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# Assessment of Physico-chemical Properties and Heavy Metals Bioavailability in Dumpsites along Enugu-port Harcourt Expressways, South-east, Nigeria

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## ABSTRACT

Physico-chemical parameters (pH, EC, %moisture, CEC, TOC, TOM, total nitrogen, $\%PO_4^{3-}$, $SO_4^{2-}$) and the chemical fractionation, mobility and bioavailability of heavy metals (Cd, Cu, Mn, Pb, Zn, Fe, Ni and Cr) in refuse waste soils of some dumpsites along Enugu-port Harcourt Expressways, South-East, Nigeria were investigated and compared with control soils from the same terrain using standard analytical methods. Results showed significant ($p>0.05$) higher changes in the soil physico-chemical properties relative to the controls, thus implicating the waste soils to be more fertile. Also, mean of total extractable metals in the samples analyzed for Cd, Cu, Mn, Pb, Zn, Fe, Ni and Cr ranged from 23.41-107.18, 10.58-238.50, 141.21-442.03, 35.11-635.31, 186.38-505.57, 76.46-371.73, 13.00-221.97 and 13.55-26.77 mg $kg^{-1}$ dry weight, respectively. Cd followed by Fe and then Pb were mostly found to be in the mobile phase of the samples indicating that the metals were potentially more bio-available to the environment than the other metals studied. Overall, the order of mobility and bioavailability of the metals is Cd>Fe>Pb>Mn>Zn>Cr>Ni>Cu. The implications of these results towards the understanding of the underlying causes of plants species diversity changes and growth, bioaccumulation and bio-toxicity of some edible plants on dumpsites were discussed.

**Key words:** Heavy metals, dumpsites, bioavailability, physico-chemical parameters, Enugu-port Harcourt expressways

## INTRODUCTION

The impact of solid waste on health and environment has been an issue of global concern over the years (Goorah *et al*., 2009; Kouznetsova *et al*., 2007; Barlaz *et al*., 2003). Solid wastes are sources of environmental pollution through introduction of chemical substances above their threshold limit into the environment. Reports have shown that solid waste introduces additional heavy metals into the surrounding soil and ground water (Nubi *et al*., 2008; Uba *et al*., 2008; Elaigwu *et al*., 2007). Soil is a natural reservoir of metals whose concentrations are associated with several factors such as biological and biogeochemical cycling, parent material and mineralogy, soil age, organic matter, soil pH, redox concentrations and microbial activities (Greenland and Hayes,

2000; Lee *et al*., 1997; Ma *et al*., 1997). However, large amounts of these heavy metals are released into soil as a result of increased anthropogenic activities such as agricultural practices, industrial activities, energy consumption and waste disposal methods, thus leading to the contamination of the soils (Ebong *et al*., 2007, 2008; Ololade *et al*., 2007; Eja *et al*., 2003; Ndiokwere and Ezehe, 1990).

The amount and variety of waste materials have drastically increased with the growing of technology and population. All solid waste occupies space and for many countries, the disposal and management of these wastes are ancient problems. Like many other geo-political zones in Nigeria, south-east zone faces problems of environmental sanitation such as improper disposal of refuse near residential areas; poor refuse collection and handling etc. (Onwurah *et al*., 2006). For example, it is a common feature in the zone to find huge refuse dumpsites within residential areas and along some minor and major roads (Elaigwu *et al*., 2007). Odukoya *et al*. (2000) and Udosen *et al*. (1990) among other researchers reported that soil at refuse dumpsites contain different kinds and concentration of heavy metals, depending on the age, contents and location of the dumpsite. Similarly, many studies have shown that continuous disposal of municipal wastes in soil may increase the heavy metal concentration in the soil and underground water (Nubi *et al*., 2008; Uba *et al*., 2008; Okoronkwo *et al*., 2005, 2006; Albores *et al*., 2000; Ukpebor and Unuigbe, 2003). Other reports have shown that metals from refuse dumpsites can accumulate and persist in soil at environmentally hazardous levels (Ebong *et al*., 2007; Amusan *et al*., 2005; Umoren and Onianwa, 2005). These data on the contamination and subsequent pollution of the environment by toxic heavy metals has become an issue of global concern due to their widespread sources, distribution and multiple effects on the ecosystem (Wyszkowska and Wyszkowski, 2003; Smith *et al*., 1996; Nriagu, 1990).

In South-East Nigeria, areas with high refuse disposal rate are association with high population density, increased commercial and industrial activities. The adverse effects of refuse dumpsites to the soil and air quality are well documented (Coskun *et al*., 2009; Ebong *et al*., 2007, 2008; Ololade *et al*., 2007; Elaigwu *et al*., 2007; Ukpebor and Unigbe, 2003). Also, most refuse dumpsites in the South-East are used extensively for cultivating varieties of edible vegetables and plant-based food stuffs without proper routine assessment. Data on the soil quality of most refuse dumpsites in South-East Nigeria is lacking. The determination of total heavy metal content of soil samples is not sufficient to evaluate the possible mobility and consequently the bioavailability of toxic metals to living organism. The application of sequential extraction procedures allows the determination of the chemical "forms" in which the elements appear to be associated in the sample. It can also help to assess how strongly they may be retained in soil and how easily they may be released into soil solutions (Uba *et al*., 2008; Takac *et al*., 2009; Iwegbue *et al*., 2007).

Bioavailability and toxicity of heavy metals depend on metal speciation in sediments (Ewa-Szarek *et al*., 2006). The mechanisms of mobility and bioavailability of heavy metals relative to the various fractions of heavy metals in sediments have been documented (Hlavay *et al*., 2004; Yu *et al*., 2001; Tsai *et al*., 1998). Heavy elements are associated with Organic Matter, adsorbed onto Fe/Mn oxides or complexed with hydroxides, sulphides and carbonates (Kabata-Pendias, 2004; Tessier *et al*., 1979). High contents in the exchangeable and soluble and easily reducible fraction may indicate pollution from anthropogenic origin (Kabata-Pendias, 2004). Even high contents in the more resistant fractions, the residual, may be significant in the long term. Organic matter and Fe/Mn oxides in the sediment matrices are the two most important sediment components for metal partition under aerobic conditions (Yu *et al*., 2001; Murray *et al*., 1999). Reports have shown that

contribution of metals bound to organic matter was high and the same magnitude as those bound to Fe/Mn-oxides (Tukura *et al*., 2011; Adekola *et al*., 2010). However, the results reported by Ikem *et al*. (2003) for the sediments of five different rivers in southern Taiwan were different.

