

Full Length Research Paper

Heavy metals in soil on spoil heap of an abandoned lead ore treatment plant, SE Congo-Brazzaville

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Accepted 10 January, 2011

Total concentrations of 4 heavy metals (Pb, Zn, Cu, and Mn), non-metal As and three reference elements (Ti, Fe and Al) of a soil profile on spoil heap were examined. 54 soil samples were collected in the soil profile at different depths: 15 to 45, 45 to 75, 75 to 105, 105 to 135 and 135 to 150 cm. The first 15 cm of top layer contained an accumulation of ores and was not sampled. Lead, zinc, copper, manganese and arsenic levels in the soil profile decreased from 11800 to 2000, 2400 to 1200, 270 to 90, 6700 to 750 and 1300 to 600 mg/kg, respectively. The levels of these trace elements were higher than the permissible limit level in soil according to European norms. The concentration levels of heavy metals and arsenic in the soil profile are listed in the following order: Pb > Mn > Zn > As > Cu. High positive correlations were observed between As, Cu, Zn and Al, Fe, Mn, Ti. Among the heavy metals, lead was not significantly correlated with Al, Fe and Ti. Evaluation of enrichment factor, geo-accumulation index and pollution load index values from the measured concentrations of heavy metals and continental crust values shows a very high contamination of the soil profile by the heavy metals studied and arsenic.

Key words: Heavy metals, spoil heap, contamination, enrichment factor, geo-accumulation index, pollution load index.

INTRODUCTION

In the environment, heavy metals in high concentration are toxic to most organisms. Human activities such as mining have continuously increased the concentration of these metals in the environment (soils, waters, sediments) (Ma and Rao, 1997; Martin et al., 1998; Adriano, 2001; Li et al., 2001). Many studies have shown that heavy metals are extremely persistent in the environment, non biodegradable and readily accumulate to toxic levels (Forstner, 1985; Giller et al., 1988; Kozak, 1991; Grzebisz et al., 2002; Ma et al., 2001; Adie and Osibanjo, 2009; Moosavi and Zarasvandi, 2009). Even low concentrations of heavy metals are toxic because there is no good mechanism for their elimination from the body. Heavy metals can accumulate to phytotoxic levels, especially in low pH soils, which reduces plant growth and enter the food chain when plants are consumed by

animals (Chaney, 1994). Heavy metals are defined as elements with densities greater than 5 g/cm³ (Duffus, 1980). In the environment, soil is the compartment which receives heavy metals coming from different sources and controls their movement to other compartments (Adriano, 2001; Osuji and Onajake, 2004; Iwegbue et al., 2007; Mahjoobi et al., 2010).

The total content of elements depends on chemical and physical properties of both the soil and the elements. In the soil profile, the content is gradually decreasing by leaching. Some factors affect the behavior of the elements in the soil, such as their sorption (Kabata-Pendias and Pendias, 1992), soil pH which influences metal solubility (Chuan et al., 1996). According to soil parameters, heavy metals may enter the food chain in significantly elevated amounts (Lock et al., 1992; Nygard et al., 2001; Hart et al., 2005; Metcheva et al., 2010). Pb, Zn, Cu and As are the most frequently reported elements with regard to potential hazards and the occurrence in contaminated soils (Alloway, 1995). Lead is classified in the list of priority pollutants by the United States

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Environmental Protection Agency (USEPA, 1999) with a carcinogenicity B (probable human carcinogen). Arsenic is not an essential element for many biological processes. When the concentration is above a certain level, As has adverse effects and may be converted to a toxin (Emsley, 1991). The background concentration of As range from 0.1 to 40 mg/kg in soil (Bowen, 1979). Some anthropogenic activities including mining and smelting of metal ores, agricultural fertilizers and pesticides led to assimilation of high As levels (10000 to 20000 mg/kg) in some agricultural areas and human habitats (Adriano, 2001).

In the district of Mfouati, south-east of Congo-Brazzaville, the activities of a treatment plant of a poly-metal ore left large quantity of deads and mining waste on the spot. The metal ore was made up mainly of galena (PbS), chalcosine (Cu_2S), Chalcopyrite (CuFeS_2), carbonates as PbCO_3 , ZnCO_3 , malachite CuCO_3 , $\text{Cu}(\text{OH})_2$, and other more complex minerals as hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$), lead chloroarsenate $\text{Pb}_4(\text{PbCl})(\text{AsO}_4)_3$, vanadite $(\text{VO}_4)_3\text{Pb}_4(\text{PbCl}_2)$. This study is important for the people of Mfouati because it can be used by the decision makers to prioritize measures to control the environment pollution by toxic metals such as lead and arsenic.

The study aims to evaluate the vertical distribution of some heavy metals (Pb, Zn, Cu, Mn) and non-metal As in soil on spoil heap and assess soil contamination using geochemical indicators such as enrichment factor (EF), geo-accumulation index (I geo) and pollution load index (PLI). Al, Fe, Mn and Ti are included in this study, as they might be indicators of geochemical behaviour of heavy metals.

