Pb, Zn, Cd, Cu, Cr and Ni fractioning from a soil profile collected in old deposit of mining waste – Ribeira Valley (Brazil).

Conference Paper · September 2015

DOI: 10.3233/978-1-61499-603-3-2442

CITATIONS
0

READS
5

4 authors, including:

Mariana Consiglio Kasemodel
University of São Paulo
6 PUBLICATIONS **14** CITATIONS
SEE PROFILE

Valéria Rodrigues
University of São Paulo
12 PUBLICATIONS **25** CITATIONS
SEE PROFILE

Joel Barbujiani Sígolo
University of São Paulo
73 PUBLICATIONS **356** CITATIONS
SEE PROFILE

Pb, Cd, Zn, Cr, Cu and Ni contamination assessment in the topsoil collected in a former mining waste deposition area...

Conference Paper · January 2015

DOI: 10.20906/CPS/CB-05-0058

CITATIONS
0

READS
43

3 authors:

Mariana Consiglio Kasemodel
University of São Paulo
5 PUBLICATIONS **14** CITATIONS
SEE PROFILE

Joel Barbujiani Sígolo
University of São Paulo
72 PUBLICATIONS **354** CITATIONS
SEE PROFILE

Valéria Rodrigues
University of São Paulo
11 PUBLICATIONS **24** CITATIONS
SEE PROFILE

XVIII Brazilian Conference on Soil Mechanics and Geotechnical Engineering
The Sustainable Future of Brazil goes through our Minas
COBRAMSEG 2016 — 19-22 October, Belo Horizonte, Minas Gerais, Brazil

Pb, Cd, Zn, Cr, Cu and Ni contamination assessment in the topsoil collected in a former mining waste deposition area - Adrianópolis, PR (Brazil)

Mariana Consiglio Kasemodel
São Carlos School of Engineering (USP), São Carlos, Brazil, mariana.kasemodel@usp.br

Joel Barbujiani Sígolo
Geosciences Institute (USP), São Paulo, Brazil, jbsigolo@usp.br

Valéria Guimarães Silvestre Rodrigues
São Carlos School of Engineering (USP), São Carlos, Brazil, valguima@usp.br

SUMMARY: The inadequate deposition of mining waste enriched in potentially toxic metals from a smelter company changed the natural metal concentration of the area. In order to evaluate the contamination by Pb, Cd, Zn, Cr, Cu and Ni, nine samples were collected in the 0-20 cm depth at the central portion of the former mining waste disposal area, located in Adrianópolis (Brazil). Samples were nominated according to the transversal line of collection, four samples were collected in the north-south (NS) transversal, and five samples were collected in the east-west (EW) transversal. The following analysis were performed: ΔpH, potential redox (Eh), soil organic matter (SOM) content, soil cation exchange capacity (CEC), particle size distribution, X-ray fluorescence (XRF) and determination of the pseudo-total concentration of metals. Metal contamination assessment was based on the calculation of the enrichment factor (EF) and Nemero Quality Index (NQI). EW samples are mainly constituted of sand, while NS samples were primarily composed of fines (silt and loam), average SOM found in samples was 1.9 % and CEC was 6.1 cmol kg^{-1}; ΔpH was mainly negative in the NS samples, while in the EW it was mainly positive and, medium Eh was +408 mV. Pseudo-total concentration of metals was especially high for Zn, Pb and Cd. Cr concentrations were under background of the area. Pseudo-total concentration of metals was found in the following order: Zn > Pb > Cu > Ni > Cr > Cd. EF and NQI were found in the following order: Zn > Pb > Cd > Cu > Ni > Cr. In both contamination assessment methods, EF and Pi (NQI) it was obtained similar results, indicating elevated indexes for Zn, Pb, Cd, Cu and Ni. According to EF method, the area was considered extremely high enrichment by all metals assessed, excluding Cr, whereas when assessed with NQI method, same area was classified as heavy polluted by Pb, Cd, Zn, Cu and Ni.

KEYWORDS: potentially toxic metals, enrichment factor, pollution index, Ribeira Valley.

1 INTRODUCTION

Potentially toxic metals are found in the environment by both anthropogenic and natural sources (Adriano, 1986). One of the pathways by which metals enter the environment is mining, which itself affects relatively small areas, however, the residues from the mining, such as tailings, slag and rock deposits are a source of metal pollution (Salomons, 1994) affecting large areas and its surroundings.

