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Quantification and risk assessment of trace metals in soils from selected solid waste dumpsites in Delta State, Nigeria.

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Abstract

This study examined the concentration of heavy metals (HMs) in soil from selected open dumpsites in Delta State, Nigeria. The potential health and ecological risks from exposure to these metals were also evaluated. 27 soil samples were collected from 9 different dumpsites at soil depths of 0-15 cm, 15-30 cm and 30-45 cm. The soil samples were digested with aqua regia and analyzed for Pb, Cd, Cr, Cu, Ni, Mn and Co using atomic absorption spectrophotometry. The ecological risk of HMs was evaluated using soil pollution assessment models-geoaccumulation index, contamination factor and ecological risk index. Health risk was assessed using the carcinogenic and non-carcinogenic risk models. The concentration of HMs across the 9 locations and depths ranged as follows: 0.85 – 207 mg kg^{-1} for Cd, 2.08 – 33.5 mg kg^{-1} for Pb, 4.65 – 307 mg kg^{-1} for Ni, 1.05 – 69.5 mg $kg^{-1}$for Cr, 4.20 – 436 mg kg^{-1} for Co, 3.50 – 405 mg kg^{-1} for Cu, 0.15 – 293 mg kg^{-1} for Mn, 7.36 – 47.7 mg kg^{-1} for Zn and 54.4 – 474 mg kg^{-1} for Fe. Cd, Co, Ni, Cu and Fe exceeded their respective regulatory limits at some soil depths. Cd showed very high geoaccumulation index values and contamination factors across depths. The non-carcinogenic risk exposures indicated significant risks in 2 locations, while the risk of developing cancer was high in all locations. The very high levels of Cd in soil call for concern, owing to its low biodegradation and associated health consequences.

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Introduction

Waste management is a major challenge, especially in towns and cities in developing countries (Anzene, 2019). This challenge is due to the increase in the generation of wastes occasioned by increasing industrialization, anthropogenic activities and population, and lack of technical capacity to manage the generated waste. Due to their cost-effectiveness, landfill practices and dumpsites have become preferable options for managing solid wastes in many developing countries, including Nigeria. A dumpsite is an unregulated area where wastes are simply dumped without any concerns about environmental safety (Tse and Adamu, 2012), and it is quite different from a landfill in terms of design and environmental impact of the latter. In developing countries, due to the low coverage in the collection of municipal solid waste, a greater fraction of such waste are illegally dumped in the open, resulting in the creation of open dumpsites (Tang and Goh, 2022). These untreated dumped wastes constitute great threat to both surface and subsoils within and around the dumpsites through spillages, leaching or waste incineration, because they usually contain toxic components, including trace metals, which can contaminate the surrounding soils. In addition, dumpsites are known to emit obnoxious odours, which can give rise to several health problems, ranging from respiratory and skin irritations to allergies (Amadi and Nwankwoala, 2013).

Improper waste disposal is one of the main contributors of heavy metals contamination of soils, and it is reported to be severe in developing countries where there is a very low level of recycling and management of wastes (Tang and Goh, 2022). Heavy metals are described in terms of their specific gravity being greater than 5 g cm-1 (Erses et al., 2005). They are ubiquitous in the environment, being natural constituents of the earth's crust, but their average levels have increased over the years due to mining and industrialization. When these metals are present in soil at concentrations above threshold levels, there is cause for concern because metals are stable and cannot be metabolized/easily degraded by soil microorganisms.

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Some heavy metals possess toxic characteristics even at low levels (e.g. Cd, Pb, Hg, etc.), and can be bioaccumulated by plants, resulting to biomagnification in the food chain (Akanchise et al., 2020). The essential metals (e.g. Cr, Ni, Zn, Mn, Fe, etc.) can also become injurious to man when present in concentrations that exceed their corresponding regulatory limits in soil. Heavy metals are reported to be exhibit carcinogenic, mutagenic, teratogenic and neurotoxic effects on living organisms (Ngole and Ekosse, 2012). Since dumpsites are often improperly managed, they are commonly sited indiscriminately within residential areas, and humans can become exposed to these metals via ingestion of vegetable crops growing on dumpsite soils, inhalation of re-suspended soil particulates and dermal contact (Iniaghe and Adie, 2018; Mohammed et al., 2020). Heavy metals are reported to be greatest in surface soils, with a decreasing trend with increasing depth; and storm water may leach heavy metal contaminants to nearby surface and ground water depending on the water table of the environment, water-rock interaction and water chemistry (Hussein et al., 2021).

Abandoned dumpsites are sometimes used for crop cultivation and human residences, while some dumpsite soils are excavated and used for soil amendments due to their potentially high mineral composition and organic matter (Agbeshie et al., 2020; Akanchise et al., 2020). There are several reported studies on metals level in dumpsite soils in Nigeria (Essien et al., 2019; Mohammed et al., 2020; Shehu-Alimi et al., 2020; Onwukeme and Eze, 2021; Njoke and Nwani, 2022; Ojiego et al., 2022) and parts of Delta State, mainly in Warri metropolis (Nwajei, 2008; Akpoveta et al., 2010; Dike, 2019; Issa et al., 2022) and Asaba (Nwajer et al., 2012). In this study, the concentration of heavy metals in soils around municipal solid waste dumpsites was carried out in rural, semi-urban and urban areas of Delta State, Nigeria, to provide insights on the human health and ecological risks posed by the presence of these metals in dumpsite soils.

Materials and Methods

Study Area: The studied locations include Aragba-Orogun, a rural community located in Ughelli North Local Government Area; Abraka, a semi-urban town in Ethiope East Local Government Area; and Ughelli, an urban town in Ughelli North Local Government Area, all in Delta State, Nigeria. The climate of the study areas is equatorial, and is marked by two distinct seasons: the dry season and the wet (rainy) season. The dry season lasts from about November to April and is significantly marked by the cool "harmattan" dust haze from the north-east wind. The rainy season spans from May to October with a brief dry spell in August, but it frequently rains even in the dry season. The climate of the study areas is tropical equatorial with a mean annual temperature of 32.8 °C and annual rainfall amount of 2673.8 mm. Figures 1 and b are maps of Nigeria indicating Delta State, and the towns wherein dumpsite soil samples were obtained.

Sampling and sample preparation: A total of twenty-seven (27) soil samples were collected. Nine (9) soil samples of three different depths 0-15 cm, 15-30 cm and 30-45 cm were collected from three different dumpsites in each of the studied locations using a soil auger. The soil samples were kept in foil paper, labeled and taken to the laboratory. In the laboratory, the samples were air dried, homogenized using agate mortar and pestle, sieved with a 2 mm sieve and kept in the refrigerator at a temperature of 4 ^{o}C before analysis.

Physicochemical characterization of the soil samples

pH: A glass electrode pH metre was used to measure the pH of the soil samples in soil- suspension (1:5 soil-to-water ratio) (Rayment and Higginson, 2002).

Conductivity: In an empty beaker, 5 g of soil sample was weighed, and 100-ml of deionized water was added. The mixture was swirled and left to stand for 15 minutes. Then, the conductivity probe was inserted into the sample suspension. The electrical conductivity value was read directly on the display while stirring the probe in the solution.

Total Organic Carbon: The Walkley and Black (1934) wet oxidation method was used to quantify the total organic carbon content in soil samples.

Soil digestion and instrumental analysis: Wet digestion method using *aqua regia*, ($HCl:HNO_3$, ratio 3:1) was used for sample digestion. In an empty beaker, 1.00 g of soil sample was weighed and placed in it, followed by the addition of 12 mL of *aqua regia*. The resulting mixture was thoroughly swirled, placed under a watch glass and allowed to stand overnight. The following day, the beaker was heated in a fume cupboard until clear fumes were seen. The digest was filtered using Whatman No. 1 filter paper and made up to 25 mL with 0.25 M HNO_3 (Radojevic and Bashkins, 1999).

