RESEARCH ARTICLE

Soils Pollution in Some Metals in a Solid Waste Dump in Yamoussoukro, Cote d'Ivoire

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ABSTRACT

Some metals inputs within the solid waste dump were studied through the Pollution Load Index (PLI). High levels in cadmium (4.00±0.62 mg.kg^{-1}), lead (138.43±51.5 mg.kg^{-1}) and zinc (266.63±42.83 mg.kg^{-1}) and low levels in copper (40.77±11.98 mg.kg^{-1}) were measured within the soils at five sites against a control. The total concentrations in metals were measured in soil samples collected from the surface to 1.5 m depth. The measurements showed in total metal concentration decrease from surface to depth in lead, zinc and copper. Cadmium was measured to be constant with the depth of study. The values of Pollution Load Index pointed out strong contaminations in metals of the soils surface layers at overall area of study. PLI decreased from 5.13 to 1.33 with respect to the increase in depth in that landfill. The soils clay contents were showed to be the major factor for controlling the metals distribution within those soils.

INTRODUCTION

The solid waste dump is the worldwide rejection method of solid waste. In developing countries, over 90% of solid wastes are treated by this method (Subramaniam *et al.*, 2003). The Municipal Solid Waste is heterogeneous and depends on the lifestyle of societies. Their composition varies in space and time with people practices (Buenrostro and Bocco, 2003). Wastes consist mainly of organic material, bulky waste (furniture, wrecks, demolition) and special harmful waste to health and environment (medical waste and chemicals for example) are sometimes subject to special legislation (Altındag *et al.*, 2005; Aloueimine, 2006). Wastes storage in dumpsites is of concern due to pollution. Soil degradation is mostly caused by metal presence in the wastes (Christian *et al.*, 2009). They result from batteries (Hg, Zn, Pb, Cd), paintings (Cr, Cd, Pb), plastics (Cd, Ni, Zn), papers and paperboards, (Pb), electronic components (Pb, Cd), ceramics, cosmetics (Harikumar *et al.*, 2009). Large variability in metal concentrations is related to the waste composition. If the levels are shown to be lower than Baize (1997) standard, the accumulation in the soils increases the contents leading to soil pollution (François, 2004). Resultant diffuse contamination and soils degradation reduce the activity of microorganisms. That negatively impacts soil fertility and requires very often some costly treatment events (Edu *et al.*, 2011). In a metal polluted soil, the variation of the physicochemical conditions likely result in the mobility of those elements. This mobility can lead to a migration by leaching events that reach groundwater (Kouamé *et al.*, 2006; Zhong *et al.*, 2010). In this study, we evaluated some heavy metals total

contents in soils in municipal solid waste landfills to better understand contamination process. The extent of that concern was assessed in soils surrounding the city dumpsite in Yamoussoukro, a town in center of Côte d'Ivoire, where more than 400 000 tons/year of various waste are stored.

MATERIALS AND METHODS

The sampling was carried out at five sites in the city landfill and a control off-landfill (Figure 1). Wells were dug and samples were collected from surface (natural compost), 0.5 m, 0.75 m, 1m and 1.5 m depth. Each sample was first screened on a sieve of 2 mm in diameter before being transferred to the laboratory. They were air dried in a room for a week before their characterization. Different parameters were performed: The pH, organic matter and cation exchange capacity (CEC) of the soils samples were performed according to the method used in Yobouet *et al.* (2010). The determination of particle size was performed using the method of wet fractionation of Robinson-Köhn (1934). It is a soil physical fractionation which consists of breaking the unstable macrostructures as well as resistant microstructures for then classified particle size (Feller *et al.*, 1991). That allows separation of fractions of materials with homogeneous surface properties. The principle relies on the destruction of coarse aggregate (greater than 250 μm) by immersion, followed by gravity separation up to 2 microns by sedimentation according to Stokes law (Rouiller *et al.*, 1994). The metal total contents (cadmium, lead, copper and zinc) within the soils in the landfill were obtained by acid attacks according to the standard NF X37-147 (AFNOR, 1996b) after digestion. In a sample of 0.3 g of soil were added, 5 mL of nitric acid, 5 ml of hydrofluoric acid and 1.5 mL of perchloric acid. All acids were concentrated. The metal analysis was performed by atomic absorption spectrometry with