The pollution of the environment with heavy metals has become a world-wide problem during recent years (Benjamin and Mwashot, 2003) because they are non-biodegradable and are toxic to flora and fauna in the ecosystem (Krissanakriangkrai *et al*., 2009; Ozturk *et al*., 2009; Ikem *et al*., 2003). The physicochemical parameters of soil have been reported to have a profound influence on the mobility and bioavailability of heavy metals (Tukura *et al*., 2007). In view of the above, the study was therefore aimed to investigate the physicochemical properties and the chemical fractionation of heavy metals in some dumpsites soils along Enugu Port Harcourt Expressway and as such not only provide their baseline data but also determine their mobility, bioavailability and fate in order to assess the human health and ecological risks associated with the refuse dumpsites.

## MATERIALS AND METHODS

**Dumpsite description and sample collection:** Soils from ten dumpsites and five control sites were collected from five major locations along Enugu Port-Harcourt Expressway, in South-East, Nigeria. The five locations include Aba, Umuahia, Okigwe, Ishiagu and Enugu. Control-site samples were collected from farm lands in each of these locations. The dumpsites are Burrow pit-Aba, Ntiga-Isiala Ngwa, Ubakala-Umuahia South, Abia Tower-Umuahia, Umuka-Okigwe, Ubahu-Okigwe, Enugu Junction-Ishiagu, Ntave-Ishiagu, Four Corner-Enugu and Amaéchi-Enugu. Triplicate sample, from each dumpsite and control site were collected seven meters within the vicinity of the sites and composite samples were made in the laboratory. The samples were air dried and sieved (using 2 mm sieve) and then stored in polycom bottles in desiccators at room temperature before further analysis.

**Physicochemical analysis of samples:** Soil pH was determined (1:2.5 w/v) using digital pH meter according to the method described by Bates (1954), Soil electrical conductivity was determined (1:2.5 w/v) using conductivity meter according to the method outlined by Godson *et al*. (2002). Cation exchange capacity was determined by the method described by Ayres *et al*. (1973). Moisture content was determined by the method of Shrivastava and Banerjee (2004). Organic carbon and organic matter were determined according to the method outlined by Osuji and Adesiyan (2005) while total nitrogen was determined by the semi-Kjeldhal method (Yeomans and Bremmer, 1991). $SO_4^{2}$-was quantified by the turbidimetric method outlined by Butters and Chenery (1959) while $PO_4^{3}$-was determined by Brays No. 1 method (Olsen and Sommers, 1982).

**Sequential extraction of heavy metals:** The conventional method developed by Tessier *et al*. (1979) as outlined with modifications in Uba *et al*. (2008) and Gupta and Sinha (2006) was used in the extraction. However, Mg $(NO_3)_2$ was used instead of $MgCl_2$ to avoid an increase in the solubility of heavy metals within the soil solution (Shuman, 1985). The sequential extraction procedures were as follows:

- **Exchangeable phase:** One gram of air dried sample in polypropylene centrifuge tube of 50 mL capacity was shaken at room temperature with 16 mL of l M Mg $(NO_3)_2$ at pH 7.0 for 1 h, centrifuged and the supernatant decanted and made up to 40 mL with double distilled-deionized water

- **Oxidizable phase (bound to organic matter):** Residue from (1)+10 mL 8.8 M $H_2O_2$+6 mL 0.02 M $HNO_3$, was shaken for 5 h at 98°C. Then, 10 mL 3.5 m $CH_3COONH_4$ 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 carbonate):** Residue from (2)+25 mL 0.05 M $Na_2$ EDTA, 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 0.1 M $NH_2OH.HCl$+17.5 mL 3.5 M $CH_3COONH_4$, Shaken for l h and centrifuged, the supernatant decanted and made up to 40 mL with distilled water prior to analysis
- **Residual phase (bound to silicates and detrital materials):** Residue from (4) was digested by using HCl-$HNO_3$/HF (0.35:12 w/v soil solution ratio) in acid Teflon Cup. It was then 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 4500 rpm for 15 min (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 mm centrifugation before the next extraction. The volume of the rinsed distilled water used was kept to a minimum. The extracts were analyzed using Atomic Absorption Spectrophotometer (Solar 32).

## RESULTS AND DISCUSSION

The analysis of the result of physico-chemical properties determined is shown in Table 1. The pH of the waste soils ranged from 7.30 to 8.60 with dumpsite B and A having the lowest and highest pH values, respectively. This suggests that the dumpsites were mostly alkaline in nature. Similar results were reported for dumpsites by other researchers (Uba *et al.*, 2008; Elaigwu *et al.*, 2007; Gupta and Sinha, 2006). The degree of acidity and/or alkalinity is considered a master variable that affects nearly all soil properties-chemical, physical and biological while some organisms are unaffected by a rather broad range of pH values, others may exhibit considerable intolerance to even minor variations in pH. For example, the amount of acid (or alkali) in soils