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The filtrates were analyzed for lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), manganese (Mn) and cobalt (Co) using a Perkin Elmer (AAnalyst 200) Atomic Absorption Spectrophotometer

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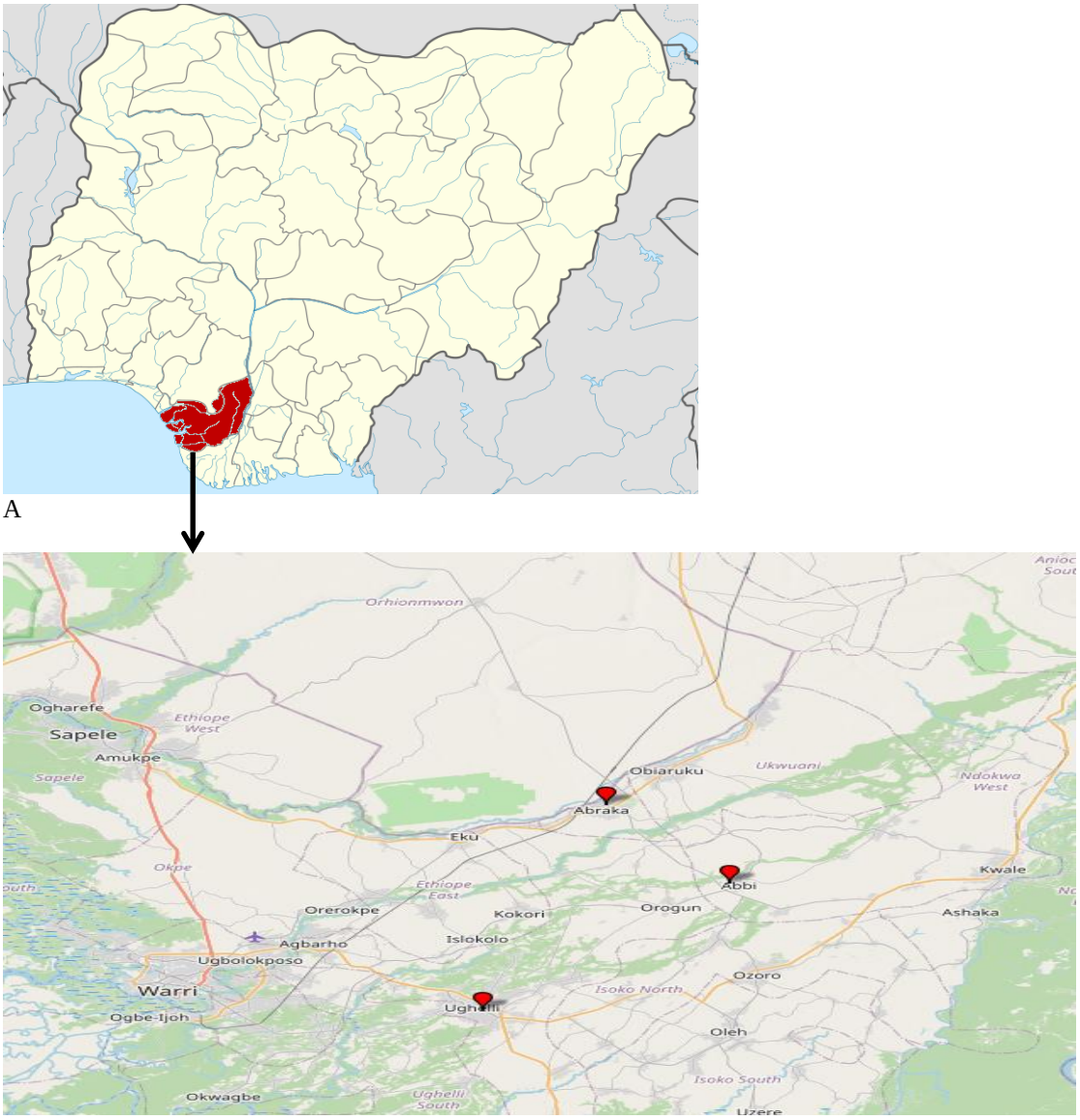

A

B

Figure 1: Map of Nigeria showing (A)Delta State, and (B) the sampling areas.

Soil pollution assessment methods

Geo-accumulation index (Igeo): This is a method proposed by Müller (1969) for the estimation of metals enrichment above background concentrations. It was calculated as:

$$Igeo = log_2 \frac{C_n}{1.5B_n} \quad (1)$$

where:

C_n is the concentration of metal (n) in soil sample;
B_n is the background concentration of metal in soil from the control area for element (n);
1.5 is a correction factor introduced to minimize the effect of possible variations in the background value.

Contamination factor: A quantification of the extent of contamination of soil in geologically comparable but uncontaminated areas is expressed as a

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Contamination factor (*Cf*) (Tijani *et al.*, 2004). The *Cf* as suggested by Håkanson (1980) is given by:

$$Cf = \frac{C_s}{C_n} \quad (2)$$

Where C_s is the metal concentration, and C_n is the background concentration of metal. The *Cf* is defined as follows: $Cf < 1$ - low contamination factor; $1 \leq Cf < 3$ - moderate contamination factor; $3 \leq Cf < 6$ - considerable contamination factor; and $Cf \geq 6$ - very high contamination factor.

Ecological risk index method

This factor quantitatively expresses the potential ecological risk of a given metal. It is given by the following expression (Håkanson, 1980):

$$Er = Tr \times Cf \quad (3)$$

Where; *Tr* is the metal's biological toxic-response factor and C*f* is the contamination factor.

The Er is described by the following terminologies: < 40 - low potential ecological risk; ≥ 40 < 80 - moderate potential ecological risk; ≥ 80 < 160 - considerate potential ecological risk; ≥ 160 < 320 - high potential ecological risk; and ≥ 320 - very high potential ecological risk.

The potential ecological risk index (RI)

The RI is defined as the sum of all ecological risk factors and is given by equations suggested by Håkanson (1980):

$$RI = \Sigma Er \quad (4)$$

It is described using the following terminologies: RI < 150 - low ecological risk; ≥ 150 < 300 - moderate ecological risk; ≥ 300 < 600 - strong ecological risk; and ≥ 600 - very strong ecological risk

Degree of pollution

The degree of pollution P_d, described by Håkanson (1980) is the sum of all contamination factors for a particular set of pollutants, i.e.

$$P_d = \sum_{i=1}^{m} C_f \quad (5)$$

where *Cf* is the single index of contamination factor and "m" is the count of heavy metal species (m = 7 in this study). The degree of pollution is described in the following ways: $P_d < 5$ – low degree of pollution, $5 < P_d < 10$ – moderate degree of pollution, $10 < P_d < 20$ – considerable degree of pollution, and $P_d > 20$ – very high degree of pollution (Caeiro *et al.*, 2005).

Human health risk assessment of metals: Humans can be exposed to metals in soil through three major pathways- ingestion, inhalation of soil particulates, and dermal contact:

Ingestion of metals: The average daily dose (ADD) of metals via ingestion of soil was estimated as follows:

$$ADD_{Ing} = \frac{C \times IngR \times EF \times ED \times CF}{BW \times AT} \quad (6)$$

Where:
ADD_{Ing} = average daily dose of ingested metals from soil (mg kg^{-1} day^{-1}),
C = metal concentration in soil (mg kg^{-1}),
IngR = ingestion rate (mg day^{-1}),
EF = exposure frequency (days $year^{-1}$),
ED = exposure duration (years),
BW = body weight of the exposed individual (kg),
AT = period over which the dose is averaged (days) and
CF = conversion factor (mg kg^{-1})

Inhalation of metals: The average daily dose (ADD) of metals via inhalation of soil particulates was estimated as follows:

$$ADD_{Inh} = \frac{C_S \times IR_{air} \times EF \times ED}{BW \times AT \times PEF} \quad (7)$$

Where:
ADD_{inh} = average daily dose of metals inhaled from soil in mg kg^{-1} day^{-1}, C_S = heavy metal concentration in soil in mg kg^{-1}, IR_{air} = inhalation rate in m^3 day^{-1}, PEF = particulate emission factor in m^3kg^{-1}, EF, ED, BW and AT are as earlier defined in equation (6) above.