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flame (air-acetylene) using a Varian AA 20 spectrometer. The Pollution Load Index (PLI) is obtained as concentration Factors (CF). The CF is the quotient obtained by dividing the concentration of each metal on the background value (natural concentration of metal in soil) of the same metal in the soil. The PLI of each site is calculated by obtaining the n-root from the n-CFs that were obtained for all the metals (Kao *et al.*, 2007; Chakravarty and Patgiri, 2009; Rabee *et al.*, 2011). For each site, it is expressed as:

$$PLI = \sqrt[n]{CFi \times CFj \times \cdots \times CFn} \qquad (1)$$

where, *n* is the number of metals.
The contamination factor (CF) is calculated from the following relation:

$$CF = \frac{Metal\ concentration\ in\ soil}{Background\ value\ of\ metal} \qquad (2)$$

The background value of the metal used is the average concentration of heavy metals in the terrestrial crust proposed by Baize (1997). The PLI greater than 1 is equivalent to site pollution.

RESULTS AND DISCUSSION

Sample characterization

Particle size results are summarized in Table 1. Soils contained mostly coarse particles (sand) from the surface to depth. The proportions for fine particles (clay and silt) from 0.75 m depth (especially sites 1, 4 and 5) increased over all sites of study. There was a high variability between the fractions obtained at both the depth and site. This dispersion is indicated by the values of standard deviations in Table 2. The calculations showed that soils from the landfill had a relatively coarse texture at all depths. The finest fraction reduced the mobility and bioavailability of the contaminants (Adriano *et al.*, 2004). The variation in pH at the sites as function of depth is presented in Figure 2. The pH values of the control site ranged from 7 to 6 (from surface to 1.5 m depth). In the landfill, there was a slight decrease in pH, which ranged from 8.5 to 7. The highest values of pH were observed at soils surface, showing the maturity of compost (Bozkurt, 1999). Those pH values gave the soil a strong adsorbent character. The observed decrease in pH with depth is due to the sites intrinsic physical and chemical characteristics, and the reactions that take place, or the infiltration of acid percolation in the lower layers (Christian *et al.*, 2009). The values and the variation of the cation exchange capacity (CEC) are shown in Figure 3.

The values of CEC obtained for the control site varied weakly with depth. At landfill surface, the values of CEC were relatively high (25.96 cmol.kg⁻¹ at site 1, 23.29 cmol.kg⁻¹ at site 2, 17.55 cmol.kg⁻¹ at site 3, 27.93 cmol.kg⁻¹ at site 4 and 29.34 cmol.kg⁻¹ at site 5), and decreased with depth. The decrease in CEC also suggests that clays in depth are not swelling clays, type T/O/T. The variation in organic matter (OM) content in samples is shown in Figure 4. The OM contents in the control site ranged from 55 to 34.5 g.kg⁻¹ from the surface to depth. These values are relatively low and varied little with depth. The low levels could result from the slow decomposition of vegetable materials. In landfill surface, the OM contents ranged between 215.3 and 29 g.kg⁻¹ at site 1, 205.6 and 33.1 g.kg⁻¹ at site 2, 172, 5 g.kg⁻¹ at site 3, 168.4 and 62.1 g.kg⁻¹ at site 4 and 164.2 and 30.35 g.kg⁻¹ at site 5. The high levels of OM were obtained from surface samples. The large variation of values obtained is due to the heterogeneity of waste (Barlaz and Reinhart, 2004; Davoli *et al.*, 2010). Contents decreased with depth, indicating a low infiltration of soluble organic matter in soils. Organic substances pile up on the surface, controlling the mobility of heavy metals in soil (De Matos *et al.*, 2001; Kim *et al.*, 2011). The organic matter content and clays were negatively correlated as shown in Figure 5. The metals retention

in depth is caused mainly by clays which are also characterized by a high buffering capacity. Averages and standard deviations of physicochemical parameters are presented in Table 3. The standard deviations showed a large dispersion of values of parameters with respect to the site and depth. The comparison of average values for each site at different depth was carried out using analysis of variance, at the risk of 5%, with SPSS 11.5 software. That analysis indicated significant differences between the soils pH, organic matter and CEC. The total metal contents of samples are presented in Figure 6. The values were compared to the average values of earth's crust given by Baize (1997). Total metal contents in soils were highly variable and also found to be high (Ashraf *et al.*, 2011).