The determination of the degree of pollution by a given metal requires that the pollutant metal concentration is compared with an unpolluted reference material (Abrahin and Parker, 2008). The enrichment factor (EF)

developed by Salomons and Förstner (1984) has been used to verify whether the concentration of metal in a site is natural or enriched; while Nemero Quality Index (NQI) takes not only the environmental quality index but also the extreme value to assess contamination in an area.

When assessing the impact of potentially toxic metals in soil, it is also necessary to integrate various factors that influence metal availability, such as ΔpH, potential redox, soil organic matter content, soil cation exchange capacity and particle size distribution.

The deposition of Pb-Zn-Ag mining waste in Adrianópolis (Paraná state - PR, Brazil), located in the Ribeira Valley, was performed directly on a non compacted soil devoid of proper coverage. The waste was exposed to weathering for 18 years before it was covered with thin layer of heterogeneous uncompressed residual soil from Eldorado Paulista (São Paulo state - SP, Brazil), city located in the Ribeira Valley, approximately 150 km from Adrianópolis.

The main objective of this study was to evaluate the properties of the topsoil of the deposit and integrate with EF and NQI contamination assessment techniques.

2 MATERIALS AND METHODS

2.1 Field Sampling and Sample Preparation

Samples were collected at the city of Adrianópolis (Paraná state, Brazil), located in an area used for the disposal of mining waste (slag enriched in potentially toxic metals). To evaluate the contamination of the superficial soil, 9 samples (consisted mainly of soil used in the coverage of the waste and slag) were collected at the central portion of the abandoned mining waste deposit: 4 were collected at the north-south (NS) direction (distanced 5-10 m from each other), and these samples were nominated NS1, NS2 and NS3 and NS4; and 5 in the east-west (EW) direction (distanced 5-10 m from each other), nominated EW1, EW2, EW3, EW4 and EW5.

Samples were collected at 0-20 cm depth with an auger (Dutch model). Prior to the analysis, samples were air dried at room temperature, disintegrated with agate mortar and subsequently homogenized (quartered).

The background sample (natural concentration of metals for the study area) was collected at Eldorado Paulista, area without influence of mining and without anthropogenic changes (Marques, 2014) located in the Ribeira Valley.

2.2 Particle Size Distribution

Particle size distribution was conducted from sedimentation and sieving assay according to the Brazilian Standard ABNT 7181.

2.3 Cation Exchange Capacity (CEC), Specific Surface (SS) and Clay Activity (Tc)

CEC was obtained experimentally using the method adapted by Pejon (1992). Analysis was conducted from 1g of sample (sieved 2 mm) and 10 mL of distilled water and, titration with a solution of 1.5 g L^{-1} of methylene blue (Merck Index). A droplet of the titration product was placed on a filter paper (Whatman nº.42); if a clear light blue halo appears around the blue dark spot, the test is positive, and finished, using the final volume of the titration to calculate the CEC. CEC was calculated using Eq. (1), SS (2) and Tc (3).

$$CEC = V \cdot C \cdot 100/M \quad (1)$$

V is titration volume (mL) used in the titration; *C* is methylene blue normal concentration; *M* is bulk mass (g).

$$SS = 3.67 \cdot V/M \quad (2)$$

V titration volume (mL) used in the titration; *M* is bulk mass (g).

$$T_c = 100 \cdot CEC/(\%clay) \quad (3)$$

2.4 Delta pH (ΔpH) and Potential Redox (Eh)

ΔpH determination was conducted from (1) soil and distilled water solution (1:2.5 ratio) and (2) soil and 1M KCl solution (1:2.5 ratio); Eh was

determined only in aqueous solution. The solution was stirred constantly during 5 minutes and then left resting during 60 minutes before pH determination in pHmeter (Digimed DM21) and Eh determination (MicroNal pHmetro B374) (EMBRAPA,1997).

ΔpH was determined from Eq. (4):

$$\Delta pH = pH(KCl) - pH\ (H_2O) \quad (4)$$

2.5 Soil Organic Matter (SOM) Content

SOM was obtained using digestion with hydrogen peroxide (30%) on a soil solution (1:10) (Eusterhues et al., 2005). The analysis was conducted on a heating plate (40-60 ^{o}C) and additional hydrogen peroxide was added until attack ceased. The sample was transferred to an oven (60 °C) until complete drying. SOM was calculated from Eq. (5).

$$SOM(\%) = 100 \cdot (m1 - m2)/m1 \quad (5)$$

$m1$ is soil mass used (g) and; $m2$ is the mass of soil at the end of the experiment (g).

