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# TRACE METALS DISTRIBUTION IN DIFFERENT GEOCHEMICAL PHASES OF SOILS AROUND AUTOMOBILE JUNK MARKETS IN SOUTHERN NIGERIA

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#### ABSTRACT

Chemical forms of some trace metals in soils around some selected automobile junk markets were studied using five step sequential extraction procedure. The results revealed that nickel, chromium and iron were of lithogenic origin while copper, lead, manganese and cadmium were from anthropogenic sources. The residual fraction was the most important phase for nickel, chromium and iron with the average amounts of 20.38%, 29.93% and 31.09% respectively. Copper and lead were mainly associated with the organic fraction having the average amounts of 24.06% and 22.89% respectively. Manganese predominated in Iron-Manganese oxide phase with an average amount of 23.76% while cadmium existed mainly in the exchangeable phase with an average amount of 30.36%. These results suggest that nickel, chromium and iron cannot be mobilized while cadmium is the most mobile and is easily available for plant uptake. Lead, manganese and copper are relatively stable but may become mobile if there are changes in soil pH or redox potential. The amounts of the metals in the non exchangeable phases were generally high but with relative high mobility factor values obtained for all the metals, changes in the soils physicochemical conditions may lead to remobilization of the metals and they may become bioavailable to plants and may enter food chain which implies a contamination risk for the metals.

Key words: Automobile junks, geochemical phases, sequential extraction, soil pollution, trace metals.

### **INTRODUCTION**

The rapid increase in automobile waste transfer from industrialized countries to developing countries like Nigeria has led to the establishment of many automobile junk markets in the country. Container loads of automobile parts regarded as automobile wastes by these developing nations are transferred to Nigeria where they are refurbished and sold in the automobile junk markets. These include fairly used automobiles parts, knockdown engines, used engines and transmissions (Nwachukwu *et al.*, 2013).

In most Nigerian cities automobile mechanic workshops and automobile dumpsites are usually located close to automobile junk markets. In these markets, vehicles are dismantled, and solid waste are generated and discharged. Other activities include fossil fuel combustion, waste incineration, spray painting scrapping of vehicles, disposal of petroleum by-products etc (Asagba *et al.*, 2007). All these activities constitute possible sources of environmental contamination by trace metals. Since these metals are among the pollutants that are not biodegradable and can not undergo any other breakdown processes, they accumulate gradually in the soil and when they exceed certain limits, they increase the health risk of metal accumulation of food chain (Wang *et al.*, 2013).

Among metals chosen for this study, copper, nickel, manganese and chromium are essential micronutrients required for growth of all living organisms. However at toxicity levels they constitute serious health risk to plants, microorganism, animals and humans. Copper at toxicity levels can cause liver and kidney damage, anemia and irritation of stomach and intestine and when tolerable amount of Nickel is exceeded, it results to various kinds of cancer on different sites within the human and animal bodies (Wuana and Okieimen, 2011). High level of manganese leads to malfunctioning of liver and pancreas and kidney failure (Underwood, 1977). Chromium accumulates on skin, muscles, lungs, liver and placenta and it is traceable to various health conditions (Reves-Gutierrez et al., 2007). The other metals are cadmium, lead and iron. Cadmium is extremely biopersistent and it has adverse effects on several enzymes. It causes kidney dysfunction and itai-itai disease (Wuana and Okieimen, 2011). High lead exposure may

lead to anemia, brain damage; muscle weakness and severe stomach ache (A. Thirulogachandar, *et al.*, 2014). There was a reported case of lead poisoning which led to the death of many people in a village in Zamfara State, Nigeria (Idugboe *et al.*, 2014). High concentration of iron in the body may cause cancer, diabetes and heart disease (A. Thirulogachandan *et al.*, 2014).

Metals in the soil exist in different chemical forms and their ease of bioavailability, mobility, and toxicity depends on their chemical forms in the soil (Urunmatsoma et al., 2010). Therefore the determination of total metal concentration alone is not adequate to evaluate the possible health risk of metals because it only gives limited information (Tessier et al., 1979; Kalis et al., 2007; Ogubanjo et al., 2015). The best way to predict these geochemical forms of the metals in the soil is to apply sequential extraction procedure which will reveal the fate, toxicity and the environmental impact of the metals in the soils (Mortatti et al., 2013). Many sequential extraction schemes have been reported in literature and studies have shown that all of them generally have some disadvantages (Davison et al., 1999, Ahmadipour, et al., 2014). However Tessier et al., (1979) procedure has been reported as the most properly researched and most widely applied (Woszczyk and Spychalsk, 2013; Liang et al., 2014).

