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RESEARCH PAPER

Seasonal variation in bioavailability of some toxic metals in waste dump soils of Makurdi, North-Central Nigeria

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Abstract

Seasonal changes in the bioavailable forms of cadmium (Cd), copper (Cu) and lead (Pb) in waste dump soils of a rapidly expanding city were assessed by sequential chemical extractions. Three major waste dumps at Apir Mechanic Village (AMV), Benue Industrial Layout (BIL) and Integrated Waste Dump (IWD) all located in Makurdi, north-central Nigeria, were selected for the study. Composite soil samples were collected from each waste dump during dry (January) and wet (July) seasons in 2011; characterized and subjected to the modified Tessier et al's sequential extraction to separate the metals into operationally defined pools with varying bioavailability – water-soluble (F_1), exchangeable (F_2), carbonate-bound (F_3), Fe, Mn and Al oxide-bound (F_4), organic matter-bound (F_5) and residual (F_6) in soil. The soils were essentially mineral soils with sandy clay loam texture, moderately contaminated with Cd (1.36 – 2.98 mg kg^{-1}), Cu (2.70 – 10.86 mg kg^{-1}) and Pb (32.26 – 74.56 mg kg^{-1}). Metal forms and their partitioning in the soils varied markedly among the waste dumps possibly due to different anthropogenic sources of these metals coupled with seasonal effects. The metals were more bioavailable in the wet than dry season. Across the waste dumps metal bioavailability followed the order: BIL > IWD > AMV. Depending on the metal, mobility factors, M_f were high enough and appeared to vary in the order: Cd ($20 \le M_f (\%) \le 65$) > Pb ($37 \le M_f (\%) \le 50$) > Cu ($7 \le M_f (\%) \le 37$) suggesting the potential long-term risk of these elements (especially Cd) in the soils.

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Introduction

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 (Abdus-Salam, 2009). 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. In Nigeria, the waste dumps are frequently put to agricultural use or scavenged for recyclable materials (plastics, metals, glass) by the urban populace in a bid to augment personal incomes and offset food insecurity occasioned by rural-urban drift (Wuana *et al.*, 2012). Risks or hazards frequently associated with waste dumps are categorized into three groups: biological (bacteria, helianthus, viruses, protozoa, micro-fauna), chemical (heavy metals, nitrogenous compounds, phosphorus compounds, minerals, pesticides, petrochemicals) and physical (sharp objects, psychosocial discrimination, insecurity and land tenure problems (Hope, 2006; Nabulo *et al.*, 2008). Unlike most organic contaminants which are oxidized to carbon (IV) oxide by microbial action, the heavy metals as chemical hazards do not undergo microbial or chemical degradation (Kirpichtchikova *et al.*, 2006) and their total concentration in soils persists for a long time after their introduction. Heavy metals that are most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg) and nickel (Ni) (Wuana and Okieimen, 2011). As chemical hazards, heavy metals are particularly notorious for their toxicity to humans, crops and other biological systems owing to their chemical reactivity, radioactivity and cumulative tendency in such systems (D'amore *et al.*, 2005).

The heavy metals, once introduced in the soil, are adsorbed by initial fast reactions followed by slow adsorption reactions and are, therefore, redistributed into different geochemical forms with varying bioavailability, mobility and toxicity (Shiowatana *et al.*, 2001). The total metal content of the soil, though an excellent criterion to define the extent of metal build up or degree of contamination in soil, is not a good indicator for metal availability to biota (Shiowatana *et al.*, 2001; Voegelin *et al.*, 2003; Rao *et al.*, 2008; Wuana *et al.*, 2009). In order to assess the bioavailability, hence toxicity, of heavy metals in soils, approaches involving only total metal content of soils have now been increasingly relegated in favour of those relating some kind of biological response to the available fraction of metal. Of these approaches, the sequential extraction procedures have been commonly used to study metal partitioning among the various solid phases of the soils and provide qualitative evidence regarding the metal forms and their bioavailability (Morera *et al.*, 2001; Rao *et al.*, 2008;). During sequential extraction, the soil sample is treated with a series of reagents in order to partition the heavy metal content among operationally defined fractions; which will be more or less, water-soluble, exchangeable/non-specifically sorbed, specifically sorbed, organically complexed, carbonate-bound, hydrous (Fe and Mn) oxide-bound, silicate-bound fractions (Rao *et al.*, 2008). Various fractionation schemes have been extensively used for heavy metal partitioning in the soil (Tessier *et al.*, 1979; Ure *et al.*, 1993; Ma and Rao, 1997; Salbu *et al.*, 1998; Maiz *et al.*, 2000; Kabala and Singh, 2001).

