International Scholars Journals

African Journal of Environmental and Waste Management ISSN 2375-1266 Vol. 9 (5), pp. 001-009, May, 2022. Available online at www.internationalscholarsjournals.org © International Scholars Journals

Full Length Research Paper

Assessment of heavy metals bioavailability in dumpsites of Zaria Metropolis, Nigeria

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Accepted 18 December, 2021

The objectives of this study was to investigate the chemical fractionation, mobility and bioavailability of Cd, Cu, Mn, Pb and Zn in refuse waste soils of some dumpsites in Zaria metropolis. The heavy metals in the waste soils samples were sequentially extracted and measured using atomic absorption spectrometry. Mean of total extractable metals in the samples analysed for Cd, Cu, Mn, Pb and Zn ranged from 25.86 – 95.71, 1.70 – 446.43, 141.92 – 423.22, 39.9 – 739.10, and 122.45 – 511.57 mgKg^{-1} dry weight, respectively. Cd and Pb were mostly found to be in the mobile phase of the samples indicating that the metals are potentially more bioavailable to the environment than the other metals studied. Overall, the order of mobility and bioavailability of the metals is Cd > Pb > Zn > Mn > Cu.

Key words: Heavy metals, Zaria metropolis, dumpsites, bioavailability.

INTRODUCTION

Zaria Metropolis is located at latitude 11° 3'N and longitude 07° 40'N and is presently one of the most important cities in Northern Nigeria. As at 2007 Census, it had a population of 1,018,827 (TWG, 2007). Like many cities in Nigeria, Zaria faces problems of environmental sanitation such as improper disposal of refuse near residential areas; poor refuse collection and handling, etc. For example, it is a common feature to find huge refuse dumpsites within residential areas and along some minor and major roads.

As many studies have shown, municipal refuse may increase heavy metal concentration in soil and underground water (Carlson, 1976; Albores et al., 2000; Okoronkwo et al., 2005; Okoronkwo et al, 2006) 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 municipal refuse are greatly influenced by their heavy metal contents. However, while total heavy metal content is a critical measure in assessing risk of a refuse dumpsite, total heavy metal content alone does not provide predictive insights on the bioavailability, mobility and fate of the heavy metal contaminants (Albores et al., 2000). Thus, it is the chemical form or species of the heavy metal that is an important factor in assessing their impacts on the environment. This is because it is the chemical form of the heavy metal that controls its bioavailability or mobility (Norvell, 1984).

Past investigation on the heavy metals impacts of municipal refuse dumpsites in Nigeria were concerned with total heavy metal determination only (Bamgbose et al., 2000; Okoronkwo et al., 2006). The objective of this study, therefore, was to investigate the chemical fractionation of Cd, Cu, Mn, Pb and Zn heavy metal in some refuse dumpsites in Zaria and determine their mobility, bioavailability and fate in order to assess the human health and ecological risks associated with the refuse dumpsites.

MATERIALS AND METHODS

Quality assurance

All reagents used were of analytical grade. Double distilled-deionized water was used. 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