Dermal contact with soil

The average daily dose (ADD) of metals via dermal contact with soil was estimated as follows:

$$ADD_{derm} = \frac{C_S \times SA \times FE \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (8)$$

where:
ADD_{derm} = exposure dosage by means of dermal contact (mg kg^{-1} day^{-1}), Cs = metal concentration in soil in mg kg^{-1}, SA = exposed skin area in cm^2, FE = fraction of the dermal exposure ratio to soil, AF = soil adherence factor in mg cm^{-3}, ABS = fraction of the applied dose absorbed across the skin, EF, ED, BW, CF and AT are as earlier defined in equation (6).

Non-carcinogenic risk assessment: The non-carcinogenic hazard is characterized by the "Hazard quotient (HQ)". It is a measure of ADD per the threshold value (chronic reference dose, R*f*D) of a given metal as shown in the equation below:

$$HQ = \frac{ADD}{R_fD} \quad (9)$$

For "n" metals, the non-carcinogenic effect is thus the sum of all HQs by individual metals (called the "Hazard Index (HI)") (USEPA, 1989). Equation (10) shows the mathematical representation of this parameter:

$$HI = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{derm} \quad (10)$$

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If HI values > 1, there are potential non-cancerous effects, but if HI values < 1, there are no likely adverse health effects (Luo *et al.*, 2012).

Total lifetime carcinogenic risk assessment: Carcinogenic risk assessment approximates the increasing prospects of an individual getting cancer over a lifetime due to exposure to the identified carcinogen. It was estimated as the product of the dose and corresponding slope factor as:

$$Risk_{pathway} = \sum_{k=1}^{n} ADD_k \,.\, CSF_k \qquad (11)$$

where:

ADI_k (mg kg^{-1} day^{-1}) and CSF_k (mg kg^{-1} day^{-1}) are the average daily intake and cancer slope factor respectively for the kth heavy metal for n number of metals. The slope factor converts the estimated daily intake of metals averaged over a lifetime of exposure directly to the incremental risk of an individual developing cancer (USEPA, 1989). The carcinogenic risk assessment is calculated using the R*f*D and CSF values derived from the USEPA and the Department of Environmental Affairs (South Africa).

In general, the total cancer risk lower than 10^{-6} (i.e. the carcinogenic target risk, which is the probability of 1 individual in every 1,000,000-developing cancer) are negligible, while cancer risks above 10^{-4} are considered unacceptable by most international regulatory agencies (USEPA, 1989; Luo *et al.*, 2012).

Quality control/assurance: Procedural blank samples were analyzed for impurities in reagents. All reagents used were of Analytical grade. Beakers and sample bottles were soaked in 5% nitric acid for 24 h and rinsed with deionized water before use. Samples were analyzed in triplicates to check for the precision of the chosen method. Method validation was done using a recovery study.

Statistical analysis: Analysis of variance (ANOVA) was used to establish the difference in concentration and composition of metals across the different sampling locations, while T-test was used to establish the difference in concentrations among the different depths.

Results and Discussion

Physicochemical properties of soils

Table 1 gives the physicochemical properties of the studied soil samples. The soil pH, electrical conductivity, and total organic carbon ranged from 5.3-7.8, 52-124 µs/cm and 0.03-1.36 % for rural, 4.8-7.4, 42-108 µs/cm, 0.06-1.57 % for sub-urban, and, 5.2-7.5, 41-118 µs/cm and 0.09-1.94 % for urban dumpsite soils, respectively. Soil samples from the rural location were all acidic except locations 1 (depth 15-30 cm), and 2 (depths 0-15 cm and 15-30 cm). Sub-urban area soil samples were all acidic except location 6 depth 0-15 cm. For urban area, soil samples were all acidic except top-soils from site 8. Acidity of soils arise from decomposition of organic matter that produced proton (H^+) during respiration (Fageria and Nascente, 2014). The electrical conductivity is a basic property of soils, which is related with the nature of soil composition, soil structure, water content in soil and the temperature of the soil. The average EC values in dumpsite soils followed the order: rural > urban > sub-urban.

The average percent TOC level of soils in this study ranged from 0.03 to 2.29% across all studied locations and depths. There was no observed pattern of distribution of TOC across most of the locations and depths; a decrease in the percent TOC from top to bottom soil was observed in only two locations (i.e., locations 3 and 8). Generally, organic carbon in soil accounts for less than 5% on average of the mass of upper soil layers, and it may also diminish with depth (Iwegbue *et al.*, 2013).

Table 1: Physicochemical properties of dumpsite soils

Sites	Depth (cm)	pH	EC (µs/cm)	TOC (%)
1	0-15	6.8	73	0.29
	15-30	7.2	54	1.36
	30-45	5.3	67	0.06
2	0-15	7.8	106	0.64
	15-30	7.3	74	0.09
	30-45	6.2	52	0.26
3	0-15	5.6	91	0.29
	15-30	6.9	124	0.12

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	30-45	5.8	65	0.03
4	0-15	6.7	62	0.35
	15-30	6.3	61	0.20
	30-45	4.8	53	0.58
5	0-15	5.4	108	1.22
	15-30	6.2	83	0.23
	30-45	5.8	105	0.09
6	0-15	7.4	92	0.58
	15-30	4.9	44	1.57
	30-45	5.6	42	0.06
7	0-15	6.9	63	0.87
	15-30	6.2	80	0.58
	30-45	6.7	97	0.96
8	0-15	7.5	118	0.70
	15-30	5.8	77	0.44
	30-45	5.2	41	0.12
9	0-15	6.3	61	1.94
	15-30	5.9	76	2.29
	30-45	6.4	54	0.09

Concentrations of Heavy Metals in Soils Around Dumpsites

The concentration of heavy metals in dumpsite soils is shown in Figures 2 – 10. The concentration across the three locations and depths ranged as follows: 0.85 – 207 mg kg^{-1} for Cd, 2.08 – 33.5 mg kg^{-1} for Pb, 4.65 – 307 mg kg^{-1} for Ni, 1.05 – 69.5 mg $kg^{-1}$for Cr, 4.20 – 436 mg kg^{-1} for Co, 3.50 – 405 mg kg^{-1} for Cu, 0.15 – 293 mg kg^{-1} for Mn, 7.36 – 47.7 mg kg^{-1} for Zn and 54.4 – 474 mg kg^{-1} for Fe. The average metal levels followed the order: Fe > Ni > Co > Cu > Mn > Zn > Cd > Cr > Pb for 0-15 cm, Fe > Co > Mn > Cu > Ni > Cd > Zn > Cr > Pb for 15-30 cm, and Fe > Ni > Co > Mn > Cu > Cd > Zn > Pb > Cr for depth 30-45 cm, respectively. Out of all the determined metals, Fe was detected at high levels. The average concentration of Cd, Co, Cu and Ni (except at depth 30-45 cm) exceeded their NESREA (2009) regulatory limits of 5.0, 50.0, 40 and 100 mg kg^{-1}, respectively; while Cr, Pb and Zn were within their respective NESREA limits of 100, 164 and 421 mg kg^{-1}, respectively.

Lead

Lead occurs in soil naturally, but increased input of Pb into the environment is on the increase due to industrialization and rapid urbanization, which ultimately increases the number of wastes (solid and liquid) required for disposal. The concentration of Pb in dumpsite soils ranged as follows: 5.64 – 13.2 mg kg^{-1} for 0-15 cm, 2.08 – 11.3 mg kg^{-1} for 15-30 cm and 6.90 – 16.5 mg kg^{-1} for 30 – 45 cm, respectively. A decrease in the average Pb levels from 0-15 cm to 15-30 cm was observed, but increased again at depth 30-45 cm in about 66% of the studied soils. This trend shows that leaching of Pb from top-soil to bottom soil is evident. Hussein *et al.* (2021) reported that heavy metals were greatest in surface soils, with a decreasing trend with increasing depth. There was however no significant difference ($p<0.05$) in the average Pb levels in the soil profile across the studied locations. Variation in Pb levels across depth are shown in Figure 2. Also, the effect of urbanization was not evident in the metals' distribution, as the greatest concentration was observed in the semi-urban dumpsite soils (site 6). All Pb levels were within the NESREA (2009) regulatory limit of 164 mg/kg in soil. However, with leaching being evident in bottom soil, there is a high tendency for Pb to contaminate groundwater. Children are more exposed to contamination by Pb via hand-to-mouth transfer; and the effect of even low-level exposure on brain development results in intellectual impairment (Malcoe *et al*., 2002), shortened attention span, lower intelligence quotient, mental deterioration and hyperactivity (Wuana and Okieimen, 2011).