MATERIALS AND METHODS

Description of the study area

The site retained for sampling is the spoil heap of a treatment plant in which activity was stopped for more than twenty years. The ore treatment plant was built on the side of a hill located at 442 m of altitude in Mfouati, south-east Congo-Brazzaville, which is located between 367178.59 to 370507.20 UTM South latitude and 9512957.94 to 9515800.06 UTM East longitude. The area is in the equatorial climate zone. Temperature varies from 25 to 36°C in rainy season, while it is between 18 and 24°C in dry season. The annual rainfall varies from 1050 to 1650 mm. The vegetation is of savanna type with leguminous plants. The soils are of ferralitic type, which have been derived from schisto-limestone. Soil samples were collected from the spoil heap (Figure 1).

Soil sampling, preparation and analyses

A soil profile having 1.50 m of depth and 1 m broad was sampled on the spoil heap. The first 15 cm of top layer present an accumulation of ore and was not sampled. 54 soils samples were collected in the soil profile at different depths: 15 to 45, 45 to 75, 75 to 105, 105 to 135 and 135 to 150 cm. Soil samples were collected with a polyethylene scoop and stored in plastic bags. The soil samples were air-dried and passed through a 2 mm plastic sieve to

move gravel and rocks, put in plastic bags then sent to the Service Central du CNRS, Vernaison (France) for analysis. The total concentration of heavy metals (Pb, Zn, Cu, and Mn), non-metal As and reference elements (Al, Fe and Ti) was determined by ICP-MS Quad PQ2+ (Thermo-fisher X7). Briefly, 0.1 g of each homogenized sample was digested by triacid attack ($\text{HF-HClO}_4\text{-HNO}_3$) in a Teflon vessel and heated in a microwave oven at 180°C for 10 min. The digested solution was diluted to a known volume with double distilled water, and then it was analyzed for metals and non-metal As by ICP-MS. Precision was achieved by triplicate analyses of the same sample and standards. Soil pH was measured in a suspension at a soil/water ratio of 1:2 according to McLean (1982).

Elements are divided into two groups: the first, those that occur naturally in modest abundances in most environments, such as Al, Fe, Mn and Ti. The second is related to those that occur in nature but are also products of anthropogenic activities (Pb, Zn, As, Cu) (Bricker, 1993). Correlation analysis is widely used in heavy metals analyses (Dudka and Market, 1992; Tume, 1997; Lewandoski et al., 1998). Correlations between metals indicate whether there is any common source of pollution. Correlation analysis was conducted using STATISTICA 7.1 for Windows. To evaluate the magnitude of contaminants in the soil profile, three geochemical parameters were used: Enrichment Factor (EF), Geo-accumulation index (I geo) and Pollution Load Index (PLI). Enrichment Factor (EF): The enrichment factor were computed according to the abundance of species in source material to that found in the Earth's crust and the following equation was used to calculate the EFs :

$$EF = (\text{Me/Al}) \text{ sample} / (\text{Me/Al}) \text{ background} \quad (1)$$

where (Me/Al)sample is the metal to Al ratio in the sample at a given depth in the soil profile; (Me/Al)background is the natural background value of metal to Al ratio (Feng et al., 2004).

Aluminum with a high crustal abundance was selected as the reference element. As we do not have heavy metals and Al background of our study area, we adopted the continental crust value of Taylor (1964) for Pb, Zn, Cu, Mn and As. In this study, the average Al concentration of 68,400 mg/kg or 6.84% was adopted as the background value (Feng et al., 2004). EF values were interpreted as follows: $EF < 1$ indicates no enrichment; the range as 1 to 3 is minor; 3 to 5 is moderate; 5 to 10 is moderately severe; 10 to 25 is severe; 25 to 50 is very severe; and > 50 is extremely severe (Acevedo-Figueroa et al., 2006). Geo-accumulation Index (I geo): The geo-accumulation Index (I geo), introduced by Müller (1979) has been used to evaluate the intensity of heavy metal pollution in the soil profile at the different depths. Mathematically, I geo is expressed as:

$$I \text{ geo} = \log_2 (\text{Cn}/1.5\text{Bn}) \quad (2)$$

where, Cn is the concentration of element 'n', Bn is the geochemical background value and 1.5 is the background matrix correction factor due to lithogenic effects. The geo - accumulation index (I geo) scale consists of seven grades or classes (0 to 6) ranging from unpolluted to highly polluted (Table 1).

The average value of each element in the earth's crust after Taylor (1964) was adopted as background value in this study. Pollution Load Index: Pollution load index (PLI) for the soil profile, has been evaluated following the method proposed by Tomilson et al. (1980). PLI is expressed as:

$$PLI = (\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \dots \times \text{CF}_n)^{1/n} \quad (3)$$

where, n is the number of metals (five in this study) and CF is the contamination factor which can be calculated from the following relation:

