

## Chemical speciation and mobility of heavy metals in soils of refuse dumpsites in some urban towns in the Niger Delta of Nigeria

Godswill O. TESI\*,<sup>1</sup> Joshua O. OJEGU,<sup>2</sup> and Samuel O. AKPORIDO<sup>3</sup>

<sup>1</sup>Department of Chemical Sciences, University of Africa, Toru-Orua, Bayelsa State, Nigeria

<sup>2</sup>Department of Chemistry, Delta State University, P.M.B.1 Abraka, Delta State, Nigeria

<sup>3</sup>Department of Chemistry, Taraba State University, Jalingo, Taraba State, Nigeria

**Abstract.** Refuse dumpsites often contain materials which are capable of polluting surrounding soils especially if the dumpsites are not adequately shielded from the surrounding area. This study examined chemical speciation and mobility of heavy metals in three urban towns in the Niger Delta. Soil samples were collected from three dumpsites in each of the three selected urban towns at 0-15 cm, 15-30 cm and 30-45 cm depths. The chemical speciation of the heavy metals in the soils was determined using the Tessier's sequential extraction procedure. The results showed that on the average, the residual fraction was the predominant fraction of all the metals except Pb which was dominant in the organic fraction. The mobility factor followed the order Zn > Fe > Pb > Cr > Ni > Cd > Cu. The study indicates that the metals studied do not pose environmental risk considering their relatively low concentrations and the chemical forms they are associated with. It is however recommended that the sites be continuously monitored because of the deleterious health effects of exposure to heavy metal pollution in the events of reclaim.

**Keywords:** heavy metals; speciation; mobility; dumpsite; soil; Niger Delta.

### 1. Introduction

Soil acts as a sink for contaminants and natural buffer for transportation and distribution of chemical materials and elements in the atmosphere, hydrosphere and biomass, and is thus regarded as the most important component of biosphere [1]. The presence of heavy metals in soils is of environmental, ecological and human health importance because they do not degrade, persistent and toxic in nature. The concentrations of total heavy metals in soil can be an indicator to measure or evaluate the degree of contamination and/or pollution of the soil. However, the information provided by the total heavy metal concentrations is limited since it does not give the specific forms of the heavy metals in the soil and their impact on the environment [2, 3]. The fate or behaviour, mobility, availability, and toxicity of heavy metals in soil are not only a function of the total heavy metal concentration but also a function of other parameters like the specific chemical forms, binding state, metal characteristic, environmental and soil characteristics like pH, the content of total organic matter, cation exchange capacity, redox conditions and root exudates acting as chelates [3]. Thus, chemical speciation is crucial to assess heavy metal behaviour and impact on the environment.

Heavy metals are present in different chemical forms in soils namely: water soluble/exchangeable, carbonates, bound to Fe, Mn and Al oxides/hydroxides, bound to organic matter and residual forms [4]. The mobility and bioavailability of heavy metals in water

soluble/exchangeable and carbonates forms are very high, while for those bound to Fe, Mn and Al oxides/hydroxides, bound to organic matter and residual forms are very low and they are relatively not bioavailable [4]. Although, heavy metals bound to Fe-Mn oxides/hydroxides or bound to organic matter can be relatively mobile or strongly bound, depending on the physicochemical characteristics of the soils [2].

Several studies have been conducted to determine the chemical speciation and mobility of heavy metals in soil of dumpsites in different parts of Nigeria. However, only a few studies [5-8] have been carried out in the Niger Delta area. Therefore, information regarding chemical forms of heavy metals in soils of dumpsites in the Niger Delta is still scanty. Thus, the objective of the present study is to determine the chemical speciation and mobility of heavy metals in soils of refuse dumpsites in some urban towns in the Niger Delta of Nigeria.

### 2. Experimental

#### 2.1. Description of study area

A detailed description of the study area has been reported elsewhere [9]. Briefly, the study area comprised of three urban towns of Ughelli (UGH) which lies within Longitude 5.30° N and Latitude 5.59° E, Sapele (SAP) which lies within Longitude 5.54° N and Latitude 5.54° E, and Orhuwhorun (UDU) which lies within Longitude 5.45° N and Latitude 5.43° E in the Niger Delta of Nigeria. The map of the study area is shown in Figure 1.