Cadmium

The concentration of Cd in dumpsite soils ranged as follows: 7.15 – 207 mg kg^{-1} for 0-15 cm, 0.85 – 41.4

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mg kg^{-1} for 15-30 cm, and 1.00 – 40.9 mg kg^{-1} for 30-45 cm. As shown in Figure 3, there was no particular trend in Cd distribution in the soil profile across the studied locations. The average Cd levels across the studied locations greatly exceeded the NESREA regulatory limit of 3 mg kg^{-1} in soil. However, in terms of individual locations, only location 3, was within the limit at depth 15-30 cm. Like with Pb, dumpsite soils from location 6, a semi-urban area, had the greatest Cd concentration across all depths. High Cd concentrations can be associated with leaching from Cd wastes on the dumpsite. The results obtained in this study are comparable to those of Ojiego *et al.* (2022) for dumpsite soils in Kuje and Kwali area Councils of Abuja. The high Cd concentrations in this study is of serious health concern because, Cd is a cumulative poison, and, with very high concentrations in bottom soil, there is a very strong tendency for groundwater contamination by Cd.

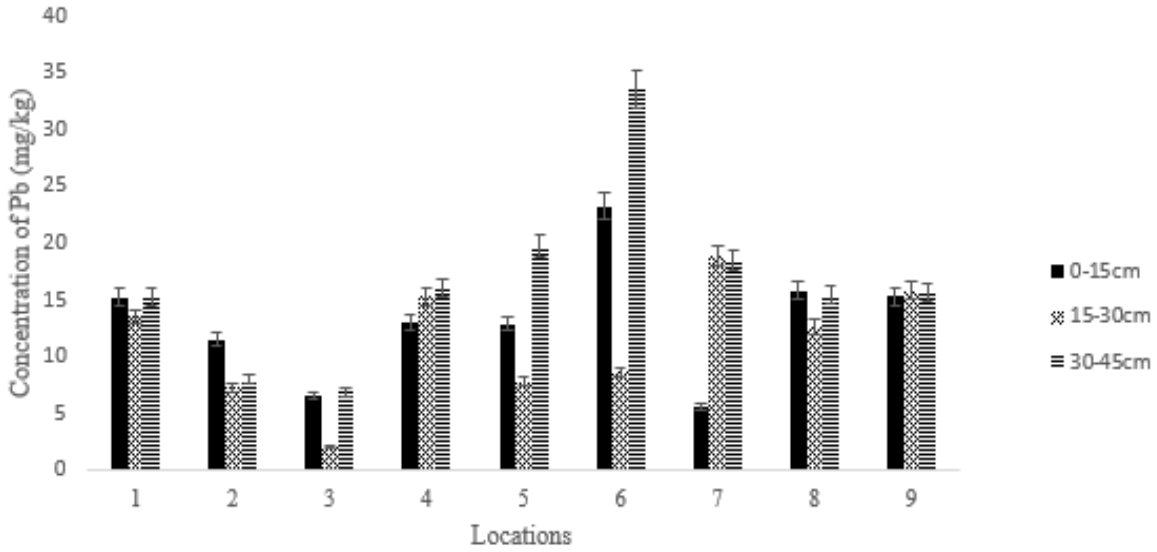

Figure 2: Average concentration of Pb in soil across the studied locations and depths

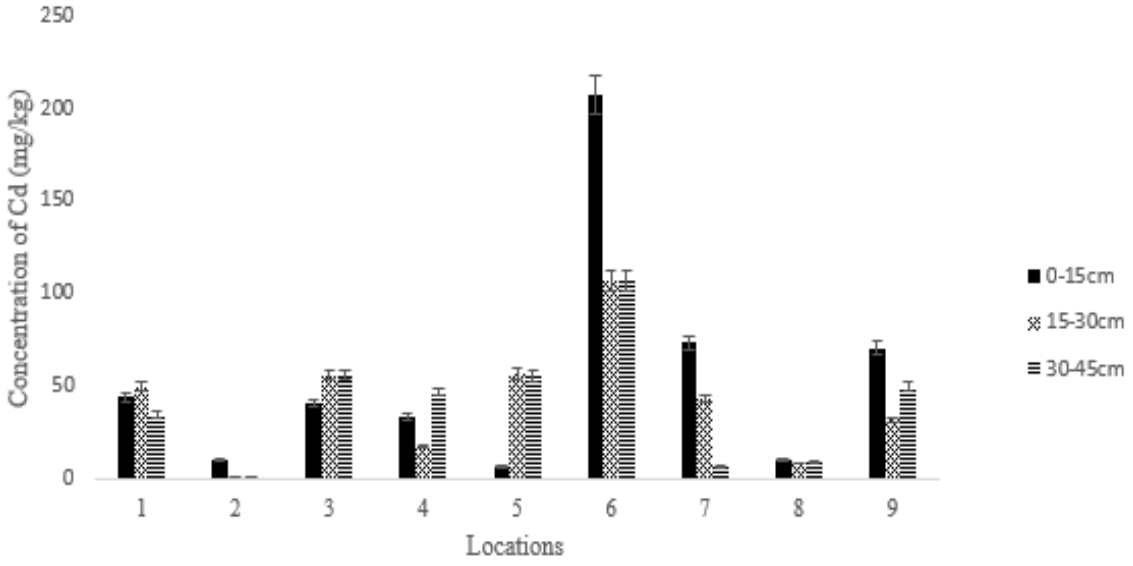

Figure 3: Average concentration of Cd in soil across the studied locations and depths

Nickel

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There was no observed distribution pattern for Ni in the soil profile across the locations. Ni concentrations ranged as follows: 52.4 – 307 mg kg^{-1} for 0-15 cm, 6.80 – 306 mg kg^{-1} for 15-30 cm, and 4.65 – 307 mg kg^{-1} for 30-45 cm, respectively. Except for locations 1 and 4 (depth 30-45 cm) and location 7 (depth 15-30 cm), all other locations and depths greatly exceeded the NESREA regulatory limit of 40 mg kg^{-1} in soil (Figure 4).

Chromium

For Cr, the sub- soil (i.e. 15-30 cm) had the greatest concentration in about 44% of all studied soils. Cr concentration ranged as follows: 1.05 – 41.5 mg kg^{-1} for topsoil, 3.10 – 50.2 mg kg^{-1} in sub-soil, and 1.10 – 69.5 mg kg^{-1} in bottom soil. The concentrations in the soil profile were significant ($p<0.05$) in locations 2, 3, 4 and 7. However, all concentrations were within the NESREA regulatory limit of 100 mg kg^{-1} (Figure 5).

Cobalt

Very high concentrations of Co were recorded across the soil profiles in the different locations. Its concentration ranged from 4.20 – 155 mg kg^{-1} in topsoil, 11.9 – 151.8 mg kg^{-1} in sub-soil, and 25.3 – 232 mg kg^{-1} in bottom soil (Figure 6). The average Co concentration across the study locations indicated significant pollution, as the average concentrations at all depths and locations exceeded the NESREA regulatory limit of 50 mg kg^{-1}. Chronic exposure to Co in the form of dust or fumes has been reported to cause respiratory disease with symptoms ranging from cough to permanent disability and even death, respiratory hypersensitivity, progressive dyspnea, decreased pulmonary function, weight loss, dermatitis, and diffuse nodular fibrosis (Haneke, 2002).