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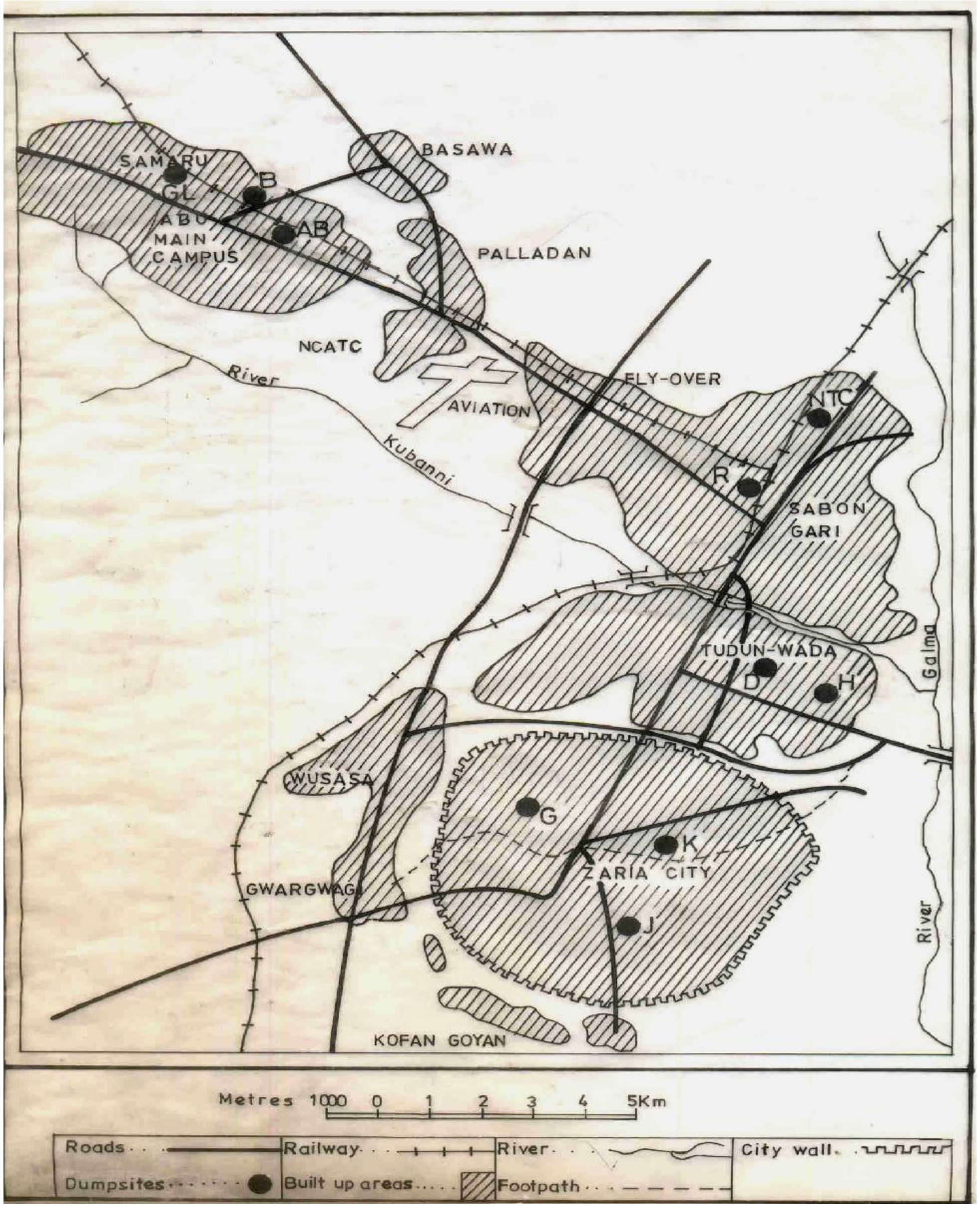

Figure 1. Zaria Metropolis showing dumpsite. Source: Modified from Zaria Topographic map and fieldwork, 2006.

water and dried. The analytical results obtained were validated with spiked samples. The percentage recovery of metals obtained by the summation of sequential fractions in relation to the total metal content extracted with aqua-regia was computed. The analytical precision was confirmed with triplicates throughout the study.

Dumpsite description

Soils from ten dumpsites were collected from four major settlements in Zaria metropolis. These dumpsites are: Basawa (B), Railway Station (R), Ali Basawa (AB), NTC, Babban Gwani (G), Galadima (GL), Anguwan Karfe (AK), Alkali Jae (J), Hajiya (H) and Dandutse (D) dumpsites. The map indicating the location of the dumpsites is shown in Figure 1.

Refuse characterization

To ascertain the percentage compositions of the waste types, known weight (1 kg) of refuse samples were sorted and weighed which revealed the presence of the following: plastics, papers, textiles, polythene bags, wood, metal scraps, waste leaves, rubber tubes and charcoal in various compositions.

Refuse waste soil collection

Refuse waste soils were collected from ten dumpsites in Zaria metropolis as follows: Triplicate sample from each dumpsite were collected and composite samples were made in the laboratory. The samples were air dried and sieved (using 2 mm sieve). The samples were stored in polythene bottles in desiccators at room temperature before extraction.

Physico-chemical properties of refuse waste soil

Soil pH and electrical conductivity were measured (1:2.5, w/v) by digital pH and conductivity meter. Soil organic matter content was determined by Walkley Black method (Walkley and Black, 1934). Exchangeable cations were extracted by 0.1 M $BaCl_2$ and subsequently determined by AAS (Hendershot and Duquette, 1986). The available phosphorous was determined by the method described by Udo and Ogunwale (1978). Finally, moisture content was determined using the method of Shrivastava and Banerjee (2004).

Chemical fractionation of heavy metals in waste soils of refuse dumpsites

Extraction

The extraction was carried out with an initial mass of 1.0 g air dried waste soil samples in polypropylene centrifuge tube of 50 ml capacity. The conventional method developed by Tessier (1979) was used in the extraction. However, $Mg(NO_3)_2$ was use instead of $MgC1_2$ to avoid an increase in the solubility of heavy metals within the soil solution (Shuman, 1985). The extractions were carried out on three sub-samples as follows:

Exchangeable phase

Each sample was shaken at room temperature with 16 ml of 1M Mg $(NO_3)_2$ at pH 7.0 for 1 h, centrifuged and supernatant decanted and made up to 40 ml with double distilled-deionsed water.

Oxidizable Phase (bound to organic matters)

Residue from 1 + 10 ml H_2O_2 8.8M + 6 ml HNO_3 O.02 M, was shaken for 5+1 h at 98ºC. 10 ml CH_3COONH_4 3.5 M was added as an extracting agent, centrifuged and supernatant made up to 40 ml with distilled water prior to analysis.

