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Chemical speciation of some heavy metals and human health risk assessment in soil around two municipal dumpsites in Sagamu, Ogun state, Nigeria

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ABSTRACT

Environmental and health risk posed by heavy metals from municipal landfill cannot be over emphasized. However, the toxicity and fate of metal in the soil is dependent on its chemical form and therefore quantification of the different forms of metal is more meaningful than the estimation of its total concentration. This study investigated the chemical form and potential hazards of heavy metal pollution at two municipal landfills in Sagamu, Ogun state, Nigeria. Soil samples were collected around the landfills and chemical form of Cu, Zn, Cd, Pb, and Fe were studied, using the Tessier Five-step sequential chemical extraction procedure. The results showed that Cu and Fe were speciated into residual fractions with averages of 23.9 and 31.3% respectively, while Cd and Zn were associated with Carbonate fractions with respective averages of 20.3 and 20.6%. The order of mobility and bioavailability of these metals are: Cd > Pb > Cu > Zn > Fe. A comparison of the result of total extractable metals with standard set by USEPA reveals that Cd and Cu level in the dumpsite soils are far above the critical permissible limit of 3.0 and 250 mg kg⁻¹, respectively which potent a health risk. Assessment of soil pollution level using geoaccumulation index (I_{geo}) revealed that the landfill was extremely polluted by Cd ($I_{geo} > 5$). Pearson correlation and principal component analysis showed that there were no significant correlations ($p < 0.05$) among all the metals, suggesting that they are all from different anthropogenic sources. The cancer risk ranged from 1.36E–01 to 2.18E–04 and 5.82E–01 to 9.35E–04 for Children and Adult respectively. The level of cancer risk falls above the threshold values (10⁻⁴–10⁻⁶) which US Environmental Protection Agency considered as unacceptable risk. Based on the above findings, it was suggested that environmental management policy should be implemented to decrease the environmental risks.

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1. Introduction

It is commonly accepted that soil contamination with heavy metals is potentially damaging to the ecosystem health.[1,2] Unlike organic pollutants, metals cannot be biodegradable and their residence time in the soil can be thousands of years. Therefore, a better understanding and evaluation of the distribution and potential hazards of heavy metals in municipal landfill are increasingly needed to ensure the safety of public health.

Solid waste management has become a serious environmental problem and a major growing concern for urban areas, especially in the developing parts of the world.[3] In most of the developing countries, it is commonplace to find huge waste dumps within residential and industrial areas and on shoulders of minor and major roads owing to inadequate regulatory framework and enforcement system. This practice constitutes serious health and environmental concern due to the

phytotoxicity effect of these metals to the plants and the animals feeding on such vegetables and plant based foodstuff.[4,5] Thus, waste deposited at open dumpsites and poor management of these sites could create a number of adverse environmental impacts including leachate, which could pollute underground soil bed.[6] Leachate from dumpsites are said to be of particular interest when it contains potentially toxic heavy metals.[7] These metals are known to bioaccumulate in soil and have long persistence time through interaction with soil components and consequently enter into the food chain.[8]

However, it is generally recognized that the particular behavior of trace metals in the environment is determined by their specific chemical forms rather than their total concentration because knowledge of the total content of heavy metals present in the soil provides limited information about their potential behavior and bioavailability.[9–14]

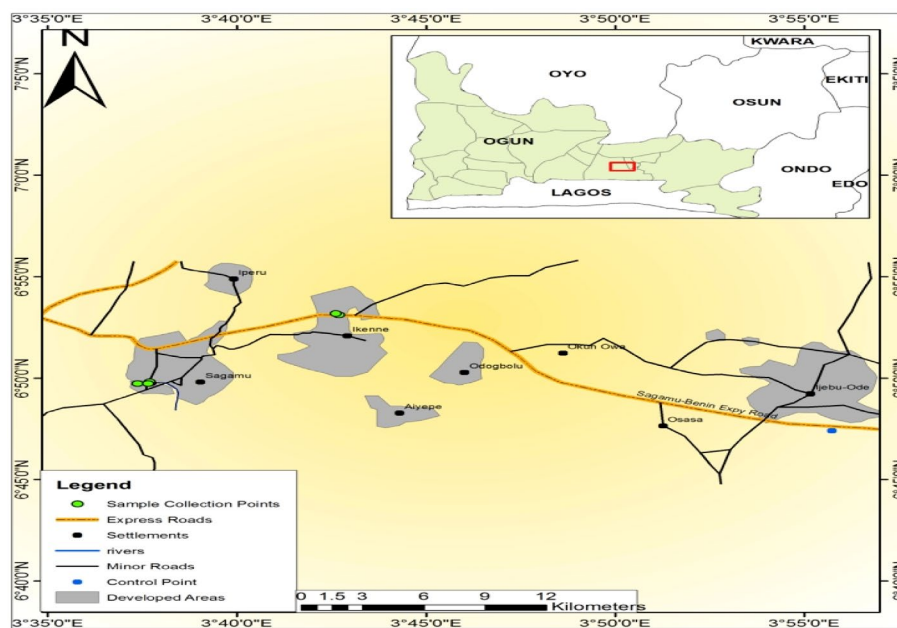


Figure 1. Map of the study area showing the sampling points.