Table 1: Physico-chemical parameters of waste soils in studied dumpsites

| Dumpsites parameter | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH ($H_2O$) | 8.60 | 7.30 | 7.05 | 7.60 | 7.74 | 7.23 | 7.51 | 7.90 | 7.18 | 8.20 | 7.80 | 7.31 | 7.65 | 7.90 | 7.10 |
| EC (mS $cm^{-1}$) | 3.12 | 3.08 | 1.25 | 2.46 | 1.53 | 0.80 | 2.10 | 1.93 | 1.05 | 1.38 | 1.45 | 0.52 | 1.96 | 2.78 | 0.95 |
| MOISTURE (%) | 44.70 | 38.50 | 40.90 | 40.54 | 47.90 | 46.00 | 41.65 | 79.10 | 69.65 | 88.56 | 50.96 | 49.35 | 43.00 | 39.60 | 40.15 |
| Cation exchange acidity (%) | 28.80 | 18.00 | 8.20 | 16.75 | 22.40 | 7.58 | 15.80 | 17.05 | 10.70 | 13.20 | 16.13 | 9.95 | 18.40 | 15.10 | 10.20 |
| Total organic carbon (%) | 4.25 | 2.76 | 0.85 | 2.97 | 3.82 | 1.05 | 3.60 | 3.28 | 1.30 | 3.96 | 3.39 | 1.14 | 3.18 | 3.00 | 1.02 |
| Total organic matter (%) | 7.33 | 4.76 | 1.47 | 5.12 | 6.59 | 1.81 | 6.21 | 5.65 | 2.24 | 6.83 | 5.67 | 1.97 | 5.48 | 5.17 | 1.78 |
| Total nitrogen (%) | 0.11 | 0.16 | 0.20 | 0.21 | 0.28 | 0.24 | 0.20 | 0.25 | 0.29 | 0.36 | 0.33 | 0.27 | 0.24 | 0.28 | 0.25 |
| $PO_4^{3-}$ (mg $L^{-1}$) | 167.98 | 146.40 | 132.70 | 132.14 | 176.80 | 154.45 | 154.54 | 168.05 | 159.80 | 225.62 | 338.50 | 218.50 | 165.50 | 186.70 | 142.40 |
| $SO_4^{2-}$ (mg $L^{-1}$) | 6.36 | 5.50 | 6.15 | 8.60 | 12.42 | 9.10 | 9.17 | 11.65 | 8.20 | 31.40 | 30.08 | 27.60 | 12.00 | 13.59 | 12.26 |
| C:N ratio | 20.45 | 17.25 | 9.25 | 14.14 | 13.64 | 12.71 | 18.00 | 17.1 | 11.38 | 11.00 | 10.27 | 13.11 | 13.25 | 10.71 | 11.52 |

A: Burrow pit-Aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu

determines the availability of many nutrients for plant growth and maintenance (Arias *et al.*, 2005). Thus, being a key player in soil microbial reactions, the measured pH values may well have implications on the availability and uptake of metals by plants and microorganisms.

The electrical conductivity of the refuse waste soils ranged from 1.38 to 3.12 mS $cm^{-1}$. Similar results were reported for some dumpsites at Zaira (Uba *et al.*, 2008). 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 dumpsite and this implicates that there are more soluble salts in the soil (Arias *et al.*, 2005; Karaca, 2004; Singer and Munns, 1999). The moisture content which is directly proportional to the water holding capacity of the soil ranged from 38.50 to 88.56%. The general high moisture contents of the samples are to be expected, considering the overall climatic predisposition of the area under study.

The Cation Exchanges Capacity (CEC) of the waste soils ranged from 13.20 to 28.80 C mol $kg^{-1}$, with dumpsite G and A having the lowest and highest exchangeable cations, respectively. CEC gives the soil a buffering capacity which may slow down the leaching of nutrient cations and positively charged pollutants because they affect both soluble and exchangeable metal levels (Yoo and James, 2002). The total mean percentages of organic carbon (TOC) and Total Organic Matter (TOM) ranged from 2.25 to 4.28 and 3.88 to 7.39%, respectively. These values compares favorably with those reported by Uba *et al.* (2008), however, the values are high based on the classification of soil organic matter given by Enwezor *et al.* (1998). While soil organic carbon is not a requirement for plant growth, the levels of organic matter in soils influence a number of soil chemical and physical processes and it is an important indicator of the soil as a rooting environment (Okalebo *et al.*, 1993).

The total nitrogen, $PO_4^{3}$ -and $SO_4^{2-}$ in the refuse waste soils ranged from 0.11 to 0.36%, 132.14 to 338.50% and 5.50 to 31.40%, respectively. The high concentration of these parameters may be attributed to have contributed to the good growth of plants observed in these sites. Also, the ratio of carbon to Nitrogen (C:N) ranged from 11.00 to 20.45 which implicates that the soils would support plant species diversity and growth (Obute *et al.*, 2010; Okalebo *et al.*, 1993).

The results of the sequential extractions of Cd, Cu, Mn, Pb, Zn, Fe, Ni and Cr in samples of waste soils of studies dumpsites along Enugu-port Harcourt Expressway, South-East, Nigeria are presented in Table 2-9 while the total extractable metals and percentage (%) mobile phase of the total extractable metals are shown in Fig. 1 and 2. The heavy metals were categorized into five fractions: exchangeable phase, oxidizable phase (bound to organic matter), Acid soluble phase

Table 2: Cadmium (Cd) concentrations in each fraction of waste soils in studied dumpsites

| Dump sites parameter | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable | 24.89 | 11.29 | 1.02 | 12.90 | 8.96 | 0.05 | 10.11 | 8.98 | 0.11 | 16.43 | nd | 0.36 | nd | 9.63 | 0.98 |
| Oxidizable | 18.86 | 13.06 | 2.45 | 12.85 | 8.12 | 1.80 | 9.88 | 8.90 | 1.05 | 16.40 | 3.76 | 1.16 | 3.02 | 9.61 | 0.64 |
| Acid soluble | 19.86 | 13.15 | 1.10 | 12.90 | 11.15 | 1.02 | 8.75 | 6.75 | 0.96 | 10.12 | 4.85 | 0.88 | 5.82 | 6.18 | nd |
| Reducible | 19.43 | 10.98 | 1.39 | 16.18 | 9.45 | 1.75 | 9.85 | 9.00 | 0.98 | 11.42 | 6.75 | 1.38 | 7.04 | 9.63 | 1.05 |
| Residual | 23.14 | 14.66 | 4.58 | 17.30 | 13.05 | 2.16 | 15.48 | 12.25 | 1.14 | 1. 20 | 8.05 | 1.50 | 10.06 | 11.70 | 1.12 |
| Total extractable metals | 107.18 | 63.14 | 10.54 | 72.13 | 50.73 | 6.78 | 54.07 | 45.88 | 4.24 | 77.57 | 23.41 | 5.28 | 25.94 | 46.75 | 3.79 |
| Non-residual (%) | 78.41 | 76.78 | 58.44 | 76.02 | 74.28 | 68.14 | 71.37 | 73.30 | 73.11 | 76.54 | 65.61 | 79.59 | 61.22 | 74.97 | 70.45 |
| Residual (%) | 21.59 | 23.32 | 41.56 | 23.98 | 25.72 | 31.86 | 28.63 | 26.70 | 26.89 | 23.46 | 34.39 | 28.41 | 38.78 | 25.03 | 29.55 |
| Mobile phase (%) | 41.75 | 38.71 | 20.11 | 35.77 | 39.64 | 15.78 | 34.88 | 34.29 | 25.24 | 34.22 | 20.72 | 23.48 | 22.44 | 33.82 | 25.86 |