2.6 X-Ray Fluorescence – XRF

The contents were determined in compressed sample using X-ray fluorescence spectrometer (Axios Advantage, Panalytical). The calibration STD-1 (Standardless) was used regarding the analysis without patterns of chemical components between fluoride and uranium. The loss on ignition was performed at 1,020 °C during 2 hours. Values were normalized to 100%.

2.6 Determination of Pseudo-total Concentration of Metals (Pb, Cd, Zn, Cr, Cu and Ni)

Pb, Cd, Zn, Cr, Cu and Ni concentrations in samples were obtained by digestion with HNO_3 and HCl 50% (3:1) according to Method 3030F (APHA, 2013). The analysis was performed on FS-AAS (fast sequential atomic spectrometer - Varian AA240FS) as described in Method B3111 (APHA, 2013).

Pseudo-total concentration of Pb, Cd, Zn, Cr, Cu and Ni were compared to background of the area (MARQUES, 2014) and to CONAMA (2009) standard for industrial investigation, since the area is located in a former industrial area.

2.7 Contamination Assessment (Pb, Cd, Zn, Cr, Cu and Ni)

Contamination assessment was conducted using Nemero Quality Index (NQI) and enrichment factor (EF) (Salomons and Förstner, 1984).

EF is calculated from normalization of metal concentrations above uncontaminated background levels with respect to a reference metal. The EF is calculated according to Eq. (8).

$$EF = (X/Al)_{sample}/(X/Al)_{background} \quad (8)$$

X_{sample} is the concentrations of potentially toxic metal in soil sample and Al_{sample} is the concentration of Al in the sample obtained by XRF analysis, while $X_{background}$ and $Al_{background}$ are their concentrations in a suitable background or baseline reference material.

To obtain NQI, it was first calculated the single factor pollution index (P_{ij}) and then the compressive pollution index (P_j) according to Eq. (6) and (7) respectively.

$$P_{ij} = C_{ij}/S_j \quad (6)$$

C_{ij} is the concentration of potentially toxic metal j in the i-th functional area soil, and S_j is the background concentration value of potentially toxic metal j.

$$P_i = \sqrt{\left[(P_{ijmax})^2 + (P_{ijave})^2\right]/2} \quad (7)$$

P_{ijmax} is the corresponding maximum value in the single factor pollution index, and P_{ijave} is the corresponding average value in the single factor pollution index. The site pollution grade is classified according to Table 2.

Table 1. Grade standard of Nemero index method (Hong-gui et al., 2012).

Grade	P_i	Pollution grade
I	$P_i \leq 0.7$	Clean
II	$0.7 < P_i \leq 1$	Warning limit
III	$1 < P_i \leq 2$	Slight pollution
IV	$2 < P_i \leq 3$	Moderate pollution
V	$P_i > 3$	Heavy pollution

2.8 Statistical Treatment

Pearson correlation index was calculated as a statistical treatment in effort to determinate specific correlations in between soil characteristics and metal concentration.

3 RESULTS AND DISCUSSION

The particle size distribution is shown on Figure 1. The NS samples were mainly constituted of fines (silt and loam), while EW were majority composed by sand. The samples with higher content of fines were samples NS1 (65.0%) and NS2 (61.5%); while samples with lower fine content were samples EW4 (20%) and EW5 (20.5%).

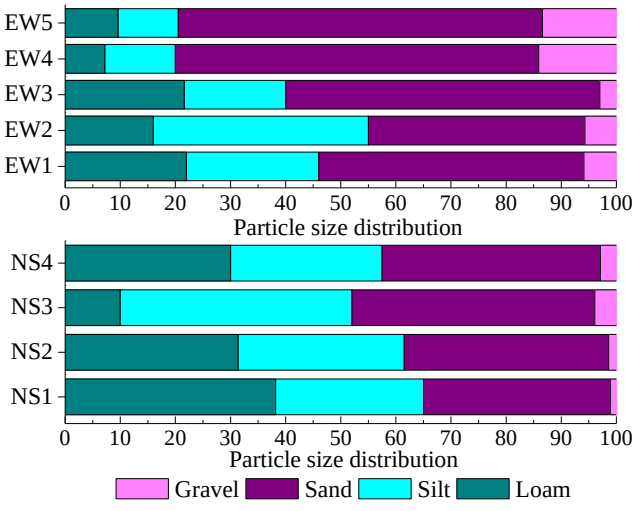

Figure 1. Particle size distribution of samples collected in a former disposal area of mining waste (Adrianópolis, PR).

