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Full Length Research Paper

Metals bioavailability in the leachates from dumpsites in Zaria Metropolis, Nigeria

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Landfill leachates pose a significant threat to both surface water and groundwater especially the wells adjacent to landfills. The study investigated the bioavailability of zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd) and mercury (Hg) from leachates of ten huge dumpsites across the metropolitan city of Zaria. The trends in the mean concentrations of the metals (mg/L) among the fractions were; Zn: total > mobile > particulate > dissolved; Pb: total > mobile > particulate > dissolved; Cd: mobile > dissolved > total > particulate; Hg: particulate > mobile > total > dissolved, respectively. All the concentrations of the metal ions were above the world Health Organization (WHO) (2006) and United States Environmental Protection Agency (USEPA) (2000) tolerable limits across the sites, with the exception of lead at the control site which was not detected. The order of the metals bioavailability was; Cd > Hg > Zn > Pb > Cu, with more than 49% found in the bioavailable phase. Thus, the underground waters within the vicinity of the dumpsites were greatly at the risk of being polluted by these toxic metals and subsequently affecting the inhabitants who use the water for drinking and other domestic activities untreated, through the food chain transfer. The health implications associated with the toxic metals include an irreversible damage to nervous system, gastric and intestinal disorder, heart disease, liver, brain damage, mental retardation and teratogenic effects.

Key words: Fractionation, heavy metals, leachates, dumpsites, Zaria.

INTRODUCTION

Inadequate municipal and industrial waste collection and disposal creates a range of environmental problems in Zaria metropolis wHere considerable amount of waste ends up in open dumps or drainage system, threatening both surface water and groundwater quality. This provides a breeding ground for disease carrying pests, create health hazards, pollute the air, soil and sometimes groundwater and surface water, as well as deteriorating the beauty of the area (Botkin and Keller, 1998). The situation is high in Zaria metropolis where most households could not make use of garbage collection containers; lack of most solid wastes services in crowded, low-income neighbors is a major contributor to the high mobility and mortality among the urban poor.

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The incoming wastes in the city originate mainly from households and industries (Benedine et al., 2011).

The open dumpsites are well known to release large amounts of hazardous and otherwise deleterious chemicals to nearby groundwater, surface water, soil and to the air via leachates and landfill gases. It is known that such releases contain a wide range variety of potential carcinogens and potentially toxic chemicals that represent a threat to public health (Fredlee et al., 2003). Leachates have been implicated as environmental pollutants such as air, soil, plants, surface and ground water pollution. Sufficient number of individuals near dumpsites would experienced an average increased cancer risk, at least 1 in 1000 (Fredlee et al., 2003).

As many studies have shown, municipal refuse may increase heavy metals concentrations in soils and underground water (Carlson et al., 1976; Albores et al., 2000; Okoronkwo et al., 2005a, b) which may have effects on the host soils crops and human health (Smith et al., 1996; Nyle and Ray 1999). Thus, the environmental impacts of leachates emanating from dumpsites are greatly influenced by their heavy metals contents. However, while total heavy metals contents is a critical measure in assessing risk of a refuse dumpsite, it does not provide a predictive insight on the bioavailability, mobility and fate of the heavy metals contaminants (Albores et al., 2000). Thus, it is the chemical form or species of the heavy metals that is an important factor in assessing their impacts on the environment as it controls their bioavailability and mobility (Norvell, 1984).

Past investigations on the metals impact of municipal refuse dumpsites leachates in Nigeria were concerned only with total heavy metals determination (Amadi et al., 2011; Aiyesanmi et al., 2011). The objective of this study therefore was to investigate the chemical fractionation of cadmium (Cd), copper (Cu), lead (Pb), mecury (Hg), and zinc (Zn) in dumpsites leachates of Zaria metropolis so as to assess their potential mobility, bioavailability and fate. Thus, the human health and ecological risks associated with the refuse dumpsites to the underground water (hand-dug wells) will be assessed.

MATERIALS AND METHODS

Quality assurance

All reagents used were of analytical grade, de–ionized water was used for the preparation of the standard solutions, all the glassware and polythene sample bottles were washed with liquid soap, rinsed with water, soaked in 10% HNO_3 for 24 h, cleaned thoroughly with double distilled de- ionized water and dried. The analytical results obtained were validated with spiked samples. The percentage recoveries of the metals and the analytical precision was confirmed with the triplicates throughout the study (Todorovi et al., 2008). Procedural blanks, reagents blanks and preparation of standard solutions were carried under clean laboratory environment.