Generally metals of lithogenic origin fractionate in the residual fraction while those of anthropogenic sources are associated with other fractions depending on some soil physicochemical properties (Wilike *et al.*, 1999). Therefore, the main aim of this study was to determine the chemical forms of some selected trace metals in the soils around automobile junk markets in Obosi, Effurun and Ughelli in Southern Nigeria, in order to assess the anthropogenic degree, mobility and bioavailability of the metals in the soils, which is important for the prediction of their potential hazards to the environment.

## **MATERIALS AND METHODS**

#### The Study Area

Different automobile junk markets were chosen

for this study. These include Mgbuka Obosi near Onisha in Anambra State, Uwelu near Benin City in Edo State, Effurun and Ughelli both in Delta State. All these selected junk markets have existed for over ten years.

Mgbuka Obosi junk market is located at Obosi in Idemili North Local Government Area of Anambra State. Its geographical coordinates are longitude  $6.70^{\circ}$   $6.50^{\circ}$  E and latitude  $6.12^{\circ}$ N,  $6.83^{\circ}$ E. Uwelu junk market is located at Uwelu in Egor Local Government Area of Edo State. It lies on longitude 5.45' N and latitude 5.04° E. It is very close to Benin City which is a University town and also the administrative capital of Edo State. Effurunjunk market is located at Effurun-Warri in Uvwie Local Government Area of Delta State with the geographical coordinates of longitude 5°46' E and latitude 5°. 32' N. Effurun has two tertiary institutions, Federal University of Petroleum Resources (FUPRI) and Petroleum Training Institute (PTI). Ughelli is the Local Government headquarter of Ughelli North Local Government Area of Delta State and it is sited at longitude 5.98°E and latitude 5.5°N.

# Sample collection and preparation

Soil auger was used to collect the soil samples within the immediate vicinity of each of the automobile junk markets. The samples were collected at the depths of 0 - 15 cm, 15 - 30 cm and 30 - 45 cm to represent the top, sub and bottom soils respectively. The soil samples collected at the same depths at each location were thoroughly mixed to form composite or representative samples and they were air dried at room temperature, ground and sieved to pass a 2 mm sieve.

#### Sequential Extraction

The method used in this study was Tessier *et al.*, (1979) five steps sequential extraction procedure. The extraction procedure applied in this study is described below and shown on table 1.

| Fraction                                     | Test   |
|--|--|
| F1 Exchangeable Fraction                     | 8 ml of 1 M MgCl <sub>2</sub> was added to 1g of soil samples in a 50 ml centrifuge tube. The mixture was shaken at room temperature and at pH 7 for 1 hour.   |
| F <sub>2</sub> Carbonate Fraction            | The residue from the exchangeable fraction was extracted with 8 ml of 1M NaOA <sub>C</sub> adjusted to pH 5 with acetic acid and was subjected to continuous agitation at room temperature for 2 hours.  |
| F <sub>3</sub> Iron-Manganese Oxide Fraction | 20 ml of 0.04 M NH <sub>2</sub> OH/HCl in 25% HOA $_{\rm C}$ was added to residue from the carbonate fraction. The mixture was adjusted to pH 2 with HCl and was heated at 96 $^{\circ}$ C with occasional shaking for 6 hours.  |
| F4 Organic Fraction                          | Residue from Iron-Manganese Oxide fraction $F_3$ was<br>treated with 5 ml 30% Hydrogen peroxide and heated at<br>85°C for 3 h ours with occasional agitation. On cooling,<br>another 5 ml portion of 30% hydrogen peroxide was<br>added. The mixture was adjusted to pH2 with<br>concentrated Nitric Acid and heated for 3 hours at 85 °C<br>with occasional shaking. It was allowed to cool. 5 ml of 3.2<br>M CH <sub>2</sub> CONH <sub>3</sub> in 20% CH <sub>3</sub> COOH was added to the<br>mixture with continuous agitation for 30 minutes. |
| F5 Residual Fraction                         | Residue from the organic fraction $F_4$ was subjected to Hydrofluoric acid/Aqua regia digestion.   |
| <b>RESULTS AND DISCUSSION</b>                | while the percentages of their total concentrations  |