In Nigeria, though recent studies have investigated the partitioning of a number of heavy metals in waste dump soils from other urban areas in other regions of the country (Iwegbue, 2007; Umoren *et al.*, 2007; Uba *et al.*, 2008; Omuku *et al.*, 2009; Umoren and Udousoro, 2009; Yahaya *et al.*, 2009; Nwachukwu *et al.*, 2010; Osakwe, 2010; Achi *et al.*, 2011; Omotunde *et al.*, 2011), seasonal effects have not been reported. In north-central Nigeria, heavy metal fractionation studies, though conducted on soils in the vicinity of an Industrial Layout (Wuana *et al.*, 2009; Wuana and Okieimen, 2011), are yet to be extended to waste dumps. The objective of this study was, therefore, to assess the seasonal changes in the forms of Cd, Cu and Pb in dumpsite soils within Makurdi, a rapidly expanding city in north-central Nigeria using the modified Tessier et al's sequential extraction procedure.

Materials and methods

Chemicals and apparatus

Chemicals and apparatus used for the study included lead nitrate, copper nitrate, calcium chloride, glassware, weighing balance (Gallenkamp 80), pH meter (Fisher Hydrus 300 model), mechanical shaker (Model TT 12F, Techmel and Techmel, Texas, US), electric heater, centrifuge (Model TGL-16G, Shanghai, China), atomic absorption spectrophotometer (Buck Scientific Model 200A, Norwalk, Connecticut, US).

Study area

Makurdi is a rapidly growing city located at the coordinates 7.44°N, 8.33°E in the Lower Benue River Basin, a major agricultural zone in North-Central Nigeria (Fig 1). The city is the capital of Benue State and doubles as the headquarters of Makurdi Local Government Area (LGA). Though the land mass and census figures for urban Makurdi are difficult to retrieve, owing to its rapid expansion, Makurdi LGA has an approximate land mass of 804.35 km² and an estimated population of 297398 inhabitants (NPC, 2006). The inhabitants are engaged in civil, commercial, industrial and agricultural activities. The city is itself bisected by the Benue River into the North- and South-Bank areas. The soils are derived from Precambrian basement complex rocks and quaternary alluvial deposits of the River Benue as parent materials (Okezie, 1985). The range of annual rainfall is 1200 – 1650 mm and is distributed between March/April and October/November, followed by a marked dry season (of up to 4 months). The ranges of daily maximum and minimum temperatures during the rainy season are 30 – 34°C and 22 – 24°C, respectively and 33 – 37°C and 18 – 24°C, respectively in the dry season. Daily global irradiation and mean hours of insulation are, respectively, 314 – 433 cal.cm^2.day^{-1} and 4.00 – 7.74 h (Sha'Ato *et al.*, 2002). Solid wastes generated by humans and industries within the city are disposed at the waste dumps. Potential risks from heavy metal contamination of these soils as well as nearby water sources are possible.

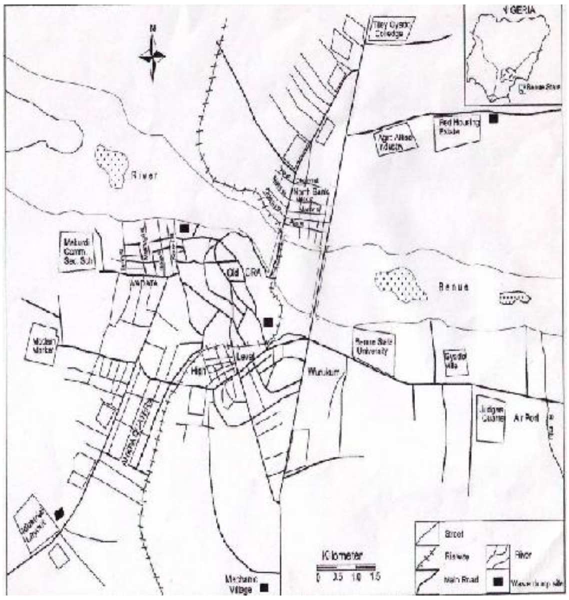


Fig. 1. Map of Makurdi town showing major waste dump sitee (Source: Ministry of Lands and Survey Makurdi, 2011).