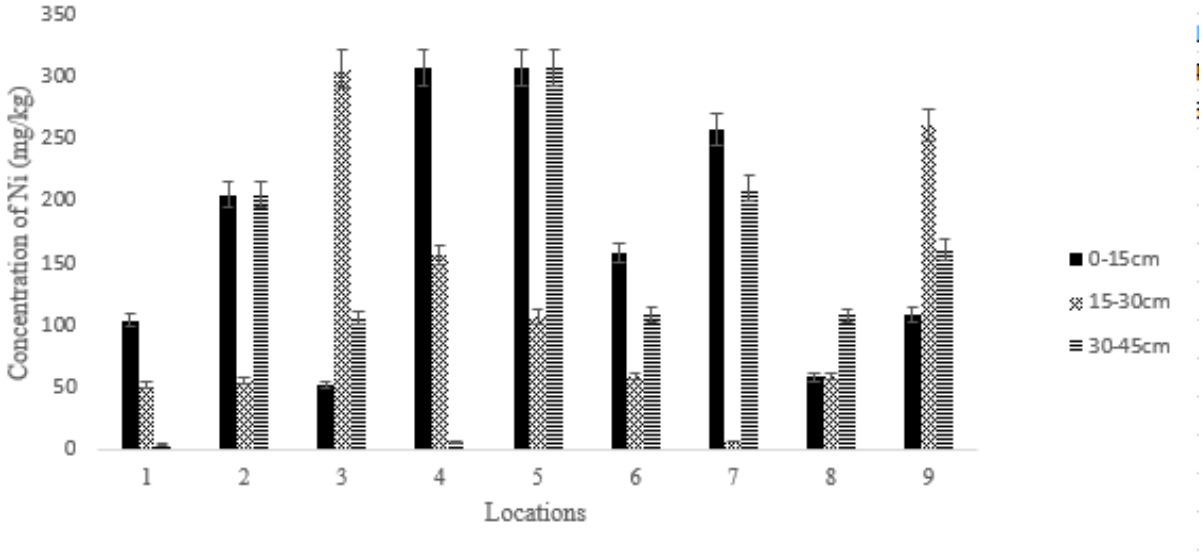

Figure 4: Average concentration of Ni in soil across the studied locations and depths

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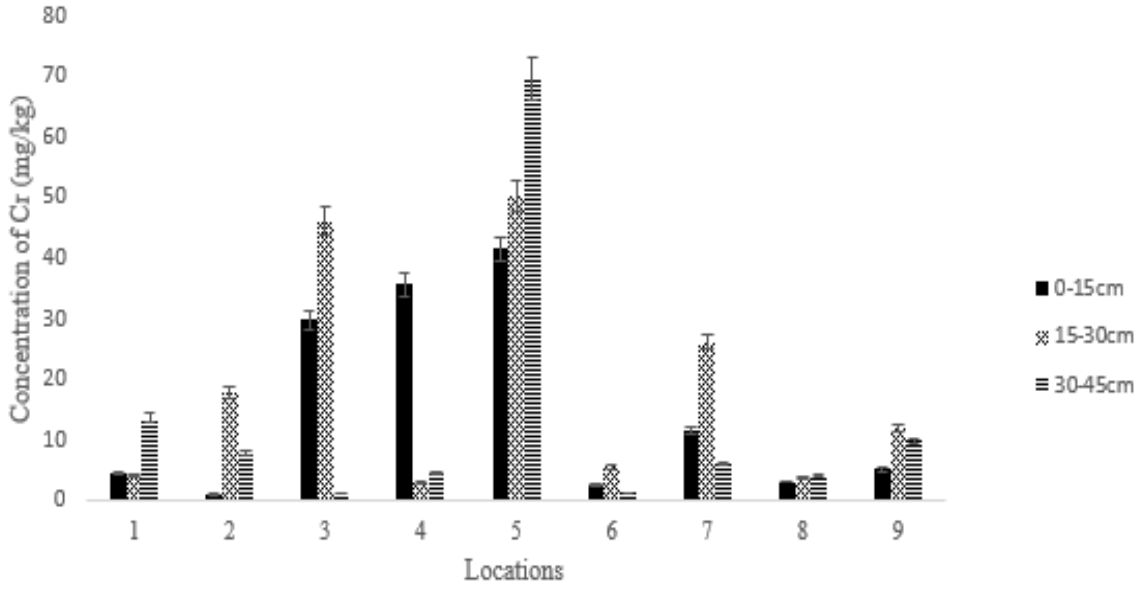

Figure 5: Average concentration of Cr in soil across the studied locations and depth

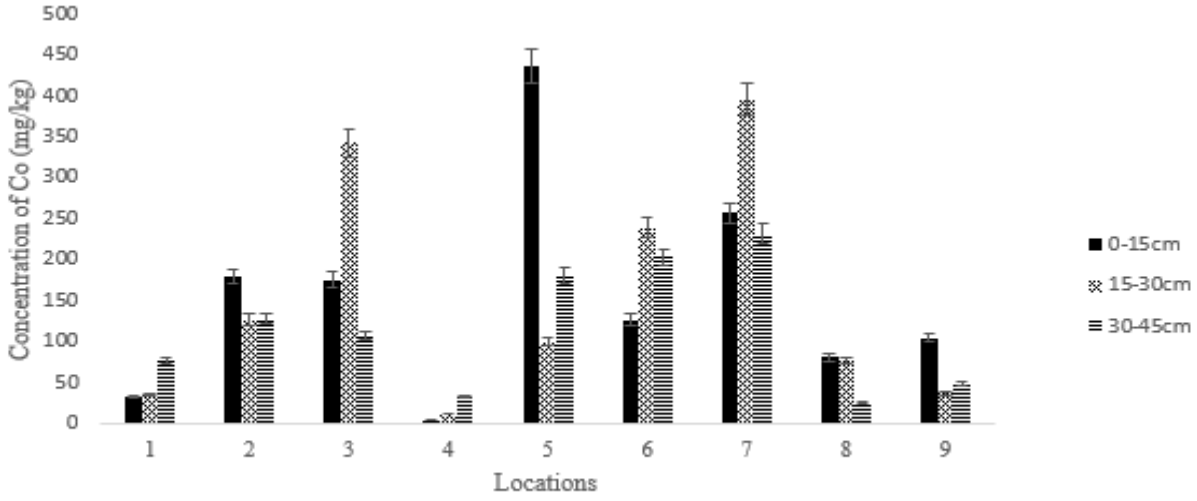

Figure 6: Average concentration of Co in soil across the studied locations and depth

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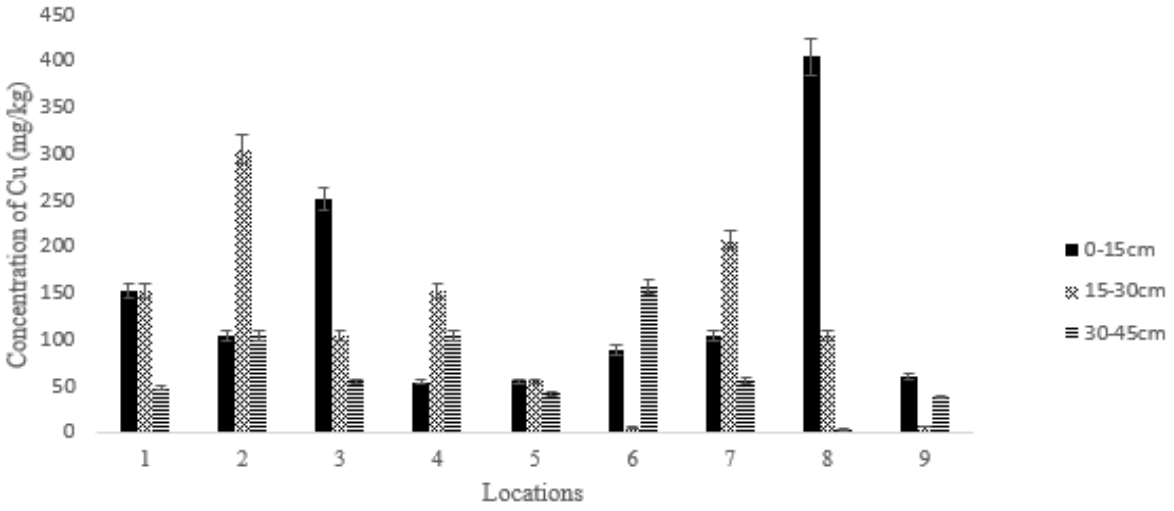