Chronic low-level intake of heavy metals may deplete body stores of iron and vitamin C, induce anemia and immunosuppression, promote renal damage and neurotoxicity, generate vascular complications, and lead to epidermal hyperpigmentation and keratosis.[15–17] These manifestations are detrimental to human health due to the severity and irreversibility of the damage invoked upon the individual and the prolonged period of time required for producing clinical symptoms. Moreover, exposure to heavy metals such as Cd, As and Pb may induce carcinogenesis of various organs including the liver, lung, bladder, and skin.[17,18] Risk assessment has emerged in recent years as a powerful tool in the analysis of environmental and/or occupational hazards.[19] This discipline is becoming increasingly important in modern toxicological and epidemiological practice, both in terms of hazard evaluation as well as at the level of efficient disease control and prevention.[20–22]

Many research works have been carried out on the speciation of heavy metals in soils in different parts of Nigeria,[23–33] but no data available regarding the chemical forms and health risk assessment of heavy metals in soils around municipal dumpsites in Sagamu, the industrial capital of Ogun state. Therefore, the objective of the present study was to determine the speciation or different forms of heavy metals and to assess their human health risk in the dumpsite contaminated soils in Sagamu, south-western Nigeria. This study will reveal the chemical behavior of heavy metals in the soil environment which is the basis of health risk assessment, decontamination and remediation of soils contaminated with heavy metals as a result of anthropogenic activities. Since no speciation and health risk assessment studies on heavy metals in soils in this part of the country have been reported, it is expected that the results from this

study would form the baseline data for future heavy metal pollution status of soils in the area under study.

2. Materials and methods

2.1. Description of the study area

Sagamu, a town in the southwestern part of Nigeria is located in latitude 6°40' and 7°50' N and longitude 3°35' and 3°55' E (Figure 1). It is about 63 km southeast of Abeokuta, 72 km southeast of Ibadan, 67 km northwest of Lagos and 32 km west of Ijebu-ode, all in South-west Nigeria.

The area stands on a low-lying gently undulating terrain with altitude ranging from 30 to 61 m above sea level. The area is characterized by high annual temperature, high rainfall, high evapo-transpiration and high relative humidity which make it be classified as humid tropical region.[34] The soil type of Sagamu is ferralitic [35,36]; the climate is classified to be the humid tropical climatic zone [36] and controlled by the tropical maritime and tropical continental air masses.[35] The monthly relative humidity is at least 70% with temperature ranging from 24 to 28 °C.[36]

2.2. Chemicals and apparatus

Chemicals and apparatus used for the study included: Acetic acid, Hydroxylamine hydrochloride, Perchloric acid, Ammonium acetate, Nitric acid, Hydrofluoric acid, Hydrogen peroxide, glassware, weighing balance (Gallenkamp 80), pH meter (Fisher HydruS 300 model), mechanical shaker (Model TT 12F, Techmel and Techmel, TX, USA), electric heater, centrifuge (Model TGL-16G, Shanghai, China), atomic absorption spectrophotometer (Buck Scientific Model 200A, Norwalk, CT, USA).

2.3. Sampling and analysis

A total of five Soil samples were collected. While four samples were taken within and around two dumpsites, a soil sample from a farmland with no anthropogenic input was also taken and used as control sample. Samples were collected at depth ranging from 0 to 20 cm using a stainless steel hand auger. At each location, the dumpsite was divided into two sections. In each section, five soil samples are collected and composited to obtain a representative sample using a coning and quartering method. It implies that two composite or representative samples were obtained from each of the Dumpsites under study. All the samples were air dried and ground to pass through a 2-mm sieve.

The procedure [9] modified by Uba et al. [37] was used to separate the heavy metals into five operational defined geochemical fractions (F1–F5). One gram of the soil was placed in a 50 mL polypropylene centrifuge tube and subjected to the following extraction processes:

Exchangeable fraction (F1): Soil sample was extracted with 20 mL of 1M NaOAc, pH 8.2 for 1 h.

Carbonate-bound fraction (F2): Residue from F1 was leached with 20 mL 1M NaOAc, pH 5 for 6 h.

Fe–Mn oxide-bound fraction (F3): Residue from F2 was extracted with 20 mL 0.04M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) HOAc at 96 °C for 6 h with occasional agitation.

Organic-bound fraction (F4): To the residue from (3) were added 3 mL of 0.02M HNO_3 and 5 mL of 30% H_2O_2 (pH 2, adjusted with HNO_3); heated at 85 °C for 2 h with occasional agitation.

