



Chemical Speciation and Mobility of Some Heavy Metals in Soils around Automobile Waste Dumpsites in Northern Part of Niger Delta, South Central Nigeria

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ABSTRACT: The mobility of some heavy metals (Fe, Co, Ni and Mn) in soils around automobile waste dumpsites in Northern part of Niger Delta was assessed using Tessier et al. five steps sequential chemical extraction procedure. The results showed that majority of iron and manganese were associated with the residual fraction with the average levels of 29.2% and 24.43% respectively. The exchangeable fraction was the most important fraction for cobalt with the average level of 39.53%, while the organic fraction contained the predominant species of nickel with an average level of 22.97%. For the total concentrations of the metals, iron ranging from (mg kg^{-1}) 768.30 to 2897.00 was the highest followed by manganese ranging from 1.78 to 19.92 and then cobalt and nickel which ranged from 0.28 to 2.42 and 0.084 to 0.512 respectively. The mobility factors for the metals in all the sites ranged from 20.37 to 90.90 for cobalt, 15.83 to 62.07 for nickel, 25.50 to 60.43 for manganese and 16.49 to 32.13 for iron following the order $\text{Co} > \text{Ni} > \text{Mn} > \text{Fe}$. The relatively high mobility factors observed for cobalt in some sites coupled with its comparatively high concentration in the exchangeable fraction, indicates high mobility, lability and bioavailability for cobalt in the soils studied. The other metals (Fe, Ni and Mn) which are strongly bound to soil matrix are not readily available for introduction into the food chain. The results suggest that there is no serious contamination hazard with the metals studied, considering the geochemical phases in which Fe, Ni and Mn were associated with, and the low total metal concentration of Co, even with its relatively high mobility. @JASEM

The behaviour and fate of metals are governed by a range of different physicochemical processes which dictate their availability and mobility in the soil or sediment system. The knowledge of the chemical forms of soluble heavy metals or of heavy metals associated with particulates or colloids is essential for estimating the bioavailability, mobility and chemical reactivity in soils and sediments (Hickey and Kittrick, 1984). To assess the bioavailability of heavy metals, sequential extraction procedure consists of a series of chemical extractants, each being more drastic in action and of different nature than the previous one (Chaudhary and Banerjee, 2007).

Soil is relatively heterogeneous in terms of its physical chemical and biological characteristics, (Hakanson, 1992). Heavy metals are associated with various soil components in different ways and these associations determine their mobility and availability (Ahumuda *et al.*, 1999).

In recent years there has been increased interest in the studies on speciation or chemical forms of heavy metals in polluted soils using sequential extraction techniques because these provide knowledge on metal affinity to soil components and the strength with which they are bound to matrix (Kotoky *et al.*, 2003). The use of sequential extractions, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals (Tessier *et al.*, 1979). Among the numerous extraction schemes described in literature, the procedure of Tessier *et al.*, (1979) is one of the most thoroughly researched and widely used procedures to evaluate the possible chemical association of metals in soils and sediments.

The soils around automobile waste dumpsites are

considered to be contaminated by heavy metals since these waste dumpsites consist primarily of automobile and machine parts and scraps at various stages of corrosion, discarded motor batteries and tyres, cans, cables, etc.

The aim of the present study is to investigate the different chemical forms of Fe, Co, Ni and Mn in the soils around the automobile waste dumpsites and to assess the association and bioavailability of these metals and their environmental contamination risk between the different geochemical phases based on chemical speciation.

MATERIALS AND METHODS

The study Area: The study area located in the Northern part of the Niger Delta, South Central of Nigeria, lies within the coordinates of latitude $6^{\circ}05'N$ to $6^{\circ}16'N$ and longitude $6^{\circ}07'E$ to $6^{\circ}12'E$. The undulating rugged sedimentary terrain with steep slopes marks the principal relief feature of the area. The mean annual rainfall in this area ranges between 2540-3500mm and temperature varies between $28^{\circ}C$ to $33^{\circ}C$ around March and $23^{\circ}C$ – $30^{\circ}C$ around August. The area experiences an average industrialization and commercial activities and large population of automobiles attracts many mechanic workshops and automobile dumpsites.

Sampling and Analysis: Soil samples were collected from selected automobile waste dumpsites at depths of 0-15cm, 15-30cm, and 30-45cm, representing top soils, sub soils and bottom soils respectively. The soil samples were air-dried, homogenized by grinding, and filtered through a 2mm mesh sieve. They were then oven-dried at $105 \pm 0.5^{\circ}C$ to a constant mass, cooled and stored in labelled plastic cans until analysis (Allen *et al.*, 1974). The samples for

atomic absorption spectroscopic analysis were digested using a mixture of 2ml 60% perchloric acid, 15ml nitric acid, and 1ml sulphuric acid (Burrell 1974). For the chemical fractionation of the metals under study, the procedure of Tessier *et al.*, (1979) was selected. In this method heavy metals, were separated into five operationally defined fractions: Exchangeable (F_1), bound to carbonate (F_2), bound to Fe-Mn oxide (F_3), bound to organic matter (F_4), and residual fraction (F_5).