Table 1: Sequential extraction procedure applied for the speciation of the metals in this study

#### **RESULTS AND DISCUSSION**

The concentrations of the metals in sequential extraction of the soils are presented on Table 2

while the percentages of their total concentrations are presented on Table 3.

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| Sample sites                          |      | Cu           |              |      | Cd    |            |      | ïŻ    |             |        | $\mathbf{Pb}$ |       |      | Ċ     |       |                | Мn             |                |                | Fe           |               |
|---------------------------------------|------|--------------|--------------|------|-------|------------|------|-------|-------------|--------|---------------|-------|------|-------|-------|----------------|----------------|----------------|----------------|--------------|---------------|
| Depth (cm)<br>fraction                | 0.15 | 15-<br>30    | 30-<br>45    | 0.15 | 15-30 | 30-45 0.15 | 0.15 | 15-30 | 30- (<br>45 | 0.15   | 15-30         | 30-45 | 0.15 | 15-30 | 30-45 | 0.15           | 15-30          | 30-45          | 0.15           | 15-30        | 30-45         |
| A: Mgbuka Obosi                       | iosi |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Exchangeable                          | 1.43 | 1.22         | 1.02         | 0.06 | 0.05  | 0.07       | 0.12 | 0.07  | 0.10 1      | 1.57   | 1.31          | 1.08  | 0.09 | 0.06  | 0.03  | 24.90          | 22.40          | 18.30          | 6.78           | 5.56         | 4.32          |
| F1                                    |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Carbonate $F_2$                       | 1.45 | 1.32         | 1.07         | 0.04 | 0.02  | 0.01       | 0.12 |       |             |        | 1.21          | 1.04  | 0.04 | 0.04  | 0.01  | 23.80          | 21.30          | 17.30          | 6.65           | 4.87         | 3.34          |
| Fe-Mn Oxide                           | 1.67 | 1.34         | 1.12         | 0.06 | 0.04  | 0.04       | 0.11 | 0.06  | 0.30 1      | 1.56   | .33           | 1.13  | 0.05 | 0.05  | 0.03  | 26.32          | 21.24          | 20.13          | 8.43           | 6.71         | 4.87          |
| $\mathrm{F}_3$                        |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Organic $F_4$                         | 2.31 | 1.83         | 1.02         | 0.04 | 0.02  | 0.05       | 0.13 |       |             |        | 1.45          | 1.32  | 0.04 | 0.04  | 0.01  | 16.30          | 19.30          | 21.60          | 12.30          | 11.50        | 10.30         |
| Residual $F_5$                        | 1.46 | 1.56         | 1.32         | 0.09 | 0.07  | 0.04       | 0.17 | 0.14  | 0.07 1      |        | 1.23          | 1.02  | 0.08 | 0.07  | 0.08  | 14.10          | 12.40          | 11.70          | 13.40          | 12.10        | 14.40         |
| B: Uwelu                              |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Exchangeable                          | 1.44 | 1.02         | 1.50         | 0.07 | 0.05  | 0.06       | 0.13 | 0.09  | 0.10 1      | 1.67 1 | 1.37          | 1.06  | 0.08 | 0.06  | 0.03  | 24.50          | 21.40          | 17.50          | 6.58           | 5.52         | 4.35          |
| $F_1$                                 |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Carbonate $F_2$                       | 1.51 | 1.52         | 1.06         | 0.05 | 0.03  | 0.01       | 0.14 |       | 0.08 1      |        | 1.23          | 1.07  | 0.05 | 0.05  | 0.01  | 23.70          | 21.10          | 18.40          | 5.65           | 4.83         | 3.38          |
| Fe-Mn Oxide                           | 1.73 | 1.37         | 1.13         | 0.07 | 0.05  | 0.04       | 0.13 | 0.09  |             | 1.66 1 | .34           | 1.17  | 0.06 | 0.07  | 0.03  | 26.52          | 23.17          | 20.63          | 7.43           | 6.81         | 4.76          |