Description of the study area

Zaria metropolis is located at latitude 11° 07' N and longitude 07° 42' E, and is presently one of the most important cities in Northern Nigeria (Uba et al., 2008) (Figure 1). It has problems of environmental sanitation such as improper disposal of refuse near residential areas resulting in the contamination of the underground water via leachates emanating from the dumpsites since most of the wells near the dumpsites were poorly covered and opened (Figure 2). It has a total area of 300 km^2 and constitutes four major settlements; Zaria City, Tudun Wada, Sabon Gari and Samaru (Zaria at a glance, 2013). It has a tropical continental climate with a pronounced dry season, lasting up to seven months (October to May). During the dry season, a cool period is usually experienced between November and February. This emanates from the influence of the North-eastern winds (the Harmattan) which control the tropical continental air mass coming from the Sahara. This weather prevails over most parts of the country. The North-East (NE) winds are characterized by hazy to dusty conditions and low temperatures, as low as 10°C at night. In the afternoon, up to 40°C is sometimes recorded. The humidity also drops to less than 15% in December/January.

Zaria experiences a brief period of hot but dry weather in March and April, followed by a progressive incursion of tropical maritime air mass from the Atlantic Ocean which displaces the NE (Harmattan) winds. During this short period, the mean daily maximum temperatures are fairly stable, and they range from 38 to 42°C. After that, the South Westerly Monsoon winds laden with moisture bring the rain in thunderstorms and squalls with heavy fall of high intensities. The rainy season lasts from May to September/ October with long-term annual rainfall of 1,040 mm in about 90 rain days (Zaria at a glance, 2013). The relatively deep tropical ferruginous soils and climate conditions of Zaria are suitable and sustain a good cover of savanna woodland (Northern Guinea Savanna), with a variety of grasses woody shrubs and short trees. Ten huge dumpsites were selected which covered the metropolitan city, and a control/uncontaminated site was selected 300 m away from the Kusfa dumpsite which is a new settlement without any dumping activities as summarized in Table 1.

Samples collections

Leachate samples were collected from ten dumpsites and a control site from June to August, 2011 in the rainy season from randomly selected leachate drains at the sites. The samples were collected in the well labeled clean polythene bottles that were rinsed with the leachates prior to sample collection. The samples for elemental analysis were collected in 1 L polyethylene bottles while those for mercury analysis were collected in glass bottles (American Public Health Association (APHA), 2005).

Samples pre-treatment

Samples for mercury analysis were preserved in 1 ml concentrated H_2SO_4 and 1 ml 5% $K_2Cr_2O_7$ solution for every 100 ml samples. The samples for elemental analysis were preserved in 2 ml concentrated HNO_3 (Aiyesanmi et al., 2011; APHA, 2005).