The high surface area and the nature of the fine grained particles lead to many sites for adsorption of metals (Salomons, 1994). So samples with higher concentration of fines, such as NS1, NS2, NS3, NS4 and EW2 may favor metal adsorption.

SOM, ΔpH and Eh values are shown in Table 2. SOM content varied from 0.40% (EW5) to 3.3% (EW2). Usually, SOM controls metals retention by adsorption or chelation (Adriano, 1986), so higher SOM is expected to retain more potentially toxic metals.

Medium pH was neutral (7.0) with little variation (dp = ±0.3). Sample ΔpH was mainly negative in the NS samples (indicating the susceptibility to retain cations) and positive in the EW samples, favoring anion retention.

Potential redox (Eh) varied from +383 mV (EW1) to +466 mV (NS2), which indicates an oxidant environment, i.e. able to capture electrons.

Table 2. SOM, ΔpH and Eh of samples collected in a former disposal area of mining waste (Adrianópolis, PR).

Samples	SOM (%)	ΔpH	Eh (mV)
NS1	1.7	+0.7	+396.0
NS2	1.5	-0.2	+466.0
NS3	2.7	-0.5	+429.0
NS4	1.8	-0.5	+388.0
EW1	2.5	-0.4	+383.0
EW2	3.3	+0.2	+428.0
EW3	1.5	+0.4	+384.0
EW4	1.4	+0.6	+410.0
EW5	0.4	-0.6	+387.0

CEC, SS and Tc are shown in Table 3.

Table 3. CEC, SS and Tc of samples collected in a former disposal area of mining waste (Adrianópolis, PR).

Samples	CEC (cmol kg^{-1})	SS (m^2 g^{-1})	Tc (cmol kg^{-1})
NS1	7.6	59.2	19.8
NS2	7.6	59.2	24.1
NS3	7.6	59.2	75.6
NS4	5.7	44.4	18.9
EW1	10.9	85.2	49.5
EW2	4.0	39.2	25.3
EW3	5.0	39.2	23.2
EW4	4.5	35.0	62.1
EW5	2.0	15.5	20.6

CEC varied from 2.0 cmol kg^{-1} (EW5) to 10.9 cmol kg^{-1} (EW1). SS varied from 15.5 m^2 kg^{-1} (EW5) to 85.2 m^2 kg^{-1} (EW1). Medium

CEC and SS values obtained for NS samples were higher than those found for EW samples, indicating that generally NS samples has a greater content of fines and greater ability to retain cations.

Activity clay (Tc) varied from 18.9 cmol kg^{-1} (NS4) to 75.6 cmol kg^{-1} (NS3). Activity clay refers to the corresponding CEC of clay, and it is considered high activity when the value is equal or greater than 27 cmol kg^{-1} (IBGE, 2007). High Tc was only obtained in samples NS3, EW1 and EW4.

XRF analysis results are available in Tables 4 and 5. XRF analysis results indicated the presence of As in NS4 sample, which can be due to its association with Pb or from the arsenopyrite present in rocks of the area; As was not detected in other samples.

Table 4. XRF results for samples NS collected in a former disposal area of mining waste (Adrianópolis, PR).

Metal oxides (%)	NS1	NS2	NS3	NS4
Cr_2O_3	0.108	0.071	0.081	0.071
MnO	0.190	0.328	0.501	0.325
Fe_2O_3	9.79	11.0	11.4	13.5
Co_3O_4	<0.001	<0.001	<0.001	<0.001
NiO	0.019	0.016	0.016	0.017
CuO	0.020	0.038	0.045	0.087
ZnO	0.694	2.35	1.96	3.70
As_2O_3	<0.001	<0.001	<0.001	0.076
SrO	0.012	0.016	0.018	0.023
BaO	0.081	0.103	0.162	0.228
PbO	0.263	0.603	0.749	1.10
Al_2O_3	15.3	13.0	11.9	14.9
CaO	1.25	4.01	3.96	4.25

Table 5. XRF results for samples EW collected in a former disposal area of mining waste (Adrianópolis, PR).