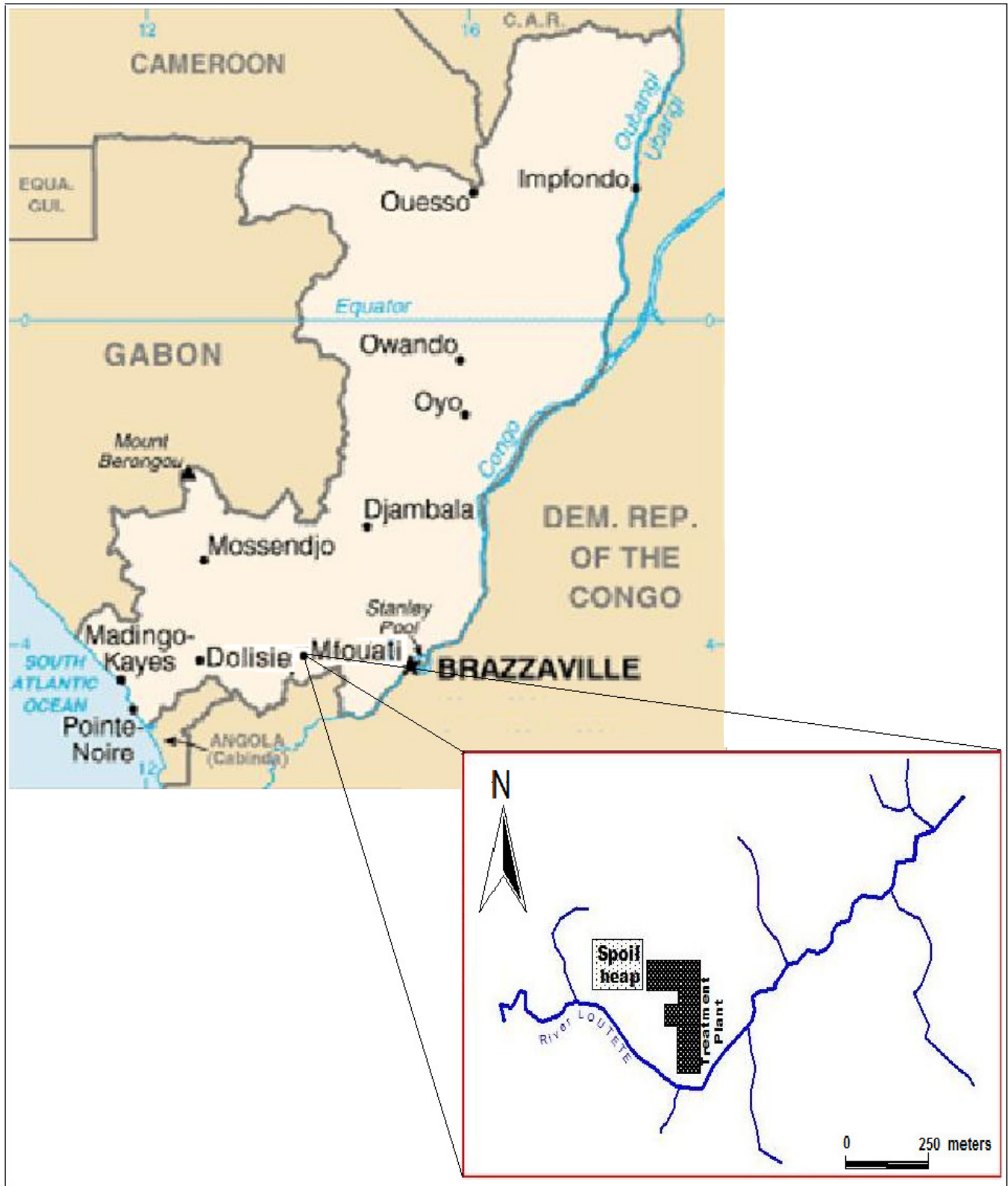


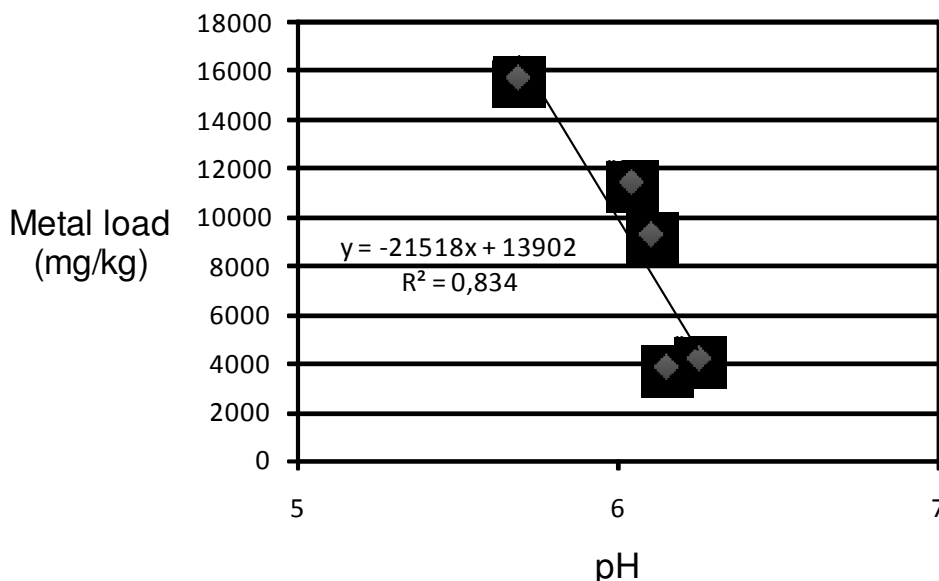
Figure 1. Location of the spoil heap in the study area.

