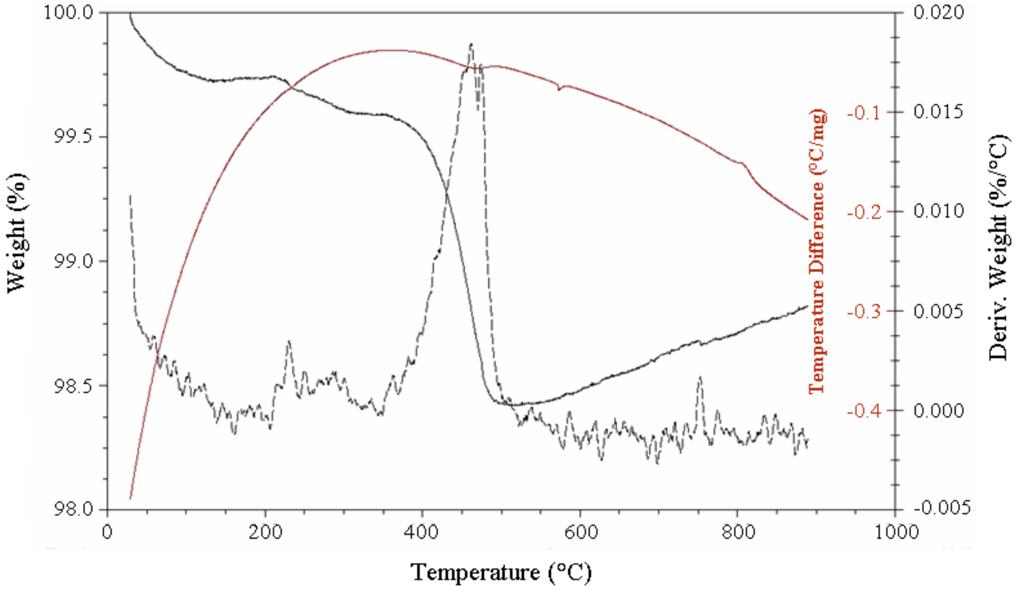

Figure 3. TG/DTG/DTA curves of contaminated soil.

The TG/DTG curves from contaminated soil sample show three decomposition stages. The first one may be related to water loss and the other two may be related to loss of hydroxyl groups. The last decomposition stage can not be assigned to organic matter decomposition due to the presence of an endothermic event at 600 °C. The small gain in mass at the end of TG curve may be related to lead oxide or equipment noise. As thermogravimetric analysis does not indicate the presence of organic matter we can assume that its percent in soil sample is negligible, which corroborates with the metals determined in oxidizable fraction, 3 and 5 % of lead and zinc, respectively.

The small amount of organic matter in soil has an important environmental implication, once it can act as a natural barrier preventing the metal lixiviation to deeper horizons.

The residual fraction was obtained through aqua regia digestion and was found 1 and 17 % of the total lead and zinc content, respectively. The metal species extracted in this fraction are not considered bioavailable, once they are retained within the crystal lattices of minerals and inside crystallized oxides.

3.2. Comparison of BCR sequential extraction procedure and pseudototal metal concentration

In order to evaluate the sequential extraction procedure an aliquot of 1.0 g of the same soil sample was subjected to 3050B open digestion procedure. The sample was transferred to a 100 mL Erlenmeyer flask and 10 mL of 7 mol L^{-1} HNO_3 solution were added. The flask was covered and heated at 95 °C for 15 minutes and after cooling, an aliquot of 5.0 mL of 14 mol L^{-1} HNO_3 was added and sample was refluxed at 95 °C for 30 minutes. After cooling an aliquot of 3.0 mL of H_2O_2 (30% m:m) was added and the mixture was heated again. After digestion, the extract was filtered, the supernatant was transferred to a volumetric flask and, then were carried the determination of metal concentrations. The results are summarized in Table 1. Table 1 compares the results of 3050B digestion and the results of the sum of the three extraction steps plus the residual step. Considering that no significant differences were found, it can be inferred that metal species under investigation were not present as silicates, once this form is not soluble in aqua regia solution.

Table 1. Comparison of results from sequential extraction and aqua regia extraction

	Zinc (mg Kg^{-1})	Lead (mg Kg^{-1})
Step 1	15 ± 1.5	174 ± 2.97
Step 2	9.7 ± 0.1	3155 ± 92.3
Step 3	1.6 ± 0.07	99 ± 5.1
Aqua regia	5.5 ± 0.08	38 ± 0.8
Sum of the three extraction steps and the residual step	31.8 ± 1.5	3466 ± 92
3050B	33.4 ± 2.2	3428 ± 13

3.3. Comparison of lead and zinc soil content and determination of individual contamination factor

In order to evaluate environmental implications of the results the individual contamination factor of lead and zinc was calculated according to Equation 1. [26]

$$C_f^i = \frac{c_1 + c_2 + c_3}{c_{res}} \tag{1}$$

Where c_1, c_2 and c_3 represent the metal concentration in each extraction step, and c_{res} represents the metal concentration in the residual phase and the value obtained for each metal specie was 90.2 and 4.8 for lead and zinc, respectively. The results indicate that lead possess a higher potential of pollution than zinc, once more than 90 % of the total metal content is associated with the first two fraction.

Table 2 exhibit results obtained for lead and zinc concentration in soil samples from several countries. In all cases the contamination is related to some industrial activity, such as mining and fuel burning. Through the comparison of guidelines values provided by CETESB (Brazilian Society of Environmental Sanitation Technology) was possible to conclude that the soil was severely contaminated and represents an environmental risk to local population.

Table 2. Comparison of lead and zinc concentration in several soil samples.

Location	Metal specie (mg kg^{-1})		Ref.
	Zinc	lead	
Bauru (Brazil)	31.8	3466	This study
Hong Kong (CC)	--	393	[3]
Newcastle (UK)	4626	4134	[7]
Piura (PG)	772	341	[8]
Prievidza (SK)	375	142	[9]
CETESB guidelines (Society of Environmental Sanitation Technology-Brazil)			
	Quality reference	Prevention	Industrial Intervention
Lead (mg Kg^{-1})	17	72	900
Zinc (mg Kg^{-1})	60	300	2000

The soil, collected in a secondary smelting lead recycling plant neighborhood, in Bauru city presented high concentration of lead and the results obtained in sequential extraction procedure indicated that more than 90% of all lead content is associated with the labile fractions, which can be easily mobilized. The absence or the low content of organic matter can be an aggravating factor related to the contamination of underground water, once organic substances can act as buffer or a metal bind layer.

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