A: Burrow pit-Aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu, nd: Not detected

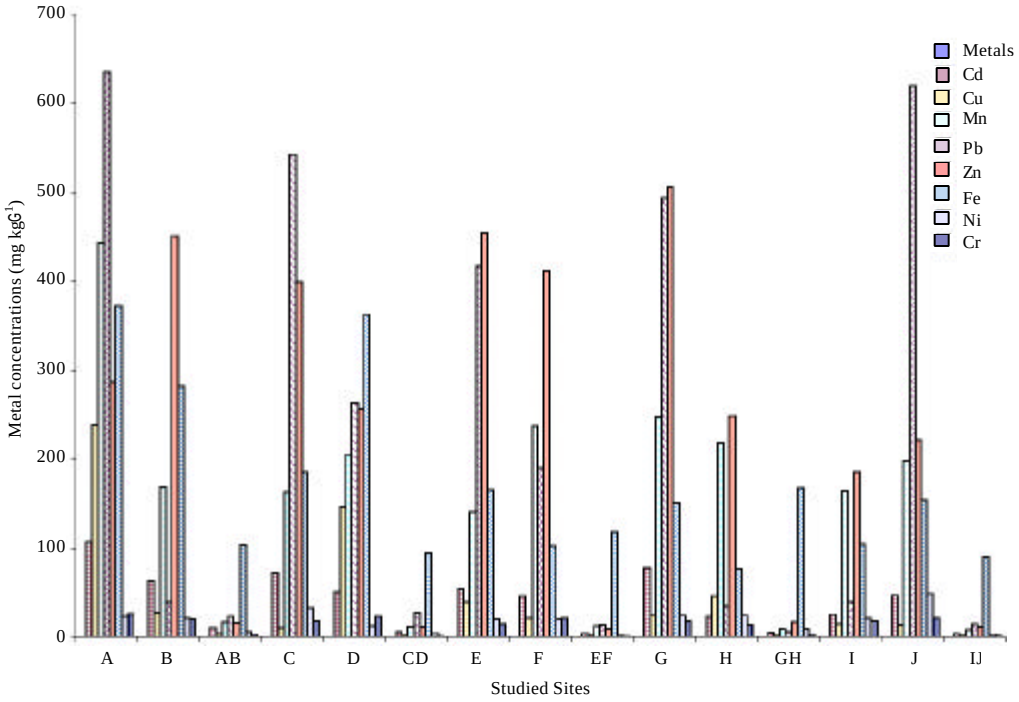


Fig. 1: Total extractable metals in the studied sites

Table 3: Copper (Cu) concentrations in each fraction of waste soils in studied dumpsites

| Dumpsites fraction | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable | 13.56 | nd | nd | nd | nd | nd | nd | 1.85 | nd | nd | nd | nd | 2.10 | nd | nd |
| Oxidizable | nd | 9.57 | 0.97 | 3.86 | 12.18 | 1.10 | 8.80 | nd | 0.83 | 6.18 | nd | 0.70 | nd | 4.02 | 0.74 |
| Acid soluble | 3.50 | nd | nd | nd | nd | nd | nd | nd | nd | nd | 6.85 | nd | nd | nd | nd |
| Reducible | nd | nd | 0.92 | nd | 49.68 | 0.08 | 6.50 | 2.70 | 0.33 | 7.92 | 13.43 | 0.22 | nd | nd | 0.26 |
| Residual | 221.44 | 18.42 | 2.04 | 6.72 | 84.70 | 1.96 | 24.16 | 17.18 | 1.67 | 11.57 | 26.05 | 1.84 | 13.18 | 9.44 | 2.10 |
| Total extractable metals | 238.50 | 27.99 | 3.93 | 10.58 | 146.56 | 3.14 | 39.46 | 21.73 | 2.83 | 25.67 | 46.33 | 2.75 | 15.28 | 13.46 | 3.10 |
| Non residual (%) | 7.15 | 34.19 | 48.09 | 36.48 | 42.21 | 37.58 | 38.77 | 20.94 | 40.99 | 54.93 | 43.77 | 33.09 | 13.74 | 29.87 | 32.26 |
| Residual (%) | 92.85 | 65.81 | 51.91 | 63.52 | 57.79 | 62.42 | 61.23 | 79.06 | 59.01 | 45.07 | 56.23 | 66.91 | 86.26 | 70.13 | 67.74 |
| Mobile phase (%) | 7.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 8.51 | 0.00 | 0.00 | 14.79 | 0.00 | 13.74 | 0.00 | 0.00 |

A: Burrow pit-Aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu, nd: Not detected

(bound to carbonate), reducible phase (bound to Fe-Mn oxides) and residual phase (bound to silicates and detrital materials).