A second 3 mL aliquot of 30% H_2O_2 were added and heated at 85 °C for 3 h with occasional agitation. After cooling, 5 mL of 3.2M NH_4OAc in 20% (v/v) HNO_3 was added; diluted to 20 mL; agitated for 30 min and centrifuged.

Residual fraction (F5): Residue from F4 was digested using a HF–HCl/ HNO_3 (hydrofluoric/aqua regia) digestion procedure.

All the solid phases from F1 to F5 were washed with 10 mL of deionised water before further extraction. The washes were collected with supernatant from the previous fraction. After each extraction, the supernatant was separated by centrifugation at 10,000 rpm for 30 min.

The heavy metals content of each fraction was analyzed using Atomic absorption spectrophotometry (Perkin-Elmer Model Analyst 2002). The following metals were analyzed for; Pb, Cd, Fe, Zn, and Cu. All samples were run in triplicates.

2.4. Pollution assessment method

In the study, contamination levels of all analyzed heavy metals in the soil were characterized by Geo-accumulation index (I_{geo}), commonly applied in the literature. [38–40] I_{geo} is computed by the following Equation [41]:

$$I_{\text{geo}} = \log_2 \frac{C_i}{1.5B_i} \quad (1)$$

where C_i is the measured concentration of the element i and B_i is the geochemical background value of the element. The constant 1.5 is introduced to minimize the variation of background values. The following classifications were given according to I_{geo} [38,42]: unpolluted ($I_{\text{geo}} \leq 0$), unpolluted to moderately polluted ($0 < I_{\text{geo}} \leq 1$), moderately polluted ($1 < I_{\text{geo}} \leq 2$), moderately to strongly polluted ($2 < I_{\text{geo}} \leq 3$), strongly polluted ($3 < I_{\text{geo}} \leq 4$), strongly to extremely polluted ($4 < I_{\text{geo}} \leq 5$), and extremely polluted ($I_{\text{geo}} > 5$).

2.5. Potential human health risk of metals in the study sites

The health risk assessment model used in this study to calculate the exposure risk to children and Adults from heavy metals in soil is based on those models developed by USEPA [43] and the Dutch National Institute of Public Health and Environmental Protection [44] which defines guidelines or screening levels of contaminants in soils in urban exposed scenarios. Human exposure to heavy metals in soil can occur via the following three main paths: (a) direct ingestion of substrate dust particles (CDI_{ing}); (b) inhalation of suspended dust particles through mouth and nose (CDI_{inh}); (c) dermal absorption of heavy metals in particles adhered to exposed skin ($\text{CDI}_{\text{dermal}}$). The dose received through each of the three paths was calculated using the following Equations (2)–(4). [43,45]

For cancer risk, only the carcinogen risk for inhalation exposure modes was considered in the model, and was used in the assessment of cancer risk. [46,47]

$$\text{CDI}_{\text{ing}} = C_{\text{UCL}} \times \frac{R_{\text{ing}} \times F_{\text{exp}} \times T_{\text{exp}}}{\text{ABW} \times T_{\text{avg}}} \times 10^{-6} \quad (2)$$

$$\text{CDI}_{\text{inh}} = C_{\text{UCL}} \times \frac{R_{\text{inh}} \times F_{\text{exp}} \times T_{\text{exp}}}{\text{PEF} \times \text{ABW} \times T_{\text{avg}}} \quad (3)$$

$$\text{CDI}_{\text{dermal}} = C_{\text{UCL}} \times \frac{\text{SAF} \times A_{\text{skin}} \times F_{\text{exp}} \times T_{\text{exp}}}{\text{ABW} \times T_{\text{avg}}} \quad (4)$$

where CDI ($\text{mg kg}^{-1} \text{ day}^{-1}$) is the chemical daily intake (CDI) through ingestion (CDI_{ing}), inhalation (CDI_{inh}), dermal contact ($\text{CDI}_{\text{dermal}}$) R_{ing} is the ingestion rate at 200 mg day^{-1} for children (1–6 years) and 100 mg day^{-1} for adults [45]; R_{inh} is the inhalation rate at 7.6 $\text{m}^3 \text{ day}^{-1}$ for children and 20 $\text{m}^3 \text{ day}^{-1}$ for adults. [46] Exposure frequency (F_{exp}) in this study was 180 day years^{-1} [48] while exposure duration (T_{exp}), in this study was 6 years

Table 1. Heavy metal concentration in each fraction of the soil samples (mg kg⁻¹), mean \pm SD (n = 3).