Lead: The content of Pb in surface of the control site is high (60.83 mg.kg⁻¹). That high value could be due to the influence of external discrete sources like atmospheric pollutants deposition, including vehicle emissions, waste incineration in the dumpsite and other anthropogenic inputs. Values varied weakly with respect to depth and are higher than the average content in the earth's crust. That slight variation could be due either to a geochemical anomaly, characterized by the presence of Pb in the structure of the geological formation or to a migration of the element in depths (Galan *et al.*, 2008). The values observed in the landfill surface are high (139.33 mg.kg⁻¹, 107.83 mg.kg⁻¹, 133.83 mg.kg⁻¹, 142.67 and 222 mg.kg⁻¹, 67 mg.kg⁻¹, respectively, at sites 1 to 5). They indicated the presence of lead in the waste. Variation of Pb content obtained from the different sites could be explained by the heterogeneity of the waste and the period of use of different sites for storage. Contents decreased with depth, indicating a surface pollution in those metals. These values remained very high (superior to 13-16 mg.kg⁻¹) and suggested a contamination due to migration of this element to depth.

Cadmium: Cadmium is a highly toxic element known for its high bioavailability (Edu *et al.*, 2011). Values obtained at different sampling points indicated a high level of contamination of the different sites. They ranged from 3.5 to 5.02 mg.kg⁻¹ at over all sampling points. The values were widely higher than the average concentration of the terrestrial crust. Regarding to the control site, the value obtained at surface indicated a soil contamination that would be caused, as lead, by external discrete sources. In the landfill, cadmium contents found at the surface were high. They decreased slightly in depth, resulting in surface contamination (Galan *et al.*, 2008). For a so mobile and highly bioavailable element, these high contents represent a major environmental risk.

Copper: Copper is a trace element which content in the soil becomes toxic beyond a certain threshold (45-70 mg.kg⁻¹) (Baize, 1997). The values measured in the control site from the surface to depth range between 12 and 9 mg.kg⁻¹. The values found in the landfill did not show a sign of copper contamination. But the observed decline with respect to depth suggests a contribution of the item by the waste discharged.

Zinc: This element was found to be present in very small quantities in the control site from surface to depth, where the contents range between 19.7 and 15.5 mg.kg⁻¹. Those contents varied lower and were below the average content in the terrestrial crust. There is therefore, a priori, no contamination of soils of the control site. Higher concentrations (288.33 mg.kg⁻¹, 190.17 mg.kg⁻¹, 288 mg.kg⁻¹, 281.5 mg.kg⁻¹, 285.17 mg.kg⁻¹, respectively, at the sites 1 to 5) were found at surface of the sampling sites in the landfill. Contents felt by over a third from 0.5 m depth for site 2 (21.67 mg.kg⁻¹), site 3 (46.67 mg.kg⁻¹) and site 5 (96.5mg.kg⁻¹), and from 1 m for site 1 (51.17 mg.kg⁻¹) and site 4 (97.67 mg.kg⁻¹). The low values observed could be explained by the buffer role of clays that prevent the progression of the element in depth (Kao *et al.*, 2007).

The averages of total metal contents in the five sampling sites are resumed in the Table 4. At surface, the metal total contents were important, except Cu. The amounts of metal were measured to be

equal to 4.00±0.62 mg.kg⁻¹, 138.43±51.5 mg.kg⁻¹, 40.77±11.98 mg.kg⁻¹ and 266.63±42.83 mg.kg⁻¹, respectively, for Cd, Pb, Cu and Zn. Overall, the metal total contents decreased significantly with respect to depth, suggesting high surface contamination (Yobouet *et al.,* 2010). Consequently, soils under the landfill could exhibit highest available quantities of metal when changes in pH occur (Gonzalez Corrochano *et al.,* 2011). Zinc contents ranged from 266.63 to 24.27mg.kg⁻¹. Copper contents appeared to be far of concern (40.77 to 21.30 mg.kg⁻¹), but those of cadmium and lead remained higher enough in the depths (values greater than 2 mg.kg⁻¹ and 60 mg.kg⁻¹, respectively). A higher dispersion of values was observed, showing the diversity and heterogeneity of waste in the sites. Analysis of variance (ANOVA) was employed to determine whether heavy metal variables have the same mean on data. That data manipulation indicated significant difference between the values at the sites with depth, except for lead. That suggests that lead distribution in soil is similar whatever the site and the depth.