Total extractable cadmium ranged from 23.41 to 107.18 mg $kg^{-1}$ (Table 2). This value is above the critical permissible concentration of 3.0 mg $kg^{-1}$ for agricultural soils (MAFF, 1992; USEPA, 1986). This high concentration may be attributed to the dumping of cadmium containing substances like cadmium batteries and metals from residence and industries to these sites. The availability of this metal in the sequentially extracted fractions follows the order: residual>reducible>exchangeable>acid soluble>oxidizable. The mobile phase contained 20.72 to

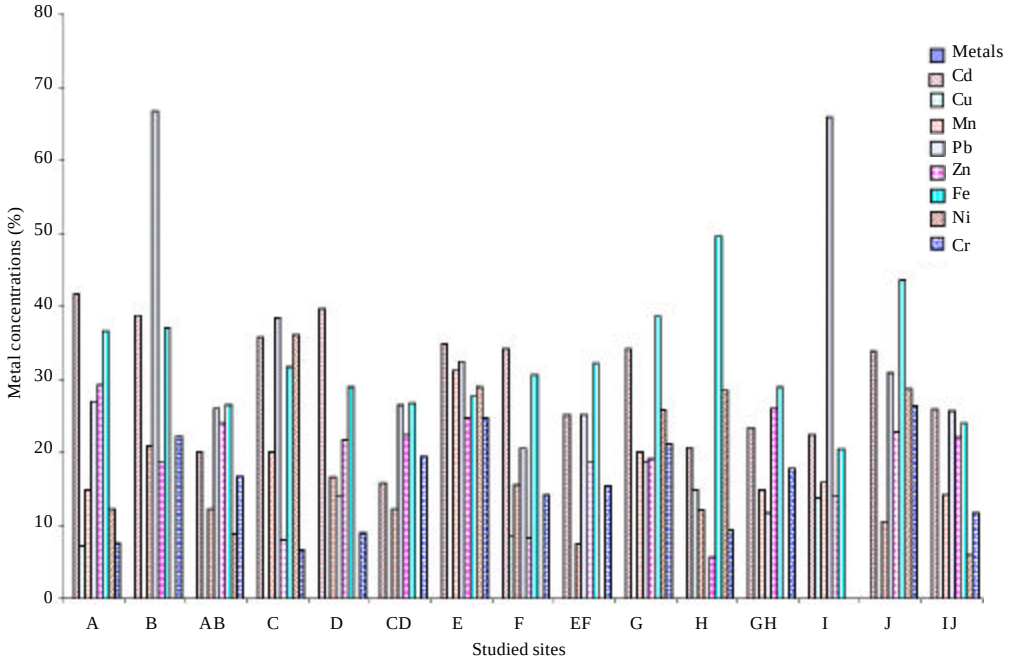


Fig. 2: Percentage mobile phase of total extractable metals in the studied sites

41.75% of the total extractable fraction of the metals (Fig. 2). The high percentage of the total extractable fraction in the mobile phase suggests that Cd in these soils was potentially more bioavailable for plants uptake (Xian, 1989). This result was in agreement with the observation of Uba *et al.* (2008), Gupta and Sinha (2006) and Kuo *et al.* (1993). Harrison *et al.* (1981) reported similar Cd concentration levels in waste soils of dumpsites, sewage and tannery sludge. The potential mobility and bioavailability of Cd in the waste soils of the dumpsites were found to be in the order: A>D>B>C>E>F>G>J>I>H. The potential mobility of the metals was generally higher in dumpsites compared to the control sites.

The results of the sequential extraction of Copper in the samples of waste soils of the dumpsites shown in Table 3 ranged from 10.58 to 238.50 mg $kg^{-1}$. The concentrations of this metal in the studied samples were all below the toxic limit of 250 mg $kg^{-1}$ set by USEPA (1986) for agricultural lands. The availability of Cu in each fraction is of the order: residual>oxidizable>reducible>acid soluble>exchange. The results indicated that Cu was most found in the residual phase (i.e., bound to silicates and detrital materials) which is in agreement with the reports of Uba *et al.* (2008), Hickey and Kittrick (1984) and Gupta and Chen (1975). The results also indicated Cu to be mostly associated with the Oxidizable fraction (bound to organic matter) which may be attributed to the high formation constants of organic copper complexes (Stumm and Morgan, 1981). The mobile phase had only reasonable percentage in dumpsite H (14.79%), I (13.74%), F (8.51%) and A (7.15%). Thus, Cu is more bioavailable in these dumpsites than the others and as well as the control sites.

Total extractable manganese ranged from 141.21 to 442.03 mg $kg^{-1}$ (Table 4). The concentrations of this metal in all the samples were within the tolerable limits (100-300 mg $kg^{-1}$)

Table 4: Manganese (Mn) concentrations in each fraction of waste soils in studied dumpsites

| Dumpsites fraction | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable | 35.11 | 3.08 | 0.24 | 16.30 | 1.12 | 0.52 | 5.74 | 19.66 | 0.11 | 13.54 | 13.80 | 0.62 | nd | 7.26 | 0.41 |
| Oxidizable | 187.94 | 14.11 | 3.72 | 36.15 | 14.76 | 3.80 | 9.35 | 35.05 | 5.21 | 8. 07 | 41.35 | 3.45 | 11.68 | 73.58 | 3.15 |
| Acid soluble | 30.66 | 32.25 | 1.86 | 16.55 | 33.05 | 0.94 | 38.44 | 17.11 | 0.87 | 36.13 | 12.45 | 0.82 | 26.13 | 13.57 | 0.85 |
| Reducible | 160.14 | 118.03 | 7.55 | 86.10 | 141.78 | 3.74 | 72.12 | 158.74 | 5.13 | 86.88 | 135.40 | 3.79 | 108.34 | 96.05 | 3.40 |
| Residual | 28.18 | 1.46 | 3.85 | 8.90 | 14.83 | 2.46 | 15.56 | 6.42 | 1.86 | 24.32 | 14.53 | 0.99 | 18.61 | 7.20 | 1.07 |
| Total extractable metals | 442.03 | 168.93 | 17.22 | 164.00 | 205.54 | 11.94 | 141.21 | 236.98 | 13.18 | 246.94 | 217.53 | 9.67 | 164.76 | 198.26 | 8.88 |
| Non-residual (%) | 93.62 | 99.14 | 77.64 | 94.57 | 92.78 | 79.40 | 88.98 | 97.29 | 85.89 | 90.15 | 93.32 | 88.85 | 88.70 | 96.37 | 87.95 |
| Residual (%) | 6.38 | 0.86 | 22.35 | 5. 43 | 7.22 | 20.60 | 11.02 | 2.71 | 14.11 | 9.85 | 6.68 | 11.15 | 11.30 | 3.63 | 12.05 |
| Mobile phase (%) | 14.88 | 20.03 | 12.19 | 20.03 | 16.62 | 12.23 | 31.29 | 15.52 | 7.44 | 20.11 | 12.07 | 14.89 | 15.86 | 10.51 | 14.19 |

A: Burrow pit-Aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu, nd: Not detected