Metal oxides (%)	EW1	EW2	EW3	EW4	EW5
Cr_2O_3	0.053	0.083	0.059	0.062	0.056
MnO	0.630	0.644	0.407	0.598	0.489
Fe_2O_3	14.3	12.1	16.5	23.2	21.8
Co_3O_4	<0.001	<0.001	<0.001	<0.001	<0.001
NiO	0.013	0.018	0.018	0.021	0.016
CuO	0.072	0.057	0.092	0.187	0.124
ZnO	4.82	3.39	5.28	14.6	13.1
As_2O_3	<0.001	<0.001	<0.001	<0.001	<0.001
SrO	0.053	0.027	0.030	0.045	0.038
BaO	0.382	0.093	0.099	0.452	0.251
PbO	1.57	0.935	1.74	2.82	2.89
Al_2O_3	10.1	7.09	11.1	5.22	6.10
CaO	8.75	7.75	11.3	18.9	18.3

Considerable concentrations of metals such as Cr, Mn, Co, Ni, Cu, Zn, Sr, Ba and Pb were also detected in the XRF analysis. Since the topsoil collected in Adrianópolis is highly composed with slag, XRF analysis was compared to data from Piatak et al. (2015), which provides an average Pb-Zn-Ag slag composition based on published studies; slags may content an average of 4.94% of Al_2O_3; 26.1% of FeO; 9.41% of CaO and 2.45% of MnO; As corresponding average is 491 mg kg^{-1} and Ba is 20,630 mg kg^{-1}. In this study, average concentration of CaO, PbO, BaO, SrO, ZnO, CuO, Fe_2O_3 and MnO were superior in EW samples (Table 6).

Pseudo-total concentrations of metals for the analyzed samples are shown in Figure 2.

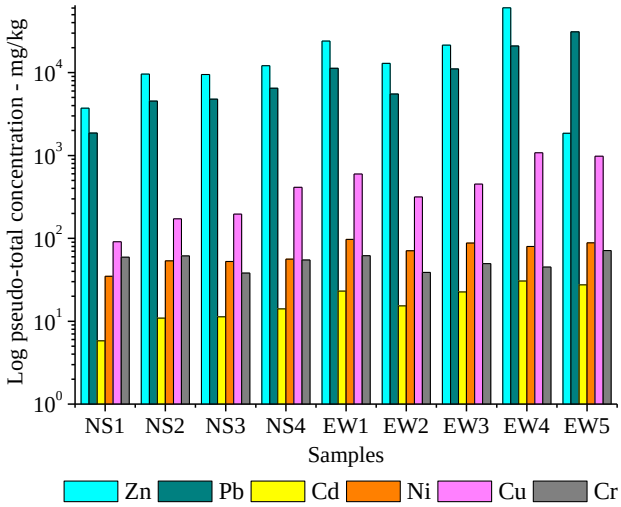

Figure 2. Pseudo-total concentration of metals in samples collected in a former disposal area of mining waste (Adrianópolis, PR).

Background values (MARQUES, 2014): Zn: 19.4 mg kg^{-1}; Pb: 16.5 mg kg^{-1}; Cd: 0.08 mg kg^{-1}; Ni: 11 mg kg^{-1}; Cu: 16.2 mg kg^{-1}; Cr: 71 mg kg^{-1}.

Industrial investigation (CONAMA, 2009): Zn: 2000 mg kg^{-1}; Pb: 900 mg kg^{-1}; Cd: 20 mg kg^{-1}; Ni: 130 mg kg^{-1}; Cu 600 mg kg^{-1}; Cr: 400 mg kg^{-1}.

Zn medium concentration in EW (24,152 mg kg^{-1}) was superior to NS (8,739 mg kg^{-1}); Zn pseudo-total concentration varied from 1,857 mg kg^{-1} (EW5) to 60,541 mg kg^{-1} (EW4). Zn pseudo-total concentration was approximately 890 times superior the background of the area; and all analyzed samples except for EW5 were above CONAMA (2009) Zn concentration for Industrial Investigation standard.

Pb medium concentration in EW (16,002 mg

kg^{-1}) was superior to NS (4,410 mg kg^{-1}); Pb pseudo-total concentration varied from 1,860 mg kg^{-1} (NS1) to 31,100 mg kg^{-1} (EW5). Pb pseudo-total concentration was approximately 660 times the background of the area; and all analyzed samples were above CONAMA (2009) Industrial Investigation standard for Pb.

Cd pseudo-total concentration varied from 5.8 mg kg^{-1} (NS1) to 30.5 mg kg^{-1} (EW4). Cd medium concentration in EW (23.8 mg kg^{-1}) was superior to NS (10.5 mg kg^{-1}); Cd medium pseudo-total concentration was considerably higher than the natural background of the area (220 times). Samples EW1, EW3, EW4 and EW5 had Cd concentration above CONAMA (2009) Industrial Investigation.