Chemical fractionation of heavy metals in the dumpsite-leachates

The chemical fractionations of the samples were carried out on the

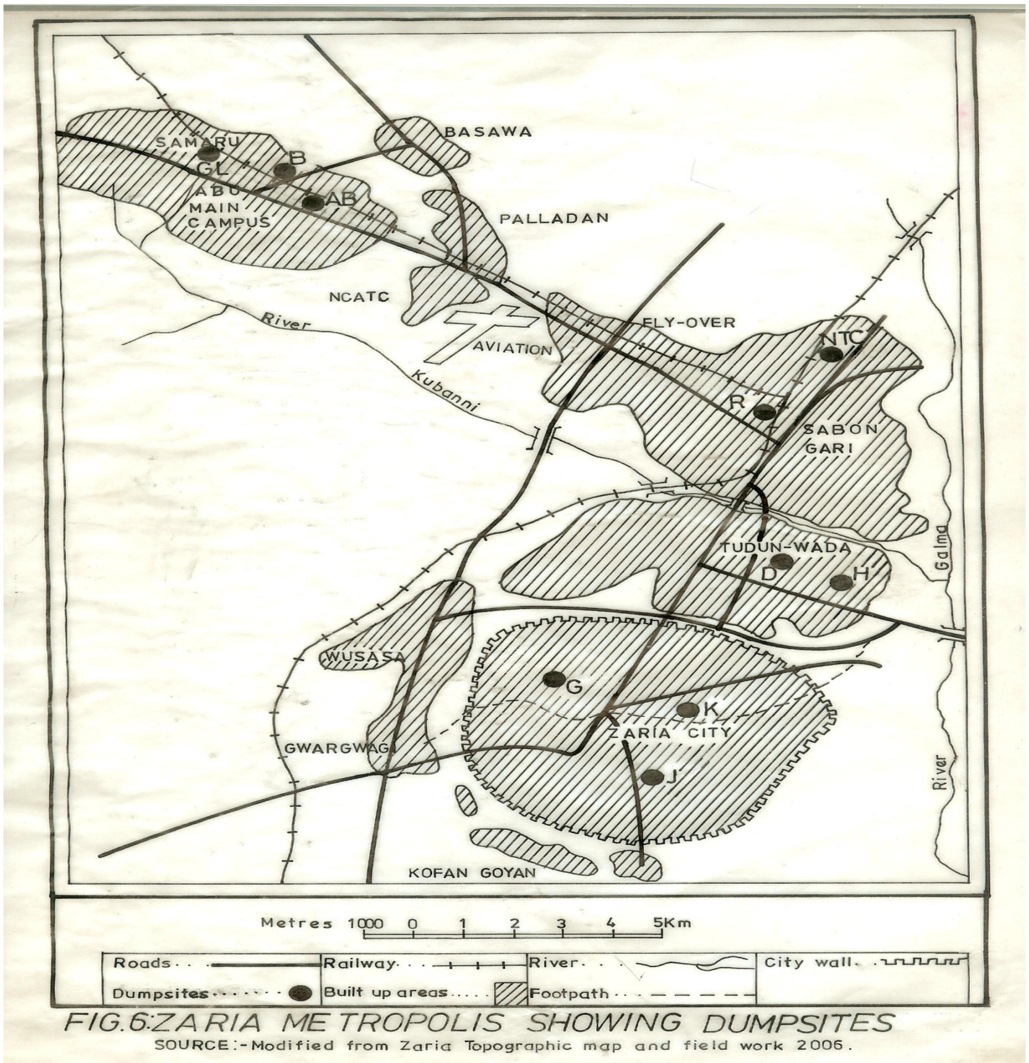

Figure 1. Zaria map showing different sampling points.

principle proposed by Bäckström et al., 2003; Wakawa et al., 2008). Basically, there are three steps that were involved, while fraction (IV) was taken as the difference between fractions (III) and (I) and the fractionation was carried out as follows;

Fraction I (dissolve phase): 50 ml of the leachate samples were decanted from the sampling vessel and filtered through 0.5 µm teflon filters and the solution was then acidified with 5 ml 2% HNO_3 and made up to 25 ml with de-ionized water (Bäckström et al., 2003).

Fraction II (mobile phase): 50 ml of the samples were decanted and acidified with 2% HNO_3 (5 ml). These were followed by filtration through 0.5 µm teflon filters after 24 h. The solutions were then made up to 25 ml with de-ionized water (BäckstrÖm et al., 2003).

Fraction III (total fraction): 5 ml of 2% HNO_3 were added to the 50 ml of the samples and the solution were stirred vigorously to suspend all the particulate matter and then filtered through 0.5 µm teflon filter after 24 h (Bäckström et al., 2003).

Fraction IV (particulate fraction): Particulate fraction was the difference between total residual fraction and dissolve phase (BäckstrÖm et al; 2003).

Samples analysis

The digests of the samples were analysed for Zn, Pb, Cu, Cd and Hg using AAS-650 (varian double beam) and the validation of the procedure for metal determination was conducted by spiking samples with multi-element standard solutions containing 5 mg/L of the metals with the exception of Cd where 4 mg/L of the spiked sample was used. Spiked samples were used under the same experimental conditions used for the procedural blanks as samples the acceptable recoveries (>98.4%) from the spiking experiment had validated the experimental procedure (Table 2).

Figure 2. One of the dumpsites in Zaria metropolis showing one of the sampling point (RA).

Statistical analysis

The data were expressed as means ± standard deviation. To show whether there is significant difference between the mean concentrations of the metals across the sites, one way analysis of variance (ANOVA) was used and the Pearsons moment correlation (r) was used to establish the degree of relationship among the fractions of the analysed metal ions across the sites using a statistical software package for social science (SPSS version 16).