$CF = \text{Metal concentration} / \text{Cbackground concentration of the same metal}$ (4)

Metal contamination in the soil profile has been assessed for Pb, Zn, Cu, Mn and As.

Table 1. Geoaccumulation Index (I_{geo}) in relation to pollution intensity.

I _{geo} value	I _{geo} class	Pollution intensity
< 0	0	Unpolluted
0 - 1	1	Unpolluted to moderately polluted
1 - 2	2	Moderately polluted
2 - 3	3	Moderately to strongly polluted
3 - 4	4	Strongly polluted
4 - 5	5	Strongly to very strongly polluted
> 5	6	Very strongly polluted

**Figure 2.** Graph showing the variation of metal load with pH.

RESULTS AND DISCUSSION

Concentrations of Pb, Zn, As, Cu, Ti, Fe, Al and Mn at different depths of the soil profile as well as pH values are listed in Table 2 together with mean values and standard deviations. The soil profile showed very high levels of Pb, Zn and As decreasing from 11800 to 2000, 2400 to 1200 and 1300 to 600 mg/kg, with an average of 4267.55, 500 and 304.96 mg/kg, respectively. Adie and Osibanjo (2009) found very strong lead concentrations varying between 243 and 126000 mg/kg in the soil from an automobile battery manufacturing plant in Nigeria. Very high amounts of some heavy metals (Pb, Zn, and As) up to 13600, 6150, and 40600 mg/kg, respectively, were also found in soils of historic metal ore mining activities in the Sudety Mts, Poland (Karczewska et al., 2006).

The concentrations of Cu in this soil profile were lower, decreasing from 270 to 90 mg/kg, with an average of 75.7 mg/kg. These values were far higher than the standard values in soils from European norms (Table 2)

(Rademacher, 2003). About the reference elements, Fe showed the higher concentrations decreasing from 53130 to 18620 mg/kg, followed by Al and Ti as: 25835.3 to 13394.11 mg/kg and 154 to 68 mg/kg, respectively (Table 2). The soil profile showed high levels of Pb, Zn, Cu, Mn, As and reference elements (Al, Fe and Ti) at the depth 15 to 45 cm. This can be explained by the presence of the ore in the top layer 0 to 15 cm, having undergone a strong dissolution by action of water in rainy season. Strong concentrations observed at the depth 15 to 45 cm are due to leaching of heavy metals and reference elements from the top layer (0 to 15 cm). The pH value in the soil profile was in the range from 5.69 to 6.25 which is characteristic of slightly acidic nature. Metal load in the soil profile decreases with pH value (Figure 2). This negative relationship is significant at $P < 0.05$ probability level. This tendency implies that more soil acidity induces more dissolution of heavy metals.

The soil profile have a reddish brown soil color which is indicator of very high Fe levels and were contributory to the acidic nature of the soil (Ekosse, 2008). Heavy metals

Table 2. Summary of soil profile properties.

Depth (cm)	Pb	Zn	As	Cu	Mn	Metal load	Ti	Fe	Al	pH
	(mg/kg)						(mg/kg)			
15 - 45	11800	2400	1300	270	6700	15770	154	53130	25835.3	5.69
45 - 75	6100	2000	1000	210	3400	9310	128	41440	22235.3	6.1
75 - 105	9000	1600	700	160	2500	11460	85	23590	15882.35	6.04
105 - 135	2200	1300	600	100	700	4200	75	21210	14347.06	6.25
135 - 150	2000	1200	600	90	750	3890	68	18620	13394.11	6.15
Mean	6220	1700	840	166	2810	8926	102	31598	18338.82	6.05
SD	4267.55	500	304.96	75.7	2463.33	5027.56	37.26	15008	5426.75	0.21
¹ Standard values	50 -100	100 - 200	1 - 20	30 - 60	-					
² Continental crust	13	70	1.8	55	720		3800	35900	68400	-

¹From European norms (Rademacher, UN/ECE; 2003). ²Taylor (1964).

at the different depths of the soil profile are found to be correlated with the reference elements in the correlation analysis. Table 3 displays the inter-element Pearson correlation matrix in the soil profile. A very high positive correlation with high significant probability ($P < 0.01$) was observed between Zn/As, Zn/Cu and As/Cu. A high positive correlation ($P < 0.01$) was also noticed between Ti/Zn, Ti/As, Ti/Cu, Ti/Mn, Fe/Zn, Fe/As, Fe/Cu, Fe/Mn, Al/Zn, Al/As, Al/Cu, Mn/Zn, Mn/As, Mn/Cu and Mn/Al. In addition, high positive correlation ($P < 0.01$) was also noticed between the reference elements Ti/Fe, Ti/Al and Fe/Al.