Ni concentration varied from 34.9 mg kg^{-1} (NS1) to 96.9 mg kg^{-1} (EW1); average pseudo-total Ni concentration in EW samples (84.8 mg kg^{-1}) was superior than NS samples (49.3 mg kg^{-1}). All samples had Ni concentration superior to the natural background of the area and under CONAMA (2009) Industrial Investigation.

The average pseudo-total concentration of Cu in EW (217.6 mg kg^{-1}) was higher than NS (684.8 mg kg^{-1}). Cu concentration varied from 91.1 mg kg^{-1} (NS1) to 1,080 mg kg^{-1} (EW4) and, all analyzed samples had Cu concentration above the background of the area (Figure 2). Cu concentrations were above CONAMA (2009) Industrial Investigation values in samples EW4 and EW5.

Cr had little variation among analyzed samples, and all concentrations obtained were under the background of the area and CONAMA (2009) Industrial Investigation, which leads to affirming that the slag deposited in the soil did not alter Cr natural concentration (Figure 2).

In a general manner, concentration of metals in EW was higher than NS. The pseudo-total concentration of metals was found in the following order of concentration: Zn > Pb > Cu > Ni > Cr > Cd. Elevated concentrations of Zn and Pb were expected since the slag deposited in the area is mainly from Pb-Zn foundry waste.

According to Piedade et al. (2014), the average Pb concentration in 57 soils collected at 10-20 cm depth, in the area of the former company Plumbum in Adrianópolis (PR - Brazil) was 2,752.30 mg kg^{-1}. Pb average concentration detected in the topsoil collected 2,000 m from the former smelting area was 10,850.4 mg kg^{-1}.

Rodríguez et al. (2009) studied metal distribution around a Pb-Zn mining area; the authors found concentration of metals in mine tailings in the following order: Pb > Zn > Cu > Cd. According to Onyeobi and Imeokparia (2014), the average abundance order of potentially toxic metal contents in the soils around Pb-Zn mines of Abakaliki district (Nigeria) is: Pb (85.8 mg kg^{-1}) > Zn (63.2 mg kg^{-1}) > Cu (20.0 mg kg^{-1}) > Cd (15.0 mg kg^{-1}) > Ni (7.1 mg kg^{-1}) > Cr (5.8 mg kg^{-1}).

Since the topsoil collected in Adrianópolis is highly composed with slag, the pseudo-total concentration of metals obtained was compared to average metal concentration in Pb-Zn-Ag slags (Piatak et al., 2015). According to Piatak et al. (2015) data, average Pb-Zn-Ag mining slags are constituted in Pb (90,657 mg kg^{-1}) > Zn (31,162 mg kg^{-1}) > Cu (2,502 mg kg^{-1}) > Cd (99.2 mg kg^{-1}) > Ni (97.1 mg kg^{-1}) > Cr (82.3 mg kg^{-1}).

Enrichment factor (EF) is shown on Figure 3.

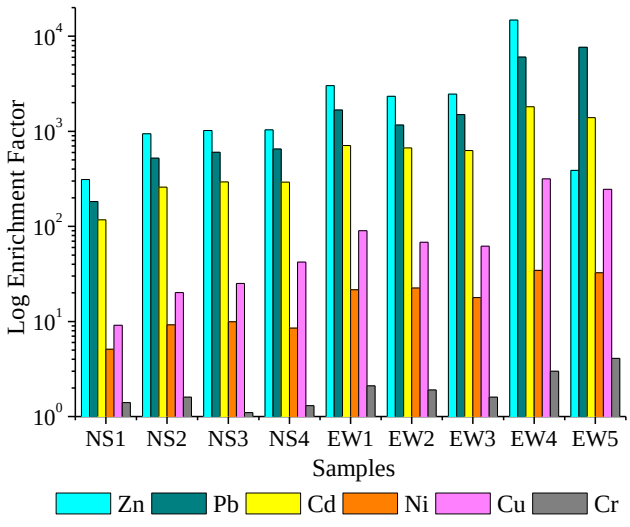

Figure 3. Enrichment factor (EF) obtained in samples collected in a former disposal area of mining waste (Adrianópolis, PR).

EF calculated for Zn, Pb, Cd, Ni, Cu and Cr were higher in EW samples, probably due to the fact that EW samples were collected closer to the former mining company. Slag deposition was performed unevenly, which may cause

significant alteration in the EF values. Average EF in EW samples was approximately 5 times higher than those obtained in NS samples.