RESULTS

Chemical fractionation of metals in the leachates (dumpsite-leachates)

Tables 3 to 7 showed the percentages of the bioavailable of zinc, lead, copper cadmium and mercury in the fractionated leachates across the sites in addition to the concentrations of various fractions (mg/L). The highest total extractable fraction of zinc (Table 3) was recorded at the control site, with 98.674% in the bio-available phase. The order of the bioavailable fractions of zinc across the sites followed the trend: CTR > SA > AJ > JK > PR > SH > BG > DD > KU > RA > NTC. Table 9 showed the results for the analysis of variance (ANOVA), and a significant difference of the mean concentrations of the metal were recorded across the sites at $p < 0.05$, with the exception of cadmium which was not significant at 95% confidence.

Furthermore, Table 4 showed the elevated levels of lead recorded across the sites, with the extractable fractions predominantly found in the bio-available phase (>65%) except the control site which was below the detection limit (BDL). The highest bio-available lead was recorded at BG-dumpsite leachates. The order of mobility Table 7 showed the concentrations of mercury in the fractionated leachate samples in which 29.23 (CTR) to 100% (SH, SA, PR and DD) were in the bioavailable

Table 1. Description of the sampling points (dumpsites) and various activities being discharged at each dumpsite.

Sampling site	Sampling site	Activities	No./wells	House holds
NTC	National tobacco company	Tobacco wastes, residential waste and workshops	2	Household and shops
DD	Dandaji	Household wastes	2	Households
SH	Shafi	Households wastes, brick molding and automobile	2	Households and shops
RA	Railway station	Carpentry, wood workshops mechanic workshops, residential and wood wastes	2	Market and households
JK	Jeka da Kwarinka	Household	3	Households
PR	Prince road	School and households wastes	2	Schools & households
SA	Samaru	Households wastes	3	Households
KU	Kusfa	Households wastes	3	Households
BG	Babban Gwari	Residential waste	2	Households
AJ	Alkali Jae	Households waste	4	Households
CTR	Control	No dumping activity	3	Households

Table 2. Fractions descriptions and WHO limits.

Symbol	Description	Unit	Tolerable limit (WHO, 2006)
I	Dissolved fraction	mg/L	Depends on the metal
II	Mobile fraction	mg/L	Depends on the metal
III	Total fraction	mg/L	Depends on the metal
IV	Particulate fraction	mg/L	Depends on the metal
Zn	Zinc	mg/L	5
Pb	Lead	mg/L	0.001
Cu	Copper	mg/L	1.5
Cd	Cadmium	mg/L	0.003
Hg	mercury	mg/L	0.001
Bioavailable	Equal to the sum of dissolved and mobile phases	%	-

phase. The bioavailability trend across the sites was: PR > SH > SA > DD > RA > JK > AJ > BG > NTC > KU > CTR. It was observed that the levels obtained were well above the WHO (2006) limits both across the sites and among the fractions. The distribution trend among the fraction was: particulate > mobile > total > dissolved. Similarly, one way ANOVA showed a significant difference among the fractions at $p < 0.05$ as shown in Table 9. The metal was positively correlated with the lead however, negative correlation of the metal ion was recorded with copper, cadmium and zinc, revealing an inverse relationship. The high concentrations recorded at the sites may not be unconnected with dumpsites constituents where cadmium containing waste formed part of the constituents and the total fraction was significantly not different at $p < 0.05$.Table 8 showed the degree of association of the metal ions, the variables showed significant positive correlations with each other and with different metal ions with

Table 3. Concentrations (mean ± SD) mg/L of zinc in the fractionated dumpsites leachates.

Fraction	Sites											
	AJ	BG	CTR	DD	JK	KU	SA	SH	RA	PR	NT	STD
I	0.30±0.02	0.16±0.01	0.04±0.06	0.29±0.02	1.16±0.08	0.39±0.03	2.71±0.02	0.47±0.03	0.15±0.03	0.12±0.09	0.04±0.03	5.00
II	0.13±0.09	0.13±0.06	0.06±0.04	0.17±0.01	1.19±0.08	0.18±0.01	0.20±0.01	4.64±0.03	0.10±0.07	3.71±0.03	0.10±0.02	5.00
III	0.34±0.001	0.46±0.03	0.35±0.03	0.53±0.04	1.53±0.01	4.12±0.03	2.72±0.02	2.82±0.02	0.83±0.05	1.01±0.07	1.26±0.09	5.00
IV	0.04±0.03	0.31±0.02	0.01±0.05	0.24±0.02	0.37±0.03	3.73±0.02	0.2±0.02	2.35±0.02	0.80±0.06	0.89±0.06	1.23±0.09	5.00
Bioavailable (%)	95.63	70.77	98.67	80.52	91.310	55.680	96.650	77.150	57.580	84.490	53.390	-

Table 4. Concentrations (mean ± SD) mg/L of lead in the fractionated dumpsites leachates.