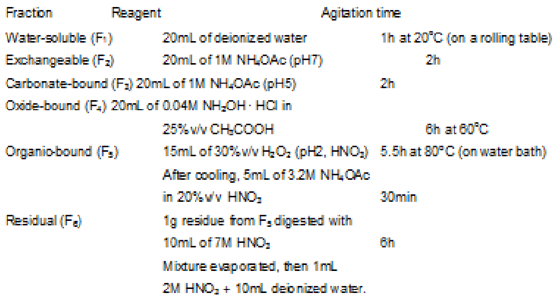
Soil sampling, pretreatment and characterization

Five top (0 – 15 cm) soil samples were randomly collected with the aid of a chrome-plated hand trowel at five different points from each of the three major waste dumps located at Apir Mechanic Village (AMV); Benue Industrial Layout (BIL) and Integrated Waste Dump (IWD) within Makurdi metropolis. Sampling was done in the dry (January) and wet (July) seasons in 2011. Soil samples were collected with the aid of a chrome-plated trowel into polythene bags and taken to the laboratory, air-dried, ground, sieved to give < 2mm particle size and composited. Standard operating procedures were used to test soil properties: pH (1:25 soil/water ratio) (Maxted *et al.*, 2007), particle size distribution by the hydrometer method (Bouyoucos, 1962); organic matter by the Walkley-Black rapid acid dichromate oxidation (Schumacher, 2002) and soil pseudototal metal by digestion with aqua regia (Golia *et al.*, 2007).

Sequential extractions to assess metal partitioning in soil

The procedure of Salbu *et al.* (1998) adopted by Kabala and Singh (2001), which is a modified version of Tessier *et al.* (1979), was used to separate the metals into six operationally defined fractions: water-soluble (F_1), exchangeable (F_2), carbonate-bound (F_3), Fe, Mn and Al oxide-bound (F_4), organic matter-bound (F_5) and residual (F_6). One gram of the air-dried soil sieved to obtain < 2 mm particle size was placed in a 15-mL polycarbonate centrifuge tube and extracted sequentially according to the scheme in Table 1. All solid phases (except F_6), were washed with 10 mL of water before the next extraction step. The washes were collected and analyzed with supernatant from the previous fraction. After each extraction, the supernatant was separated by high-speed centrifugation for 30 minutes at 10,000 x g. To verify the sum of sequential extraction, the pseudototal concentrations of Cu, Pb and Cd was determined after digestion with aqua regia (Golia *et al.*, 2007). The metals in the extract were assayed by flame atomic absorption spectrophotometry.

Table 1. Sequential extraction scheme used for heavy metal fractionation in soil (Kabala and Singh, 2001; Wuana *et al.*, 2009).



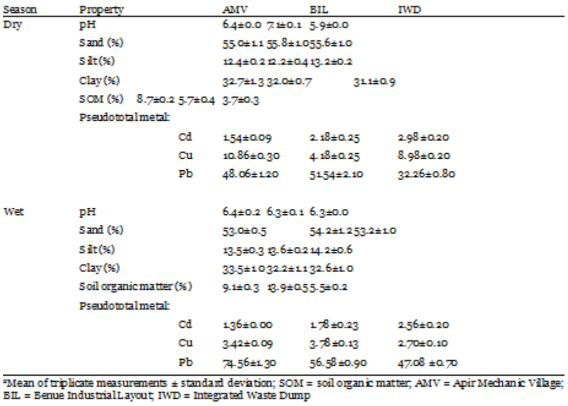
Fraction	Reagent	Agitation time
Water-soluble (F_1)	20mL of deionized water	1h at 20°C (on a rolling table)
Exchangeable (F_2)	20mL of 1M NH_4OAc (pH7)	2h
Carbonate-bound (F_3)	20mL of 1M NH_4OAc (pH5)	2h
Oxide-bound (F_4)	20mL of 0.04M $NH_2OH \cdot HCl$ in 25% v/v CH_3COOH	6h at 60°C
Organic-bound (F_5)	15mL of 30% w/v H_2O_2 (pH2, HNO_3)	5.5h at 80°C (on water bath)
	After cooling, 5mL of 3.2M NH_4OAc in 20% v/v HNO_3	30min
Residual (F_6)	1g residue from F_5 digested with 10mL of 7M HNO_3	6h
	Mixture evaporated, then 1mL 2M HNO_3 + 10mL deionized water.	

Results and discussion

Changes in soil physicochemical attributes

Some physicochemical properties of soils collected during the dry and wet seasons at at AMV, BIL and IWD all located in urban Makurdi are recorded in Table 2.

Table 2. Some properties[a] and pseudototal heavy metal levels of waste dumps soils in urban Makurdi collected in dry and wet seasons.