Figure 7: Average concentration of Cu in soil across the studied locations and depth

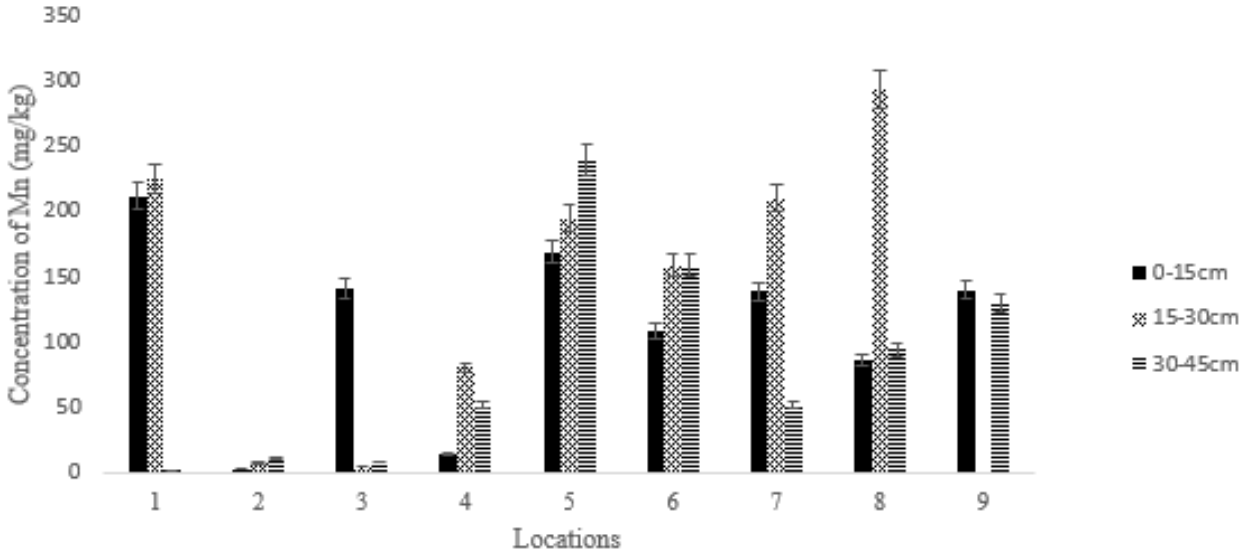

Figure 8: Average concentration of Mn in soil across the studied locations and depth

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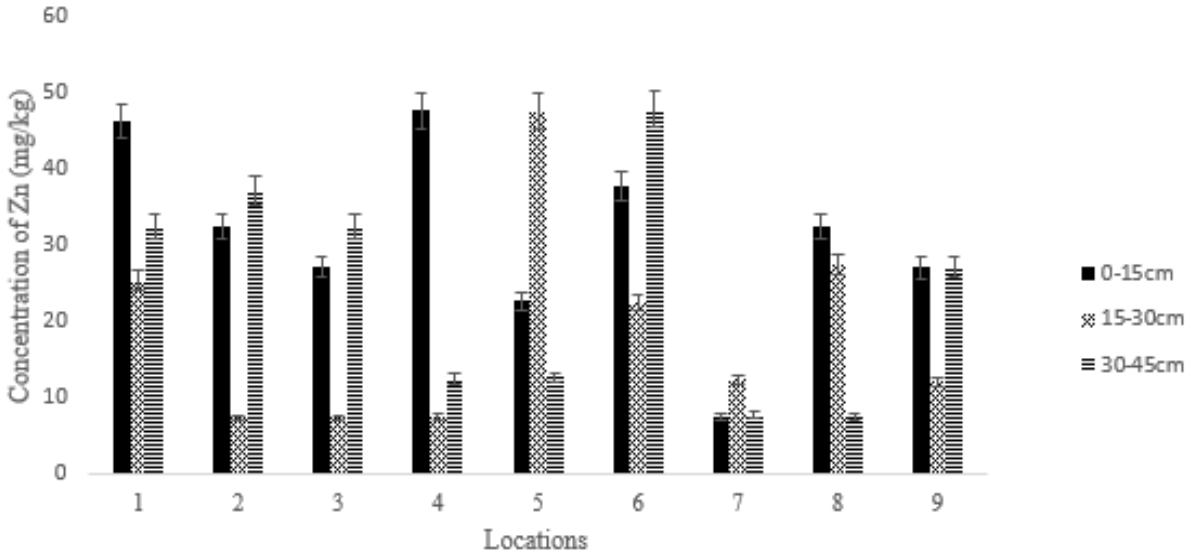

Figure 9: Average concentration of Zn in soil across the studied locations and depth

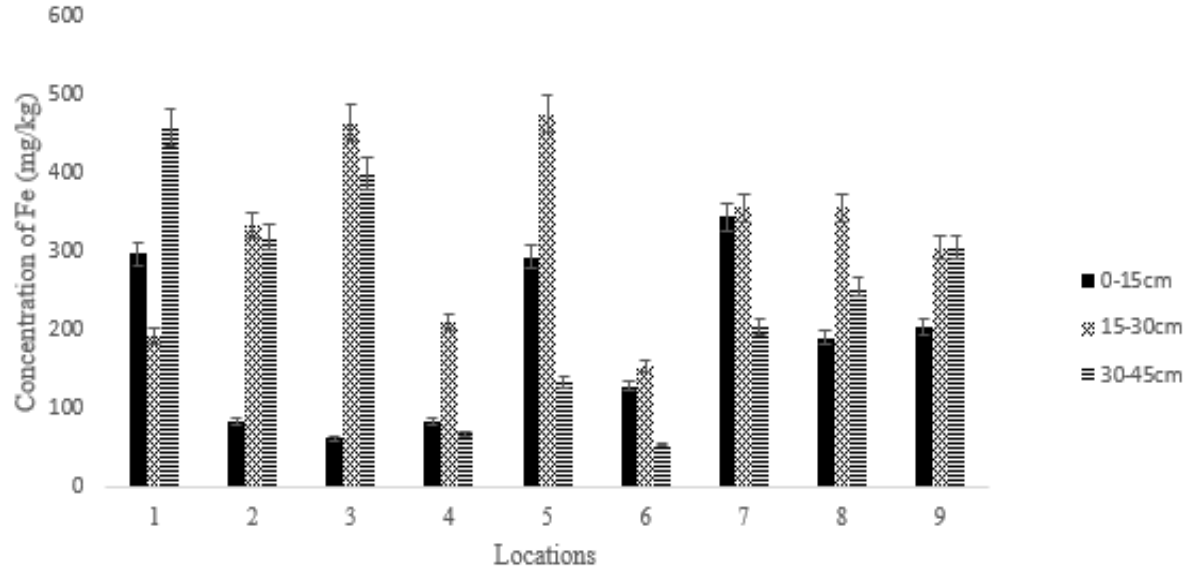

Figure 10: Average concentration of Fe in soil across the studied locations and depth

Copper

Like Co, very high concentrations were observed for Cu (Figure 7). Topsoils had the highest concentrations in 5 out of the 9 locations. The concentration of Cu in about 48% of the studied soils were within the NESREA regulatory limit of 100 mg kg^{-1}. However, the average level showed that the bottom soil concentration was within the regulatory limit.

Manganese and Zinc

For Mn, the concentration ranged as follows: 3.15 – 112.5 mg kg^{-1} for topsoil, 0.15 – 130.6 mg kg^{-1} for subsoil, and 2.35 – 239 mg kg^{-1} for bottom soil. The concentration across the studied locations indicates significant variation in Mn input in the different dumpsite soils. However, all dumpsite soils had concentrations that were within the 100 – 300 mg kg^{-1} regulatory limit for agricultural soils.