\*Corresponding author. E-mail addresses: godswillinfodesk@yahoo.com; godswill.tesi@uat.edu.ng (Godswill O. Tesi)

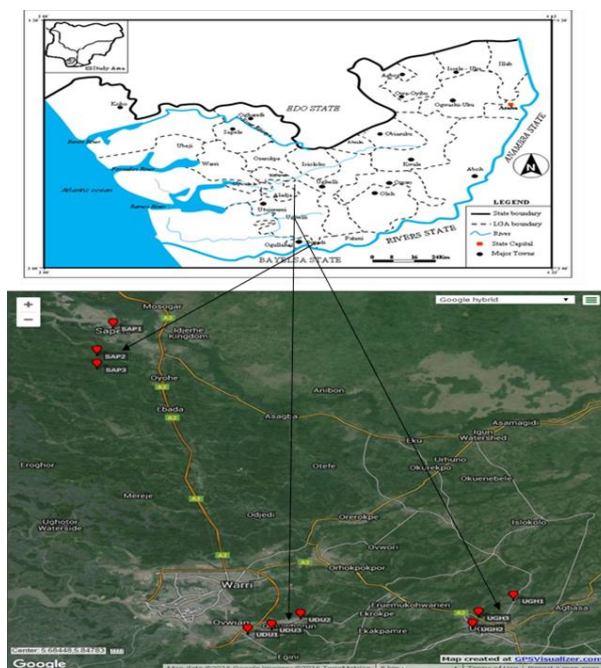


Figure 1. Map of the study area

## 2.2. Sample collection

Soil samples were collected using soil corer from three dumpsites each from the three urban towns, totalling nine dumpsites. Soil samples were collected at 0-15 cm, 15-30 cm and 30-45 cm depths. Soil samples were air dried, sieved (< 2 mm) and stored at 4 °C prior to analysis.

## 2.3. Reagents

The reagents used in this study include: nitric acid (HNO<sub>3</sub>) (Merck, USA), magnesium chloride (MgCl<sub>2</sub>) (Fisher Scientific, USA), sodium acetate (NaCH<sub>3</sub>COO) (Fisher Scientific, USA), acetic acid (CH<sub>3</sub>COOH) (Fisher Scientific, USA), hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) (Merck, USA), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (Merck, USA) and ammonium acetate (NH<sub>4</sub>CH<sub>3</sub>COO) (Merck, USA).

## 2.4. Determination of some soil physicochemical properties

The soil pH was determined in soil suspension (1:2 soil to water ratio) using a glass electrode pH meter. The soil electrical conductivity (EC) was determined in soil suspension (1:2 soil to water ratio) using a conductivity meter. The total organic carbon of the soil was determined by the wet oxidation digestion method of Walkley and Black [10] as described by Radojevic and Bashkin [11]. Total metal concentrations were determined using air-acetylene atomic absorption spectrophotometry (Perkin Elmer Analyst 200) after digestion with *aqua regia* as described Radojevic and Bashkin [11].

## 2.5. Chemical speciation of metals in soil

For the chemical speciation of the metals under study, the procedure of Tessier *et al.* [12] was employed. In this method heavy metals were separated into five operationally defined fractions (F1-F5).

1 g of the soil sample was weighed and extracted into five fractions as follows:

1. **F1 - Exchangeable:** the soil sample was extracted at room temperature for 1 h with 8 ml of 1 M MgCl<sub>2</sub> solution at pH 7.0 with continuous agitation;
2. **F2 - Metals bound to carbonates:** the residue from step (1) was extracted at room temperature with 8 ml of 1 M NaCH<sub>3</sub>COO solution adjusted to pH 5.0 with 0.5 M CH<sub>3</sub>COOH solution. Continuous agitation was maintained;
3. **F3 - Metals bound to Fe-Mn oxide:** the residue from step (2) was extracted with 20 ml of 0.04M NH<sub>2</sub>OH·HCl in 25% (v/v) CH<sub>3</sub>COOH and was heated to 96 °C with occasional agitation for 6 h;
4. **F4 - Metals bound to organic matter:** the residue from step (3) was extracted with 3 ml of 0.02 M HNO<sub>3</sub> and 5 ml of 30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 2.0 with HNO<sub>3</sub>, and the mixture was heated to 86 °C for 3 h with intermittent agitation. The mixture was cooled and 5 ml of 3.2 M NH<sub>4</sub>CH<sub>3</sub>COO in 20% (v/v) HNO<sub>3</sub> were added and the solution was then be diluted to 20 ml and agitated continuously for 30 min;
5. **F5 - Residual metals:** the residue from step (4) was digested with 15 ml of *aqua regia*.

After each successive extraction, the supernatant solution was separated by centrifuging the suspension at 7,500 rpm for 30 min and filtering through Whatman 42 filter paper. The concentration of Cd, Pb, Zn, Ni, Cu, Fe and Cr was determined using atomic absorption spectrometer (Perkin Elmer Analyst 200).

The wavelength (analytical lines) used for each metal were 228.8 nm, 283.31 nm, 357.9 nm, 232.0 nm, 324.8 nm, 213.9 nm and 248.3 nm for Cd, Pb, Cr, Ni, Cu, Zn and Fe respectively. The instrument conditions are as follows: the slit was 0.7 nm for Cd, Pb, Cr, Cu and Zn but 0.2 nm for Ni and Fe; the lamp current (mA) were 10 for Cd, 8 for Pb, 12 for Cr, 30 for Ni, 25 for Cu, 15 for Zn and Fe; the flame used for all the metals analysis was composed of air (9.5 l/min) and acetylene (2.3 l/min).