Season	Property		AMV	BIL	IWD
Dry	pH		6.4±0.0	7.1±0.1	5.9±0.0
	Sand (%)		55.0±1.1	55.8±1.0	55.6±1.0
	Silt (%)		12.4±0.2	12.2±0.4	13.2±0.2
	Clay (%)		32.7±1.3	32.0±0.7	31.1±0.9
	SOM (%)		8.7±0.2	5.7±0.4	3.7±0.3
	Pseudototal metal:				
		Cd	1.54±0.09	2.18±0.25	2.98±0.20
		Cu	10.86±0.30	4.18±0.25	8.98±0.20
		Pb	48.06±1.20	51.54±2.10	32.26±0.80
Wet	pH		6.4±0.2	6.3±0.1	6.3±0.0
	Sand (%)		53.0±0.5	54.2±1.2	53.2±1.0
	Silt (%)		13.5±0.3	13.6±0.2	14.2±0.6
	Clay (%)		33.5±1.0	32.2±1.1	32.6±1.0
	Soil organic matter (%)		9.1±0.3	13.9±0.5	5.5±0.2
	Pseudototal metal:				
		Cd	1.36±0.00	1.78±0.23	2.56±0.20
		Cu	3.42±0.09	3.78±0.13	2.70±0.10
		Pb	74.56±1.30	56.58±0.90	47.08 ±0.70

[a]Mean of triplicate measurements ± standard deviation; SOM = soil organic matter; AMV = Apir Mechanic Village; BIL = Benue Industrial Layout; IWD = Integrated Waste Dump

Across the waste dumps, ranges of soil pH in the dry and wet seasons were 5.9 ≤ pH ≤ 7.1 and 6.3 ≤ pH ≤ 6.4, respectively. Soil pH values recorded in the wet season are within the 6.0 ≤ pH ≤ 6.5 range proposed for ideal agricultural soils (Eriksson *et al.*, 1997). The soils were characterized by a sandy clay loam texture with the fractions ranging from 55.0 ≤ sand (%) ≤ 55.8; 12.2 ≤ silt (%) ≤ 13.2 and 31.1 ≤ clay (%) ≤ 32.7 during the dry season and 53.0 ≤ sand (%) ≤ 54.2, 13.5 ≤ silt (%) ≤ 14.2 and 32.2 ≤ clay (%) ≤ 33.5 in the wet season. Based on the organic matter content; the soils may be said to be mineral soils with soil organic matter (SOM) content falling in the range 0 ≤ SOM (%) ≤ 10. Actual ranges were found to be 3.71 ≤ SOM (%) ≤ 8.65 in the dry season and 5.54 ≤ SOM (%) ≤ 13.87 in the wet season.

Pseudototal Cd concentrations recorded in the dry season at AMV, IWD and BIL, respectively were 1.54, 2.18 and 2.98 mg kg^{-1}; while corresponding levels during the wet season were 1.36, 1.78 and 2.56 mg kg^{-1}. Pseudototal Cu levels in the soils during the dry season at AMV, IWD and BIL, respectively were 10.86, 4.18 and 8.98 mg kg^{-1}; while corresponding amounts during the wet season were 3.42, 3.78 and 2.70 mg kg^{-1}. In the case of Pb, 74.56, 56.58 and 47.08 mg kg^{-1}, respectively were found at AMV, IWD and BIL, respectively in the dry season and 48.06, 51.54 and 32.26 mg kg^{-1}, respectively during the wet season. Pseudototal metal levels appeared to be higher in the dry season than the wet season for all soil samples. The seasonal variations may be attributed to the dilution and run-off effects of rainfall which are capable of respectively leaching and removing the metals during the wet season. Furthermore, dumping and burning of wastes are a common practice at the dumpsites. This and the intense evaporation in the dry season concentrate the soil solution (Yahaya *et al.*, 2009). The pseudototal metal levels in the study soils appeared to follow the order: Cd < Cu < Pb and were lower than their corresponding upper critical levels – Cd (8 mg kg^{-1}), Cu (125 mg kg^{-1}) and Pb (400 mg kg^{-1}) (Maiz *et al.*, 2000). The critical total metal concentration in soil is defined as the range of values above which toxicity is considered to be possible (Maiz *et al.*, 2000). This implies that the study soils were moderately contaminated in terms of Cd, Cu and Pb. Pseudototal heavy metal content is an excellent criterion used to define the extent of metal build-up or degree of contamination of soil and provides an estimate of the degree of saturation of the total cation exchange capacity of soil colloids by metals.