Acid soluble phase (bound to carbonates)

25 ml of 0.05 M Na_2EDTA was added to the residue from 2, shaken for 6 h and centrifuged. The supernatant was decanted and made up to 40 ml with distilled water prior to analysis.

Reducible Phase (bound to Fe-Mn Oxides)

Residue from 3+17.5 ml $NH_2OH.HCI$ 0.1M + 17.5M CH_3COONH_4 3.5M, shaken for 1 h, centrifuged, the supernatant decanted and made up to 40 ml with distilled water prior to analysis.

Residual phase fraction (bound to silicates and detrital materials)

Residue from 4 was digested by using HCI – HNO_3/HF (0.35:12w/v soil solution ratio) in acid digestion Teflon cup. It was dry ashed for 2 h and evaporated to dryness. The residue was diluted to 40 ml with distilled water prior to analysis.

After each successive extraction, the sample was centrifuged at 4500rpm for 15min (Legret et al., 1988). The supernatant was removed with Whatman No.42 filter paper. The residue was washed with de-ionized water followed by vigorous handshaking and then 15 min centrifugation before the next extraction. The volume of the rinsed distilled water used was kept to a minimum. The extracts were analysed using Atomic Absorption Spectrophotometer.

Table 1. Percentage recovery of the sequential extraction compared with the aqua regia digestion.

Metals	Sequential extraction	Aqua regia digestion
Pb	98.98 ± 0.90	85.94 ± 0.83
Cu	105.13 ± 0.13	104.17 ± 0.36
Cd	106.27 ± 0.55	106.55 ± 0.27
Zn	102.33 ± 0.29	91.05 ± 9.24
Mn	109.13 ± 1.95	89.60 ± 0.88

RESULTS AND DISCUSSION

Quality assurance

The recovery of added metal ions obtained with spiked samples was found to be >98.93%. The percent recovery of metals computed by the summation of sequential extractions in relation to the total metal content extracted with the aqua regia digest is presented in Table 1. For all metals, except Cd, recovery ranged from 102 to 109%, which is within the acceptable range. This variation may be attributed to the differences in leaching time, reagents and the total volume of extractant (Ciba et al., 1999). Similar ranges have already been reported in literature for sequential extraction (Albores et al., 2000).

Characterization

The results of the characterization of the refuse dumpsites are presented on Table 2. Based on the result, all the dumpsites were being dumped with polythene bags and textile materials. Pieces of papers and plastics materials were the next most abundant sources of the dumpsites contamination. Metal scraps were attributable to the locations. Woody materials were also found in most of the dumpsites studied. G, K and J dumpsites have waste leaves being dumped although G has the highest percentage (48%). Bone scraps were found only in GL and B dumpsites; these dumpsites were located some kilometers away from the Abattoir which may probably act as their bone supplier. Little percentage of rubber tubes was also found in B and 0% was found in other dumpsites. The presence of these materials could probably alter the physico-chemical parameters of the soils studied.

Physico-chemical properties of refuse waste soils

The selected physico-chemical properties determined are

Table 2. Characterization of refuse dumpsites (%).

Site	H	G	K	J	AB	NTC	D	GL	R	B
Plastic	13.94±0.14	-	13.02±0.03	9.15±0.09	44.02±0.03	7.32±0.42	31.19±0.18	7.99±0.01	4.21±0.25	12.33±0.57
Paper	21.48±0.78	0.85±0.02	-	1.69±0.08	17.38±0.20	26.28±0.01	11.19±0.18	6.43±0.33	34.13±0.03	18.03±0.05
Textiles	28.38±0.11	33.93±0.98	8.35±0.48	60.59±0.35	1.24±0.02	26.09±0.09	0.97±0.01	34.01±0.57	14.26±0.05	16.37±1.17
Polythene	17.59±1.27	17.29±0.13	18.79±0.26	12.37±0.61	11.64±0.03	30.01±0.96	38.87±0.58	14.97±0.02	28.71±0.23	18.34±0.55
Wood	4.89±0.18	0.40±0.02	-	-	3.95±0.01	-	7.71±0.25	10.23±0.05	-	11.31±0.23
Metals	14.45±0.41	-	16.29±0.53	11.01±0.04	4.51±0.23	9.28±0.16	9.28±0.04	18.04±0.02	19.02±0.04	-
Hair	-	-	-	-	-	-	-	-	-	-
Bones	-	-	-	-	-	-	-	8.51±0.02	-	10.43±0.06
Waste leaves	-	48.02±0.06	43.69±1.39	5.64±0.57	-	-	-	-	-	-
Rubber	-	-	-	-	-	-	-	-	-	10.23±0.12
Charcoal	-	-	-	-	-	-	-	-	-	2.83±0.06

Table 3. Mean (±SD) of physico-chemical parameters of waste soil in studied dumpsites.