Fraction	Sites											
	AJ	BG	CT	DD	JK	KU	SA	SH	RA	PR	NT	STD
I	BDL	0.35±0.03	BDL	BDL	BDL	0.25±0.02	BDL	BDL	0.36±0.03	0.10±0.07	BDL	0.001
II	0.33±0.02	0.32±0.02	BDL	0.33±0.02	0.32±0.02	0.35±0.03	0.27±0.02	0.36±0.0	0.34±0.02	0.36±0.03	0.33±0.02	0.001
III	0.38±0.03	0.38±0.03	BDL	0.30±0.02	0.33±0.02	0.39±0.03	0.33±0.02	0.38±0.02	0.39±0.03	0.33±0.02	0.32±0.02	0.001
IV	0.38±0.03	0.03±0.02	BDL	0.30±0.02	0.33±0.02	0.13±0.09	0.33±0.02	0.02±0.01	0.39±0.03	0.23±0.02	0.32±0.02	0.001
Bioavailable (%)	65.260	97.580	BDL	67.650	66.390	88.140	64.240	97.210	73.690	77.500	66.940	-

Table 5. Concentrations (mean ± SD) mg/L of cadmium in the fractionated dumpsites leachates.

Fraction	Sites											
	AJ	BG	CTR	DD	JK	KU	SA	SH	RA	PR	NT	STD
I	0.04±0.02	0.06±0.4	0.002±0.001	0.05±0.03	0.055±0.3	0.07±0.04	0.05±0.040	0.07±0.05	0.06±0.004	0.05±0.00	0.05±0.03	0.003
II	0.07±0.05	0.06±0.04	0.02±0.01	0.06±0.04	0.07±0.05	0.06±0.04	0.06±0.03	0.05±0.04	0.06±0.033	0.138±0.02	0.02±0.01	0.003
III	BDL	0.07±0.05	0.03±0.02	0.06±0.04	0.06±0.04	0.03±0.02	0.07±0.05	0.05±0.04	0.02±0.01	0.03±0.02	0.03±0.02	0.003
IV	BDL	0.01±0.05	BDL	0.02±0.01	0.01±0.03	BDL	0.02±0.09	BDL	BDL	BDL	BDL	0.003
Bioavailable (%)	100.00	96.45	100.00	90.68	97.43	100.00	89.94	100.00	100.00	100.00	100.00	-

few exceptions. For example, the dissolved fractions of zinc (ZnLI) was positively correlated and significant with the particulate fractions (0.433). Other variables that were positively correlated with the fraction of zinc were PbLII, PbLIII, PbLIV, CdLI, CdLIII, CdLIV and HgLI respectively. ZnLI was highly positively correlated to HgLIV (particulate phase) but negatively correlated to HgLII. Similarly, the mobile fraction (ZnLII) of zinc was strongly positively correlated to CdLIV, CuLIV and HgLI fractions with r-values of 0.885, 0.687 and 0.557, respectively. Other mild positive correlations were observed with the PbLII, PbLII, PbLIII, CdLI, CdLII, CuLIII and CuLIII. Furthermore, the ZnLII (mobile fraction) of

Table 6. Concentrations (mean ± SD) mg/L of copper in the fractionated dumpsites leachates.

Fraction	Sites											
	AJ	BG	CTR	DD	JK	KU	SA	SH	RA	PR	NT	STD
I	0.091±0.07	0.05±0.03	BDL	1.11±0.08	0.06±0.04	0.07±0.05	0.08±0.06	0.03±0.02	0.03±0.02	0.001±0.01	0.07±0.05	1.500
II	0.003±0.001	0.03±0.02	BDL	0.08±0.01	0.12±0.01	0.08±0.05	0.03±0.002	0.07±0.01	0.07±0.01	0.09±0.01	1.39±0.01	1.500
III	0.002±0.001	0.21±0.02	BDL	1.60±0.01	0.33±0.02	0.10±0.01	0.07±0.01	0.4±0.03	0.49±0.04	0.59±0.04	0.08±0.06	1.500
IV	0.001±0.09	0.16±0.01	BDL	0.48±0.03	0.27±0.01	0.04±0.03	BDL	0.36±0.03	0.47±0.03	0.59±0.04	0.006±0.001	1.500
Bioavailable (%)	63.920	58.440	0.000	100.000	100.000	79.050	50.000	49.910	100.000	78.470	63.430	-