Multivariate analysis of variance

We used the MANOVA statistical model to determine the effects of physical and chemical parameters for a better appreciation of the results (Table 5). The sites, depths and interaction site-depth showed significant influence on the physical and chemical parameters ($p = 0.000 < 0.05$ in the three cases). Indeed, the sites receive waste at different times, and the waste composition differs from a site to another.

Study of correlation

The correlations were performed using SPSS 11.5. Table 6 shows the linear correlations between physicochemical parameters. The considered significant correlation coefficients were those with probability level smaller than 5% ($P < 0.01$ and $P < 0.05$). For the linear correlation, a very high positive correlation with a very significant probability ($P < 0.01$) was observed between pH/OM, pH/CEC and OM/CEC. Indeed, the CEC is a parameter that depends strongly on the pH and the organic matter content of soil (Sens, 1998). A very high correlation ($P < 0.01$) is also noticed between pH/metals, OM/metals and CEC/metals (except correlation between

OM and Cd). The strong correlations of metals with organic matter content and CEC showed their affinity for soil organic matter (Rooney *et al.,* 2007.). There were also significant correlations between total contents of the different metals. The adsorption of a metal is strongly influenced by the adsorption of other metals (Rabee *et al.,* 2011).

Pollution load index (PLI)

The determination of the total metal contents leaded to the calculation of the PLI. The evolution of the PLI values is presented in Figure 7. The PLI values showed that sites surfaces were about 4 to 5 times, more polluted than the control site (the medium PLI of the control site was of 0.95). The relatively higher values of PLI at the different sites and their fluctuations might be due to the increase of waste dumping. The pollution decreased by half from 0.75 m in the sites 1, 3 and 4, whereas it decreased by third on the sites 2 and 5. The reduction of the PLI values could be due as previously mentioned, to the role (buffer) acted by the textural characteristic of soils, notably clays (Kao *et al.,* 2007). However, the PLI values were all greater than 1. That indicated a soil contamination at the different levels. The contamination factor (CF) were higher for Pb and Cd (the CF values of these metals vary from 3.59 to 15.35 for Pb, and of 5.83 to 42.5 for Cd) whatever the depth. That contamination could be, therefore, essentially due to these two metals (Pb and Cd). Two hypotheses are plausible to explain that. Each metal goes into solution to migrate towards depths because of the particles size, or it could be due to the abnormally high amount of both the Pb and Cd in the structure of soils in depths. Considering the control site unpolluted, the calculation of the average of metals content at different levels of depth shown the results in Table 4. Concentration levels of lead and cadmium in the sites exceeded the earth's crust average concentration (2.13 and 56.20 mg.kg⁻¹, respectively). In other hand, copper and zinc are well below. Also, coefficients of variation calculated for different metals have shown the large variability in the distribution of total metal content with depth (38.49%, 33.75% and 33.26% respectively for Cd, Cu and Zn). Only the coefficient of variation of Pb is less than 15%, indicating a lower variability of that element with depth (5.92%) (Feinberg, 1996). Values measured at the different levels of depth fluctuated, when those of Pb were homogenous. The CF values of both metals Pb and Cd decreased. They range from 0.88 to 3.66 for