| $F_3$                                 |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Organic $F_4$                         | 2.36 | 1.93         | 1.05         | 0.05 | 0.02  | 0.06       | 0.15 |       |             | _      | 1.49          | 1.42  | 0.06 | 0.05  | 0.01  | 16.50          | 19.70          | 20.30          | 13.30          | 11.70        | 11.30         |
| Residual $F_5$                        | 1.51 | 1.66         | 1.32         | 0.08 | 0.05  | 0.05       | 0.19 | 0.14  | 0.07 1      | 1.41 1 | 1.25          | 1.07  | 0.07 | 0.06  | 0.04  | 14.80          | 13.60          | 14.30          | 12.30          | 12.70        | 15.40         |
| C: Effurun                            |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Exchangeable                          | 2.03 | 1.32         | 1.07         | 0.07 | 0.04  | 0.06       | 0.14 | 0.08  | 0.10 1      | 1.64 ] | 1.35          | 1.04  | 0.09 | 0.06  | 0.03  | 23.50          | 21.40          | 19.20          | 5.58           | 5.52         | 4.12          |
| $F_1$                                 |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Carbonate $F_2$                       | 1.95 | 1.21         | 1.05         | 0.05 | 0.03  | 0.01       | 0.14 |       |             | 1.51   | 1.26          | 1.01  | 0.05 | 0.04  | 0.01  | 22.60          | 20.30          | 16.10          | 6.15           | 4.81         | 3.21          |
| Fe-Mn Oxide                           | 1.87 | 1.24         | 1.12         | 0.06 | 0.04  | 0.06       | 0.13 | 0.09  | 0.06 1      |        | .38           | 1.04  | 0.06 | 0.06  | 0.03  | 26.02          | 23.08          | 21.03          | 7.63           | 6.79         | 4.75          |
| $\mathrm{F}_3$                        |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Organic F <sub>4</sub>                | 3.01 | 1.51         | 1.04         | 0.05 | 0.03  | 0.05       | 0.16 |       |             | 1.64   | 1.49          | 1.27  | 0.05 | 0.04  | 0.01  | 18.30          | 21.20          | 17.20          | 11.60          | 11.30        | 10.70         |
| Residual $F_5$                        | 1.58 | 1.46         | 1.37         | 0.08 | 0.06  | 0.05       | 0.19 | 0.16  | 0.08 1      |        | .27           | 1.02  | 0.06 | 0.07  | 0.08  | 15.20          | 13.40          | 12.40          | 12.80          | 12.20        | 13.40         |
| D: Ughelli                            |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Exchangeable<br>F1                    | 1.39 | 1.62         | 1.12         | 0.06 | 0.06  | 0.07       | 0.17 | 0.10  | 0.09 1      | 1.47   | 1.47          | 1.01  | 0.08 | 0.07  | 0.05  | 22.40          | 23.40          | 16.50          | 6.52           | 6.52         | 4.32          |
| Carbonate F <sub>2</sub>              | 1.31 | 1.52         |              | 0.05 | 0.04  | 0.04       | 0.18 | 0.15  | 0.09 1      | 1.43   | 77            | 1.07  | 0.05 | 0.06  | 0.04  | 19.70          | 22.10          | 17.40          | 5.54           | 5.63         | 3.18          |
| Fe-Mn Oxide                           | 1.63 | 1.37         | 1.12         | 0.08 | 0.06  | 0.05       | 0.16 | 0.10  |             |        | 1.38          | 1.14  | 0.06 | 0.08  | 0.03  | 20.12          | 24.12          | 21.03          | 7.81           | 6.21         | 4.66          |
| $F_3$                                 |      |              |              |      |       |            |      |       |             |        |               |       |      |       |       |                |                |                |                |              |               |
| Organic F <sub>4</sub><br>Residual F. | 2.21 | 1.75<br>1.66 | 1.09<br>1.31 | 0.04 | 0.04  | 0.07       | 0.17 | 0.09  | 0.06 1      | 1.73   | 1.59          | 1.41  | 0.06 | 0.06  | 0.01  | 17.20<br>12.70 | 19.90<br>14.60 | 20.30<br>15 30 | 13.70<br>11.20 | 7.71<br>9.71 | 6.31<br>10.40 |
| C. T TENTISANT                        | 1.74 | 1.00         | 10.1         | 10.0 | 10.0  | 0.00       | 17.0 |       |             |        | 11            | 1.0.1 | 10.0 | 0.01  | 10.0  | 14.10          | 11.00          | 1000           | 11.40          | 7.11         | 01.01         |