Table 7. Concentrations (mean ± SD) mg/L of mercury in the fractionated dumpsites leachates

Fraction	Sites											
	AJ	BG	CTR	DD	JK	KU	SA	SH	RA	PR	NT	STD
I	1.05±0.08	0.59±0.42	BDL	1.94±0.14	0.92±0.07	0.65±0.05	2.16±0.02	5.13±0.36	1.10±0.78	3.37±0.02	1.20±0.09	0.001
II	3.71±0.03	0.80±0.01	0.69±0.02	0.84±0.005	1.07±0.08	0.85±0.01	0.69±0.05	0.74±0.01	2.17±0.01	1.03±0.01	1.94±0.01	0.001
III	2.72±0.01	1.15±0.08	BDL	0.92±0.07	1.24±0.08	14.96±0.11	1.71±0.11	0.72±0.05	1.45±0.01	1.62±0.01	2.74±0.02	0.001
IV	0.75±0.01	0.57±0.004	1.67±0.01	BDL	0.32±0.02	14.31±0.10	BDL	BDL	0.34±0.002	BDL	1.54±0.01	0.001
Bioavailable (%)	90.850	81.860	29.230	100.000	90.900	53.490	100.000	100.000	93.260	100.000	79.380	-

mercury was strongly positively correlated to HgLIII and HgLIV (at r = 0.696 and 0.656) while CdLI, CdLII, CdLIII, HgLI, ZnLIV, PbLI and PbLII were negatively correlated as show in Table 8. The particulate fraction of zinc (ZnLIV) had the highest significant positive correlation with HgLIII and HgLIV with r-values of 0.791 and 0.781 at $p < 0.05$. Other positive correlations of dissolved zinc (ZnLI) were observed with the PbLIV, CdLI, CdLIV and HgLI respectively.

As shown in Table 8, zinc was strongly positively correlated to dissolved, mobile, total and particulate fractions while the mobile phase of zinc was positively correlated to the particulate fraction (r = 0.312). Furthermore, all the variables (fractions) were positively correlated, the highest r-value was observed on correlating mobile and total lead (r = 0.948) at $p < 0.05$ as shown in Table 7.

Similarly, cadmium fractions were positively correlated with the exception of mobile and particulate fractions which showed negative correlation. Copper fractions, were strongly positively correlated with the dissolved and particulate, particulate and total fractions (r = 0.869 and 0.748), respectively. However, negative correlations were recorded among the fractions of mercury across the sites with the exception of particulate and total fractions which were strongly positively correlated (0.974) at $p < 0.05$ (Table 8).

DISCUSSION

On comparing the results obtained for zinc with the standard limits (USEPA, 2000; WHO, 2006), sites KU, SA, SH and PR were contaminated (concentration > 5 mg/L). Thus, the zinc in the analysed leachate samples was readily bio-available to the environment contaminating especially, the underground water due to leachates percolation. Zinc pollution is known to induce vomiting, dehydration, abdominal pain, dizziness and lack of muscular co-ordination (WHO, 1999). Overall, the mobile fractions had the highest concentrations of the total extractable Zinc across the sites. The concentrations recorded were

Table 8. Correlation matrices for the fractionated metals in the leachates.