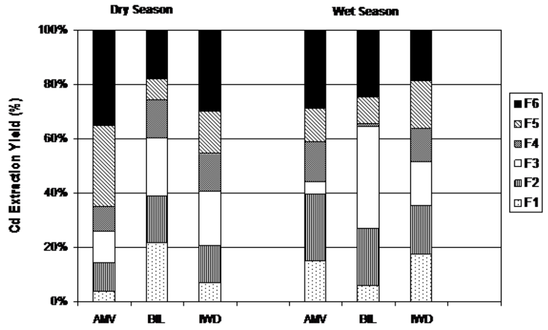


Fig. 2. Cd extraction yields (%) in operationally defined pools of soil at different dumpsites extracted by the modified Tessier *et al.* sequential procedure (F_1-water soluble, F_2- exchangeable, F_3-carbonate bound, F_4-Fe, Mn and Al oxide bound, F_5-organic matter-bound, and F_6-residual); AMV = Apir Mechanic Village; BIL = Benue Industrial Layout; IWD = Integrated Waste Dump.

Assessment of metal bioavailability in waste dump soils

Pseudototal metal levels become inadequate whenever an assessment of changes in the metal bioavailability status in the soil is intended. In this study, the modified Tessier *et al.*, (1979) sequential extraction procedure separated the metals into six operationally defined fractions: water-soluble (F_1), exchangeable (F_2), carbonate-bound (F_3), Fe, Mn and Al oxide-bound (F_4), organic matter-bound (F_5) and residual (F_6). Ma and Rao (1997) observed that metal bioavailability decreases in the order: $F_1 > F_2 > F_3 > F_4 > F_5 > F_6$. Metal concentrations (mg kg^{-1}) in the various fractions (Tables 3 – 5) were converted to extraction yields (%) by using the equation:

$$\text{Extraction Yield (\%)} = \frac{F_i}{\sum_{i=1}^{6} F_i} \text{x}\,100 \qquad (1)$$

where $\sum_{i=1}^{6} F_i = F_1 + F_2 + F_3 + F_4 + F_5 + F_6$. The results are illustrated in Figs 2 – 4.

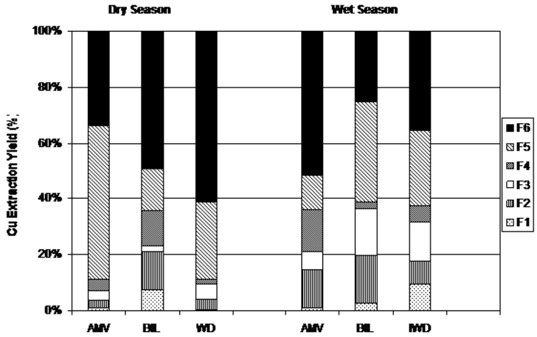


Fig. 3. Cu extraction yields (%) in operationally defined pools of soil at different dumpsites extracted by the modified Tessier et al's sequential procedure. (F_1-water soluble, F_2- exchangeable, F_3-carbonate bound, F_4-Fe, Mn and Al oxide bound, F_5-organic matter-bound, and F_6-residual); AMV = Apir Mechanic Village; BIL = Benue Industrial Layout; IWD = Integrated Waste Dump.

Salbu *et al.* (1998) considered F_1, F_2 and F_3 as constituting the most weakly bound metal species and defined the mobility factor, M_f (%) relative to their sum:

$$M_f = \left(\frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6}\right) x100 \qquad (2)$$

The efficiency of the sequential extraction scheme was assessed by comparing the sum of metal concentrations obtained as $\sum_{i=1}^{6} F_i$ with their pseudototal concentrations (aqua regia-extracted). This approach furnished recovery factors, R_f defined as:

$$R_f = \frac{F_1 + F_2 + F_3 + F_4 + F_5 + F_6}{\text{Pseudototal Concentration}} \quad (3)$$

Table 3. Mean Cd concentrations (mg kg^{-1}) in fractions of waste dump soils.

Season	Fraction, F_i	AMV	BIL	IWD
Dry	F_1	0.06 ± 0.02	0.46 ± 0.10	0.20 ± 0.05
	F_2	0.16 ± 0.03	0.36 ± 0.03	0.38 ± 0.07
	F_3	0.18 ± 0.00	0.46 ± 0.02	0.56 ± 0.15
	F_4	0.14 ± 0.05	0.30 ± 0.05	0.40 ± 0.09
	F_5	0.46 ± 0.07	0.16 ± 0.00	0.44 ± 0.10
	F_6	0.54 ± 0.15	0.38 ± 0.00	0.84 ± 0.10
	$\sum_{i=1}^{6} F_i$	1.54 ± 0.15	2.12 ± 0.20	2.86 ± 0.22
	R_f(%)	100	97	95
	M_f(%)	26	60	40
Wet	F_1	0.20 ± 0.03	0.10 ± 0.00	0.42 ± 0.05
	F_2	0.32 ± 0.05	0.34 ± 0.10	0.42 ± 0.07
	F_3	0.06 ± 0.02	0.62 ± 0.06	0.38 ± 0.00
	F_4	0.20 ± 0.00	0.02 ± 0.00	0.38 ± 0.03
	F_5	0.16 ± 0.02	0.16 ± 0.03	0.42 ± 0.08
	F_6	0.38 ± 0.10	0.40 ± 0.15	0.44 ± 0.01
	$\sum_{i=1}^{6} F_i$	1.32 ± 0.15	1.64 ± 0.40	2.38 ± 0.50
	R_f(%)	97	92	93
	M_f(%)	44	65	51