| Metal Fraction               | Α     | В     | С      | D     | Average |
|------------------------------|-------|-------|--------|-------|---------|
| Cu                           |       |       |        |       |         |
| F <sub>1</sub> Exchangeable  | 17.33 | 18.57 | 19.34  | 19.02 | 18.57   |
| F <sub>2</sub> Carbonate     | 18.18 | 18.34 | 18.42  | 18.32 | 18.31   |
| F <sub>3</sub> Fe – Mn Oxide | 19.46 | 18.98 | 18.55  | 19.16 | 19.04   |
| F <sub>4</sub> Organic       | 24.43 | 23.96 | 24.34  | 23.50 | 24.06   |
| F5 Residual                  | 20.60 | 20.19 | 19.34  | 20.00 | 20.03   |
| Cd                           |       |       |        |       |         |
| F <sub>1</sub> Exchangeable  | 50.00 | 25.00 | 25.00  | 21.43 | 30.36   |
| F <sub>2</sub> Carbonate     | 5.56  | 12.50 | 12.50  | 14.29 | 11.21   |
| F3 Fe – Mn Oxide             | 13.89 | 20.83 | 20.83  | 21.43 | 19.25   |
| F <sub>4</sub> Organic       | 11.11 | 16.67 | 16.67  | 17.86 | 15.58   |
| F5 Residual                  | 19.44 | 25.00 | 25.00  | 25.00 | 23.61   |
| Ni                           |       |       |        |       |         |
| F1 Exchangeable              | 17.24 | 14.29 | 19.64  | 19.05 | 17.56   |
| F <sub>2</sub> Carbonate     | 17.24 | 14.29 | 21.43  | 22.22 | 18.80   |
| F <sub>3</sub> Fe – Mn Oxide | 27.59 | 11.69 | 16.07  | 17.46 | 15.53   |
| F <sub>4</sub> Organic       | 15.52 | 11.69 | 17.86  | 17.46 | 15.63   |
| F5 Residual                  | 22.35 | 18.46 | 16.92  | 20.00 | 20.38   |
| Pb                           |       |       |        |       |         |
| F1 Exchangeable              | 15.17 | 19.94 | 20.21  | 19.50 | 18.71   |
| $F_2$ Carbonate              | 18.66 | 18.63 | 19.00  | 18.61 | 18.73   |
| F <sub>3</sub> Fe – Mn Oxide | 20.33 | 20.23 | 19.91  | 20.53 | 20.25   |
| F <sub>4</sub> Organic       | 22.91 | 23.14 | 22.17  | 23.34 | 22.89   |
| F5 Residual                  | 18.06 | 18.05 | 18.70  | 18.02 | 18.21   |
| Cr                           |       |       |        |       |         |
| F1 Exchangeable              | 25.00 | 24.00 | 25.00  | 25.00 | 24.75   |
| F <sub>2</sub> Carbonate     | 12.50 | 16.00 | 12.50  | 17.86 | 14.72   |
| $F_3$ Fe – Mn Oxide          | 16,67 | 20.00 | 20.83  | 21.43 | 19.73   |
| F <sub>4</sub> Organic       | 12.50 | 16.00 | 12.50  | 14.29 | 13.83   |
| $F_5$ Residual               | 33.33 | 24.00 | 29.17  | 21.43 | 26.98   |
| Mn                           |       |       |        |       |         |
| F <sub>1</sub> Exchangeable  | 22.31 | 21.45 | 22.09  | 21.73 | 21.90   |
| $F_2$ Carbonate              | 21.22 | 21.39 | 20.34  | 20.64 | 20.90   |
| $F_3$ Fe – Mn Oxide          | 24.03 | 23.59 | 23.86  | 22.76 | 23.56   |
| F <sub>4</sub> Organic       | 19.46 | 19.12 | 19.57  | 20.01 | 19.54   |
| F <sub>5</sub> Residual      | 12.99 | 14.45 | 14.13  | 14.86 | 14.11   |
| Fe                           |       |       | 1 1110 | 1.100 |         |
| F <sub>1</sub> Exchangeable  | 1326  | 13.05 | 12.62  | 15.87 | 13.70   |
| $F_2$ Carbonate              | 11.83 | 11.00 | 11.75  | 13.10 | 11.92   |
| $F_3$ Fe – Mn Oxide          | 15.94 | 15.07 | 15.90  | 17.08 | 16.00   |
| $F_4$ Organic                | 27.17 | 28.81 | 27.87  | 25.33 | 27.30   |
| F <sub>5</sub> Residual      | 31.79 | 32.07 | 31.86  | 28.62 | 31.09   |