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Zn was present at relatively low concentrations compared to its NESREA regulatory limit of 421 mg kg^{-1} (Figure 9).

Pollution indices for assessing heavy metals pollution in dust

Geo-accumulation index (Igeo):

The geoaccumulation index for the studied metals in soils is shown in Table 2. In this study, metals such as Pb, Cr, Fe, Mn and Zn had negative Igeo values in all the locations and across depths, and were categorized into class 1 (Igeo< 0), which indicated that the dumpsite soil samples in all the studied locations were practically unpolluted with these metals. For Cd, about 77% of the studied dumpsite soil samples were in the class 6 category (i.e. Igeo > 5), indicating extreme pollution by Cd. This calls for serious concern, because of the health hazards associated with Cd. For Cu, about 22% of the soil samples were categorized in Class 2 (i.e. unpolluted-moderately polluted range) while only 7% of soil samples were in Class 3. The Igeo values for Ni ranged from -4.69 to 1.36, while Co ranged from -2.84 to 3.86.

Contamination factor (*Cf*)

The computed *Cf* values are shown in Table 3. From the Table, very high contamination factors (*Cf* > 6) were obtained for Cd in 93% of soil profiles across the studied location, with the remaining 7% in the considerable contamination range (*Cf* > 3 < 6). Very high contamination was also observed for Co in locations 2, 3, 5, 6 and 7 at all depths, while low contamination was observed for Cr, Zn, Mn, and Fe, with *Cf* values all less than 1 in the soil profiles across all studied locations.

Ecological risk factor/ risk index

The computed ecological risk factors/risk indices of metals in the studied soils are shown in Table 4. The potential ecological risk (Er) of all metals indicated low ecological risk for Pb in approximately 88% of the studied soils across depths. However, Cd posed serious ecological risk (with risk values > 320) in about 67% of the studied soils, while approximately 18% were in the high ecological risk category. On a general note, Cd, Co, Ni and Cu presented the greatest ecological risks of the determined metals.

The risk index values indicated significant ecological risk, with values ranging from 1150 – 8349. This shows that the studied dumpsite soils pose a significant risk of metals arising from the nature of wastes dumped in them, which calls for serious concern.

Degree of pollution

The values for the degree of pollution (P_d) are also presented in Table 3 above. The results indicated that all but one location had very high degree of pollution (with P_d values > 20) by several orders of magnitude. In location 2, sub- and bottom soil samples were considerably polluted, with P_d values > 10. This implies that the studied dumpsite soils were highly polluted with heavy metals based on the criteria for classification. The high pollution of the soils can be attributed to the exceptional high levels of Cd, Co and Ni in them.

Human exposure and health risk assessment of metals

Non-carcinogenic health risk

Table 5 depicts the HQ values for individual metals and the HI values across the studied locations for ingestion, inhalation and dermal pathways. The average non-carcinogenic risk exposure for the three pathways followed the order: $HI_{dem} > HI_{ing} >> HI_{inh}$. The HI values for ingestion were less than 1 in all but locations 6 and 7, indicating that there is the risk of developing non-carcinogenic risk in these two locations.

Carcinogenic health risk

The average carcinogenic risk for all studied metals are shown in Table 6. The sequence of carcinogenic risk for the different exposure pathways followed the order: $HQ_{ing} > HQ_{dermal} > HQ_{inh}$. Similar sequences of carcinogenic pathways for metals in soil have been reported for the Gold mining Basin in South Africa (Kamunda *et al.,* 2016), Steel rolling mill in Nigeria (Bello *et al.,* 2017) and Pb-Zn mining areas in China (Huang *et al.,* 2017). The total carcinogenic risk indicates a significant risk of developing cancer, as the values obtained were all above the acceptable limit of $1x10^{-4}$. Thus, there is concern for possible adverse health effect on individuals around such vicinities.

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Tablele 2: Geo-accumulation Index of metals studied

Location	Depth (cm)	Geo-accumulation index								
		Pb	Cd	Cr	Ni	Cu	Fe	Co	Mn	Zn
1	0-15	-0.47	7.21	-5.08	-0.21	1.03	-7.89	0.15	-2.82	-1.28
	15-30	-0.64	7.37	-5.21	-1.18	1.03	-8.52	0.27	-2.74	-2.15
	30-45	-0.47	6.87	-3.45	-4.69	-0.62	-7.27	1.38	-9.32	-1.80
2	0-15	-0.87	5.14	-7.16	0.77	0.47	-9.73	2.58	-8.90	-1.79
	15-30	-1.53	1.50	-3.07	-1.12	2.02	-7.73	2.08	-7.56	0.00
	30-45	-1.39	1.74	-4.23	0.77	0.49	-7.79	2.09	-7.04	-1.60
3	0-15	-1.67	7.10	-2.33	-1.20	1.75	-10.13	2.55	-3.41	-2.05
	15-30	-3.34	7.55	-1.70	1.35	0.49	-7.25	3.52	-8.21	-3.93
	30-45	-1.61	7.56	-7.09	-0.18	-0.44	-7.47	1.85	-7.45	-1.79
4	0-15	-0.69	6.80	-2.08	1.36	-0.46	-9.72	-2.84	-6.74	-1.24
	15-30	-0.46	5.91	-5.60	0.38	1.03	-8.40	-1.33	-4.22	-3.90
	30-45	-0.38	7.30	-5.04	-4.29	0.49	-10.01	0.15	-4.85	-3.17
5	0-15	-0.70	4.57	-1.85	1.36	-0.43	-7.91	3.86	-3.15	-2.32
	15-30	-1.43	7.57	-1.58	-0.17	-0.44	-7.22	1.73	-2.94	-1.24
	30-45	-0.09	7.54	-1.11	1.36	-0.82	-9.04	2.59	-2.65	-3.15
6	0-15	0.14	9.43	-5.82	0.40	0.25	-9.09	2.08	-3.78	-1.58
	15-30	-1.28	8.48	-4.76	-1.02	-3.67	-8.84	2.99	-3.24	-2.33
	30-45	0.67	8.48	-6.91	-0.14	1.07	-10.34	2.76	-3.24	-1.24
7	0-15	-1.90	7.94	-3.69	1.10	0.49	-7.68	3.10	-3.43	-3.91
	15-30	-0.15	7.19	-2.52	-4.14	1.47	-7.63	3.72	-2.84	-3.18
	30-45	-0.18	4.45	-4.63	0.81	-0.42	-8.43	2.95	-4.85	-3.86
8	0-15	-0.41	5.09	-5.57	-1.04	2.43	-8.54	1.43	-4.13	-1.79
	15-30	-0.74	4.87	-5.36	-1.02	0.49	-7.63	1.37	-2.36	-2.03
	30-45	-0.45	4.95	-5.12	-0.15	-4.42	-8.11	-0.25	-3.99	-3.90
9	0-15	-0.46	7.88	-4.86	-0.14	-0.32	-8.43	1.81	-3.42	-2.06
	15-30	-0.41	6.73	-3.66	1.12	-3.33	-7.85	0.30	-13.29	-3.22
	30-45	-0.43	7.38	-3.93	0.42	-0.96	-7.85	0.71	-3.53	-2.05

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Table 3: Contamination factors of metals studied