Parameter	H	G	K	J	AB	NTC	D	GL	R	B
pH(H_2O)	7.80±0.01	8.71±0.01	8.81±0.01	8.51±00.02	9.21±0.02	8.61±0.01	8.11±0.02	9.31±0.01	8.42±0.03	9.21±0.01
EC(Scm^{-1})	1.53±0.03	1.53±0.03	2.21±0.03	1.52±00.02	3.00±0.01	1.21±0.01	0.42±0.01	0.86±0.01	0.90±0.02	4.00±0.01
Moisture content (%)	47.86±0.02	17.87±0.02	23.54±0.01	82.49±0.02	32.52±0.03	40.02±0.03	32.02±0.03	60.04±0.04	24.04±0.04	32.04±0.04
Organic matter (%)	4.35±0.03	3.90±0.02	4.46±0.04	3.72±00.01	6.10±0.22	3.21±0.02	3.77±0.03	3.78±0.02	5.03±0.02	5.30±0.03
Nitrite-NO_2-N (%)	8.33±0.15	5.63±0.06	6.27±0.12	9.17±00.06	5.03±0.15	4.27±0.12	4.20±0.03	4.27±0.12	5.30±0.30	8.37±0.12
Nitrate-NO_3-N (%)	11.33±0.15	4.17±0.35	8.33±0.12	11.27±00.12	5.67±0.12	5.67±0.12	5.60±0.20	5.60±0.20	5.60±0.20	11.30±0.17
Ammonia Nitrogen NH_3-N (%)	5.57±0.06	5.50±0.17	2.77±0.06	5.67±00.12	11.23±0.06	5.60±0.20	5.67±0.12	5.67±0.12	2.87±0.12	2.87±0.12
Chloride Cl (Meq/l)	6.97±0.02	25.06±0.02	6.82±0.03	5.81±00.01	15.21±0.01	4.32±0.02	2.02±0.03	5.01±0.01	5.62±0.02	15.82±0.03
Phosphorus (Meq/l)	267.99±0.02	386.43±0.03	397.10±0.03	198.57±0.01	187.77±0.01	230.76±0.01	57.76±0.01	177.10±0.01	118.11±0.02	246.86±0.01
Sulphate- SO_4	5.45±0.02	20.53±0.01	12.69±0.01	33.21±0.01	102.64±0.01	14.49±0.02	3.62±0.01	3.62±0.01	43.48±0.01	36.25±0.02

shown in Table 3. The pH of the waste soils ranged from 7.80 to 9.21 with dumpsites H and AB having the lowest and highest pH values respectively. This suggests that the dumpsites were alkaline in nature. The total mean percentage of organic matter ranged from 2.63 to 6.10% which is high based on the classification of soil organic matter given by Enwezor et al. (1988). The electrical conductivity of the refuse waste soils also ranged from 0.42 to 4.0 $mScm^{-1}$. The high conductivity value of the waste soil may be attributed to the presence of metal scraps which is one of the constituents of the refuse dumpsites. The moisture content which is directly proportional to the water holding capacity of the soil ranged from 17.87 to 82.49%. Available phosphorous in the refuse waste soil ranged from 38.52 to 129.52 meq per 100 g. The high concentration of phosphorous contributes to good growth of plants as was observed.

The results of the exchangeable cations in 0.1M $BaCl_2$ are presented in Table 4. The cation exchange capacity (CEC) was determined by the sum of cations (Ca, Mg, Na, K, Mn and Fe). Exchangeable Fe and Mn were found to be the dominant cations ranging from 5.15 to 254.52 and 53.92 to 137.70 $Cmolkg^{-1}$. Overall, total exchange-

Table 4. Mean (±SD) of exchangeable cations in waste soils of studied dumpsites.

Dumpsite	Ca	Mg	K	Na	Fe	Mn	∑cation
H	17.69±0.04	7.40±0.01	6.53±0.02	4.16±0.03	251.47±1.27	96.27±1.11	383.52±1.08
G	12.54±0.04	9.86±0.03	9.70±0.02	7.07±0.02	335.72±4.98	94.63±0.93	469.54±4.74
K	13.55±0.02	6.15±0.01	8.14±0.01	3.93±0.02	354.52±3.46	70.79±0.65	457.07±3.07
J	18.81±0.01	9.21±0.01	7.21±0.01	3.91±0.01	207.70±1.73	137.70±2.34	384.54±2.14
AB	17.71±0.01	9.84±0.01	14.43±0.02	8.09±0.01	146.49±2.33	95.29±0.06	291.85±2.36
NTC	16.71±0.02	6.76±0.02	7.06±0.02	3.66±0.01	45.76±0.58	55.75±0.34	135.70±0.93
D	18.91±0.01	4.93±0.02	2.73±0.03	2.08±0.01	112.68±0.59	68.22±2.35	209.54±2.93
GL	20.61±0.01	11.06±0.02	7.66±0.01	3.13±0.02	155.11±2.25	53.92±1.73	251.49±0.56
R	22.02±0.03	16.02±0.03	15.97±0.02	2.25±0.01	5.15±0.13	71.39±0.57	132.83±0.68
B	25.21±0.01	8.61±0.01	11.23±0.02	4.17±0.01	147.14±1.16	66.03±0.87	262.39±1.39

Table 5. Cd concentrations in each fraction of waste soils in studied dumpsites.