 Table 3: Percentage of the total concentrations of the trace elements in each of the geochemical fractions

## Copper

The majority of copper in the soils was associated with organic fraction. The contents ranged from 23.50 to 24.43% with an average of 24.06%. Predominance of copper in organic fraction has been reported by other researchers (Osakwe and Egharevba, 2008; Swietlik *et al.*, 2012; Helali*et al.*, 2013). Devutluoglu *et al.*, (2010) reported 30% while Liang *et al.*, (2014) also reported 33.34% of copper contentsin this fraction. Studies have shown that substantial amount of copper in various soils is often bound to organic phase because the metal is strongly fixed by organic matter to form organic-copper compounds easily (Fagbote and Olanipekun, 2010). This implies that organic matter retains copper by complexation and not by ion exchange (Wu *et al.*, 1999). As a result, high amount of organic bound copper would be relatively immobile in the soil (Froste, 1985).

The next important fraction for copper is residual fraction with an average copper content of

20.03%. High proportion of copper in this phase has been reported in other similar studies (Kumar *et al.*, 2014, Ogubanjo *et al.*, 2016).

Fe-Mn oxide phase contained an average of 19.04% of copper. Asagba *et al.*, (2007) reported an average of 25.8% while Osakwe *et al.*(2012) and Kumar *et al.* (2014) reported 10.88% and 9.50% of copper contents respectively in this phase. Studies have shown that this fraction sequestrates metals in the environment (Nachtegaal and Sparks, 2004, Asagba *et al.*, 2007).

The amount of copper associated with the exchangeable and carbonate fractions were 18.57% and 18.31% respectively. Relatively low proportion of copper in these two phases has been reported (Iwegbue, 2011; Osakwe, 2012; Liang, 2014). These two phases are of special importance because metals associated with them are highly mobile and labile and are readily available for plant uptake and may eventually leach into both surface and groundwater sources thereby posing some ecological risks.

## Cadmium

Cadmium predominated in the exchangeable fraction ranging from 21.43-50% with an average of 30.36%. This is consistent with the findings of Ramos et al., (1994); Ogundiran and Osibanjo, (2009); Iwegbue et al., (2011); Liang et al., (2014). Studies have shown that cadmium compounds in soil solution are relatively soluble, therefore, its high amount in this fraction implies a high ecological risk (Jamnika et al., 2013). This relatively high percentage of exchangeable associated cadmium shows that cadmium in the studied soil is of anthropogenic origin and can enter food chain easily through plant uptake (Tokalioghe et al., 2003). The next important fraction is Residual fraction with an average of 23.61% amount of cadmium. Osakwe (2013) reported 37.69% residual bound cadmium in contaminated soils of Eastern Nigeria.. The amount of cadmium associated with Fe-Mn oxide phase was an average of 19.25%. Ahmadepour et al., (2014) reported an appreciable amount of cadmium associated with Fe-Mn oxide fraction. Carbonate and organic phases contained 11.21% and 15.58% of cadmium respectively. Kotoky et al., (2003) reported 15.30% while Jaradat et al. (2006)

reported 13.0% of this metal associated with the organic phase. Osakwe 2013) and Asagba *et al.*, (2007) reported 14.86% and 34.0% of the carbonate bound cadmium respectively.