Table 1. Particles size distribution in the soils at the sites

SITES	Depth (m)	% Clay	% Fine silt	% Coarse silt	%Fine sand	% Coarse sand
Size (μm)		< 2	2 – 20	20 – 50	50 – 200	200 – 2000
CONTROL	0	9.23	7.27	10.61	12.81	60.08
	0.5	5.07	3.40	4.45	8.70	78.38
	0.75	26.25	7.76	3.14	10.88	51.97
	1	36.40	5.75	6.29	9.71	41.85
	1.5	23.40	7.65	4.65	8.26	56.04
SITE 1	0	3.23	10.93	15.25	13.72	56.87
	0.5	3.50	11.70	8.87	18.82	57.11
	0.75	6.75	8.53	12.71	21.34	50.67
	1	51.30	8.18	7.38	8.98	24.16
	1.5	40.23	8.27	4.17	10.54	36.79
SITE 2	0	2.60	11.25	7.03	16.8	62.32
	0.5	20.05	11.00	4.70	16.15	48.10
	0.75	21.10	10.95	4.73	14.51	48.71
	1	17.70	15.15	5.85	15.52	45.78
	1.5	13.00	15.38	7.00	17.19	47.43
SITE 3	0	4.25	14.10	10.79	21.42	49.44
	0.5	23.23	9.90	5.80	13.68	47.39
	0.75	8.18	4.85	5.50	15.87	65.60
	1	24.00	7.85	5.39	13.92	48.84
	1.5	9.70	2.88	6.59	16.19	64.64
SITE 4	0	3.10	5.22	14.00	14.98	62.70
	0.5	2.52	9.87	10.01	19.21	58.39
	0.75	20.77	8.77	8.98	10.80	50.68
	1	30.82	5.65	5.72	8.48	49.33
	1.5	24.55	6.37	6.62	11.08	51.38
SITE 5	0	6.07	6.62	16.24	15.99	55.08
	0.5	18.80	17.15	21.60	12.01	30.44
	0.75	38.40	17.42	5.97	9.09	29.12
	1	41.55	14.45	10.37	7.39	26.24
	1.5	48.95	9.80	2.46	10.11	28.68

Table 2. Averages and standard deviation of particles size

Depths (m)	% Clay	% Fine silt	% Coarse silt	%Fine sand	% Coarse sand
Size (μm)	< 2	2 - 20	20 - 50	50 - 200	200 - 2000
0	3.85 ± 1.38	9.62 ± 3.63	12.66 ± 3.76	16.58 ± 2.94	57.28 ± 5.51
0.5	13.62 ± 9.83	11.92 ± 3.02	10.20 ± 6.73	15.97 ± 3.15	48.29 ± 11.17
0.75	19.04 ± 12.76	10.10 ± 4.64	7.58 ± 3.29	14.32 ± 4.78	48.96 ± 13.00
1	33.07 ± 13.49	10.26 ± 4.27	6.94 ± 2.06	10.86 ± 3.62	38.87 ± 12.57
1,5	27.29 ± 17.01	8.54 ± 4.61	5.37 ± 1.98	13.02 ± 3.38	45.78 ± 13.81

Table 3. Averages, standard deviation of physicochemical parameters in the landfill and the one-way ANOVA results.

Depth (m)	pH	Organic matter (g.kg^{-1})	CEC (cmol.kg^{-1})
0	8.17 ± 0.36	185.2 ± 23.5	24.21± 4.33
0.5	7.62 ± 0.48	122.3 ± 60.8	20.09± 10.11
0.75	7.36 ± 0.32	72.3 ± 37.8	15.11± 10.84
1	7.27 ± 0.24	47.5 ± 5.6	9.80± 3.74
1.5	7.15 ± 0.38	32.6 ± 6.9	5.91± 1.89
Test ANOVA	0.000	0.000	0.000

Table 4. Averages, standard deviation of total metals contents (mg/kg) and the one-way ANOVA results

Depths (m)	Cadmium	Lead	Cooper	Zinc
0	4.00 ± 0.62	138.43 ± 51.5	40.77 ± 11.98	266.63 ± 42.83
0.5	4.57 ± 2.39	102.67 ± 27.14	31.93 ± 9.19	138.70 ± 121.05
0.75	3.37 ± 1.57	73.70 ± 21.66	28.57 ± 8.28	68.57 ± 62.18
1	2.93 ± 1.05	72.37 ± 13.02	24.93 ±7.76	30.97 ± 15.57
1.5	2.93 ± 0.71	66.33 ± 16.74	21.30 ± 6.23	24.27 ± 7.93
Test ANOVA	0,000	0,204	0,018	0,067

Table 5. Multivariate tests of significance of physicochemical values

EFFECTS	Test	value	F	Effect df	Error δf	p
SITES	Wilks	0.000	8.708	40	24.589	0.000
DEPTHS	Wilks	0.003	190.423	8	5.000	0.000
SITES*DEPTHS	Wilks	0.000	4.512	40	24.589	0.000

Table 6. Correlation coefficients for the relationship between determined parameters

	pH	OM	CEC	Pb	Cd	Cu	Zn
pH	1						
OM	0.806(**)	1					
CEC	0.736(**)	0.841(**)	1				
Pb	0.562(**)	0.621(**)	0.554(**)	1			
Cd	0.538(**)	0.384	0.449(*)	0.454(*)	1		
Cu	0.443(*)	0.702(**)	0.644(**)	0.595(**)	0.248	1	
Zn	0.754(**)	0.938(**)	0.846(**)	0.706(**)	0.468(*)	0.763(**)	1

** Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05level (2-tailed)

Table 7. Averages of total metals contents at the control site compared to the total background contents

Metals	Averages of metals total contents on the control site (mg/kg)	Averages of background of metals total contents (mg/kg)
Cadmium	2.13 ± 0.82	0.2
Lead	56.20 ± 3.33	13 - 16
Cooper	8.77 ± 2.96	45 - 70
Zinc	14.13 ± 4.70	70 - 132
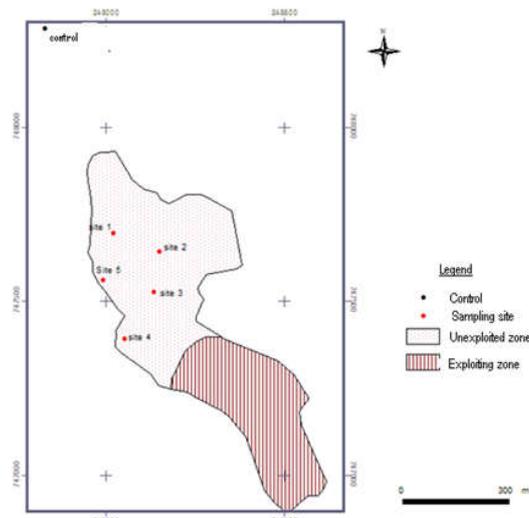
Fig. 1. Sampling sites location in city landfill, Yamoussoukro

Fig. 2: Evolution of pH

$$y = -5.137x + 191.5$$
$$R^2 = 0.892$$
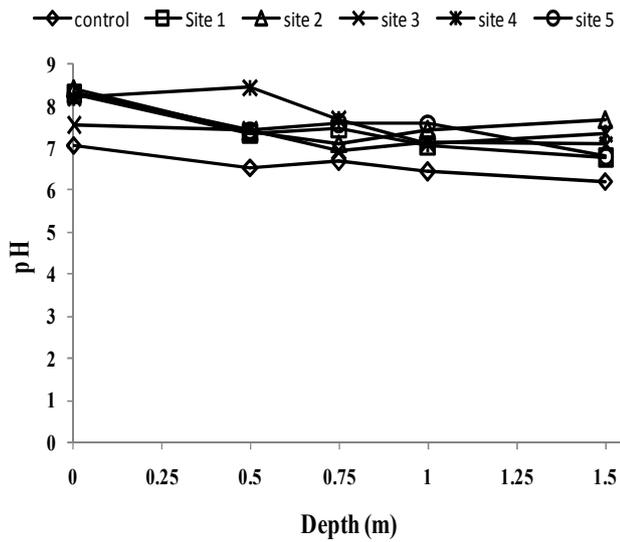
Fig. 5: Clay and OM correlation plot
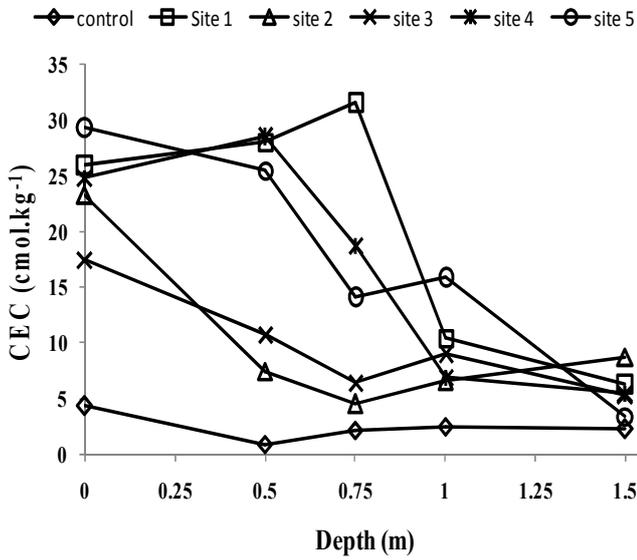
Fig. 3: Evolution of CEC
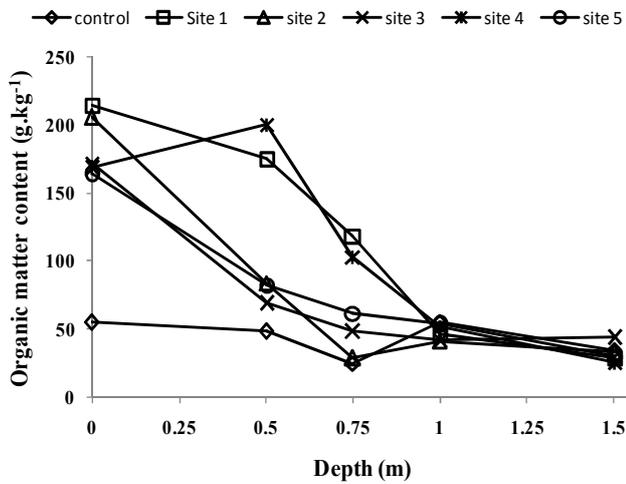
Fig. 4: Evolution of OM contents