Fraction	H	G	K	J	AB	NTC	D	GL	R	B
Exchangeable	9.68±0.45	12.90±0.45	13.98±1.86	12.90±0.23	12.90±0.45	8.60±0.92	9.68±0.68	9.68±0.23	ND	9.68±0.23
Oxidizable	9.68±0.23	12.90±0.45	9.68±0.32	12.90±0.23	12.90±0.45	8.60±0.92	9.68v0.23	12.90±0.23	3.23±0.23	12.90±0.45
Acid soluble	5.38±0.93	9.68±0.23	9.68±0.23	12.90±0.45	12.90±0.23	12.90±0.23	9.68±0.45	9.68±0.23	5.05±0.00	12.90±0.23
Reducible	9.68±0.45	9.68±0.23	9.68±0.23	16.13±0.00	12.90±0.23	9.68±0.23	9.68±0.45	12.90±0.23	7.68±0.23	9.68±0.45
Residual	12.90±0.45	12.90±0.23	52.69±0.04	16.75±0.40	16.13±0.23	12.90±0.55	12.90±0.45	17.20±0.86	9.90±0.45	16.13±0.23
∑extracted metals	47.32±0.72	58.06±0.53	95.71±0.04	71.58±0.61	67.73±0.58	52.68±0.40	51.62v0.45	62.36±0.11	25.86±0.63	61.29±0.23
Non-residual %)	72.74	77.78	44.95	76.60	76.18	75.51	75.01	72.42	61.72	73.68
Residual (%)	27.26	22.22	55.05	23.40	23.82	24.49	24.99	27.58	38.28	26.32
Mobile phase (%)	31.83	38.89	24.72	36.04	38.09	40.81	37.50	31.05	19.53	36.84

able cations ranged from 132.83 to 469.54 Cmolkg^{-1}, with dumpsites NTC and G having the lowest and highest exchangeable cations, respectively.

Sequential extractions

The sequential extraction scheme is useful in assessing the mobility and bioavailability of heavy metals in the waste soils. The results of the sequential extractions of Cd, Cu, Mn, Pb and Zn in samples of waste soils of studied dumpsites in Zaria metropolis are presented in Tables 5 - 9.

Cadmium

From the results as presented in Table 5. Total extractable cadmium was found to be above the critical permissible concentration of 3.0 mgKg^{-1} (MAFF, 1992) and USEPA (1986) in all the dumpsites. Cadmium batteries, metal scraps etc. are being dumped from the industrial and residential areas, which might have contributed to the large concentration of the metal. The mobile phase contained 19.53 to 40.81% of the total extractable fraction of the metal. This metal therefore was readily bioavailable to the environment. The availability of this metal in the sequentially extracted fractions follows the order: Residual > Exchangeable = Oxidizable = Reducible > Acid soluble.

Table 6. Cu concentrations in each fraction of waste soils in studied dumpsites.

Fraction	H	G	K	J	AB	NTC	D	GL	R	B
Exchangeable	ND	ND	ND	15.61±0.64	ND	3.40±0.33	ND	ND	ND	ND
Oxidizable	156.19±0.52	3.82±0.96	4.98±0.14	ND	11.57±0.13	ND	ND	11.00±0.05	30.53±0.94	8.91±0.00
Acid soluble	ND	ND	ND	4.05±0.00	ND	ND	8.00±0.00	ND	20.14±0.38	ND
Reducible	40.82±0.34	ND	ND	ND	ND	ND	16.41±0.67	67.63±0.08	8.00±0.00	5.31±0.50
Residual	249.42±0.99	7.88±0.67	10.18±0.47	24.03±0.31	24.08±0.33	14.42±0.78	40.90±0.00	90.96±0.16	30.89±0.59	66.67±0.42
∑extracted metals	446.44±0.12	11.70±0.99	15.16±0.33	43.69±0.68	35.65±0.88	17.82±0.48	65.31±0.33	169.59±0.70	89.56±0.69	80.89±0.65
Non-residual (%)	44.133	32.65	32.85	45.00	32.45	19.08	37.38	46.36	65.51	17.58
Residual (%)	55.87	67.35	67.15	55.00	67.55	80.92	62.62	53.64	34.49	82.42
Mobile phase(%)	9.14	ND	ND	35.73	32.45	19.08	25.13	39.88	8.93	6.56

Table 7. Mn concentrations in each fraction of waste soils in studied dumpsites.