The limit of detection (LOD) was 0.01 mg kg<sup>-1</sup> for Cd, Cr, Ni and Cu, 0.08 mg kg<sup>-1</sup> for Pb, 0.60 mg kg<sup>-1</sup> for Zn and 0.15 mg kg<sup>-1</sup> for Fe. The percentage recoveries for the metals were in the range of 90.8 to 97.9 % while the linear range of the calibration curve for the metals were 0.01 to 2.0 mg l<sup>-1</sup>, 0.1 to 10.0 mg l<sup>-1</sup>, 0.1 to 7.0 mg l<sup>-1</sup>, 0.1 to 4.0 mg l<sup>-1</sup>, 0.1 to 7.0 mg l<sup>-1</sup>, 0.1 to 10.0 mg l<sup>-1</sup> and 0.1 to 40.0 mg l<sup>-1</sup> for Cd, Pb, Cr, Ni, Cu, Zn and Fe respectively.

## 2.6. Quality assurance programme

Sterilized and disposable rubber gloves were worn during analysis. All the bottles for metal analysis were washed with metal free detergent and sterilized by soaking with 10 % HNO<sub>3</sub> analar grade overnight and then rinsed several times with distilled water. For every six samples, procedural blank was used for monitoring interferences and cross contaminations, all results were blank-corrected. Also, in the QA/QC programme, the instrument was calibrated with calibration standards before use. Matrix matching and background correction was used to overcome interference in metal analysis.

### 3. Results and discussion

#### 3.1. Physicochemical properties and total heavy metals concentrations of soil samples

The summary statistics of some physicochemical properties and total heavy metals concentrations in soils of the refuse dumpsites investigated in this study are shown in Table 1.

**Table 1.** Summary statistics of some physicochemical properties and total heavy metals concentrations (mg kg<sup>-1</sup>) in the dumpsite soils

Parameters	pH	EC (μl/cm)	TOC (%)	Cd	Pb	Cr	Ni	Cu	Zn	Fe
Minimum	4.64	60.8	0.06	ND	9.00	4.20	1.00	1.00	18.5	1650
Maximum	7.85	451	1.49	4.50	149	15.4	14.5	124	510	11865
Mean	6.83	176	0.45	1.93	44.5	9.25	3.75	26.9	157	5011
SD	0.93	105	0.35	1.09	44.4	3.12	3.25	33.8	161	2410
Kurtosis	0.17	1.91	2.32	0.14	0.40	-0.56	3.14	1.70	-0.51	1.64
Skewness	-1.08	1.44	1.50	0.63	1.29	0.36	1.59	1.38	0.91	1.35

SD = standard deviation

#### 3.2. Chemical speciation of metals in soil samples

The results of the heavy metal concentrations in the various chemical forms are shown in Table 2, while the speciation patterns of the heavy metals are displayed in

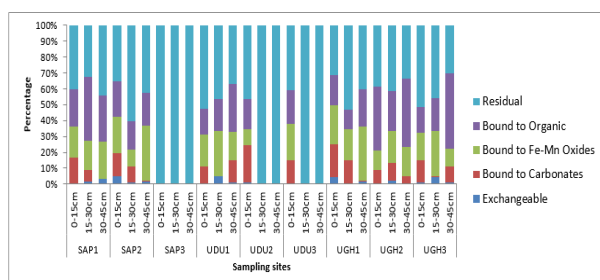
Figures 2-8. There was significant variation ( $p < 0.05$ ) in the speciation patterns of the heavy metals with respect to sampling sites and depths.