Table 5: Lead (Pb) concentrations in each fraction of waste soils in studied dumpsites

| Dumpsites fraction | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable | 171.50 | 13.12 | 3.85 | 168.40 | nd | 2.74 | 55.46 | nd | 1.60 | nd | nd | 0.18 | 12.95 | 88.30 | 1.95 |
| Oxidizable | 50.73 | nd | 6.07 | 124.85 | 38.45 | 6.39 | 98.50 | 35.00 | 4.00 | 70.03 | nd | 2.26 | nd | 187.65 | 3.92 |
| Acid soluble | nd | 12.98 | 2.30 | 39.44 | 36.88 | 4.42 | 79.85 | 39.11 | 1.95 | 92.60 | nd | 0.54 | 13.06 | 102.74 | 2.00 |
| Reducible | 144.36 | nd | 5.75 | 76.50 | 57.16 | 6.70 | 34.95 | 48.56 | 3.82 | 132.52 | 18.16 | 1.88 | nd | 37.44 | 3.81 |
| Residual | 268.72 | 13.04 | 6.73 | 132.29 | 130.59 | 5.86 | 148.00 | 67.72 | 2.71 | 197.45 | 16.95 | 1.30 | 13.48 | 202.70 | 3.24 |
| Total extractable metals | 635.31 | 39.14 | 23.70 | 541.48 | 263.08 | 27.11 | 416.76 | 190.39 | 14.08 | 492.60 | 35.11 | 6.16 | 39.49 | 618.83 | 15.42 |
| Non-residual (%) | 57.70 | 66.68 | 71.61 | 75.57 | 50.36 | 78.38 | 64.49 | 64.43 | 80.75 | 59.92 | 51.72 | 78.90 | 65.86 | 67.24 | 78.99 |
| Residual (%) | 42.30 | 33.32 | 28.39 | 24.43 | 49.64 | 21.62 | 35.51 | 35.57 | 19.25 | 40.08 | 48.28 | 21.10 | 34.14 | 32.76 | 21.01 |
| Mobile phase (%) | 26.99 | 66.68 | 25.95 | 38.38 | 14.02 | 26.44 | 32.47 | 20.54 | 25.21 | 18.80 | nd | 11.69 | 65.86 | 30.87 | 25.62 |

A: Burrow pit-aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu, nd: Not detected

set by USEPA (1986) for agricultural lands except in dumpsite A. 77.64-88.85% of this metal was associated with the non-residual fraction. The order of availability of this metal in different fractions followed the pattern: reducible>oxidizable>acid soluble>residual>exchangeable. The high percentage of Mn observed from this study in the reducible phase in all the waste soils may be attributed to the precipitation of amorphous hydrous oxides of manganese during aging of dumpsites (Staelens *et al*., 2000). The potential mobility and bioavailability follows the pattern: E>B>G>C>D>I>F>A>H>J. The metals were observed to be more bio-available in some of the control sites than some of the dumpsites.

The extractable fractions of lead (Pb) are shown in Table 5. Dumpsites B, D, F, H and I have Pb concentrations within the USEPA (1986) allowed limits of 30-300 mg $kg^{-1}$ while dumpsites A, C, E, G and J have Pb content above USEPA (1986) limits for agricultural lands. Similar results were reported by Uba *et al*. (2008) and Kabata-Pendias and Pendias (1984). The results also indicated that more than 50% of Pb were found in the non-residual fraction while 14.02-66.68% of the total extractable fraction contributed to the mobile phase (exchangeable and acid soluble phases). This indicates that the potential bioavailability of Pb in the different fractions is: residual>exchangeable>reducible>oxidizable>acid soluble. In the same way, the potential mobility and bioavailability of lead from the waste soils of the studied dumpsites indicated: B>I>C>E>J>A>F>G>D>H. Based on the mobile fraction of this metal, dumpsites B and I are at higher risks for lead contamination.

Table 6: Zinc (Zn) concentrations in each fraction of waste soils in studied dumpsites

| Dumpsites fraction | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable | 65.71 | 20.14 | 1.86 | 7.85 | 29.44 | 1.15 | 3.14 | 9.85 | 1.19 | 20.08 | nd | 2.05 | nd | 37.15 | 1.46 |
| Oxidizable | 59.56 | 131.27 | 4.40 | 78.40 | 58.60 | 3.40 | 138.70 | 76.00 | 2.64 | 167.90 | 28.63 | 4.45 | 34.40 | 48.50 | 2.96 |
| Acid soluble | 17.96 | 63.77 | 2.02 | 24.20 | 26.36 | 1.54 | 108.92 | 24.42 | 0.53 | 78.74 | 14.16 | 2.37 | 26.31 | 13.14 | 1.00 |
| Reducible | 46.38 | 44.80 | 4.98 | 67.15 | 13.36 | 3.41 | 96.50 | 56.76 | 2.66 | 46.30 | 14.24 | 4.20 | 25.38 | 42.36 | 2.64 |
| Residual | 96.48 | 190.28 | 3.38 | 220.54 | 128.54 | 2.46 | 106.86 | 244.54 | 2.20 | 194.55 | 190.83 | 3.95 | 100.29 | 79.80 | 3.08 |
| Total extractable metals | 286.09 | 450.26 | 16.14 | 398.14 | 256.30 | 11.96 | 454.12 | 411.57 | 9.22 | 505.57 | 247.86 | 17.02 | 186.38 | 220.95 | 11.14 |
| Non -residual (%) | 66.28 | 57.74 | 79.06 | 44.61 | 49.85 | 79.43 | 76.47 | 40.58 | 76.14 | 61.52 | 23.01 | 76.79 | 46.19 | 63.88 | 72.35 |
| Residual (%) | 33.72 | 42.26 | 20.94 | 55.39 | 50.15 | 20.57 | 23.53 | 59.42 | 23.86 | 38.48 | 76.99 | 23.21 | 53.81 | 36.12 | 27.65 |
| Mobile phase (%) | 29.25 | 18.64 | 24.04 | 8.05 | 21.77 | 22.49 | 24.68 | 8.33 | 18.66 | 19.15 | 5.71 | 25.79 | 14.12 | 22.76 | 22.08 |