Sampling sites	Frcations	Zn	Cu	Cd	Pb	Fe
A	Exchangeable (F1)	9.6 \pm 0.20	429 \pm 2.0	9.8 \pm 0.2	8.6 \pm 0.5	406 \pm 5.77
	Carbonate (F2)	9.9 \pm 0.20	429 \pm 3.0	10 \pm 0.1	8.7 \pm 0.5	473 \pm 30.5
	Reducible (F3)	9.8 \pm 0.30	430 \pm 1.0	10.2 \pm 0.06	9.0 \pm 0.1	936 \pm 196
	Oxidizable (F4)	9.7 \pm 0.20	428 \pm 2.0	10.4 \pm 0.06	8.5 \pm 0.6	353 \pm 5.77
	Residual (F5)	10.2 \pm 0.30	428 \pm 2.0	10.7 \pm 0.2	10 \pm 2.0	1160 \pm 34.6
	Total metal	49.2	2144	51.1	44.8	3328
B	Exchangeable (F1)	9.0 \pm 0.1	429 \pm 5.0	10.8 \pm 0.2	12.7 \pm 0.1	363 \pm 11.5
	Carbonate (F2)	8.9 \pm 0.2	429 \pm 3.0	10.4 \pm 0.06	12.8 \pm 0.1	300 \pm 78
	Reducible (F3)	8.7 \pm 0.1	426 \pm 5.0	10.4 \pm 0.1	12.8 \pm 0.3	510 \pm 170
	Oxidizable (F4)	8.5 \pm 0.1	430 \pm 2.0	10.2 \pm 0	13.1 \pm 0.2	446 \pm 150
	Residual (F5)	8.8 \pm 0.3	423 \pm 3.0	10.0 \pm 0.06	12.7 \pm 0.05	776 \pm 30.5
	Total metal	43.9	2137	51.8	64.1	2395
C	Exchangeable (F1)	9.33 \pm 0.15	293 \pm 2.1	5.25 \pm 0.05	9.9 \pm 0.2	288.7 \pm 3.2
	Carbonate (F2)	9.93 \pm 0.12	287 \pm 3.1	5.4 \pm 0.1	9.63 \pm 0.06	313.7 \pm 6
	Reducible (F3)	9.97 \pm 0.15	263 \pm 7.5	5.17 \pm 0.08	9.6 \pm 0.1	644.7 \pm 61.6
	Oxidizable (F4)	9.5 \pm 0.1	177 \pm 1.5	5.14 \pm 0.07	9.37 \pm 0.23	308.7 \pm 1.5
	Residual (F5)	9.53 \pm 0.06	260 \pm 2.6	5.22 \pm 0.01	9.33 \pm 0.06	756.7 \pm 66.6
	Total metal	48.26	1280	26.18	47.83	2312.5
D	Exchangeable (F1)	8.93 \pm 0.15	503 \pm 2.5	4.75 \pm 0.06	9.53 \pm 0.06	543.3 \pm 55.1
	Carbonate (F2)	10 \pm 0.2	493 \pm 1.5	4.71 \pm 0.06	8.47 \pm 0.23	843.3 \pm 90.2
	Reducible (F3)	9.73 \pm 0.21	423 \pm 2.3	4.48 \pm 0.05	8.27 \pm 0.15	843.3 \pm 90.2
	Oxidizable (F4)	8.6 \pm 0.1	363 \pm 1.5	4.3 \pm 0.1	8.1 \pm 0.1	450 \pm 0
	Residual (F5)	9.33 \pm 0.15	780 \pm 13.7	4.25 \pm 0.04	7.87 \pm 0.12	557 \pm 15.7
	Total metal	46.59	2562	22.49	42.24	3236.9
Control	Exchangeable (F1)	9.2 \pm 0.10	19.0 \pm 2.65	3.7 \pm 5.5	3.8 \pm 0.12	406 \pm 5.77
	Carbonate (F2)	9.6 \pm 0.06	16.0 \pm 2.08	3.87 \pm 8.8	3.8 \pm 0.1	437 \pm 11.5
	Reducible (F3)	9.5 \pm 0.12	16.3 \pm 0.6	3.73 \pm 6.3	5.8 \pm 0.17	640 \pm 43.6
	Oxidizable (F4)	9.2 \pm 0.15	16.3 \pm 0.6	3.82 \pm 1.5	5.9 \pm 0.1	390 \pm 5.77
	Residual (F5)	9.2 \pm 0.06	27.3 \pm 1.53	3.87 \pm 6.0	4.6 \pm 0.49	1220 \pm 10
	Total metal	46.7	94.9	18.99	23.9	3093

for children and 24 years for adults.[49] Average body weight (ABW) was 15 kg for children and 70 kg for adults [45] while PEF is the particle emission factor taken to be $1.36 \times 10^9 \text{ m}^3 \text{ kg}^{-1}$ for both children and adults. [49] Skin surface area (A_{skin}) was 2800 cm² for children and 3300 cm² for adults [49] and SAF is the skin adherence factor given as 0.2 mg cm² h⁻¹ for children and 0.07 mg cm² h⁻¹ for adults.[50] Dermal absorption factor (unitless) was 0.001 for both children and adults.[49] T_{avg} is the average time (for non carcinogens $T_{\text{avg}} = 365.9 T_{\text{exp}}$; for carcinogens $T_{\text{avg}} = 70 \times 365 = 25,550$ days [45]). C_{UCL} (exposure-point upper confident limit content [mg kg⁻¹]) which is the upper limit of the 95% confidence interval for the mean was calculated using Equation (5).[45]