Lead

Cadmium

Cooper
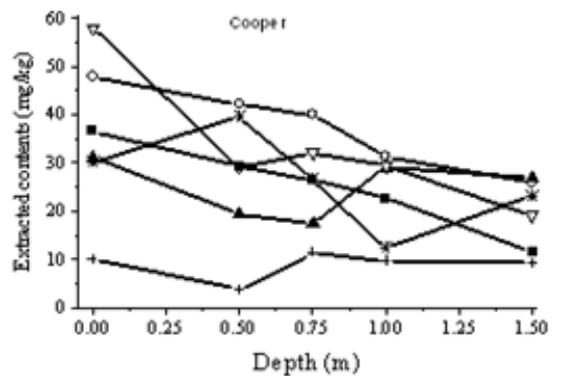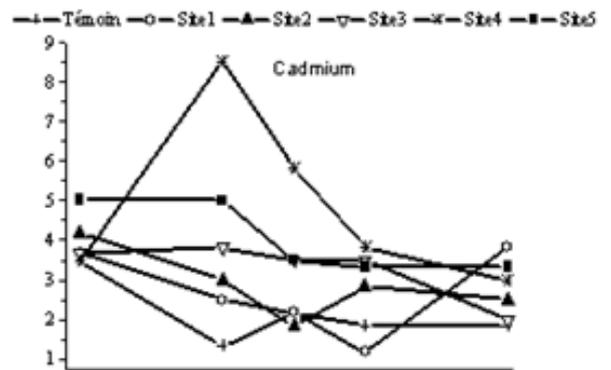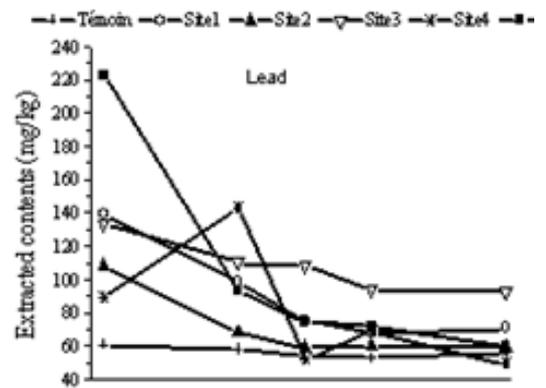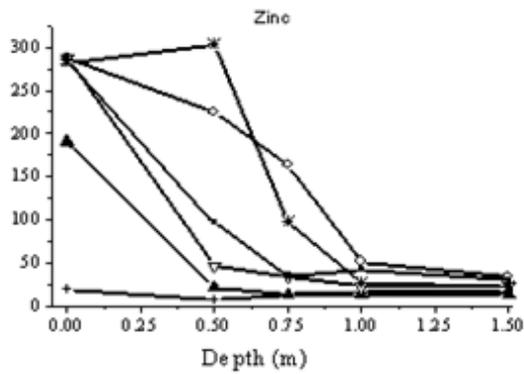
Fig. 6: Evolution of metals total contents with depth
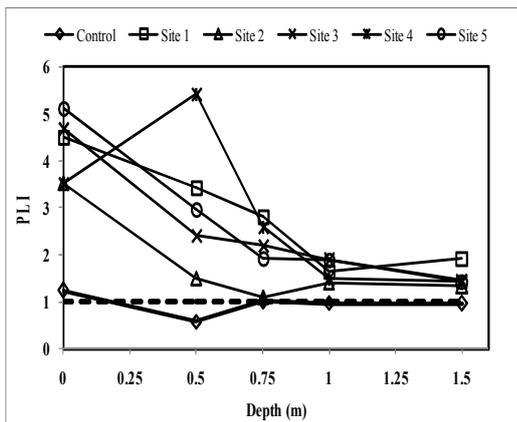
Fig. 7: Pollution load index of the different sites
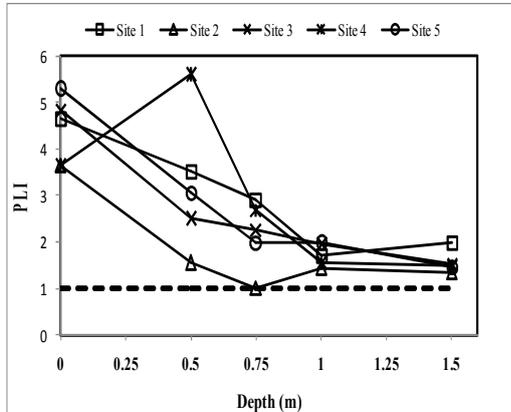
Fig. 8: Pollution load index obtained by the control site
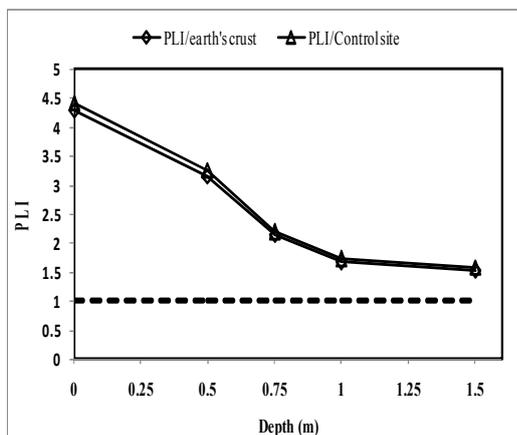
Fig. 9: Comparison of the PLI averages
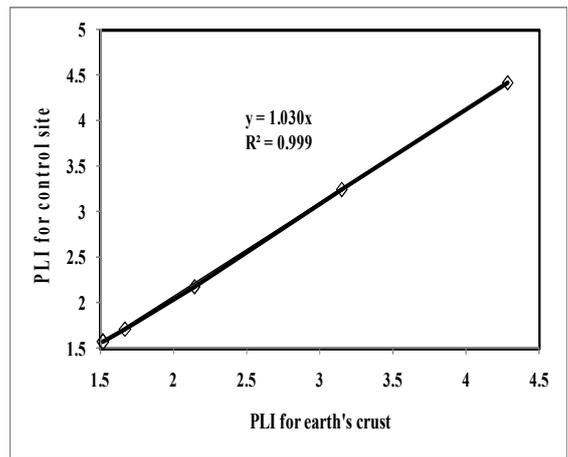
Fig. 10: Correlation plot of PLI from terrestrial crust and control site