**Table 2.** Concentrations (mg kg<sup>-1</sup>) of heavy metals in the different extraction forms in the dumpsite soils

SITES	DEPTH	Cd										Pb					Cr					Ni																																											
		F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5																																							
SAP1	0-15 cm	0.04	0.31	0.17	0.35	0.64	1.83	0.3	2.18	3.04	9.16	0.87	1.07	1.85	2.36	4.06	0.03	0.36	1.03	0.41	0.7	SAP2	0-15 cm	ND	ND	ND	ND	1.00	7.28	0.53	6.21	5.43	16.1	0.32	1.09	1.32	2.92	1.53	0.49	1.55	1.25	0.65	2.06	SAP3	0-15 cm	0.03	0.36	0.15	0.35	0.61	2.05	0.12	1.13	2.93	3.77	0.09	0.86	1.30	1.42	3.93	0.02	0.10	0.21	0.30	0.38
	15-30 cm	ND	ND	ND	ND	1.40	2.17	1.24	0.17	2.48	5.94	0.11	1.13	1.80	0.54	0.83	0.01	0.28	0.33	0.15	0.74		UDU1	0-15 cm	ND	ND	ND	ND	0.50	9.95	1.17	4.55	6.71	22.6	0.01	1.23	1.51	2.44	1.31	0.03	0.16	0.14	0.23		0.44																				
	15-30 cm	ND	ND	ND	ND	0.50	5.40	0.59	3.21	8.36	4.28	0.46	1.43	3.56	2.48	5.47	0.17	0.03	0.58	0.29	0.43																																												
30-45 cm	0.01	0.20	0.4	0.16	0.23	5.83	2.74	4.38	7.15	11.4	0.07	2.31	1.63	7.43	2.75	0.46	0.09	2.01	0.57	1.89	UDU2	0-15 cm		ND	ND	ND	ND	0.20	1.70	3.61	0.20	2.23	3.17	0.10	0.11	0.48	0.60	6.60	0.01	0.15	0.76	0.23	0.35																						
15-30 cm	0.06	0.09	0.19	0.03	0.13	2.86	0.18	1.68	3.26	8.02	1.05	0.16	1.79	3.80	2.89	0.11	0.26	0.45	0.37	0.81																																													
30-45 cm	ND	ND	ND	ND	0.20	2.43	0.41	3.02	3.32	7.33	0.69	1.29	1.09	2.31	5.22	0.09	0.01	0.31	0.37	0.72																																													
UDU3	0-15 cm	ND	ND	ND	ND	0.50	6.53	0.22	8.15	10.7	28.4	0.08	0.75	1.99	0.85	0.94	ND	0.05	0.11	0.07	0.76	UGH1	0-15 cm	0.02	0.34	0.09	0.22	1.35	8.26	5.88	14.1	12.9	28.8	0.12	1.61	1.02	1.99	5.36	0.04	0.37	0.73	0.57	1.30																						
	15-30 cm	0.04	0.48	0.53	0.38	1.07	25.4	13.8	10.2	52.1	29.5	0.04	1.10	2.81	2.00	3.95	0.04	0.85	1.00	2.87	1.24																																												
	30-45 cm	0.4	0.77	0.52	0.16	1.16	8.53	0.18	11.0	9.86	30.9	0.33	2.20	1.95	2.95	6.77	0.25	0.80	2.14	1.78	2.54																																												
UGH2	0-15 cm	0.01	0.20	1.37	0.55	0.88	19.6	1.57	17.6	22.3	51.0	3.22	0.21	1.58	7.29	2.61	0.28	2.87	2.38	2.99	5.99	UGH3	0-15 cm	0.02	0.22	0.07	0.22	0.48	18.8	1.34	31.0	27.0	70.9	0.54	1.28	1.68	1.75	3.24	0.56	0.81	1.14	2.14	3.31																						
	15-30 cm	0.10	0.01	0.85	0.42	1.63	17.2	18.9	11.1	50.4	33.4	0.94	0.08	1.35	3.92	3.71	0.22	0.97	3.77	2.59	1.95																																												
	30-45 cm	0.01	0.49	0.59	1.13	2.27	27.1	1.47	13.5	24.7	67.3	0.11	1.05	3.31	2.07	1.66	0.07	0.43	0.83	0.72	1.95																																												

SITES	DEPTH	Cu					Zn					Fe																					
		F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5																	
SAP1	0-15 cm	0.02	0.65	0.79	0.94	1.61	68.1	51.8	107	42.8	138	7.80	874	694	534	1790	SAP2	0-15 cm	0.04	0.23	0.55	1.21	0.98	4.38	3.99	15.9	7.19	8.06	586	2017	996	20.2	1436
	15-30 cm	0.14	0.01	1.04	1.32	1.98	4.09	7.03	3.48	4.72	4.18	58.3	977	880	510	2435																	
	30-45 cm	3.49	9.86	15.8	15.3	23.98	79.5	36.6	58.5	34.2	91.2	559	2125	1411	149	1290																	
SAP3	0-15 cm	0.09	1.11	1.18	2.00	6.62	10.6	9.42	11.0	19.9	13.6	95.8	579	1604	443	1269	UDU1	0-15 cm	0.04	0.01	0.87	0.51	1.06	3.64	2.00	2.79	2.26	7.81	22.8	1208	345	422	852
	15-30 cm	ND	ND	ND	ND	ND	2.50	6.10	8.13	21.1	7.65	10.5	252	820	514	10.1		1764															
	30-45 cm	ND	ND	ND	ND	ND	9.50	6.35	4.12	6.67	7.53	10.8	46.3	1612	1187	451		914															
UDU2	0-15 cm	0.40	6.93	13.1	11.0	34.58	4.45	5.04	12.0	3.16	4.90	419	777	1413	27.5	801	UDU3	0-15 cm	0.05	ND	0.28	0.20	0.46	4.03	7.39	3.43	4.79	13.4	35.8	772	2126	261	1916
	15-30 cm	0.03	0.34	0.46	0.75	0.93	22.3	19.3	50.0	14.5	26.9	298	4244	1418	980	1811																	
	30-45 cm	0.01	0.23	0.1	0.19	0.46	25.3	16.8	29.2	22.4	71.3	393	569	368	117	1342																	
UGH1	0-15 cm	ND	ND	ND	ND	2.40	5.25	9.45	8.40	7.25	19.7	239	1196	361	634	940	UGH2	0-15 cm	ND	ND	ND	ND	1.70	4.93	5.22	3.71	4.10	18.0	15.2	612	570	639	1194
	15-30 cm	0.01	0.29	0.46	0.43	0.82	10.7	11.5	20.9	13.4	14.6	585	1737	740	191	1178																	
	30-45 cm	ND	ND	ND	ND	3.30	9.88	11.2	10.3	5.66	18.5	123	1514	982	757	3444																	
UGH3	0-15 cm	1.10	5.20	6.08	4.78	7.85	52.7	40.2	49.3	37.9	105	115	292	554	632	1217	UGH3	0-15 cm	0.48	5.56	6.96	6.32	20.7	51.7	34.5	44.3	36.8	171	132	1089	910	878	2251
	15-30 cm	0.84	0.10	5.45	3.84	8.78	53.5	50.0	31.9	27.6	110	208	1756	695	570	932																	
	30-45 cm	0.10	1.30	1.36	5.95	3.79	103	65.8	81.1	93.8	167	13.4	665	491	942	1229																	