Lead showed a particular behaviour in this soil profile. High positive correlation ($P < 0.05$) was observed between Pb/Cu and Pb/Mn. Pb was negatively correlated with pH at $P < 0.05$. Mn was also negatively correlated with pH at $P < 0.05$. The relationship between Pb and Cu shows that, the two metals are mostly originated from identical source. It is the same for lead and manganese, which also indicates that, lead could be found in the fraction corresponding to reducible manganese. The positive correlation between heavy metals on the one hand, except lead, the reference elements and heavy metals on the other hand, is an indication of their possible common pollution sources, as well as their common sink in the soil profile.

Metal contamination in the soil profile has been assessed for Pb, Zn, Cu, Mn, As, Al, Fe, and Ti. Figure 3 a, b, and c presents the variation of EF values in the soil profile. The EF in soil profile shows a depletion trend for Ti (<1) while that in the case of Fe shows mild enrichment (>1). Pb, As, Zn show very high EF values (> 10) in the soil profile. It is the case of Mn down to depth 75 to 105 cm. Pb, As and Zn with EF values decreasing from 2283.7 to 746.6, 1677.3 to 1493.2 and 92.9 to 89.6, respectively, which are largely higher than the value 50, are the three major contaminants in the soil profile. Higher

concentrations of Pb, As and Zn in the soil profile (Table 2) are reflected in very high EF values. The calculated I geo values, based on the average value of each element in the earth's crust (Taylor, 1964) are illustrated in Figure 4 a, b and c. The I geo values of Pb and As decrease in the soil profile from 9.24 to 6.68 and 8.91 to 7.80, respectively. Thus, Pb and As fall in the class '6' which is very strongly polluted. For Zn, the I geo values decrease from 4.51 to 3.51 as being of the class '4' strongly polluted. In the case of Cu, the values decrease from 1.71 to 0.13, which corresponds to class '2' moderately polluted. Mn falls in the class '2' moderately polluted from the depth 15 to 45 cm to the depth 75 to 105 cm. Starting from the depth 105 to 135 cm, Mn falls into the class '0' unpolluted as one expected it, with the sight of the brutal reduction in the enrichment factor starting from depth 105 to 135 cm (Figure 3 b). From Figures 4 b and c, it is evident that the I geo values of Fe, Al and Ti fall in class '0' in all the soil profile. These findings show no contamination from Al, Fe, and Ti in the soil profile. The pollution load index is presented in Figure 5 and provides a simple means for assessing the soil profile quality. The PLI values in the soil profile are very high, varying from 18 to 60. All these values are > 1 . This is an indication of the deterioration of soil at the level of the spoil heap. The PLI of the soil profile indicates that Pb, As, Zn, Cu and Mn are the major pollutants.

Conclusion

This study has confirmed that in the overall soil profile on spoil heap of the abandoned lead ore treatment plant in Mfouati, south-east Congo-Brazzaville, high levels of lead, zinc, arsenic were observed. In the case of manganese and copper, high levels were only observed at the depth 15 to 105 cm. Trace metals concentrations as Pb, Zn, As, Mn and Cu in the soil profile are higher