Location	Depth (cm)	Contamination factor									Degree of pollution
		Pb	Cd	Cr	Ni	Cu	Fe	Co	Mn	Zn	
1	0-15	1.09	221.5	0.0445	1.30	3.06	0.006	1.7	0.21	0.62	229.5
	15-30	0.96	248.5	0.0405	0.66	3.06	0.004	1.8	0.23	0.34	255.6
	30-45	1.09	176	0.137	0.06	0.976	0.010	3.9	0.00	0.43	182.6
2	0-15	0.82	53	0.0105	2.56	2.08	0.002	9.0	0.00	0.43	67.9
	15-30	0.52	4.25	0.179	0.69	6.1	0.007	6.4	0.01	0.10	18.2
	30-45	0.57	5	0.08	2.56	2.1	0.007	6.4	0.01	0.49	17.2
3	0-15	0.47	206	0.298	0.66	5.04	0.001	8.8	0.14	0.36	221.8
	15-30	0.15	280.5	0.461	3.83	2.1	0.010	17.2	0.01	0.10	304.3
	30-45	0.49	282.5	0.011	1.33	1.106	0.008	5.4	0.01	0.43	291.3
4	0-15	0.93	167	0.356	3.84	1.094	0.002	0.2	0.01	0.63	174.1
	15-30	1.09	90	0.031	1.95	3.06	0.004	0.6	0.08	0.10	96.9
	30-45	1.15	236	0.0455	0.08	2.1	0.001	1.7	0.05	0.17	241.3
5	0-15	0.92	35.75	0.415	3.84	1.11	0.006	21.8	0.17	0.30	64.3
	15-30	0.56	284.5	0.502	1.34	1.108	0.010	5.0	0.20	0.63	293.8
	30-45	1.41	280	0.695	3.84	0.85	0.003	9.1	0.24	0.17	296.3
6	0-15	1.66	1035	0.0265	1.98	1.784	0.003	6.4	0.11	0.50	1047.4
	15-30	0.62	535	0.0555	0.74	0.118	0.003	12.0	0.16	0.30	548.9
	30-45	2.39	535	0.0125	1.36	3.14	0.001	10.2	0.16	0.64	552.9
7	0-15	0.40	369.5	0.116	3.21	2.1	0.007	12.9	0.14	0.10	388.4
	15-30	1.35	218.5	0.262	0.09	4.16	0.008	19.8	0.21	0.17	244.5
	30-45	1.32	32.75	0.0605	2.63	1.124	0.004	11.6	0.05	0.10	49.6
8	0-15	1.13	51	0.0315	0.73	8.1	0.004	4.1	0.09	0.43	65.6
	15-30	0.90	44	0.0365	0.74	2.1	0.008	3.9	0.29	0.37	52.3
	30-45	1.10	46.5	0.043	1.35	0.07	0.005	1.3	0.09	0.10	50.5
9	0-15	1.09	354	0.0515	1.36	1.2	0.004	5.3	0.14	0.36	363.5
	15-30	1.13	159.5	0.119	3.26	0.149	0.006	1.8	0.00	0.16	166.2
	30-45	1.11	250	0.0985	2.01	0.77	0.006	2.5	0.13	0.36	256.9

Table 4: Ecological risk assessment of metals in soils of the studied locations

Location	Depth (cm)	Ecological risk factors									Ecological risk index (RI)
		Pb	Cd	Cr	Ni	Cu	Fe	Co	Mn	Zn	
1	0-15	76	1329	8.90	520	765	0.006	166.5	212	46.2	3123
	15-30	67.5	1491	8.10	264	765	0.004	180.5	225	25.3	3026
	30-45	0	1056	27.4	23.3	244	0.010	390	2.35	32.3	1775
2	0-15	57.5	318	2.10	1025	520	0.002	895	3.15	32.5	2853
	15-30	36.3	25.5	35.8	277	1525	0.007	635	7.95	7.37	2549
	30-45	0	30	16	1025	525	0.007	640	11.4	37.1	2284
3	0-15	32.9	1236	59.6	262	1260	0.001	880	141	27.2	3898
	15-30	10.4	1683	92.2	1530	525	0.010	1715	5.05	7.36	5568
	30-45	0	1695	2.20	530	276.5	0.008	540	8.55	32.5	3084
4	0-15	65	1002	71.2	1535	273.5	0.002	21	14	47.6	3029
	15-30	76.5	540	6.20	780	765	0.004	59.5	80.7	7.51	2315
	30-45	0	1416	9.10	30.7	525	0.001	167	51.9	12.5	2212
5	0-15	64.5	214.5	83	1535	277.5	0.006	2180	169	22.6	4546
	15-30	39.1	1707	100.4	535	277	0.010	496.5	195	47.5	3397
	30-45	0	1680	139	1535	212.5	0.003	905	239	12.7	4723
6	0-15	116	6210	5.30	790	446	0.003	635	109	37.6	8348
	15-30	43.1	3210	11.1	295	29.5	0.003	1195	159	22.4	4965
	30-45	0	3210	2.50	545	785	0.001	1015	159	47.7	5764
7	0-15	28.2	2217	23.2	1285	525	0.007	1285	139	7.48	5509
	15-30	94.5	1311	52.4	34	1040	0.008	1975	210	12.4	4729
	30-45	0	196.5	12.1	10.5	281	0.004	1160	52	7.77	1719
8	0-15	79	306	6.30	292	2025	0.004	405.5	85.8	32.5	3231
	15-30	63	264	7.30	296	525	0.008	389	293	27.5	1864.8
	30-45	0	279	8.60	540	17.5	0.005	126.5	94.2	7.55	1073.35
9	0-15	76.5	2124	10.3	545	300	0.004	525	140	27	3747.8
	15-30	79	957	23.8	1305	37.25	0.006	184.5	0.15	12.1	2598.8
	30-45	78	1500	19.7	805	192.5	0.006	245.5	130	27.2	2997.9

Table 5: Non-carcinogenic hazard exposure to metals in dumpsite soil

Location	HQ_{Ing}	HQ_{Inh}	HQ_{Derm}	HI
1	0.31	0.00019	0.40	0.70
2	0.13	0.00004	0.11	0.24
3	0.22	0.00035	0.63	0.86
4	0.23	0.00036	0.64	0.88
5	0.20	0.00030	0.50	0.70
6	0.70	0.00075	1.67	2.37
7	0.33	0.00034	0.72	1.06
8	0.15	0.00006	0.12	0.28
9	0.31	0.00029	0.62	0.93

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Table 6: Carcinogenic hazard exposure to metals in dumpsite soils

Location	$Risk_{Ing}$	$Risk_{Inh}$	$Risk_{Derm}$	Total risk
1	$1.22x10^{-3}$	$7.08x10^{-6}$	$3.59x10^{-4}$	$1.59x10^{-3}$
2	$8.46x10^{-4}$	$5.03x10^{-6}$	$2.49x10^{-4}$	$1.10x10^{-3}$
3	$1.05x10^{-3}$	$6.17x10^{-6}$	$3.12x10^{-4}$	$1.37x10^{-3}$
4	$7.70x10^{-4}$	$4.56x10^{-6}$	$2.34x10^{-4}$	$1.01x10^{-3}$
5	$1.80x10^{-3}$	$1.09x10^{-5}$	$5.32x10^{-4}$	$2.34x10^{-3}$
6	$1.18x10^{-3}$	$5.65x10^{-6}$	$3.49x10^{-4}$	$1.53x10^{-3}$
7	$1.63x10^{-3}$	$9.35x10^{-6}$	$4.75x10^{-4}$	$2.11x10^{-3}$
8	$1.18x10^{-3}$	$7.08x10^{-6}$	$3.49x10^{-4}$	$1.54x10^{-3}$
9	$9.86x10^{-4}$	$5.47x10^{-6}$	$2.98x10^{-4}$	$1.28x10^{-3}$

Conclusion

This study has provided information on the concentration, distribution and risk assessment of heavy metals in dumpsite soils in selected areas in Delta State, Nigeria. Urbanization was shown not to positively influence metals concentration in dumpsite soils, as pollution of the soils was did not follow the trend of urbanization. Rather, the levels of metals in the dumpsite soils could be a function of the nature of wastes dumped in them. The study revealed that there was a generally low level of metal pollution in the studied dumpsite soils except for Cd, Co, Ni, Cu and Fe. Ecological risk assessments indicated that the studied dumpsite soils pose a significant risk of metals arising from the nature of the wastes dumped in them. The health index and total carcinogenic risk values indicated the absence of potential non-carcinogenic risk in these soils due to exposure to trace metals, but considerable potential carcinogenic risks are to be expected in these soils from exposure to trace metals. The ecological and health risk assessment values of metals in dumpsite soils thus call for concern, because many open dumpsites are located in proximity to large human population, with very high likelihood of exposure.

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