The enrichment factor was found in the order: Zn > Pb > Cd > Cu > Ni > Cr. This order endorses mainly the high concentration of Zn, Pb and Cd compared to their background values, indicating alarming concentration of these metals present in the samples collected.

By definition, the enrichment factor close to unity (EF = 1) is an indicative that the element considered did originate from the soil; however, some authors suggests that values of EF < 10 are merely the measurement background (Kłos et al., 2011). EF values for Cr were close to 1, suggesting that the element considered did originate from the soil and in the NS samples, Ni EF was under 10, indicating a merely the measurement background.

EF obtained for Zn, Pb and Cd are in some samples over 1,000, reaching highest values in sample EW4, when EF is 14,811.9 (Zn); 6,040.8 (Pb) and 1,809.6 (Cd). According to Sutherland (2000), when EF > 40 it is considered extremely high enrichment. Using this classification, all samples are extremely high enriched in Zn, Pb and Cd; it is also extremely high enrichment in Cu in samples NS4, EW1, EW2, EW3 and EW4.

Enrichment factor values obtained by Onyeobi and Imeokparia (2014) in soils around Pb-Zn mines of Abakaliki district (Nigeria) are in the following order: Cd > Pb > Zn > Ni = Cr > Cu. Differences in the order obtained in this study are mainly due to differences in Pb, Zn, Cu, Ni and Cr concentrations obtained by Onyeobi and Imeokparia (2014) compared to the ones obtained in this study.

NQI (P_i) indicates a general contamination assessment of the NS and EW set of samples; the results are shown in Figure 4. P_i for Zn, Pb, Cd, Cu and Ni in NS and EW are classified as heavy pollution. P_i for Cr in NS and EW set of samples were under 0.7, which indicates that the site is clean of Cr. P_i was found in the following order: Zn > Pb > Cd > Cu > Ni > Cr.

In both contamination assessment methods, EF and *Pi* (NQI) it were obtained similar results, indicating elevated indexes (enrichment factor and pollution grade) of Zn, Pb, Cd, Cu and Ni in samples collected.

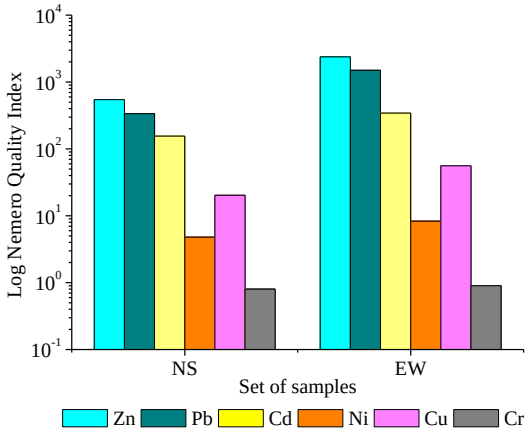

Figure 4. Nemero quality index (NQI) - Pi obtained in the set of samples NS and EW.

Using NQI contamination assessment method, a higher potentially toxic metal pollution in the EW samples is clear, especially regarding Zn and Pb. Although the classification of NQI categorized the samples as heavily polluted with Zn, Pb, Cd, Ni and Cu; according to the EF classification of Sutherland (2000), only Pb, Zn, Cd and Cu are classified as extremely high enrichment; Ni average concentration was under the classification of significant enrichment, while Cr was deficiency to minimal enrichment.

According to the statistical treatment used, it is clear that the SOM is mainly associated with the silt fraction; and that the silt fraction is responsible for greater activity clay. Positive correlations were obtained between coarse materials (sand and gravel) and especially Cu and Cd, which indicates that these metals are probably present in the slag rather than in the soil.

4 CONCLUSION

Overall, significant differences between NS and EW samples regarding mainly the concentration of metals, particle size distribution and CEC were observed; indicating that NS samples have better qualities to assess the contamination of metals, while EW samples are more contaminated with potentially toxic metals.

Differences between NS and EW samples regarding mainly metal concentration, EF and

NQI is probably because the slag deposition was performed unevenly, which may alter the distribution of slag composition in the samples.

According to background comparisons, EF and NQI, the analyzed samples are heavily contaminated with Zn, Pb, Cd and Cu. Other contaminants, such as As and Ba were obtained by XRF, but further analysis are necessary to assess contamination by these metals.