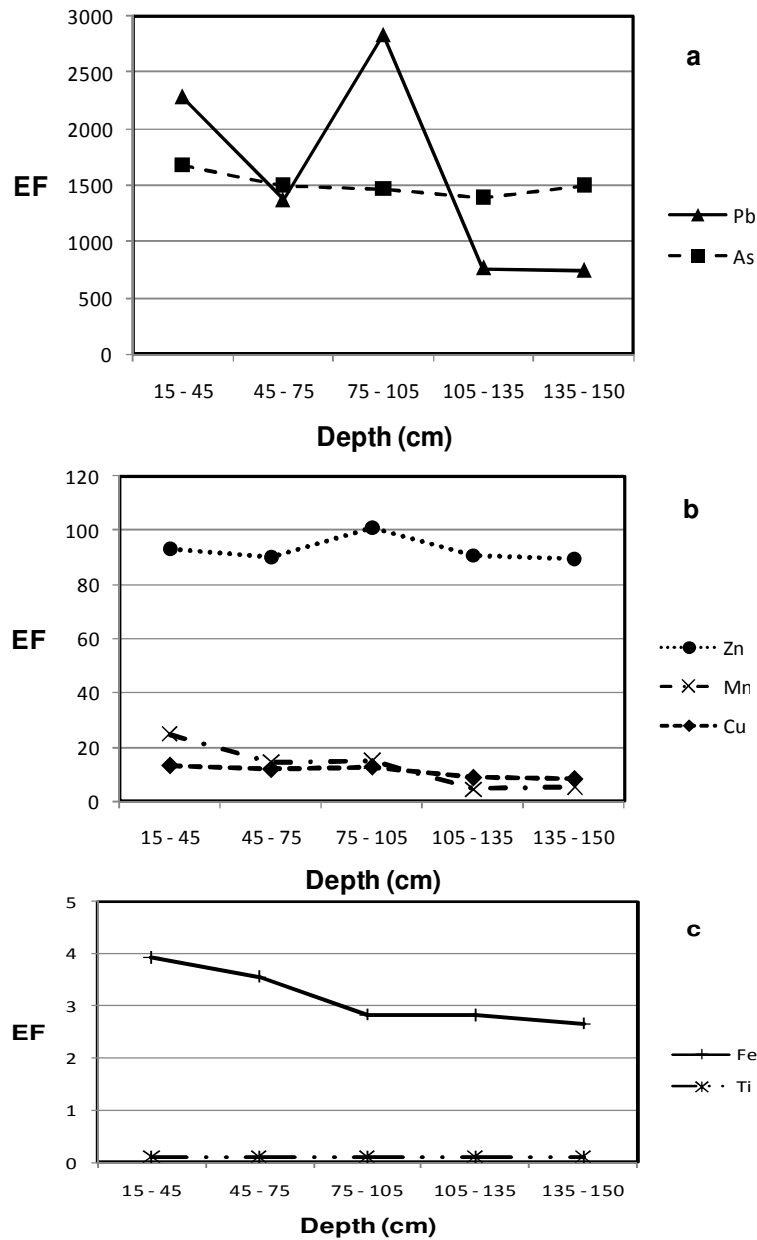


Figure 3. EF values of the elements at different depths.

Table 3. Inter-elemental correlation in the soil profile.

	Pb	Zn	As	Cu	Ti	Fe	Al	Mn	pH
Pb	1								
Zn	0.86	1							
As	0.79	0.98	1						
Cu	0.89*	1.00	0.97	1					
Ti	0.77	0.98	0.99	0.98	1				
Fe	0.75	0.98	0.99	0.97	1.00	1			
Al	0.77	0.99	0.99	0.98	1.00	1.00	1		
Mn	0.90*	0.98	0.97	0.98	0.95	0.95	0.95	1	
pH	-0.90*	-0.86	-0.88	-0.87	-0.82	-0.82	-0.81	-0.95*	1

Values in bold are statistically correlated with each element at significant level of $p < 0.01$, except * in bold at $p < 0.05$.

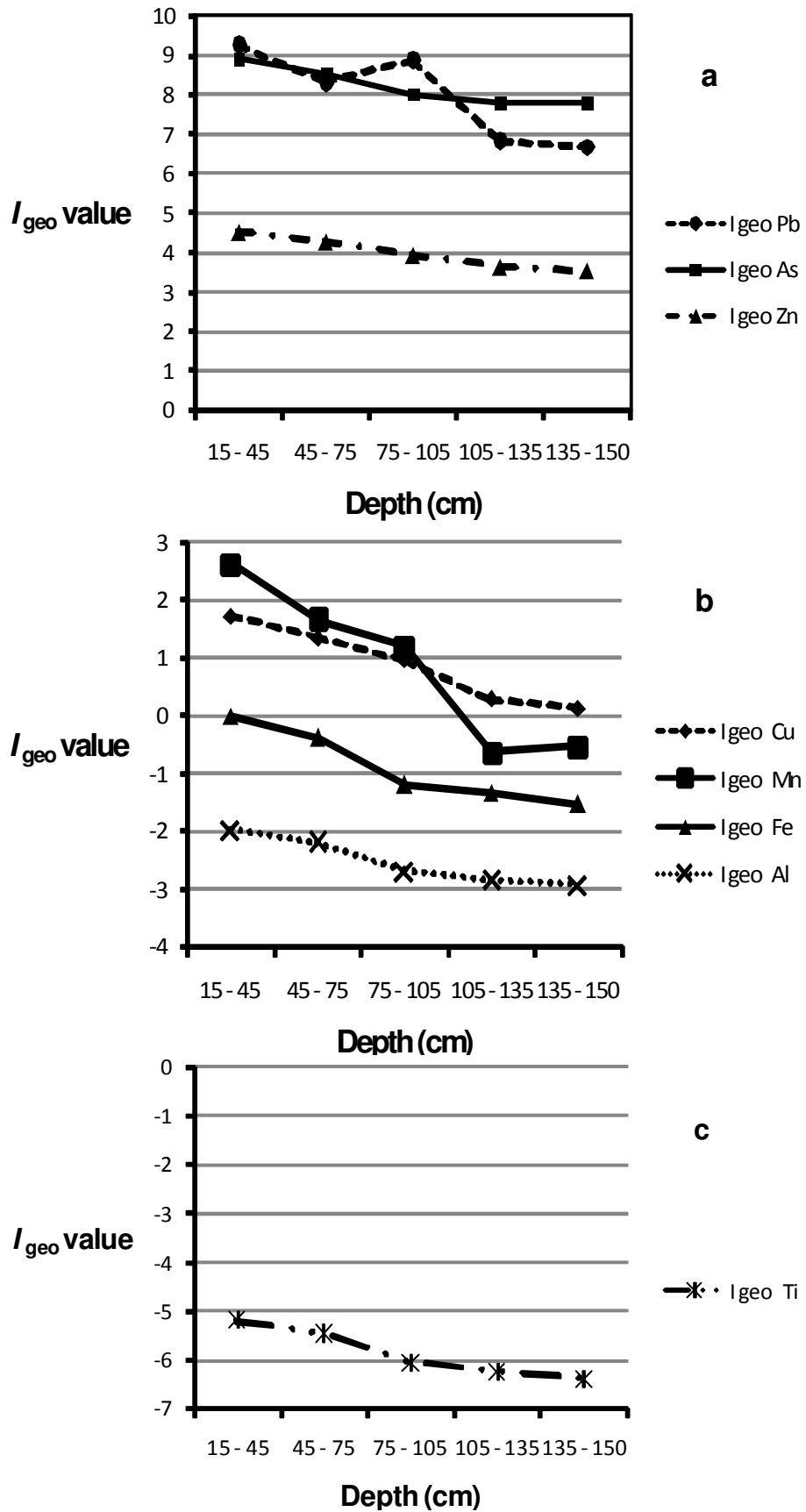


Figure 4. I_{geo} values of the elements at different depths.