Fraction	H	G	K	J	AB	NTC	D	GL	R	B
Exchangeable	3.36±0.36	ND	16.81±0.36	17.93±0.88	3.36±3.06	6.72±0.63	13.45±0.37	3.6±0.06	7.45±0.68	33.42±0.99
Oxidizable	16.81±0.73	16.81±0.36	40.34±0.73	33.61±0.73	47.06±0.72	67.23±0.73	80.67±0.72	30.25±0.72	13.45±0.73	138.17±0.42
Acid soluble	30.25±0.72	33.61±0.73	14.05±0.00	18.96±0.96	16.81±0.36	11.75±0.04	33.61±0.73	26.89±0.36	40.34±0.73	26.84±0.64
Reducible	114.29±0.73	134.45±0.37	120.45±0.73	174.79±0.72	124.37±0.72	102.25±0.44	80.67±0.72	97.48±0.72	67.23±0.36	191.34±0.73
Residual	ND	16.81±0.36	13.45±0.37	4.48±0.94	13.45±0.37	6.72±0.36	20.17±0.72	6.72±0.36	13.45±0.37	33.45±0.37
∑extracted metals	164.71±0.99	201.68±0.83	205.10±0.45	249.77±0.48	205.05±0.36	194.67±0.25	228.57±0.36	164.70±0.08	141.92±0.67	423.22±0.61
Non-residual (%)	97.04	91.67	93.44	98.21	93.44	96.55	91.18	95.92	90.52	92.10
Residual (%)	2.96	8.33	6.56	1.79	6.56	3.45	8.82	4.08	9.48	7.90
Mobile phase(%)	19.80	16.67	15.05	14.77	9.84	9.49	20.59	18.37	33.67	14.24

The potential mobility and bioavailability of this metal in the waste soils of the dumpsites were found to be in the order: NTC > G > AB > D > B > J > H > GL > K >R. The presence of appreciable percentage of the total extractable fraction in the mobile phase suggests that Cd in these soils was potentially more bioavailable for plant uptake (Xian, 1989). This result was also in agreement with the observation of Harrison (1981), Miller and Mcfee (1983), and Kuo et al. (1983) who reported similar Cd concentration levels in waste soils of dumpsites.

Copper

The concentration levels in the five fractions of the waste soils of the ten dumpsites studied are presented in Table 6. The level of copper in all the refuse waste soils studied was below the toxic limit of 250 $mgKg^{-1}$ sets by USEPA (1986) with exception of H dumpsite. Only J, AB, GL and D refuse waste soils have reasonable percentage of the total extractable fraction in the mobile phase. Thus, copper in these dumpsites is more bioavailable than in other dumpsites. The potential bioavailability of the metal is in the following order: Residual > Oxidizable > Reducible > Acid soluble > Exchangeable.

For the waste soils of H, G, K, GL and R dump-

Table 8. Pb concentrations in each fraction of waste soils in studied dumpsites.

Fraction	H	G	K	J	AB	NTC	D	GL	R	B
Exchangeable	160.00±0.00	ND	ND	160.00±0.05	73.36±0.65	12.11±0.13	80.00±0.00	ND	50.04±0.04	ND
Oxidizable	41.68±0.92	45.57±0.87	ND	145.30±0.89	56.04±0.60	ND	209.33±0.07	40.03±0.96	105.00±0.00	80.30±0.56
Acid Soluble	ND	43.20±0.72	ND	42.42±0.76	46.69±0.11	12.13±0.27	139.90±0.43	44.30±0.08	78.15±0.40	107.90±0.70
Reducible	131.67±0.58	60.47±0.61	20.25±0.49	80.00±0.05	53.33±0.41	ND	44.30±0.08	53.80±0.27	42.00±0.00	151.77±0.45
Residual	245.27±0.93	123.33±0.41	19.65±0.00	123.64±0.16	140.20±0.45	12.53±0.42	265.00±0.23	77.27±0.51	161.99±0.70	220.50±0.00
∑extracted metals	578.62±0.62	272.57±0.00	39.90±0.49	551.36±0.94	369.62±0.15	36.77±0.84	739.10±0.78	215.40±0.90	437.18±0.10	560.47±0.10
Non-Residual (%)	57.61	54.75	50.75	77.58	62.07	65.92	64.15	64.13	62.95	60.66
Residual (%)	42.39	45.25	49.25	22.42	37.93	34.08	35.85	35.87	37.05	39.34
Mobile phase (%)	27.65	15.85	0.00	36.71	32.48	65.92	29.75	20.57	29.32	19.25

Table 9. Zn concentrations in each fraction of waste soils in studied dumpsites.