Pb, and 0.33 to 3.19 for Cd. The evolution of the PLI obtained with the averages of metals contents of the control site is shown on Figure 8. The values of PLI showed the same fluctuation as those obtained beforehand. Comparison between the average values of the pollution load index from the background and the control site at the five sites showed convergent changes and were almost equal (Figure 9). A significant correlation between those two averages (R^2 = 0.999) was calculated when we plotted correlation PLI compared to the earth's crust as a function of PLI compared to control site (Figure 10). That suggests that the control site was not polluted. The levels of Pb and Cd obtained in the control site were similar to those found in depth at the different sites on the landfill. So, high levels observed in depth for Pb and Cd was mainly due to high accumulation of those metals in the soil structure. Therefore, we faced a surface pollution in the landfill.

Conclusion

The soils sampled in the landfill were relatively rich in organic matter due to the type of waste discharged, with a high pH in the surface. High levels of metals were also measured. The contents of cadmium, lead and zinc were widely greater than those of earth's crust given by Baize (1997). Values decreased, indicating a surface pollution. But in the case of cadmium and lead, the contents in depth remained high. The study of the pollution load index showed that the depths at the sites were not polluted by cadmium and lead, but the high levels observed were due to anomalies related to the presence of these metals in the soils structure in depth. The high content of metals at surface could cause metal migration into groundwater and accumulation in plants if environmental conditions change.

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