Fractions	ZnLI	ZnLII	ZnLIII	ZnLIV	PbLI	PbLII	PbLIII	PbLIV
ZnLII	-0.067							
ZnLIII	0.433*	0.245						
ZnLIV	-0.159	0.311	0.261					
PbLI	-0.290	-0.217	0.372	0.254				
PbLII	0.006	0.312	0.379	0.379	0.254			
PbLIII	0.143	0.182	-0.148	-0.148	0.379	0.948**		
PbLIV	0.296	-0.310	0.383	0.383	0.148	0.409	0.379	
CdLI	0.180	0.220	0.553	0.550	0.383	0.841	0.869**	0.145
CdLII	0.068	0.386*	0.008	0.003**	0.151	0.493**	0.388	0.210
CdLIII	0.361	-0.186	0.170	-0.060	0.116	-0.149	-0.103	-0.134
CdLIV	0.687	0.687**	-0.276	0.038	-0.384	-0.213	0.002	0.040
CuLI	-0.056	-0.0202	-0.217	-0.190	-0.230	0.118	-0.022	0.209
CuLII	-0.204	-0.138	-0.021	0.120	-0.205	0.145	0.04	0.236
CuLIII	-0.167	0.147	-0.231	-0.122	-0.055	0.289	0.094	0.178
CuLIV	-0.251	0.557**	-0.187	-0.009	0.183	0.426*	0.242	0.108
HgLI	0.138	0.885**	0.308	0.269	-0.294	0.433	0.331	-0.112
HgLII	-0.249	-0.261	-0.371	-0.215	-0.19	0.254	0.293	0.596**
HgLIII	-0.044	-0.194	0.696**	0.791**	0.333	0.254	0.308	-0.062
HgLIV	-0.118	-0.223	0.656**	0.781**	0.331	0.063	0.118	-0.233
Fractions	**CdLI**	**CdLII**	**CdLIII**	**CdLIV**	**CuLI**	**CuLII**	**CuLIII**	**CuLIV**
CdLII	0.176							
CdLIII	0.43	-0.119						
CdLIV	0.154	0.019	0.515					
CuLI	0.89	-0.270	0.297	0.601				
CuLII	0.128	-0.395	-0.185	-0.198	-0.590			
CuLIII	0.218	0.288	0.128	0.429*	0.869*	-0.154		
CuLIV	0.280	0.625**	-0.176	0.003	0.326	-0.246	0.748	
HgLI	0.379	0.379	-0.077	0.046	0.047	-0.720	0.302	0.526
HgLII	-0.123	-0.017	-0.381	-0.365	-0.128	0.192	-0.225	-0.174
HgLIII	0.347	0.030	0.060	-0.211	-0.107	0.021	-0.225	-0.301
HgLIV	0.219	-0.089	0.087	-0.259	-0.121	-0.01	-0.251	-0.345
Fractions	**HgLI**	**HgLII**	**HgLIII**	**HgLIV**				
HgLI								
HgLII	-0.207	1						
HgLIII	-0.232	-0.023	1					
HgLIV	-0.309	-0.130	0.974	1				

*Correlation significant at $p < 0.05$, **correlation significant at $p < 0.01$.

higher than the values of 0.37 to 0.65 mg/L reported by Aiyesanmi et al. (2011) in Benin City for the total elemental analysis of leachates. The difference might be attributed to the different composition of the analysed dumpsites.

The lead concentrations recorded suggests that there was a common source of pollution by the metal ions as significant difference among the fractions was observed at $p < 0.05$. When the concentrations (total extractable) across the sites were compared with those of the international standard (USEPA, 2000; WHO, 1999) they all exceeded the tolerable limit of 0.05 mg/L with the exception of the fractions at the control site. The total extractable fractions were higher than the range of 0.05

Table 9. ANOVA for leachates across the sites.

Fractions	Parameter	Sum of squares	df	Mean square	F	P
	Between groups	11.609	10	1.161		
ZnL1	Within groups	0.023	11	0.002	559.924	0.000
	Total	11.632	21			
	Between groups	49.561	10	4.956		
ZnLII	Within groups	0.090	11	0.008	604.118	0.000
	Total	49.651	21			
	Between groups	28.885	10	2.888		
ZnLIII	Within groups	0.095	11	0.009	335.592	0.000
	Total	28.979	21			
	Between groups	24.853	10	2.485		
ZnLIV	Within groups	0.056	11	0.005	491.905	0.000
	Total	24.909	21			
	Between groups	0.416	10	0.042		
PbLI	Within groups	0.001	11	0.000	573.362	0.000
	Total	0.416	21			
	Between groups	0.196	10	0.020		
PbLII	Within groups	0.003	11	0.000	80.510	0.000
	Total	0.198	21			
	Between groups	0.228	10	0.023		
PbLIII	Within groups	0.003	11	0.000	82.211	0.000
	Total	0.231	21			
	Between groups	0.423	10	0.042		
PbLIV	Within groups	0.002	11	0.000	242.765	0.000
	Total	0.425	21			
	Between groups	0.006	10	0.001		
CdL1	Within groups	0.000	11	0.000	93.537	0.000
	Total	0.006	21			
	Between groups	0.018	10	0.002		
CdLII	Within groups	0.000	11	0.000	157.957	0.000
	Total	0.018	21			
	Between groups	0.003	10	0.000		
CdLIII	Within groups	0.005	11	0.000	0.701	0.708
	Total	0.009	21			
	Between groups	0.001	10	0.000		
CdLIV	Within groups	0.000	11	0.000	575.287	0.000
	Total	0.001	21			

Table 9. Contd.