Fraction	H	G	K	J	AB	NTC	D	GL	R	B
Exchangeable	8.57±0.08	24.49±0.16	ND	16.33±0.17	ND	7.24±0.17	20.41±0.08	4.08±0.08	57.14±0.08	8.16±0.08
Oxidizable	74.08±0.29	53.06±0.08	36.73±0.17	20.14±0.17	30.48±0.65	86.12±0.25	172.79±0.02	151.02±0.16	50.31±0.38	38.51±0.96
Acid soluble	22.04±0.08	32.65±0.17	16.33±0.09	32.65±0.08	30.16±0.08	82.04±0.16	73.47±0.33	97.96±0.16	9.68±0.00	28.57±0.16
Reducible	65.71±0.09	16.33±0.09	12.24±0.09	ND	30.08±0.58	45.39±0.17	40.82±0.17	81.63±0.08	38.71±0.13	40.48±0.85
Residual	202.45±0.37	226.53±0.48	183.67±0.09	53.06±0.83	112.90±0.33	245.59±0.49	204.08±0.63	28.57±0.16	84.29±0.78	181.48±0.29
∑extracted metals	372.85±0.09	353.06±0.39	248.97±0.25	122.45±0.82	203.62±0.08	466.38±0.92	511.57±0.47	363.26±0.32	240.13±0.26	297.20±0.92
Non-Residual (%)	45.70	35.84	26.23	56.67	44.55	47.34	60.11	92.14	64.90	38.94
Residual (%)	54.30	64.16	73.77	43.33	55.45	52.66	39.89	7.86	35.10	61.06
Mobile phase (%)	8.21	16.18	6.56	40.00	14.81	19.14	18.35	28.09	27.83	12.36

sites copper was mostly associated with the reducible fraction. The metal was found to concentrate in the last four fractions in all the soils which is consistent with the findings of Gupta and Chen (1975) and Hickey and Kittrick (1984).

Most of the Cu in the refuse waste soils was present in the residual fraction as shown in Table 6. More than 50% of the total extracted fractions in all the dumpsites were present in the residual fraction with the exception of waste soil of R dumpsite. Also, significant amount of copper was associated with the oxidizable fraction. The major association of Cu with organic fraction in these soils may be due to high formation constants of organic copper complexes (Stumm and Morgan, 1981).

Manganese

The results of the sequential extraction of Mn in the samples of waste soils of the dumpsites are shown in Table 7. As could be readily seen from this Table, there is high percentage of Mn in the reducible phase in all the waste soils studied. This may be due to the precipitation of amorphous hydrous oxides of manganese during aging of the dumpsites (Staelens et al., 2000). The order of availability of this metal in different fractions followed the pattern: Reducible > Oxidizable > Acid Soluble > Residual > Exchangeable.

The concentration of this metal in all soils was within the tolerable limits (100 – 300 mgkg^{-1} set by USEPA (1986) except in dumpsite B waste soil. 90.50 - 98.12% of this metal was associated with non-residual fraction. The potential mobility and bioavailability follows the pattern: R > D > H > GL > G > K > J > B > AB > NTC.

Lead

Table 8 contains the results of the sequential extraction of Pb in samples of waste soils of the dumpsites studied. More than 50% of this metal was found to be in the non-residual fraction while 15.85 to 65.92% of the total extractable fraction contribute to the mobile phase (exchangeable and acid soluble). This indicates that potential bioavailability of this metal in different fraction is: Residual > Reducible > Oxidizable > Acid extractable > Exchangeable. Similarly, the order of mobility and bioavailability of this metal in the refuse waste soils revealed the following pattern: NTC > J > AB > D > R > H > GL>B>G>K.

Dumpsite NTC, GL, G, K and AB have lead concentrations within the USEPA (1986) allowed limits of 30 – 300 mgKg^{-1} while dumpsites H, J, D, R and B have lead content above the USEPA (1986) limits. Similar concentration range was reported by Kabata-Pendias and Pendias (1984). Based on the mobile fraction level of lead, only the NTC dumpsite is at risk for lead contamination. This dumpsite is located close to the railway line (Figure 1).

Zinc

The extractable fractions of Zinc are shown in Table 9. The total extractable zinc in most of the dumpsites was above the permissible limit sets by USEPA (300 mgKg^{-1}). The results also indicate the non-residual fraction of the metal to be >35% in all the dumpsite except site K. The mobile phase contained between 7 to 40%, indicating that the metal will be readily bioavailable to the environment.

The potential mobility and bioavailability of this metal in the refuse waste soils of the dumpsites followed the pattern: J > GL > R > NTC > D > G > AB > B > H > K. Similarly, the availability of the metal in the extracted fractions is: Residual > Oxidizable > Acid soluble > Reducible > Exchangeable.

Among the non-residual fractions, the reducible fraction for AB and B dumpsites contained the highest amount of Zn in all the refuse waste soils. This may be partially due to the high stability constants of Zn Oxides. Several other workers have also found Zn to be associated with reducible fractions (Kuo et al., 1983; Ramos et al., 1994).

Conclusion

A sequential extraction was used to fractionate Zn, Cu, Pb, Cd and Mn present in the refuse waste soils of ten dumpsites in Zaria metropolis, Northern Nigeria. The non-residual fraction was the most abundant pool for all the metals studied except copper. A significant amount of Cd and Pb were associated with mobile phase, which indicates that these metals will be potentially more bioavailable to the environment. Overall, the order of mobility and bioavailability of the metals was: Cd > Zn > Pb > Mn > Cu.