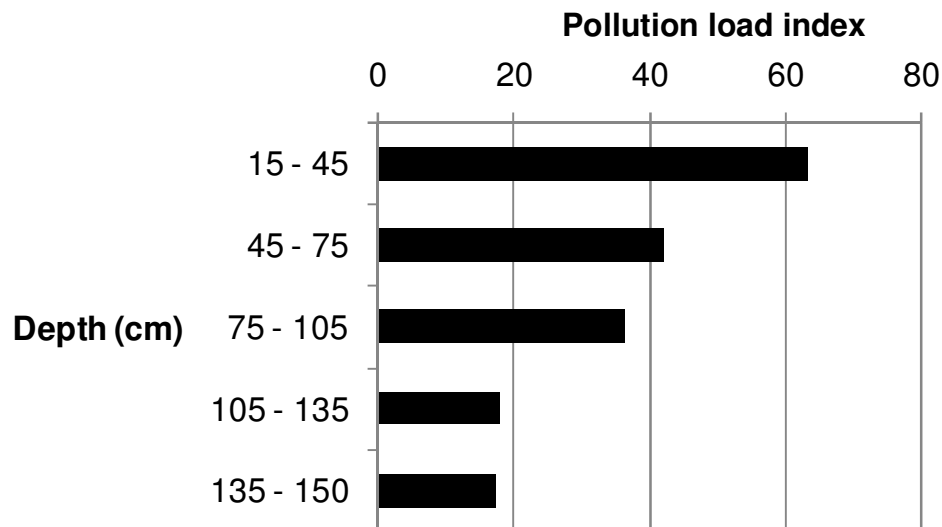


Figure 5. Pollution load index values in the soil profile.

than several times the permissible limits indicating an anthropogenic source. Trace metal concentrations were found to decrease substantially with increasing soil depth and pH. The distribution pattern of trace metals in the soil profile according to EF, I geo and PLI values shows that the soil is very strongly polluted. The results suggest the need for an examination of speciation studies to quantify the proportion of trace metals in each fraction.

ACKNOWLEDGMENT

The authors are sincerely thankful to Mr Stephane Audry, Université Bordeaux I, UMR CNRS 5805 EPOC (T.G.M) for his suggestions in the preparation of this paper.