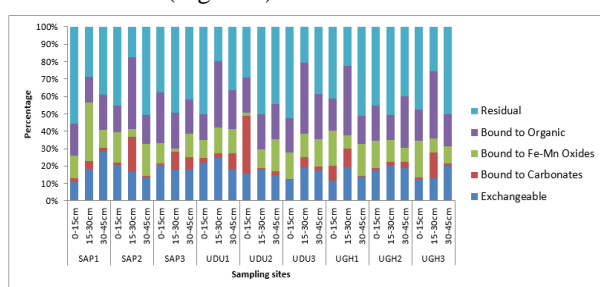
**Cadmium** was present mostly in the residual fraction (Figure 2).



**Figure 2.** Speciation pattern of Cd in the dumpsite soils

The percentage of Cd in the residual fraction in these soil profiles ranged from 21.1 to 100%. According to Osakwe [5] a relatively high percentage of Cd in the residual fraction suggests lithogenous origin and cannot be mobilized. Similar results have been reported by other researchers in literature [2, 5, 13, 14]. The next important fraction for Cd was Fe–Mn oxide fraction. The percentage of Cd in the Fe–Mn oxide fraction ranged from 6.8 to 45.5%; this is expected as Cd correlated well with Fe. The presence of Cd in this fraction may be due to the fact that Fe–Mn oxides control the fixation of Cd in these soils. The Fe–Mn oxides fraction is relatively stable but could change with variation in redox condition [5, 13]. Cd in the Fe–Mn oxide fraction has also been reported by Zuayah *et al.* [15], Hosfall and Spiff [13], and Osakwe [5]. The percentage of Cd in the carbonate and organic fractions ranged from 0.4 to 41.1% and 5.3 to 25.2% respectively, while the percentage of Cd in the exchangeable fraction ranged from 0.1 to 13.3%. This result is similar to others in the literature [3, 5]. The percentage of Cd in the exchangeable fraction indicates that Cd is potentially available to some extent in these soil profiles.

**Lead** partition was predominantly in the organic bound fraction (Figure 3).

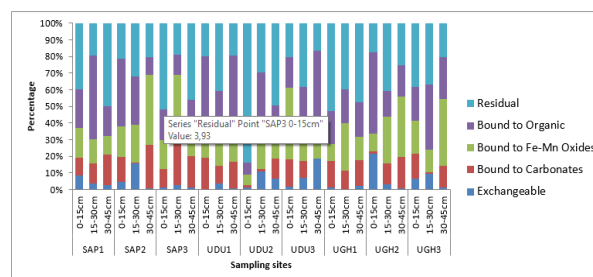


**Figure 3.** Speciation pattern of Pb in the dumpsite soils

The percentage of Pb in the organic fraction ranged from 17.4 to 55.5%. The high distribution of Pb in this fraction is as a result of the strong complexes lead formed with humic minerals [16]. The next dominant fraction of Pb in these soil profiles is Fe–Mn oxides fraction. The percentage of Pb in the Fe–Mn oxides fraction range from 14.1 to 41.6%. Higher amount of Pb in the Fe–Mn oxide fraction was also reported by Iwegbue *et al.* [17] and Iwegbue [18]. The exchangeable form of Pb was the next important fraction with a range of 11.2 to 28.4% of Pb. Metals in this fraction are

soluble and easily released into biota. The accumulation of Pb in this fraction call for concern as Pb is one of the metal that constitutes the widest possible health risk to humans through the plant uptake dietary route [16, 19]. The percentage of Pb in the residual and carbonate fraction ranged from 1.4 to 33.9% and 0.3 to 30.1% respectively.

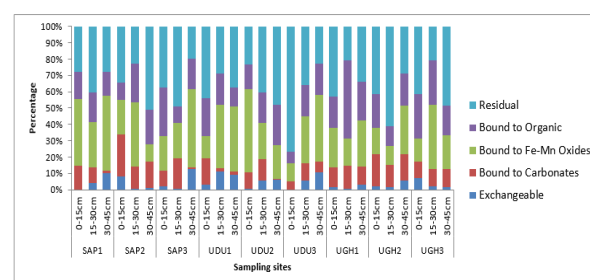
**Chromium.** In these soil profiles, the dominant species of Cr is the residual fraction (Figure 4).