REFERENCES

Albores AF, Perez-Cid B, Gomes EF, Lopez EF (2000). Comparison Between Sequential Extraction Procedures and Single Extraction Procedures and for metal Partitioning in sewage sludge samples. Analyst, 125: 1353-1357.

Bamgbose O, Arowolo TOA, Odukoya O (2000). Earthworms as bio-indicators of metal pollution in dumpsites of Abeokuta. Nigeria. Rev. Biol. Trop., Vol. 48.

Carlson CW (1976). Land application of waste materials, Soil Conserv. Soc.Am. Ankeny, IOWA, pp. 3-7.

Ciba J, Korolewicz T, Turek M (1999).The occurrence of metals in composted municipal wastes and their removal. Water Air Soil Pollut. 111: 159-170.

Enwezor WO, Ohiri AC, Opubaribo EE, Udoh EJ (Eds.) (1998). .A review of soil Fertility Investigators in South Eastern Nigeria, HFDA Lagos, Nigeria.

Gupta SK, Chen KY (1975). Partitioning of trace metals in selective chemical fractions of nearshore sediments. Environ. Lett. 10: 129-158.

Harrison RM (1981). Chemical association of Pb, Cd, Cu and Zn in street dusts and roadside soils. Environ. Sci. Technol. 15: 1378-1383.

Hendershot WH, Duquette M (1986). A simple barium chloride method for detrmining cation exchange capacity and exchangeable cations. Soil Sci. Soc. Am. J. 50: 605-608.

Hickey MG, Kittrick JA (1984). Chemical partitioning of Cd, Cu, Ni and Zn in soils and sediments containing high levels of heavy metals. J. Environ. Qual. 13: 372-376.

Kabata–Pendias A, Pendias H (1984). Trace elements in soils and plants. Boca Raton, FL: CRC – press, Inc., 107-129.

Kuo S, Heilman PE, Baker AS (1983). Distribution and forms of Cu, Zn, Cd, Fe and Mn in soils near a copper smelter. Soil Sci. 135:101-109.

Legret M, Divet L, Justo C (1988). Movement and speciation of heavy metals in a soil amended with sewage sludge containing large amount of cadmium and nickel, Water. Res. 22(8): 953-969.

MAFF and Welch Office Agriculture Department (1992). Code of good agricultural practice for the protection of soil. Draft Consultation Document, MAFF London.

Miller WP, McFree WW (1983). Distribution of Cd, Zn, Cu and Pb in soils of industrial northwestern Indiana. J. Environ. Qual. 12: 29-33.

Norvell WA (1984). Comparison of Chelating Agents for metals in diverse soil materials. Soil Sci. Soc. Am. J. 48: 1285-1292.

Nyle CB, Ray RN (1999). The nature and properties of soils. 12th ed.

Okoronkwo NE, Igwe JC, Onwuchekwe EC (2005). Risk and health implication of polluted soils for crops production. Afr. J. Biotechnol. 4(13): 1521-1524.

Okoronkwo NE, Odemelam SA, Ano OA (2006). Levels of toxic elements in soils of abandoned waste dumpsite. Afr. J. Biotechnol. 5(13): 1241-1244.

Ramos L, Hernandez LM, Gonzalez MJ (1994). Sequential fractionation of Cu, Pb, Cd and Zn in soils from or near Donana National Park. J. Environ. Qual. 23: 50-57.

Shrivastava SK, Banerjee DK (2004). Speciation of metals in sewage sludge and sludge-amended soils. Water, Air, Soil Pollut. 152: 219-232.

Shuman LM (1985). Fractionation method for soil microelements. Soil Sci. 140: 11-22.

Smith CJ, Hopmans P, Cook FJ (1996). Accumulation of Cr, Pb, Cu, Ni, Zn and Cd in soil following irrigation with untreated Urban effluents in Australia, Environ. Pollut. 94(3): 317-323.

Staelens N, Parkpian P, Polprasert C (2000). Assessment of Metal Speciation in Sewage Sludge Dewatered in Vertical flow Reeds beds using a Sequential Extraction Scheme. Chem. Speciat. Bioavail. 12: 97-107.

Stumm W, Morgan JJ (1981). Aquatic chemistry: An introduction emphasizing chemical equalibria in natural water. 2nd ed. John Wiley and Sons, New York.

TWG (2007). Current population figures for cities, towns and Administrative Divisions of the World. http://www.world-gazetter.com//home.htm.

Udo EJ, Ogunwale JA (1978). Laboratory manual for the analysis of soils, plants and water samples. Department of Agronomy University of Ibadan, p. 45.

USEPA (1986). Test Methods of Evaluation for Solid Waste (USEPA S/W 846 UEPA Washington DC).

Walkley A, Black IA (1934). An examination of the Detjare method for Determining soil organic matter and a proposed modification of the chromic Acid titration*.* Soil Sci. 37: 29-36.

Xian X (1989). Chemical partitioning of Cd, Zn, Pb and Cu in soils near smelters. J. Environ. Sci. Health A 6: 527-541.