# Nickel

Nickel was mostly associated with the residual fraction with the proportion ranging from 16.92 to 23.35% and an average of 20.38%. Highest percentage of residual bound nickel in soils has been reported in many studies (, Osakwe, 2010; Nogueirol and Alleoni, 2013, Kumar, 2014; Liang, 2014). Metals in these fractions are insoluble in the soil and are not available for plant uptake because they are held within the mineral matric (Chaudhary and Benerjee, 2007). The amount of Nickel associated with this fraction indicates that a relatively substantial proportion of nickel in these soils is of geogenic origin and its mobilization is not possible. Moral et al., (2005) reported that nickel is greatly controlled by parent materials. Theother important fractions for nickel were the carbonate and Fe-Mn oxide with the metal average contents of 18.80% and 18.20% respectively. Osakwe (2013) reported 10.47% of carbonate bound nickel and 4.98% of Fe-Mn oxide bound nickel. Organic fraction contained 15.63% of nickel. Low level of organic bound nickel has been reported (Kotoky et al., 2003; Osakwe and Okolie, 2015).

# Lead

Lead was dominant in organic phase with its proportion ranging from 22.17 - 23.34% and an average of 22.89%. This result is in agreement with those reported by Helali *et al.*, (2013); Woszczyk and Spychalsk (2013), Ogubanjo *et al.*, (2016).

The proportion of organic matter associated with lead obtained in this study is higher than those reported by Osakwe *et al.*, (2012), Ibrahim *et al.*, (2013) but lower than those reported by Asagba *et al.*,(2007), Li and Thornton (2001). Lopez-Sanchez*et al.*,(1996) suggested that lead is usually associated with organic fraction because it forms stable complex with the organic matter. Spencer *et al.*, (2003) also suggested that the lead bound organic complexes are formed as a result of early digenetic reduction of the phase. The next significant fraction was Fe-Mn oxide with an average of 20.25%. This is closely in agreement with 20.7% reported by Asagba *et al.*, (2007). The remaining proportion of lead appeared almost evenly associated with exchangeable, carbonate and residual phases with 18.71%, 18.73% and 18.21% respectively.

## Chromium

The most important fraction for chromium was the residual phase. The proportion ranged from 21.43 – 33.33% with an average of 26.98%. This result corroborates the findings of Kotoky et al., (2003), Iwegbue (2011), Osakwe (2013), Liang et al., (2014). The predominance of chromium in this fraction implies low solubility of the metal and its unavailability to biota. The finding in this study is at variant with the results of Ogunderan and Osibanjo (2009) reporting predominance of the metal in non-residual fractions linking its association with human activities on the soil. Exchangeable fraction was the next important phase for this metal with an average of 24.75%. Low levels of chromium association with this fraction have been reported (Birch and Owen 2001, Osakwe, 2013, Osakwe and Okolie 2015). A substantial amount of this metal in exchangeable fraction was reported by Kotoky et al., 2003. The speciation pattern followed the order: Residual> Exchangeable > Fe-Mn Oxide > Carbonate > Organic fraction.

#### Manganese

Fe-Mn oxide was the most significant fraction for manganese with contents ranging from 22.76 -24.30% and an average of 23.76%. Similar association of manganese with Fe-Mn oxide fraction was reported by Osakwe (2010), Iwegbue (2011), Swietliket et al., (2012), Helali et al., (2013). The proportion of manganese obtained in this study is lower than the value (38.94%) reported by Liang et al., (2014). Abeh et al., (2007) reported an average of 24.72% of manganese in this fraction and suggested that this association may be due to manganese interferences with crystals of iron (III) oxide precipitate. Metals bound to this fraction are considered relatively stable but may become available for plant uptake under some soil physicochemical conditions (Carot etal., 2002). Exchangeable fraction which was the next important phase for this metal contained 21.90% manganese. The exchangeable bound manganese obtained in this study is higher than those reported by Pizzaro *et al.*, (2003), Abeh *et al.*, (2007). The association pattern of manganese in the different phases were in the trend Fe-Mn oxide > Exchangeable > Carbonate > Organic > Residual.