$$C_{\text{UCL}} = X + t_{1-\alpha,df} \frac{s}{\sqrt{n}} \quad (5)$$

where X is the arithmetic mean, s is the standard deviation and n is the number of samples. In this study, quantified risk or hazard indexes for both carcinogenic and non carcinogenic effects were applied to each exposure pathway in the analysis. The CDI for different exposure pathway was calculated for each element and subsequently divided by the corresponding reference dose yields a hazard quotient (HQ) (non-cancer risk). For carcinogens, the CDI was multiplied by the corresponding slope factor (SLF) to produce an estimate of cancer risk. Hazard index (HI) is equal to the sum of HQ. If the value of HI (non-cancer risk) is <1 , it is believed that there is no significant risk of non-carcinogenic effects; if the value of HI >1 , there is a chance that non-carcinogenic effects may occur. If the value of HI (cancer risk) falls within the

range of threshold values (10^{-4} – 10^{-6}), the cancer risk is acceptable.[51] Therefore, HI methods and cancer risk methods were used to assess the human exposed to heavy metals in the study area.

2.6. Quality assurance

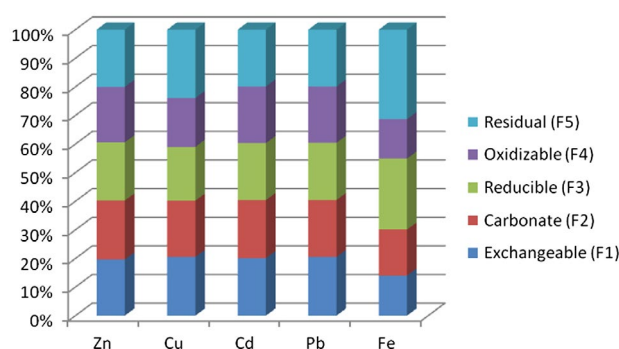
The quality assurance procedures and precautions were ensured for the reliability of the results. Samples were carefully handled to avoid contamination. Glass wares were washed with liquid soap, and rinsed properly and reagents were of analytical grades. Deionized water was used throughout the study. Reagent blank determinations (deionized water and acids) were used to correct the instrument readings. The most sensitive wavelength for each element was selected for analysis, and calibration of AAS was done using multi-elemental solution prepared by serial dilution of 20, 10, 5, 3, 2 and 1 ppm with r^2 value above 0.9 before the analysis of the samples.

2.7. Statistical analysis

The experimental results were expressed as mean \pm standard deviation (SD) of triplicate determinations. All statistical analyses were performed using SPSS Software version 18 (SPSS, Chicago, IL, USA). Correlation analysis was used to explore the possible relationships of the studied elements concentrations. Principal component analysis (PCA) is the common multivariate statistical method used in environmental studies.[52,53] In this study, on the basis of the relationship between elements, PCA was used to explore the extents and sources of heavy-metal pollution.

Table 2. Percentage metals in each fraction of the soil samples.

Metals	Fractions	Sites					
		A	B	C	D	Control	Average
Zn	Exchangeable (F1)	19.5	20.5	19.3	19.2	19.7	19.6
	Carbonate (F2)	20.1	20.3	20.6	21.5	20.6	20.6
	Reducible (F3)	19.9	19.8	20.7	20.9	20.3	20.3
	Oxidizable (F4)	19.7	19.4	19.7	18.5	19.7	19.4
	Residual (F5)	20.7	20	19.7	20	19.7	20
Cu	Exchangeable (F1)	20	20.1	22.9	19.6	20.1	20.5
	Carbonate (F2)	20	20.1	22.4	19.2	16.9	19.7
	Reducible (F3)	20.1	19.9	20.5	16.5	17.2	18.8
	Oxidizable (F4)	20	20.1	13.8	14.2	17.2	17.1
	Residual (F5)	20	19.8	20.3	30.4	28.9	23.9
Cd	Exchangeable (F1)	19.2	20.8	20.1	21.1	19.5	20.1
	Carbonate (F2)	19.6	20.1	20.6	20.9	20.4	20.3
	Reducible (F3)	20	20.1	19.7	19.9	19.6	19.9
	Oxidizable (F4)	20.4	19.7	19.6	19.1	20.1	19.8
	Residual (F5)	20.9	19.3	19.9	18.9	20.4	19.9
Pb	Exchangeable (F1)	19.2	19.8	20.7	22.6	15.9	19.6
	Carbonate (F2)	19.4	20	20.1	20.1	15.9	19.1
	Reducible (F3)	20.1	20	20.1	19.6	24.3	20.8
	Oxidizable (F4)	19	20.4	19.6	19.2	24.7	20.6
	Residual (F5)	22.3	19.8	19.5	18.6	19.2	19.9
Fe	Exchangeable (F1)	12.2	15.2	12.5	16.8	13.1	14
	Carbonate (F2)	14.2	12.5	13.6	26.1	14.1	16.1
	Reducible (F3)	28.1	21.3	27.9	26.1	20.7	24.8
	Oxidizable (F4)	10.6	18.6	13.3	13.9	12.6	13.8
	Residual (F5)	34.9	32.4	32.7	17.2	39.4	31.3