Both contamination assessment methods (NQI and EF) provided the same information regarding metal availability in the area. The order of contamination was Zn > Pb > Cd > Cu > Ni > Cr.

According to results obtained using EF method, samples are highly enriched with potentially toxic metals and those are of anthropogenic nature (deposition of mining waste). According to the data obtained using NQI, it is concluded that soil samples are strongly polluted, especially by Pb, Zn and Cd.

ACKNOWLEDGEMENTS

The support provided by FAPESP in the research fellowship 2014/07180-7 and the scholarship provided by CNPq.

REFERENCES

ABNT - Associação Brasileira de Normas Técnicas (1984) *NBR 7181: Solo: Análise Granulométrica*, Rio de Janeiro, Brasil, 13 p.

Abrahim, G.M.S. and Parker, R.J. (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand, *Environmental Monitoring Assessment*, Vol. 136, p. 227-238.

Adriano, D. C. (1986) *Trace Elements in the Territorial Environment*, Springer–Verlag, New York, NY, USA, 533 p.

APHA - American Public Health Association (2013) *Standard methods for the examination of water and wastewater*, 20th Edition, Washington, D. C., USA.

CONAMA - Conselho Nacional de Meio Ambiente. (2009). Resolução nº 420, de 28 de dezembro de 2009. Diário Oficial da União, Brasília, 249, 81-84. http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620. Acessed: June 22 2016.

EMBRAPA - Empresa Brasileira de Pesquisa Agropecuária (1997) *Manual de métodos de análise de solo*, 2nd ed., Empresa Brasileira de Pesquisa Agropecuária, Rio de Janeiro.

Eusterhues, K., Rumpel, C. and Kögel-Knabner, I. (2005) Stabilization of soil organic matter isolated via oxidative degradation, *Organic Geochemistry*, Vol. 36, p. 1567-1575.

Hong-gui, D., Teng-feng, G., Ming-hui, L. and Xu, D. (2012) Comprehensive Assessment Model on Heavy Metal Pollution in Soil, *International Journal of Electrocheminal Science*, Vol. 7, p. 5286-5296.

IBGE – Instituto Brasileiro de Geografia e Estatística (2007) *Manual técnico de Pedologia*, IBGE, Rio de Janeiro, Brasil, 94 p.

Kłos, A., Rajfur, M. and Wacławek, M. (2011) Application of Enrichment Factor (EF) to the interpretation of results from the biomonitoring studies, *Ecological Chemistry and Engineerings*, Vol. 18, p. 171-183.

Marques, J. P. (2014) *Caracterização geológica-geotécnica de solo residual de Eldorado paulista (SP) para uso como barreira selante*, Monografia de Conclusão de Curso em Engenharia Ambiental, Escola de Engenharia de São Carlos, Universidade de São Paulo.

Onyeobi, T.U.S. and Imeokparia, E.G. (2014) Heavy Metal Contamination and Distribution in Soils around Pb-Zn Mines of Abakaliki District, South Eastern Nigeria, *Frontiers in Geosciences*, Vol. 2, p. 30-40.

Pejon, O. J. (1992) *Mapeamento geotécnico da Folha Piracicaba-SP (escala 1:100.000): Estudo de aspectos metodológicos, de caracterização e de apresentação dos atributos*, Tese de Doutorado, Programa de Pós-Graduação em Geotecnia, Escola de Engenharia de São Carlos, Universidade de São Paulo 2v.

Piatak, N.M., Parsons, M.B. and Seal II, R.R. (2015) Characteristics and environmental aspects of slag: A review, *Applied Geochemistry*, Vol. 57, p. 236-266.

Piedade, T.C., Melo, V.F., Souza, L.C.P. and Dieckow, J. (2014) Three-dimensional data interpolation for environmental purpose: lead in contaminated soils in southern Brazil. *Environmental Monitoring and Assessment*, Vol. 186, p. 5625-5638.

Rodríguez, L., Ruiz, E., Alonso-Azcárate, J. and Rincón, J. (2009) Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain, *Journal of Environmental Management*, Vol. 90, p. 1106-1116.

Salomons,W. (1994) Environmental impact of metals derived from mining activities: Processes, predictions, prevention, *Journal of Geochemical Exploration*, Vol. 52, p. 5-23.

Salomons, W. and Förstner, U. (1984) *Metals in the Hydrocycle*, Springer-Verlag, Berlin Heidelberg, Germany, 352 p.

Sutherland, R.A. (2000) Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii, *Environmental Geology*, Vol. 39, p. 611-627.