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

ii. **F₁:** Exchangeable: The soil sample was extracted at room temperature for 1 hour with 8ml of 1M magnesium chloride solution at pH 7.0 with continuous agitation.

iii. **F₂:** Metals Bound to Carbonate: The residue from (i) was leached at room temperature with 8ml of 1M sodium acetate solution adjusted to pH 5.0 with acetic acid. Continuous agitation was maintained.

iv. **F₃:** Metals Bound to Fe-Mn Oxide: The residue from (ii) was extracted with 20ml of 0.04M hydroxylamine chloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in 25% (v/v) acetic acid and was heated to 96°C with occasional agitation for 6 hours.

v. **F₄:** Metals Bound to Organic Matter: The residue from (iii) was extracted with 3ml of 0.02M nitric acid (HNO_3) and 5ml of 30% Hydrogen peroxide (H_2O_2) adjusted to pH 2.0 with nitric acid and the mixture was heated to 86°C for 3 hours with intermittent agitation. The mixture was cooled and 5ml of 3.2M ammonium acetate (NH_4OAc) in 20% (v/v) nitric acid (HNO_3) was added and the sample

was diluted to 20ml and agitated continuously for 30 minutes.

vi. **F₅:** Residual Metals: The residue from (iv) was digested with a mixture of Hydrofluoric acid, nitric acid and perchloric acid.

The supernatant from each extraction step was removed with a pipette and analyzed for total metal concentrations using acetylene flame Atomic Absorption Spectrophotometer (Perkin Elmer Model Analyst 2002), fitted with deuterium lamp for background correction, following the procedure of Sakata (1983). When continuous agitation was required, the samples were shaken lengthwise on a mechanical shaker at 265 oscillations per minute with a stroke of 8cm.

Heating of the samples was done using Al block heater. Standards for all metals were prepared for each extraction step in the same matrix as the extracting reagent to minimize matrix effects. Standard addition technique and background corrections using blanks were employed to overcome interferences. At least one duplicate and one spike sample was run for every two samples to verify the precision of the method. The spike recovery and the precision was found within $100 \pm 10\%$.

Appropriate quality control measures and recovery study were carried out. All reagents used in this study were of pure analytical grade and were checked for possible trace metal contamination. All glasswares for metal analysis were previously soaked in 14% nitric acid (HNO_3) (v/v), for 24 hours to remove all entrained metals, washed with detergents and rinsed with deionized water.

RESULTS AND DISCUSSION

Tables 1-4 present the concentrations of the metals in various geochemical fractions of the soil while the percentage metals in the fractions are presented in Table 5.

Table 1: Concentrations (mgkg^{-1}) of iron (Fe) in various geochemical fractions of the soil (F_1 = Exchangeable, Carbonate = F_2 ; non-manganese Oxide = F_3 ; Organic matter = F_4 , Residual = F_5 , SS = sampling sites

| SS | D (cm) | F_1 | F_2 | F_3 | F_4 | F_5 |
|----|--------|--------|--------|--------|--------|--------|
| A | 0-15 | 280.50 | 277.30 | 360.20 | 480.30 | 672.90 |
| | 15-30 | 260.30 | 548.90 | 562.30 | 802.40 | 720.30 |
| | 30-45 | 101.46 | 121.66 | 151.29 | 122.46 | 263.70 |
| B | 0-15 | 207.50 | 232.70 | 633.70 | 973.90 | 622.00 |
| | 15-30 | 311.40 | 386.10 | 592.80 | 921.30 | 638.00 |
| | 30-45 | 241.30 | 208.90 | 541.30 | 806.30 | 538.20 |
| C | 0-15 | 186.30 | 200.30 | 248.40 | 742.90 | 554.90 |
| | 15-30 | 155.90 | 231.60 | 255.60 | 682.30 | 603.70 |
| | 30-45 | 232.30 | 281.60 | 242.30 | 637.20 | 531.60 |
| D | 0-15 | 286.30 | 336.00 | 284.00 | 714.00 | 639.20 |
| | 15-30 | 312.40 | 302.00 | 329.00 | 622.00 | 543.90 |
| | 30-45 | 211.40 | 228.00 | 240.00 | 623.70 | 581.20 |
| E | 0-15 | 364.20 | 433.20 | 596.30 | 488.70 | 599.30 |
| | 15-30 | 392.30 | 320.30 | 629.40 | 733.90 | 484.70 |
| | 30-45 | 128.10 | 173.60 | 386.30 | 391.60 | 488.00 |
| F | 0-15 | 106.10 | 90.30 | 118.30 | 200.50 | 392.50 |
| | 15-30 | 74.20 | 68.30 | 150.60 | 198.40 | 282.70 |
| | 30-45 | 92.30 | 83.70 | 120.60 | 151.70 | 233.70 |