**Figure 4.** Speciation pattern of Cr in the dumpsite soils

The percentage of Cr in the residual fraction ranged from 16.6 to 83.6%. This is similar to the report of other researchers [5, 14, 17]. The amount of Cr in the residual fraction indicates that Cr is not available for plant uptakes or biota in these soils [5, 17]. The organic bound fraction followed the residual fraction with a range of 7.6 to 52.3%. Cr in the organic bound fraction might be due to its strong affinity for organic matter. However, according to Kotoky *et al.* [14] the existence of Cr in the organic bound fraction results from the existing physicochemical conditions which include the pH and total organic carbon. The percentage of Cr in the Fe–Mn oxide ranged from 6.1 to 43.2%. The carbonates and exchangeable fractions constituted 0.2 to 26.2% and 0.2 to 21.6% respectively.

**Nickel.** The speciation of Ni follows the order: residual > Fe–Mn oxides > organic > carbonate > exchangeable (Figure 5).



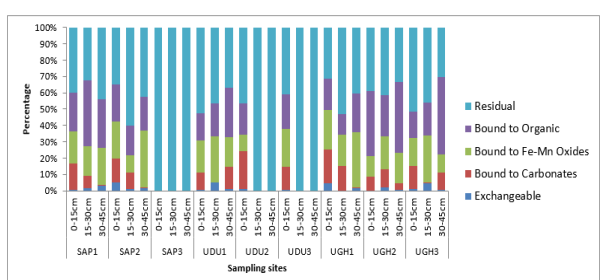
**Figure 5.** Speciation pattern of Ni in the dumpsite soils

The percentage of Ni in the different fractions ranged from 20.2 to 76.1%, 11.2 to 50.8%, 7.1 to 47.8%, 0.8 to 25.9% and 0.1 to 12.4% for residual, Fe–Mn oxides, organic, carbonates and exchangeable fractions respectively. The dominance of the residual fraction is an indication that Ni is controlled by parent materials in these soil profiles [17, 20]. This result is in agreement with the results of other researchers [5, 17, 20].

**Copper** also existed mainly in the residual fraction in the soil profiles in this study (Figure 6).

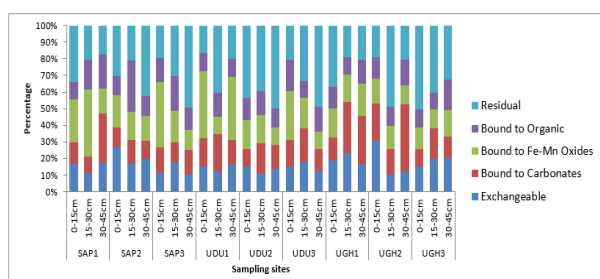
The percentage of Cu in the residual fraction ranged from 30.3 to 100%. This is in agreement with the results

reported by Iwegbue [21]. The next predominant species of Cu is the organic bound fraction. The percentage of Cu in the organic bound fraction ranged from 12.4 to 47.6 % in these soil profiles. Higher percentages of Cu in the organic bound fraction have also been reported by Iwegbue *et al.* [17] and Iwegbue [18]. Cu in the organic fraction might be as a result of the high formation constant of the Cu-organic complex [22]. Significant amount of Cu was found in the Fe-Mn oxide fraction (10.2 to 34.9%). The significant amount of Cu in the Fe-Mn oxide fraction suggests that Cu in these soil profiles is controlled by adsorption that Cu may be immobilized under reducing condition [17]. The result of this study is similar to that of Iwegbue *et al.* [17]. The amount of Cu in the carbonate and exchangeable fractions ranged from 0.1 to 23.0% and 0.1 to 5.4% respectively. The low percentage of Cu in the exchangeable fraction might be as a result of complex formation with organic matter and low precipitation with hydrous Fe-Mn oxides.



**Figure 6.** Speciation pattern of Cu in the dumpsite soils

**Zinc.** The speciation of Zn follows the order residual > Fe-Mn oxides > carbonate > exchangeable > organic (Figure 7).



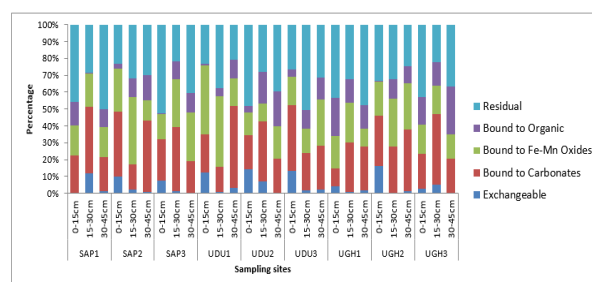
**Figure 7.** Speciation pattern of Zn in the dumpsite soils

The percentage of Zn in the different fractions ranged from 10.2 to 30.5 %, 10.1 to 40.2 %, 10.3 to 40.5%, 10.1 to 30.8 % and 16.6 to 50.5 % for exchangeable, carbonates, Fe-Mn, organic and residual fractions respectively. The dominance of the residual fraction is an indication that Zn is controlled by parent materials in these soil profiles [17, 20]. This result is in agreement with the results of other researchers [5, 20].