**Figure 2.** Percentages of metals in each fraction.

3. Result and discussion

3.1. Chemical partitioning and distribution of metals in soil

The speciation patterns of the heavy metals in the soils based on their geochemical fractions are presented in Table 1 and expressed as a percentage in Table 2. The mean concentration of total extractable metals in the two dumpsite studied were generally higher than the control site but statistically insignificant at $p < 0.05$.

The total extractable Zinc contents in the dumpsite was higher than the control site but statistically insignificant ($p < 0.05$) and were within the permissible limits

of 30–300 mg kg⁻¹ for agricultural lands set by USEPA [54]. Zn was uniformly bound to the residual fractions and the non residual fractions as depicted in Figure 2 indicating that these fractions are of major importance as Zn carriers in soil which is in agreement with previous findings by Lee et al. [55]. Among the non residual fractions, Carbonate fractions contained the highest Zn content which may be attributed to high soil pH. Decreasing order of Zn contents in the geochemical fractions is shown as: Carbonate > Reducible > Residual > Exchangeable > Oxidizable.

The concentrations of total extractable Cu in the dumpsite were significantly higher comparing to the

Table 3. Geoaccumulation index values of metals in the soil of the study sites.

Element	Average crustal values (Hakanson 1980 [85])	Mean conc. of metal in soil	I_{geo} value	Pollution intensity
Cu	50	1643.58	4.5	Strongly to extremely polluted
Zn	28.8	46.7	0.11	Unpolluted
Fe	—	3093	—	—
Pb	12.5	47.6	1.3	Moderately polluted
Cd	0.15	34.1	7.2	Extremely polluted

Table 4. Cancer and non-cancer risks for children and adults.

Children Element	C (95% UCL) (mg kg ⁻¹)	CDI _{ing} (mg kg ⁻¹ day)	CDI _{inh} (mg kg ⁻¹ day)	CDI _{dermal} (mg kg ⁻¹ day)	RfD _{ing} (mg kg ⁻¹ day)	RfD _{dermal} (mg kg ⁻¹ day)	RfD _{ing} (mg m ⁻³)	HQ _{ing}	HQ _{dermal}	HQ _{inh}	HI	CR
Zn	40	2.25E-05	6.30E-10	0.0632	3.00E-01	3.00E-01	NA	7.50E-05	2.11E-01	2.11E-01	2.11E-01	2.11E-01
Cu	1961.5	1.11E-03	3.09E-08	3.992	4.00E-02	2.30E-02	NA	2.76E-02	1.74E+02	1.74E+02	1.74E+02	1.74E+02
Cd	39.5	2.23E-05	6.22E-10	0.0624	1.00E-03	2.50E-05	2.0E-05	2.23E-02	2.50E+03	2.50E+03	2.50E+03	1.36E-01
Pb	45.6	2.57E-05	7.18E-10	0.07205	3.50E-03	3.50E-03	NA	7.34E-03	2.06E+01	2.06E+01	2.06E+01	2.18E-04
Fe	2417.9	1.36E-03	3.81E-08	3.8203	7.00E-01	7.00E-01	NA	1.95E-03	5.48E+00	5.48E+00	5.48E+00	2.70E+03
ΣHI												1.36E-01
ΣCR												
Adult												
Zn	40	9.66E-05	1.42E-09	3.86E-02	3.00E-01	3.00E-01	NA	3.22E-04	1.29E-01	1.29E-01	1.29E-01	1.29E-01
Cu	1961.5	4.74E-03	6.96E-08	1.89E+00	4.00E-02	2.30E-02	NA	1.19E-01	8.22E+01	8.22E+01	8.22E+01	8.22E+01
Cd	39.5	9.54E-05	1.40E-09	3.81E-02	1.00E-03	2.50E-05	2.0E-05	9.54E-02	1.52E+03	1.52E+03	1.52E+03	5.82E-01
Pb	45.6	1.10E-04	1.62E-09	4.40E-02	3.50E-03	3.50E-03	NA	3.14E-02	1.26E+01	1.26E+01	1.26E+01	9.35E-04
Fe	2417.9	5.84E-03	8.58E-08	2.33E+00	7.00E-01	7.00E-01	NA	8.34E-03	3.33E+00	3.33E+00	3.33E+00	3.33E+00
ΣHI												1.62E+03
ΣCR												5.83E-01