REFERENCES

- Acevedo-Figueroa D, Jimenez BD, Rodriguez-Sierra CJ (2006). Trace metals in sediments of two estuarine lagoons from Puerto Rico. *Environ. Pollut.*, 141: 336-342.
- Adie GU, Osibanjo O (2009). Assessment of soil-pollution by slag from an automobile Battery manufacturing plant in Nigeria. *Afr. J. Environ. Sci. Technol.*, 3 (9):239 – 250.
- Adriano DC (2001). *Trace Elements in Terrestrial Environments Biogeochemistry Bioavailability and Risk of Metals*, second ed. Springer-Verlag, New-York.
- Alloway BJ (1995). *Heavy metals in soils*, 2nd Ed. Chapman and Hall, India: Australia.
- Bricker SB (1993). The history of Cu, Pb and Zn inputs of Narrangansett Bay, Rhode Island as recorded by salt-marsh sediments. *Estua*, 16: 589-606.
- Bowen HJM (1979). *Environmental Chemistry of the Elements*. Academic Press, New-York.
- Chaney RL (1994). Trace metal movement in soil-plant systems and bioavailability of biosolds. In Clapp, CE (ed.). *Sewage sludge Land Utilization and the Environment*. Soil Sci. Soc. Am. Pub., Madison, Wisconsin, pp. 27-31.
- Chuan MC, Shu GY, Liu JC (1996). Solubility of heavy metals in a contaminated soil: effects of redox potential and pH. *Water Air Soil Pollut.*, 90: 543-556.
- Dudka S, Market B (1992). Baseline concentrations of As, Ba, Be, Li, Nb, Sr and V in surface soils of Poland. *Sci. Total Environ.*, 122: 279–290.
- Duffus JH (1980). *Environmental Toxicology*. Edward.
- Ekosse Georges-Ivo E (2008). Spatial distribution of iron in soils and vegetation cover close to an abandoned manganese oxide ore mine, Botswana. *J. Appl. Sci.*, 8(1): 14-25.
- Emsley J (1991). *The Elements*. Oxford chemistry Guides. Clarendon Press, Oxford, p. 250.
- Feng H, Han X, Zhang W, Yu L (2004). A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. *Marine Pollut. Bull.*, 49: 910-915.
- Forstner U (1985). Chemical forms and Reactivity of Metals in Sediments. In: *Chemical Methods for Assessing Bioavailability Metals in Sludges and Soils*, Leschber, R. (Ed.). Elsevier, London, pp. 1-30.
- Giller KE, Witter E, McGrath SP (1988). Toxicity of heavy metals to micro-organisms and microbial processes in agricultural soils. A review. *Soil Biol. Biochem.*, 30: 1389–1414.
- Grzebisz W, Ciesla L, Komisarek J, Potarzycki J (2002). Geochemical assessment of heavy metals pollution of urban soils. *Polish J. Environ. Stud.*, 11(5): 493–499.
- Hart AD, Oboh CA, Barimalao IS, Sokari TG (2005). Concentrations of trace metals (lead, iron, copper and zinc) in crops harvested in some oil prospecting locations in Rivers State, Nigeria. *Afr. J. Food. Nutr. Sci.*, 5(2): 1-21.
- Iwegbue CMA, Emuh FN, Isirimah NO, Egun AC (2007). Fractionation, Characterization and speciation of heavy metals in composts and compost-amended soils. *Afr. J. Biotechnol.*, 6(2): 067–078.
- Kabata-Pendias A, Pendias H (1992). *Trace elements in soils and plants*, 2nd ed., CRC, press, Boca Rotan FL.
- Karczewska A, Bogda A, Galka B, Szulc A, Czwarakiel D, Duszynska D (2006). Natural and anthropogenic soil enrichment in heavy metals in areas of Former metallic ore mining in the sudety MTS. *Polish J. Soil Sci.*, 39(2): 131-142.
- Kozak J (1991). Heavy metals in soil. In: Cibulka J. et al.: lead, cadmium and mercury transport in the biosphere. *Academica, Praha*, pp. 62–104.
- Lewandoski P, Burghardt W, Ilnicki P (1998). Heavy metals in surface soils of the Warta River valley in an urban area. *Z. Pflanzenernähr, Bodenk.*, 161: 303–308 (in German).
- Li XD, Poon CS, Liu PS (2001). Heavy metals contamination of urban soils and street dusts in Hong Kong. *Appl. Geochem.*, 16: 1361-1368.
- Lock JW, Thompson DR, Furness RW, Bartle JA (1992). Metal concentration in seabirds of the New Zealand region. *Environ. Pollut.*, 75(3): 289–300.
- Ma LQ, Rao GN (1997). Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. *J. Environ. Qual.*, 26: 259-264.
- Ma LQ, Komar KM, Tu C, Zhang W, Cai Y, Kenelly ED (2001). A fern that Hyper accumulates arsenic. *Nature*, 409: 579-582.

- Mahjoobi A, Albaji M, Torfi K (2010). Determination of heavy metal levels of kondok soils-haftgel. *Res. J. Environ. Sci.*, 4: 294-299.
- Martin AC, Rivers VC, Marin MTL (1998). Contamination by heavy metals in soils in the neighborhood of a scrapyard of discarded vehicles. *Sci. Total Environ.*, 212: 142-152.
- McLean EO (1982). Soil pH and Lime Requirement. In: *Methods of Soil Analysis Part 2: Chemical and Microbiological Properties*, Page AL, Miller RH and Keeney DR(Eds.). ASA and SSSA, New York, USA, pp: 199-224.
- Metcheva R, Yurukova L, Bezrukov V, Betcheva M, Yankov Y, Dimitrov K (2010). Trace and toxic metals accumulation in food chain representatives at Livingston Island (Antarctica). *Int. J. Biol.*, 2(1): 155-161.
- Moosavi MH, Zorasvandi A (2009). Geochemistry of urban soils in the Masjed-i-Soleiman (MIS) city, Khuzestan Province, Iran: *Environmentals Marks. Res. J. Environ. Sci.*, 3(3): 392-399.
- Müller G (1979). Schwermetalle in den sedimenten des Rheins, Veränderungen Seit 1971. *Umschau* 79(24): 778-783.
- Nygaard T, Lie E, Row N, Steines E (2001). Metal dynamics in an Antarctic food chain. *Marine Pollut. Bull.*, 42(7): 598-602.
- Osuji LC, Onajake CM (2004). The Ebocha soil spillage II. Fate and associated heavy metals six months after. *Afr. J. Environ. Assess. Monit.*, 9: 78-87.
- Rademacher P (2003). Atmospheric heavy metals and forest ecosystems. Federal Research Centre for Forestry and Forest Products, Hamburg, Germany. http://www.bfaffh.de/bibl/pdf/i_03_12.pdf.
- Taylor SR (1964). Abundances of chemical elements in the continental crust: a new table. *Geochimica et Cosmochimica Acta*, 28(8): 1273-1285.
- Tomilsson DC, Wilson JG, Harris CR, Jeffrey DW (1980). Problems in assessment of heavy metals in estuaries and the formation of pollution index. *Helgol Meeresunters*, 33: 566-575.
- Tume P (1997). Study of heavy metals in low Llobregat, Ph.D. Dissertation, University of Barcelona, Spain (in Spanish).
- USEPA (1999). Integrated Risk Information System (IRIS). National Center for Environmental Assessment, Office of Research and Development, Washington, DC.