Mean of triplicate measurements ± standard deviation extracted by modified Tessier et al's sequential method (F_1-water soluble, F_2- exchangeable, F_3-carbonate bound, F_4-Fe, Mn and Al oxide bound, F_5-organic matter-bound, and F_6-residual) (Kabala and Singh, 2001; Wuana *et al.*, 2009); AMV = Apir Mechanic Village; BIL = Benue Industrial Layout; IWD = Integrated Waste Dump

Table 4. Mean Cu concentrations (mg kg^{-1}) in fractions of waste dump soils.

Season	Fraction, F_i	AMV	BIL	IWD
Dry	F_1	0.10 ± 0.00	0.28 ± 0.03	0.04 ± 0.00
	F_2	0.30 ± 0.01	0.52 ± 0.02	0.34 ± 0.10
	F_3	0.36 ± 0.02	0.08 ± 0.00	0.46 ± 0.05
	F_4	0.44 ± 0.04	0.48 ± 0.08	0.16 ± 0.02
	F_5	5.98 ± 0.10	0.58 ± 0.05	2.48 ± 0.14
	F_6	3.64 ± 0.15	1.88 ± 0.13	5.58 ± 0.20
	$\sum_{i=1}^{6} F_i$	10.82 ± 0.30	3.82 ± 0.20	8.96 ± 0.21
	R_f(%)	100	91	100
	M_f(%)	7	23	9
Wet	F_1	0.04 ± 0.00	0.12 ± 0.02	0.26 ± 0.03
	F_2	0.46 ± 0.15	0.70 ± 0.20	0.22 ± 0.01
	F_3	0.22 ± 0.05	0.70 ± 0.10	0.38 ± 0.13
	F_4	0.52 ± 0.10	0.10 ± 0.01	0.16 ± 0.01
	F_5	0.42 ± 0.08	1.50 ± 0.05	0.74 ± 0.15
	F_6	1.78 ± 0.20	1.04 ± 0.07	0.96 ± 0.12
	$\sum_{i=1}^{6} F_i$	3.44 ± 0.20	4.16 ± 0.20	2.72 ± 0.09
	R_f(%)	101	110	101
	M_f(%)	21	37	32

Mean of triplicate measurements ± standard deviation extracted by modified Tessier et al's sequential method (F_1-water soluble, F_2- exchangeable, F_3-carbonate bound, F_4-Fe, Mn and Al oxide bound, F_5-organic matter-bound, and F_6-residual) (Kabala and Singh, 2001; Wuana *et al.*, 2009); AMV = Apir Mechanic Village; BIL = Benue Industrial Layout; IWD = Integrated Waste Dump

Water-soluble metal forms

This fraction contains the water soluble species made up of free ions and ions complexed with soluble organic matter and other constituents. The water-soluble metal forms, F_1 extracted in the dry season at AMV, BIL and IWD, respectively during the dry season were Cd: 4, 22 and 7 %; Cu: < 1, 7 and < 1 %; Pb: 11, 18 and 7 %. In the wet season corresponding yields were Cd:15, 6 and 18 %, Cu: 1, 3 and 10% and Pb: 19, 19 and 2%, respectively. This fraction constitutes the most mobile and potentially the most bioavailable metal and metalloid species (Rao *et al.*, 2008). The unusually high yields of Pb in this fraction suggest that it was introduced anthropogenically.

Table 5. Mean Pb concentrations (mg kg^{-1}) in fractions of waste dump soils.