**Iron.** The speciation of Fe follows the order: residual > carbonate > Fe-Mn oxide > organic > exchangeable (Figure 8).

The residual fraction is the dominant fraction of Fe in these soil profiles; it ranged from 20.7 to 52.5%. The presence of Fe in the residual fraction may be due to its association with silicate minerals [5]. Fe has been reported in the residual fraction in a number of studies [13, 23]. The carbonate fraction ranged from 10.4 to

48.5%. The high percentage of Fe in this fraction indicates that Fe is not readily available due to the relative stability of this fraction. Fe in the carbonate fraction has also been reported by Abekh *et al.* [23], Urunmatsoma and Ikhouria [24], and Osakwe [5]. Significant fraction of Fe was found in the Fe-Mn oxide fraction. The Fe-Mn oxide fraction in these soils profiles ranged from 10.7 to 41.6%. The percentage of Fe in the organic fraction ranged from 0.3 to 28.2%. Iwegbue [2] also reported significant fraction of Fe in the organic phase. The percentage Fe in the exchangeable fraction ranged from 0.2 to 16.1%. The low percentage of Fe in the exchangeable fraction may be due to the easy utilization of Fe by plants and other organisms in the soil.



**Figure 8.** Speciation pattern of Fe in the dumpsite soils

### 3.3. Mobility of heavy metals in the soils

In any sequential extraction procedure, the early fractions are the most mobile and bioavailable fractions. Thus, the mobility factor value provides the relative mobility and biological availability of heavy metals in soils. In this study, the mobility factor of heavy metals was evaluated using the equation [25, 26]:

$$\text{Mobility Factor} = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \times 100$$

where: F1 = exchangeable fraction; F2 = carbonates fraction; F3 = Fe-Mn oxide fraction; F4 = organic fraction; F5 = residual fraction.

High mobility factor values have been interpreted as evidence of relatively high reactivity, high lability and high biological availability of heavy metals in soil [5, 18, 27]. The results of the mobility factor of heavy metals in soils of refuse dumpsites in this study are shown in Table 3. The mobility factor values of the heavy metals ranged from 0.0 to 41.4 for Cd, 12.5 to 48.7 for Pb, 2.7 to 28.1 for Cr, 5.1 to 34.0 for Ni, 0.0 to 25.2 for Cu, and 21.2 to 54.0 for Zn. The mobility of the heavy metals followed the order: Zn > Pb > Cr > Ni > Cd > Cu. On the average, the mobility factors of the heavy metals were generally low. This indicates that the heavy metals in these soil profiles around the refuse dumpsites have relatively low reactivity, lability and biological availability.

## 4. Conclusion

This study investigated the speciation and mobility of heavy metals in refuse dumpsites from three urban towns in the Niger Delta, Nigeria. The results showed that, on the average, the residual fraction was the predominant fraction of all the metals except Pb which

was dominant in the organic fraction. The mobility factor followed the order Zn > Fe > Pb > Cr > Ni > Cd > Cu. The study indicates that the metals studied do not pose environmental risk considering their relatively low concentrations and the chemical forms they are associated with.