A: Burrow pit-aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu, nd: Not detected

Table 7: Iron (Fe) concentrations in each fraction of waste soils in studied dumpsites

| Dumpsites fraction | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable | 78.50 | 82.26 | 13.14 | 36.33 | 37.80 | 12.15 | 45.74 | 18.14 | 19.86 | 38.65 | 24.83 | 23.96 | nd | 35.88 | 11.20 |
| Oxidizable | 65.12 | 73.53 | 24.62 | 28.45 | 102.39 | 22.96 | 11.74 | 12.48 | 25.60 | 31.57 | nd | 35.78 | 19.20 | 23.11 | 22.05 |
| Acid soluble | 57.60 | 22.24 | 14.40 | 22.66 | 66.90 | 13.20 | nd | 13.17 | 18.35 | 19.55 | 25.11 | 24.71 | 21.43 | 31.45 | 10.22 |
| Reducible | 78.35 | 40.50 | 25.80 | 25.35 | 24.43 | 23.50 | 37.48 | 19.00 | 23.95 | 26.83 | nd | 39.00 | 27.00 | 26.18 | 21.11 |
| Residual | 92.16 | 63.45 | 25.74 | 73.42 | 130.25 | 24.05 | 70.22 | 39.34 | 30.69 | 33.90 | 26.52 | 44.35 | 37.28 | 37.70 | 24.82 |
| Total extractable metals | 371.73 | 281.98 | 103.70 | 186.21 | 361.77 | 94.86 | 165.18 | 102.13 | 118.45 | 150.50 | 76.46 | 167.80 | 104.91 | 154.32 | 89.40 |
| Non -residual (%) | 75.21 | 77.50 | 75.18 | 60.75 | 64.00 | 74.65 | 57.49 | 61.08 | 74.09 | 77.48 | 65.32 | 73.57 | 64.46 | 75.57 | 72.24 |
| Residual (%) | 24.79 | 22.50 | 24.82 | 39.43 | 36.00 | 25.35 | 42.51 | 38.52 | 25.91 | 22.52 | 34.68 | 26.43 | 35.54 | 24.43 | 27.76 |
| Mobile phase (%) | 36.61 | 37.06 | 26.56 | 31.68 | 28.84 | 26.72 | 27.69 | 30.65 | 32.26 | 38.67 | 65.32 | 29.01 | 20.43 | 43.63 | 23.96 |

A: Burrow pit-aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu, nd: Not detected

Table 6 shows the results of the sequential extractions of zinc in the samples. Dumpsites A, D, H, I and J have Zn contents within the permissible limits of 300 mg $kg^{-1}$ for agricultural lands set by USEPA (1986) while dumpsites B, C, E, F and G have Zn contents above the USEPA (1986) set limit. The mobile phase contained between 8.05 to 29.25%, indicating that the metal will be readily bio-available to the environment. The potential mobility and bioavailability of this metal in the refuse waste soils of the dumpsites followed the pattern: A>E>J>D>G>B>I>F>C>H. Similarly, the availability of the metal in the extracted fractions is: residual>reducible>oxidizable>exchangeable>acid soluble. The association of Zinc with the reducible fraction has been reported earlier by several other workers (Ramos *et al*., 1994; Kuo *et al*., 1983).

The concentration levels of iron (Fe) in the five fractions of waste soils of the ten dumpsites studied are presented in Table 7. More than 50% of this metal was found to be in the non-residual fraction while 20.43 to 49.62% of the total extractable fraction contributed to the mobile phase. The result indicates that the potential mobility of Fe in the different fraction is: Residual>Exchangeable>Reducible>Oxidizable>Acid soluble. Similarly, the order of mobility and bioavailability of this metal in the refuse waste soils revealed the following pattern: H>J>G>B>A>C>F>D>E>I. The high level of Fe in the exchange and acid soluble phase of the fractions indicated that the metal may be potentially toxic if not regulated due to their high mobility.

Table 8 showed the sequential extraction of Nickel (Ni) in the refuse dumpsites studied. All the dumpsites except dumpsite A had Ni concentration from 13.00 to 48.61 mg $kg^{-1}$ which fall within

Table 8: Nickel (Ni) concentrations in each fraction of waste soils in studied dumpsites

| Dumpsites fraction | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable | nd | nd | nd | 3.84 | nd | nd | 1.18 | nd | nd | 1.86 | nd | nd | nd | nd | 0.20 |
| Oxidizable | 86.75 | 8.11 | 1.64 | nd | 2.20 | 1.14 | nd | 5.89 | 0.58 | 3.10 | nd | 3.06 | 8.40 | 8.00 | 0.95 |
| Acid soluble | 27.08 | nd | 0.58 | 7.88 | nd | nd | 4.68 | nd | nd | 4.43 | 6.85 | nd | nd | 13.95 | nd |
| Reducible | nd | nd | 1.90 | 11.07 | nd | 1.27 | nd | 3.28 | 0.58 | nd | 11.04 | 2.55 | 5.40 | nd | 0.80 |
| Residual | 108.14 | 13.04 | 2.43 | 9.68 | 10.80 | 1.35 | 14.35 | 11.28 | 0.68 | 15.00 | 6.15 | 3.50 | 7.85 | 26.66 | 1.35 |
| Total extractable metals | 221.97 | 21.15 | 6.55 | 32.47 | 13.00 | 3.76 | 20.21 | 20.45 | 1.84 | 24.39 | 24.04 | 9.11 | 21.65 | 48.61 | 3.30 |
| Non -residual (%) | 51.28 | 38.35 | 62.90 | 70.19 | 16.92 | 64.10 | 29.00 | 44.84 | 63.04 | 38.50 | 74.42 | 61.58 | 63.74 | 45.16 | 50.09 |
| Residual (%) | 48.72 | 61.65 | 37.10 | 29.81 | 83.08 | 35.90 | 71.00 | 55.16 | 36.96 | 61.50 | 25.58 | 38.42 | 36.26 | 54.84 | 40.91 |
| Mobile phase (%) | 12.20 | 0.00 | 8.85 | 36.09 | 0.00 | 0.00 | 29.00 | 0.00 | 0.00 | 25.79 | 28.49 | 0.00 | 0.00 | 28.70 | 6.06 |