Season	Fraction, F_i	AMV	BIL	IWD
Dry	F_1	7.72 ± 0.13	9.78 ± 0.30	3.26 ± 0.05
	F_2	8.90 ± 0.12	10.98 ± 0.42	5.34 ± 0.10
	F_3	9.78 ± 0.15	6.22 ± 0.05	8.30 ± 0.35
	F_4	4.74 ± 0.05	5.04 ± 0.18	9.50 ± 0.42
	F_5	18.98 ± 0.50	7.12 ± 0.15	9.20 ± 0.34
	F_6	22.24 ± 0.15	15.42 ± 0.15	9.50 ± 0.25
	$\sum_{i=1}^{6} F_i$	72.36 ± 1.00	54.56 ± 1.30	45.10 ± 0.80
	R_f(%)	97	96	96
	M_f(%)	37	50	40
Wet	F_1	8.90 ± 0.20	9.20 ± 0.35	0.60 ± 0.05
	F_2	7.72 ± 0.15	6.22 ± 0.25	10.08 ± 0.20
	F_3	6.42 ± 0.35	6.52 ± 0.20	1.18 ± 0.10
	F_4	8.60 ± 0.20	7.72 ± 0.30	4.12 ± 0.10
	F_5	7.12 ± 0.15	7.72 ± 0.06	12.16 ± 0.40
	F_6	7.12 ± 0.20	12.16 ± 0.30	2.02 ± 0.02
	$\sum_{i=1}^{6} F_i$	45.98 ± 1.10	49.52 ± 1.20	30.22 ± 0.50
	R_f(%)	96	96	94
	M_f(%)	50	44	39

Mean of triplicate measurements ± standard deviation extracted by modified Tessier et al's sequential method (F_1-water soluble, F_2- exchangeable, F_3-carbonate bound, F_4-Fe, Mn and Al oxide bound, F_5-organic matter-bound, and F_6-residual) (Kabala and Singh, 2001; Wuana *et al.*, 2009); AMV = Apir Mechanic Village; BIL = Benue Industrial Layout; IWD = Integrated Waste Dump

Exchangeable metal forms

The exchangeable metal form, F_2 provides a measure of those heavy metals which are released most readily into the environment. Approximately 10, 17 and 13 % of Cd; 3, 2 and 5 % of Cu; and 12, 20 and 12 % of Pb were extracted as F_2 in soils at the AMV, BIL and IWD, respectively during the dry season; while corresponding extraction yields were recorded as 24, 21 and 18 % of Cd; 13, 17 and 8% of Cu and 17, 13 and 33% of Pb in the wet season.

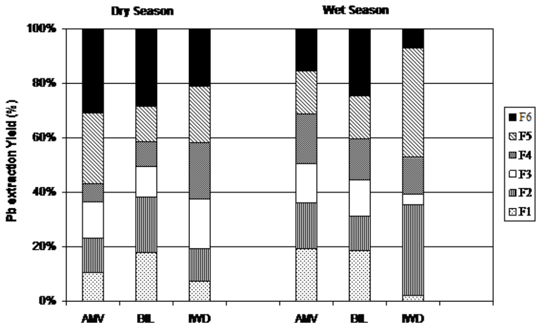


Fig. 4. Pb extraction yields (%) in operationally defined pools of soil at different dumpsites extracted by the modified Tessier et al's sequential procedure (F_1-water soluble, F_2- exchangeable, F_3-carbonate bound, F_4-Fe, Mn and Al oxide bound, F_5-organic matter-bound, and F_6-residual); AMV = Apir Mechanic Village; BIL = Benue Industrial Layout; IWD = Integrated Waste Dump.

Carbonate-bound metal forms

This phase contains loosely bound metals and may become important when the hydrous oxides and organic matter in the soil is low. The carbonate-bound fraction, F_3 retained the metals to the extent of 12, 22 and 20 % Cd; 3, 2 and 5 % Cu; and 14, 11 and 18 % Pb in soils collected at AMV, BIL and IWD, respectively during the dry season. In the wet season, corresponding extraction yields were 5, 38 and 16 % Cd, 6, 17 and 14 % Cu and 14, 13 and 4 % Pb, respectively.

The mobility factor, M_f has been defined in terms of the sum ($F_1 + F_2 + F_3$). During the dry season, M_f were calculated as Cd: 20, 60 and 40 %; Cu: 7, 23 and 9%; Pb: 37, 50 and 40 % in soils at AMV, BIL and IWD; while corresponding values in the wet season were Cd: 44, 65 and 51 %; Cu: 21, 37 and 32 %; and Pb: 50, 44 and 39 %. With the exception of Pb; higher M_f were recorded in the wet season than dry season probably due to accelerated metal leaching into the soil by rainfall with attendant increase in metal concentration in the soil solution. Considering the sites, M_f appeared to vary as: BIL > IWD > AMV; and based on the metals, M_f values appeared to follow the order: Cd > Pb > Cu. The latter sequence can be explained by the possible occurrence of Cd and Pb as Cd^{2+} and Pb^{2+}; and Cu as metallic Cu at the pH range 5.9 – 7.1 recorded for the dumpsite soils (Rastmanesh *et al.*, 2010). That Cd recorded the highest M_f among the metals investigated corroborates previous investigations (Rastmanesh *et al.*, 2010) and suggests the potential high risk of this toxic and non-essential element to biota.