**Conflicts of interest.** The authors declare no conflict of interest.

## References

- [1]. M.L. Benhaddya, M. Hadjel, Spatial distribution and contamination assessment of heavy metals in surface soils of Hassi Messaoud, Algeria, *Environmental Earth Sciences* 71(2014) 1473-1486.
- [2]. C.M.A. Iwegbue, Metal fractionation in soil profiles at automobile mechanic waste dumps, *Waste Management Research* 25 (2007) 1-9.
- [3]. X.H. Li, Z.L. Tang, F.Y. Chu, L.Y. Yang, Characteristics of distribution and chemical speciation of heavy metals in environmental mediums around Jinchang mining city, Northwest China, *Environmental Earth Sciences* 64(2011) 1667-1674.
- [4]. C.M.A. Iwegbue, G.O. Tesi, L.C. Overah, G.E. Nwajei, B.S. Marticigh, Chemical fractionation and mobility of metals in floodplain soils of the lower reaches of River Niger, Nigeria, *Transaction of Royal Society of South Africa* 73 (2018) 90-109. <https://doi.org/10.1080/0035919X.2017.1361483>
- [5]. S.A. Osakwe, Chemical partitioning of iron, cadmium, nickel and chromium in contaminated soils of South-Eastern, Nigeria, *Research Journal of Chemical Sciences* 2 (2012) 1-9.
- [6]. S.A. Osakwe, O.V. Akpoveta, B.E. Okoh, O.K. Ize-Iyamu, Chemical forms of heavy metals in soils around municipal waste dumpsites in Asaba Metropolis, Delta State, Nigeria, *Chemical Speciation & Bioavailability* 24(2012) 23-30.
- [7]. G.A. Ebong, E.U. Dan, E. Inam, N.O. Offiong, Total concentration, speciation, source identification and associated health implications of trace metals in Lemna dumpsite soil, Calabar, Nigeria, *Journal of King Saud University – Science* 31(2019) 886-897.
- [8]. K.E. Otabor, Chemical speciation and mobility study of some heavy metals in soils around municipal solid waste dumpsites in Benin City metropolis, Nigeria, *SN Applied Sciences* 1(2019) 1649. <https://doi.org/10.1007/s42452-019-1700-0>
- [9]. G.O. Tesi, J. Ojegu, S.O. Akporido, Distribution and risk of metals in soils of refuse dumpsites in some urban towns in the Niger Delta of Nigeria, *African Scientist* (2020) in press.
- [10]. A. Walkley, I.A. Black, An examination of Degtjareff method for determination soil organic matter and a proposed modification of the chromic acid titration method, *Soil Science* 37 (1934) 29-37.
- [11]. M. Radojevic, V.N. Bashkin, *Practical environmental analysis*, Royal Society of Chemistry, Cambridge UK (1999).
- [12]. A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Analytical Chemistry* 7 (1979) 844-851.
- [13]. M. Horsfall, A. Spiff, Speciation and bioavailability of heavy metals in sediment of Diobu River, Port-Harcourt, Nigeria, *European Journal of Scientific Research* 6 (2005) 20-36.
- [14]. P. Kotoky, B.J. Bora, N.K. Baruah, P. Baruah, G.C. Borah, Chemical fractionation of heavy metals in soils around oil installation, Assam, *Chemical Speciation and Bioavailability* 15 (2003) 115-125.
- [15]. S. Zuayah, B. Julian, H.R. Noorhafiza, C.L. Fauziah, A.B. Rosenanic, Concentration and speciation of heavy metal in some cultivated and uncultivated utisols and inceptisols in Peninsular Malaysia, *Proceeding of Super Soil 3rd Australian New Zealand Soil Conference*, 5-9 December 2004, University of Sydney, Australia (2004).
- [16]. L.O. Ajala, V.I. Onwukeme, M.N. Mgbemena, Speciation of some trace metals in floodplain soil of Eke-Mgbom, Afikpo, Nigeria, *American Chemical Science Journal* 4 (2014) 963-974.
- [17]. C.M.A. Iwegbue, F.N. Emuh, N.O. Isirimah, A.C. Egun, Fractionation, characterization and speciation of heavy metals in composts and compost-amended soils, *African Journal of Biotechnology* 6 (2007) 67-78.
- [18]. C.M.A. Iwegbue, Assessment of heavy metal speciation in soils impacted with crude oil in Niger Delta, Nigeria, *Chemical Speciation and Bioavailability* 23 (2011) 7-15.
- [19]. A.K. Papafilippaki, M.E. Kotti, G.G. Stavroulakis, Seasonal variation in dissolved heavy metals in the Keritis River, Chania, Greece, *Global NEST Journal* 10 (2008) 320-325.
- [20]. R. Morales, R.J. Gilkes, M.M. Jordan, Chemical fractionation of Cd, Cu, Ni and Zn in contaminated soils, *Journal of Environmental Quality* 26 (2005) 259-264.
- [21]. C.M.A. Iwegbue, Chemical fractionation and mobility of heavy metals in soils in the vicinity of Asphalt Plants in Delta State, Nigeria, *Environmental Forensics* 14 (2013) 248-259.
- [22]. O.M. Abollino, M. Malandrino, E. Menstasti, F. Petrella, Heavy metals in Agricultural soils from Piedmont, Italy: distribution, speciation and chemometric data treatment, *Chemosphere* 49 (2002) 545-557.
- [23]. T. Abeh, J. Gungshik, M.M. Adamu, Speciation studies of trace element in sediment from Zaramagada Stream in Jos, *Journal of Chemical Society of Nigeria* 32 (2007) 218-225.
- [24]. S.O. Urunmatsoma, E.U. Ikhouria, Effect of leachates (heavy metal content) from solid waste at Effurun roundabout dumpsite, Warri, Nigeria, *Chemical Technology Journal* 1 (2005) 195-202.

- [25]. R.P. Narwal, B.R. Singh, B. Salbu, Association of cadmium, zinc, copper and nickel with components in naturally heavy metal rich soils studied by parallel and sequential extraction, *Communications in Soil Science and Plant Analysis* 30 (1999) 1209–1230.
- [26]. B. Salbu, T. Kreling, D.H. Oughton, Characterization of radioactive particles in the environment, *Analyst* 123 (1998) 843–849.

- [27]. C. Kabala, B.R. Singh, Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter, *Journal of Environmental Quality* 30 (2001) 485–495

*Received:* 21.05.2020

*Received in revised form:* 06.07.2020

*Accepted:* 07.07.2020