A: Burrow pit-aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu, nd: Not detected

Table 9: Chromium (Cr) concentrations in each fraction of waste soils in studied dumpsites

| Dumpsites fraction | A | B | AB | C | D | CD | E | F | EF | G | H | GH | I | J | IJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable | nd | 1.83 | 0.21 | nd | 2.07 | 0.10 | nd | 3.08 | 0.15 | 1.90 | nd | 0.27 | nd | 2.90 | 0.22 |
| Oxidizable | 3.15 | nd | 0.55 | 3.24 | 1.54 | 0.23 | nd | 1.41 | 0.16 | nd | nd | 0.80 | 3.14 | nd | 0.40 |
| Acid soluble | 2.04 | 2.66 | 0.25 | 1.17 | nd | 0.13 | 3.66 | nd | nd | 1.80 | 1.27 | 0.29 | nd | 2.85 | nd |
| Reducible | 3.45 | nd | 0.71 | nd | 4.19 | 0.30 | nd | 2.13 | 0.15 | nd | nd | 0.68 | 2.22 | nd | 0.34 |
| Residual | 18.13 | 15.70 | 1.14 | 13.12 | 15.25 | 0.42 | 11.18 | 14.99 | 0.51 | 13.80 | 12.28 | 1.28 | 13.00 | 16.05 | 0.81 |
| Total extractable metals | 26.77 | 20.19 | 2.76 | 17.53 | 23.05 | 1.18 | 14.84 | 4.84 | 0.97 | 17.50 | 13.55 | 3.15 | 18.36 | 21.80 | 1.87 |
| Non -residual (%) | 32.27 | 22.24 | 58.70 | 25.16 | 33.84 | 64.41 | 24.66 | 30.63 | 47.42 | 21.14 | 9.37 | 59.37 | 29.19 | 26.38 | 56.68 |
| Residual (%) | 67.73 | 77.76 | 41.30 | 74.84 | 66.16 | 35.59 | 75.34 | 69.37 | 52.58 | 78.86 | 90.63 | 40.63 | 70.81 | 73.62 | 43.32 |
| Mobile phase (%) | 7.62 | 22.24 | 16.67 | 6.67 | 8.98 | 19.49 | 24.66 | 14.25 | 15.46 | 21.14 | 9.37 | 17.78 | nd | 26.38 | 11.76 |

A: Burrow pit-aba, B: Ntiga-Isiala Ngwa, AB: Control site for Aba, C: Ubakala-Umuahia South, D: Abia Tower-Umuahia, CD: Control site for Umuahia, E: Umuka-Okigwe, F: Ubahu-Okigwe, EF: Control site for Okigwe, G: Enugu Junction-Ishiagu, H: Ntave-Ishiagu, GH: Control site for Ishiagu, I: Four corner-Enugu, J: Amaéchi-Enugu, IJ: Control site for Enugu, nd: Not detected

the permissible limit of 150 mg $kg^{-1}$ by CCME (1991) for residential and agricultural lands. Most of the Ni was found in the residual and oxidizable fractions. The order of Ni in the different fractions is: residual>oxidizable>acid soluble, reducible>exchangeable similarly, the order of mobility and bioavailability of Ni in the dumpsites revealed the following pattern: C>E>J>H>G> A = B = D = F = I. The high association of Ni in the residual fraction of the studied refuse waste soils may be attributed to the alkaline stabilization process of the soils. Thus, the metal may not usually be expected to release over short period of time under the conditions usually encountered in nature because the metal is confined in the residual fraction (Su and Wong, 2003; Chlopecka *et al*., 1996). Similar results have been reported by Gupta and Sinha (2006) using tannery sludge.

The results of the sequential extraction of chromium (Cr) in the samples of waste soils of the dumpsites are shown in Table 9. Total extractable Cr ranged from 14.84 to 26.77 mg $kg^{-1}$ which is below 750 mg $kg^{-1}$ limit permissible by CCME (1991) for domestic gardens, agricultural and residential areas. The results showed Cr to be strongly associated with the residual and oxidizable fractions which are in agreement with those reported by other researchers (Alvarez *et al*., 2002; Tokalioglu *et al*., 2000) but however differ from those reported by Gupta and Sinha (2006) for tannery sludge. The results also indicated the non -residual fraction of the metal to be less than 25% in all the dumpsites. The mobile phase contained between 6.67 to 26.38%, indicating that the metal will be readily bioavailability to the environment. The potential mobility and bioavailability of this metal in the refuse waste soils of the dumpsites followed the pattern: J>E>B>G>F>H>D>A>C>I. Similarly, the availability of the metals in the extracted fraction is: residual>oxidizable>acid soluble>reducible>exchangeable. The association of this metal with the

oxidizable phase showed that is strongly bound to organic matter which is an indication that the availability of the metals to the plant may be reduced due to organic complexation. Udom *et al.* (2004) reported that metal organic complexation decrease heavily metal mobility in soils at low pH. However, the relative high mobility of this metal in the dumpsites studied may be due to the alkaline nature of the soils.

## CONCLUSION

Baseline data on the physicochemical parameters and chemical fractionation of Cd, Cu, Mn, Pb, Zn, Fe, Ni and Cr for some dumpsites along Enugu-port Harcourt Expressways, South-East, Nigeria were provided in this study. Results indicated the reuse dumpsite soils to be slightly alkaline with moderate moisture content. Total organic carbon/matter and total nitrogen content of the refuse waste soils of the dumpsites were moderate with moderate values of C:N ratio implicating the waste soils to be fertile. Thus, the overall Physicochemical parameters revealed that the soils were fertile to support plant species diversity, changes and growth.

Also, the results revealed that the non-residual fraction was the most abundant pool for all the metals studied with the exception of copper and chromium which had higher percentage of residual portion in all the dumpsites. A significant amount of Cd, Fe and Pb were associated with mobile phase, which indicated that these metals will be potentially more bio-available to the environment. This implies phyto-toxicity risk of cultivating edible hyper-accumulator plants in these dumpsites. Over all, the order of mobility and bioavailability of these metals as indicated by the results was: Cd>Fe>Pb>Mn>Zn>Cr>Ni>Cu.

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