## Iron

The highest proportion of iron in the soils was associated with Residual fraction with an average of 31.09% followed by organic fraction with an average of 27.30%. The predominance of iron in Residual fraction is in agreement with result from other related studies Helali et al., 2013, Ogubanjo, et al., 2016). The high proportion of iron in this phase implies insolubility of the metal in these soils because silicate lattice layer and oxide minerals occlude the fraction (Terus, 1995). Since insolubility of metals in the soils is related to immobility and non-bioavailability of the metal, the potential risk associated with iron in these soils will be low. Substantial amount of iron associated with organic phase has been reported (Tessier et al., 1979, Eusterhus et al., 2005). Tokalioglu et al., (2000) reported that complexes of iron with organic substances are very common. The associations of iron with other phases were 13.70%, 11.92% and 16.00% for exchangeable, carbonate and Fe-Mn oxide fractions respectively. Relatively low associations of iron in these phases have been reported (Osakwe, 2013, Ogubanjo, et al., 2016).

# Mobility Factors of the trace metals in the soil samples

Different sequential extraction schemes have been adopted by different researchers and in each of these procedures, the sequential extraction comprises using extractants, each being more drastic in action than the previous one (Chaudhary and Banerjee, 2007). As a result, the metals are fractionated in order of their decreasing solubilities as follows  $F_1 > F_2 > F_3 > F_4 > F_5$ . Since  $F_1$ and  $F_2$  are the early fractions, they are regarded as the most mobile and bioavailable fractions because they are weakly bound to soil components (Kabala and Singh, 2001). The sum of their percentages is calculated as mobility factor (Salbu et al., 1998, Kabala and Singh, 2001). The mobility factors of the trace metals in the soil samples are presented on Table 4.

|         | Cu    | Cd    | Ni    | Pb    | Cr    | Mn    | Fe    |
|---------|-------|-------|-------|-------|-------|-------|-------|
| А       | 35.5  | 25.0  | 34.48 | 33.83 | 37.50 | 43.53 | 25.09 |
| В       | 36.87 | 27.50 | 31.13 | 38.59 | 40.00 | 42.84 | 23.06 |
| С       | 37.76 | 37.50 | 41.07 | 39.21 | 37.50 | 42.43 | 24.37 |
| D       | 37.34 | 35.72 | 42.70 | 38.11 | 42.86 | 42.17 | 38.97 |
| Average | 37.37 | 31.43 | 37.35 | 37.44 | 39.47 | 42.74 | 27.87 |

 Table 4: Mobility Factors of the trace metals in the soil samples

The mobility factor values obtained in this study are relatively higher than those reported by Iwegbue (2007), Ataikiru et al., (2008), Osakwe, (2013) but lower than the values reported by Ogundiran and Osibanjo (2009). The average mobility factor values were 37.37 for Cu, 31.43 for Cd, 37.35 for Ni, 37.44 for Pb, 39.47 for Cr, 42.74 for Mn and 27.87 for Fe. These values for the metals were observed to be in the order of Mn> Cr > Cu > Ni > Pb > Cd > Fe. The average mobility factor values for all the metals in all the sites are above 20.00 which indicates that changes in the physicochemical conditions of the soil may lead to significant remobilization of the metals. This is of great concern because all the metals studied constitute potential health risk at their toxicity levels.

#### CONCLUSION

This study provided relevant information on the geochemical nature of the trace metals and their association with various phases in the studied soils. Nickel, Chromium and Iron were mainly associated with the residual fraction. Copper and Lead were predominantlybound to the organic phase while cadmium and manganese mainly existed in the fractions bound to exchangeable and Fe-Mn oxide respectively. The pattern of the metals speciation obtained in this study gives the overall picture that nickel, chromium and iron are of geogenic origin and can not be mobilized and made available to biota. On the other hand, the other four remaining trace metals copper, lead, manganese and cadmium are from anthropogenic sources. The relatively high mobility factor values above 20.00 for the metals is an indication that changes in soil physicochemical conditions may lead to significant remobilization of the metals. Although, the results obtained from the sequential extraction procedure shows that generally higher amount of the metals are in non-exchangeable phases, the high mobility factor values of the metals may lead to remobilization of the metals when there is change in the soil physicochemical conditions and they may become mobile and bioavailable to biota and may enter food chain thereby constituting health risks.

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