control site ($p < 0.05$). Also the concentrations of copper in the dumpsite were above the toxic limit of 250 mg kg^{-1} set by USEPA [54] for agricultural lands. The high concentration of Cu above the threshold may not be a cause for alarm because research shows that most Cu introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment. The results also indicated that majority of Cu in the soil was associated with the residual fraction (i.e. bound to silicates and dentrial materials) having an average of 23.9% which is similar to the reports of Iwegbue et al. [56]. The result is at variant to Refs. [57,58] in which their findings revealed Cu to be mostly abundant in the oxidizable fraction. Heavy metals with high abundance in the residual phase are not easily bioavailable to the environment. The association of Cu with different fractions was observed to be in the order; Residual > exchangeable > carbonate > Reducible > Oxidizable.

Total extractable cadmium levels in the study area were above the critical permission of 3.0 mg kg^{-1} for agricultural soil.[54,59] Also, the concentrations of Cadmium in the dumpsite were statistically insignificant compared to that of the control site ($p < 0.05$). The high values of total extractable Cadmium obtained in this study may be attributed to dumping of numerous metal containing wastes such as cadmium and lead acid batteries, metal scraps among others in the dumpsites. The result also indicated Cadmium was almost evenly distributed among the various soil fractions (Figure 1). However, an appreciable amount of cadmium was found in exchangeable and carbonate fraction (20.1 and 20.3%, respectively). The report above suggested that cadmium was potentially available to some extent in these soils because metals in these fractions were usually thought to be readily available for plants uptake.[60] This result is in agreement with Refs. [61,62]. The availability of this metal in the sequentially extracted fractions shows the order; Carbonate > Exchangeable > Reducible & Residual > Oxidizable.

The majority of Fe in the soils was associated with the residual fraction (Table 2, Figure 2). This is consistent with the results of Refs. [63–66]. The residual fraction is considered the most stable, less reactive and less bioavailable since it is occluded within the crystal lattice layer of silicates and well crystallized oxide minerals.[65,67] The fraction can be taken as a guide to the degree of pollution of the soil. The smaller the percentages of the metal present in this fraction, the greater the pollution of the area.[63] The high percentage of iron found in residual fraction is an important repository of iron in the soil. The association pattern of iron in the different phases were in the order Residual > Reducible > Oxidizable > Exchangeable > Carbonate.

Generally, the concentration of total extractible Pb from the two dumpsites studied is higher than the control site but statistically not significant at $p < 0.05$. However, the concentration of Pb in the study sites fall below 140 mg kg^{-1} set by Canadian soil quality for residential

Table 5. Varimax rotated component matrix for the total extractible.

Variables	Extracted components	
	Factor 1	Factor 2
Cu	0.07	0.077
Cd	−0.227	0.858
Pb	−0.831	0.551
Fe	0.875	0.089
Zn	0.577	−0.097
% of variance	42.336	36.508

Notes: Extracted method: principal component analysis.

Rotation method: varimax with Kaiser normalization.

Rotation converged in four iterations.

Table 6. Correlation coefficients obtained from spearman's analysis.

	Zn	Cu	Cd	Pb	Fe
Zn	1				
Cu	−0.101	1			
Cd	−0.140	0.521	1		
Pb	−0.660	0.394	0.694	1	
Fe	0.501	0.100	−0.124	−0.0695	1

area. The result also indicated that Pb was almost evenly distributed among the soil fractures with about 80% of it found in the non-residual fraction while high percentage of the total extractable fraction contributed to the mobile phase (exchangeable and acid soluble phases).

In general, the high proportion of metals with the exchangeable and acid soluble phases is indicative of anthropogenic pollution.[68–71] Appreciable quantity of Pb was associated with reducible (20.8%) and oxidizable (20.6%) soil fraction. The association of Lead with Reducible fraction is due to the formation of stable complexes.[72] The percentage quantity of reducible Pb in this study is higher than those reported by [26,73] but lower than those reported by Refs. [74–77]. The affinity of lead to soil organic matter reported in this study is at variance to the work of Fayun et al. [78]. The potential bioavailability of the metal is in the following order Reducible > Oxidizable > Residual > Exchangeable > Carbonate (Table 3, Figure 1).

3.2. Pollution index

The geoaccumulation index (I_{geo}) for the five elements investigated is presented in Table 3. The result from the study shows that the soil are very extremely polluted by Cd ($I_{geo} > 5$) and moderately polluted by Pb ($1 < I_{geo} \leq 2$). Cd and Pb are among the trace metals included in the IARC list of probable carcinogenic compounds. The soil is moderately to highly polluted with Cu ($2 < I_{geo} \leq 3$) while Zn belong to class <0, which suggested that the soil were uncontaminated with Zn.