Hydrous (Fe, Mn, Al) oxide-bound metal forms

The proportion of Cd and Cu likely associated with the hydrous (Fe, Mn, Al) oxide phase, F_4 of soils at the Industrial Layout and Integrated dumpsite appeared somewhat higher in the dry season than wet season. Extraction yields of Pb in this fraction were, however, consistently higher in the wet season than dry season in all the sites. Metal sorption by hydrous oxides occurs via the formation of inner-sphere metal surface complexes and formation of metal hydroxide precipitate phases and is a major mechanism for removal of heavy metals from soil solution.

Organic matter-bound metal forms

Cadmium appeared to have the least extraction yields as the organic matter-bound form, F_5, with its extractability appearing higher in the dry season than wet season at all the sites. Copper showed higher extraction yields in this fraction in the dry season than wet season at AMV and IWD; while the same observation was recorded for Pb at the AMV. Depending on the metals, extraction yields in this fraction followed the order: Cu > Pb > Cd. This trend is explicable in terms of formation of strong inner-sphere complexes by Cu and Pb as a result of a very strong affinity for soil organic matter due the favourable electronic properties of Cu and Pb. Strong metal adsorption by soil organic matter by formation of metal chelates reduces metal solubility in soil.

Residual metal forms

Residual metal forms are retained in the soil silicate matrix. Approximately 29, 24 and 19 % of Cd constituted the residual form, F_6 in soils collected at

AMV, BIL and IWD, respectively during the wet season. These proportions were raised to 35 and 30 % at AMV and IWD, but reduced to 20 % at the BIL during the dry season. Approximately 52, 25 and 35 % of Cu occurred as the residual form, F_6 in soils collected at AMV, BIL and IWD, respectively during the wet season. These proportions were raised to 49 and 61% at BIL and IWD, but reduced to 33 % at AMV during the dry season. The residual form of Pb, F_6, constituted about 16, 25 and 7 % of total Pb in soils collected at AMV, BIL and IWD, respectively during the wet season. Corresponding proportions were raised to 31, 28 and 21% during the dry season.

Overall, there were marked differences in the partitioning patterns of Cd, Cu and Pb among the waste dumps possibly due to different anthropogenic sources of these metals coupled with seasonal changes. In terms of metal extraction yields (%), the metal distribution patterns (Figs 2 – 4) in the dry season appeared to vary as: AMV ($F_1 > F_4 > F_5 \approx F_6 > F_2 > F_3$); BIL ($F_6 > F_1 > F_5 > F_4 > F_3 > F_1$) and IWD ($F_5 > F_2 > F_4 > F_6 > F_3 > F_1$). In the wet season corresponding variations were: AMV ($F_6 > F_5 > F_3 > F_2 > F_1 > F_4$); BIL ($F_6 > F_2 > F_1 > F_5 > F_3 > F_4$); IWD ($F_6 > F_4 > F_5 > F_3 > F_2 > F_1$). The patterns suggest that Cd, Cu and Pb were mostly associated with the residual fraction compared with any of the individual fractions during the sequential extractions.

Recovery factors, R_f (%) ranging as Cd ($92 \leq R_f(\%) \leq 100$); Cu ($91 \leq R_f(\%) \leq 100$ %) and Pb ($94 \leq R_f(\%) \leq 97$ %) were all within ±10 % indicating a good agreement between the sequential extraction and aqua regia extraction method for pseudototal metals and that the cumulative error in the sequential fractionation procedure was reasonably low.

Conclusion

This study has revealed that the waste dump soils of urban Makurdi were essentially mineral soils with sandy clay loam texture, moderately contaminated with Cd (1.36 – 2.98 mg kg^{-1}), Cu (2.70 – 10.86 mg kg^{-1}) and Pb (32.26 – 74.56 mg kg^{-1}). Metal forms and their partitioning in the soils varied markedly among the waste dumps possibly due to different anthropogenic sources of these metals coupled with seasonal effects. The metals were more bioavailable in the wet than dry season. Across the waste dumps metal bioavailability followed the order: BIL > IWD > AMV. Depending on the metal, mobility factors, M_f were high enough and appeared to vary in the order: Cd ($20 \leq M_f(\%) \leq 65$) > Pb ($37 \leq M_f(\%) \leq 50$) > Cu ($7 \leq M_f(\%) \leq 37$) suggesting the potential long-term risk of these elements (especially Cd) in the soils.

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