Table 2: Concentrations (mgkg⁻¹) of cobalt (Co) in various geochemical fractions of the soil

| SS | D (cm) | F ₁ | F ₂ | F ₃ | F ₄ | F ₅ |
|----|--------|----------------|----------------|----------------|----------------|----------------|
| A | 0-15 | 0.02 | 0.00 | 0.00 | 0.03 | 0.02 |
| | 15-30 | 0.01 | 0.00 | 0.004 | 0.004 | 0.004 |
| | 30-45 | 0.01 | 0.001 | 0.001 | 0.002 | 0.04 |
| B | 0-15 | 0.01 | 0.00 | 0.00 | 0.00 | 0.001 |
| | 15-30 | 0.02 | 0.00 | 0.004 | 0.004 | 0.03 |
| | 30-45 | 0.03 | 0.00 | 0.01 | 0.002 | 0.002 |
| C | 0-15 | 0.00 | 0.00 | 0.04 | 0.00 | 0.005 |
| | 15-30 | 0.03 | 0.04 | 0.005 | 0.02 | 0.00 |
| | 30-45 | 0.02 | 0.00 | 0.01 | 0.00 | 0.003 |
| D | 0-15 | 0.05 | 0.003 | 0.002 | 0.005 | 0.04 |
| | 15-30 | 0.03 | 0.001 | 0.004 | 0.004 | 0.06 |
| | 30-45 | 0.03 | 0.001 | 0.006 | 0.006 | 0.006 |
| E | 0-15 | 0.46 | 0.41 | 0.63 | 0.17 | 0.67 |
| | 15-30 | 0.23 | 0.33 | 0.46 | 0.42 | 0.56 |
| | 30-45 | 0.17 | 0.39 | 0.06 | 0.29 | 0.17 |

The majority of iron in the soils was associated with the residual fraction, having the range from 22.89% to 36.76% with an average of 29.2%. This is consistent with the results of Horsfall and Spiff, (2005); Gupta and Chen, (1975); Ramos *et al.*, (1994); Abeh *et al.*, (2007); Segarra *et al.*, (2008). The residual fraction is considered the most stable, less reactive and less bioavailable since it is occluded within the crystal lattice layer of silicates and well crystallized oxide minerals (Abeh *et al.*, 2007; Schawarzenbach *et al.*, 1993). The fraction can be taken as a guide to the degree of pollution of the soil. The smaller the percentages of the metal present in this fraction, the greater the pollution of the area (Horsfall and Spiff, 2005). The high percentage of iron found in residual fraction is an important repository of iron in the soil. In sandy soil that contains little clay, iron oxide could be leached through the soil and impact ground water quality.

Organic fraction with iron content varied from 23.93% to 35.64% and an average of 28.45%, had next high average percentage of iron. High iron content (28.28%) in organic fraction has been reported (Urunmatsoma and Ikhuoria, 2005). Organic compounds of heavy metals can be directly or indirectly introduced into soil through the formation of complexes and can be taken up by plants. Organic content is associated with the production of gas, and in sandy soil that contains little clay, organic matter and phosphate can leach through the soil and impact ground water (Urunmatsoma and Ikhuoria, 2005).

Next in importance for iron content was Fe-Mn oxide fraction having the range between 12.90% and 24.76% with an average of 18.52%. This fraction could be considered relatively stable, slowly mobile and poorly available but could change with variations in redox conditions. It may become more soluble under reducing conditions and less so under oxidizing ones (Horsfall and Spiff, 2005). The considerable level of iron in Fe-Mn oxide fraction can be

explained by the precipitation effect of Fe-Mn oxyhydroxides in water. Under strong oxidizing conditions and neutral pH value, Fe²⁺ can be transformed into Fe³⁺ rapidly precipitated as Fe oxyhydroxide (Stumm and Morgan, 1981).