3.3. Estimation of heavy-metal CDI and health risk assessment

The results of the carcinogenic and non-carcinogenic risk assessment for children and adults using the summation

of mobile fractions are presented in Table 4. Heavy-metal exposure has potential and serious health risk to occupants.[79] Thus, in this study, the health risk of heavy-metal exposure to humans was one of the main focus issues.

For the non-cancer effects for adults, dermal exposure to Cd ($1.52E+03$) and ingestion route to Cu ($1.19E-01$) are the major exposure routes. The non-cancer distribution pattern for both ingestion and dermal routes was: Cd > Cu > Pb > Fe > Zn. Additionally, total exposure HI from ingestion, dermal contact, and inhalation for Cu, Cd, Pb and Pb were greater for children than for adults. Children are more susceptible to a given dose of toxin and are likely to inadvertently ingest significant quantities of metals because of their hand-to-mouth behavior, which has been widely regarded as a key metal exposure pathway for children.[80] HI values for analyzed elements to both adults and children decrease in the order of Cd > Cu > Pb > Fe > Zn.

The HI summation for the sites using mobile fractions ($F1 + F2 + F3 + F4$) shows that Cadmium poses a higher risk of non-cancer effects among the studied elements while Zn poses the lowest (Table 4). The sum of hazard index (ΣHI) for all of the metals and all routes for both adult and Children is $4.32E+03$. This HI values is >1 and this is an indication that the soil poses non-cancer threat to human. The range reported for the non-cancer effects in the present study is at variant to the values reported by some Authors.[81–83]

Among the carcinogenic metals, only Pb and Cd are analyzed, and carcinogenic risk was assessed from calculated daily dose (CDI) multiplied by the corresponding SLF. The cancer risk for Children ranged from $1.36E-01$ to $2.18E-04$ for Cd and Pb, while cancer risk for Adult ranged from $5.82E-01$ to $9.35E-04$, respectively. The level of cancer risk of Cd and Pb falls above the threshold

values (10^{-4} – 10^{-6}) which some environmental and regulatory agencies considered as unacceptable risk. However, it is noteworthy that the Σ CR for all the metals and routes for Children ($1.36\text{E}-01$) and Adults ($5.83\text{E}-01$) were higher than the 10^{-5} risk factor acceptable by some authorities.[84]

3.4. Correlation and PCA on the heavy metals

Correlation and PCA were used to obtain information on the sources of heavy metals in the soil. The result of the correlation and PCA were presented in Tables 5 and 6, respectively. The result showed no significant correlation among the heavy metals studied suggesting that they are not from the same anthropogenic source. Additionally, two principal components (PC1 and PC2) with eigenvalues higher than 1.0 were extracted from the PCA. PC1 and PC2 explain 42.3 and 36.5% of the total variance respectively and characterized by weak loading in all the metal which further confirmed the fact that they are from the different anthropogenic source.

4. Conclusion

Chemical fractionation and health risk assessment of five heavy metals from two major dumpsites soil in Sagamu, Ogun state, Nigeria was carried out. The results showed that Cu and Fe were predominantly associated with residual fractions; Cd and Zn were associated with Carbonate while Pb was majorly associated with reducible fractions. Since metals associated with Carbonate and Fe–Mn oxide fractions can be remobilized and become available to the biota when the pH and redox conditions of the soil system change, the soils studied could stand the risk of contamination by Zn, Cd and Pb. The high mobility factor values indicate that the metals have high mobility as well as high availability and can be leached easily from the soil. Overall, the results indicated the order of mobility and bioavailability of these metals as: $\text{Cd} > \text{Pb} > \text{Cu} > \text{Zn} > \text{Fe}$. A comparison of the result of total extractable metals with standard set by USEPA reveals that Cd and Cu level in the dumpsite soils are far above the critical permissible limit of 3.0 and 250 mg kg^{-1} , respectively for agricultural soil which potent a health risk.

Assessment of soil pollution level using geoaccumulation index (I_{geo}) revealed that the landfill was extremely polluted by Cd ($I_{\text{geo}} > 5$). Pearson correlation and PCA showed that there were no significant correlations ($p < 0.05$) among all the metals suggesting that they are all from different anthropogenic sources. The cancer risk ranged from $1.36\text{E}-01$ to $2.18\text{E}-04$ and $5.82\text{E}-01$ to $9.35\text{E}-04$ for Children and Adult respectively. The level of cancer risk falls above the threshold values (10^{-4} – 10^{-6}) which US Environmental Protection Agency considered as unacceptable risk. Based on the above findings, it

was suggested that environmental management policy should be implemented to decrease the environmental risks.

Disclosure statement

No potential conflict of interest was reported by the authors.

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