	Between groups	1.931	10	0.193		
CuLI	Within groups	0.003	11	0.000	686.461	0.000
	Total	1.934	21			
	Between groups	3.030	10	0.303		
CuLII	Within groups	0.005	11	0.000	689.227	0.000
	Total	3.035	21			
	Between groups	3.952	10	0.395		
CuLIII	within groups	0.009	11	0.001	508.609	0.000
	Total	3.960	21			
	Between groups	0.977	10	0.098		
CuLIV	Within groups	0.003	11	0.000	419.862	0.000
	Total	0.980	21			
	Between groups	40.242	10	4.024		
HgLI	Within groups	0.126	11	0.011	351.747	0.000
	Total	40.368	21			
	Between groups	16.376	10	1.638		
HgLII	Within groups	0.069	11	0.006	262.326	0.000
	Total	16.445	21			
	Between groups	322.132	10	32.213		
HgLIII	Within groups	0.614	11	0.056	577.196	0.000
	Total	322.746	21			
	Between groups	328.814	10	32.881		
HgLIV	Within groups	0.517	11	0.047	699.358	0.000
	Total	329.331	21			

ANOVA run at $p < 0.05$, if p is < 0.05, there was a significant difference among the fractions with the variable at 95% confidence otherwise, there was not.

to 0.12 mg/L reported by Manpanda et al. (2007) in Zimbabwe and lower than 0.35 to 0.97 mg/L reported by Ahlberg et al. (2006) in Sweden, respectively. It was also noted that if significant quantity of lead was leached into the groundwater, cytogenetic alteration such as kidney and brain damage or birth defects results especially when ingested through the food chain or drinking water (Ademoroti et al., 1996; Aiyesanmi et al., 2011).

The extractable fractions of cadmium were compared with the WHO (2006) standard limits of 0.003 and 0.001 mg/L (WHO, 2006; USEPA, 2003) respectively, overall, the results showed higher values with few exceptions. The recorded concentrations in this study were below the ranges of 0.02 ± 0.01 to 0.24 ± 0.31 mg/L and 3. 62 ± 0.01 to 8.15 mg/L reported by Aiyesanmi et al (2011) in Benin City and Ahlberg et al. (2006) in Sweden, respectively. Analysis of variance (ANOVA) showed a significant difference (at $p < 0.05$) both among the fractions and across the sites. In addition, there was a positive correlation between the lead and Zinc (Pb to Zn) across the sites suggesting a common source of pollution. Cadmium is toxic when inhaled even in trace amount in dust/particulates during incineration/burning at dumpsite because of its carcinogenicity (Aiyesanmi et al., 2011). It is also known that it is very hazardous and of no use to biological processes (Watanabe et al., 2008).

The levels of copper recorded in this study were lower than > 1.5 mg/L reported by Ikem et al. (2002) in Lagos. The distribution pattern among the fractions was Cu: total > particulate > mobile > dissolved. Copper in the blood exist in two forms: bound to ceruplasmin (85 to 95%) and the rest ‘freely’ loosely bound to albumin. The free copper is toxic as it generates reactive oxygen species such as superoxide, hydrogen peroxide and the hydroxyl radical. These damages proteins and DNA (Brew et al., 2010). The levels of mercury recorded were significantly high, quiet above the WHO tolerable limit across the sites, and significant amount was found in the bioavailable fraction, thus the metal was readily leachable into the nearby open wells resulting to serious health problems such as chromosomal segregation, disruption and inhibition of cell division.

CONCLUSION

The leachates samples were heavily polluted by zinc, copper, cadmium and mercury including those at the control site. However, lead was not detected at the control in all the fractions of the samples. Furthermore, significant amounts of the fractionated metals were found in the mobile phase showing a threat to the open wells within the vicinity of the dumpsites. Overall, more than 49% of the analysed toxic metals were found in the bioavailable fractions (dissolved + mobile fractions) resulting to serious health problems such as typhoid fever, cholera and other water borne related diseases to the residents who relied heavily on the untreated well waters for drinking and other domestic activities due to erratic and inadequate water supply in the city.

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