The concentrations of iron found in carbonate fraction varied from 10.53% to 19.95% with an average of 13.57%. The iron concentration reported here is in agreement with the result obtained by Abeh *et al.*, (2007). Low iron content in this fraction has been reported (Horsfall and Spiff, 2005; Urunmatsoma and Ikhuoria, 2005; Zhang *et al.*, 1998). The exchangeable fraction of iron ranged between 9.68% and 13.18% with an average of 11.61%. Low iron in exchangeable fraction has been reported (Horsfall and Spiff, 2005). The carbonate and exchangeable fractions are released into solutions of low pH, which can be related to stomach conditions (Evans *et al.*, 1992). The association pattern of iron in the different phases were in the order residual > organic > Fe-Mn oxide > carbonate > exchangeable.

Table 4: Concentrations (mgkg⁻¹) of manganese in geochemical fractions of the soil

| S S | D (cm) | F ₁ | F ₂ | F ₃ | F ₄ | F ₅ |
|-----|--------|----------------|----------------|----------------|----------------|----------------|
| A | 0-15 | 2.63 | 3.16 | 3.28 | 3.11 | 3.28 |
| | 15-30 | 2.43 | 2.67 | 2.24 | 2.33 | 2.94 |
| | 30-45 | 1.28 | 1.44 | 1.48 | 2.06 | 2.37 |
| B | 0-15 | 2.92 | 2.45 | 3.21 | 4.26 | 5.62 |
| | 15-30 | 1.28 | 3.06 | 2.98 | 3.48 | 6.22 |
| | 30-45 | 1.98 | 1.66 | 2.31 | 1.74 | 3.42 |
| C | 0-15 | 1.96 | 1.19 | 4.31 | 1.16 | 1.16 |
| | 15-30 | 1.93 | 1.94 | 2.67 | 2.01 | 2.05 |
| | 30-45 | 1.25 | 1.63 | 2.51 | 1.22 | 2.82 |
| D | 0-15 | 3.16 | 3.21 | 3.46 | 5.44 | 4.26 |
| | 15-30 | 3.14 | 3.06 | 3.28 | 3.71 | 4.08 |
| | 30-45 | 2.63 | 2.84 | 2.97 | 3.82 | 5.19 |
| E | 0-15 | 3.54 | 8.48 | 3.01 | 1.15 | 2.63 |
| | 15-30 | 1.85 | 2.99 | 1.97 | 3.67 | 1.18 |
| | 30-45 | 1.81 | 1.58 | 1.47 | 2.33 | 1.15 |
| F | 0-15 | 0.44 | 0.84 | 0.56 | 0.58 | 1.42 |
| | 15-30 | 0.29 | 0.33 | 0.12 | 0.09 | 0.96 |
| | 30-45 | 0.37 | 0.53 | 0.42 | 0.44 | 0.92 |

The exchangeable fraction was the most important fraction for cobalt having the range of 14.43% to 68.97 with an average of 39.53%. This fraction represents heavy metals soluble in water as well as those held by electrostatic adsorption. The amount of metal in this phase indicated the environmental conditions of the soil. The high percentage of cobalt in this fraction suggests a greater contamination risk for cobalt.

Next in importance for cobalt content was the residual fraction having the range from 4.62% to 43.84% and an average of 27.00%. Fe – Mn oxide fraction contained cobalt in the range of 3.42% and 31.79 with an average of 14.19%. This was followed by organic bound fraction with the range between 5.31% and 24.66% and an average of 11.86%. Carbonate fraction was of the least importance with range between 0.00% and 23.12% with an average of 7.46%. Cobalt was not available in this fraction in sites B and F.

Nickel was predominantly associated with organic and residual fractions averaging 22.97% and 22.24% respectively. Organic nickel varied from 13.63% to 35.21% while residual nickel varied from 10.12% to 34.38%. This predominance of inactive forms of nickel is consistent with other reports of contaminated soils (Gupta and Chen, 1975; Tessier and Campbell, 1980; Ma and Rao, 1997; Iwegbue, 2007; Abeh *et al.*, 2007), although high levels of soluble nickel were found in Kaolin soil (Reedy *et al.*, 2001). Tessier *et al.*, 1979; Hickey and Kittrick 1984; Ryan *et al.* 2002; Kotoky *et al.* 2003; Horsfall and Spiff 2005; Egila and Nomyel (2002). Segarra *et al.*, (2008) reported high levels of nickel in residual fraction. Norrish (1975) reported that nickel is commonly occluded by silicate during soil weathering. Nickel in Fe-Mn oxide fraction varied from 10.36% to 32.35% with an average of 19.67%. Hickey and Kittrick (1984) similarly reported significant amount of nickel in this fraction. Jenne (1968) had suggested that the levels of nickel in this fraction depend on how much Mn oxide is adsorbed in a given soil sample because Ni^{2+} could substitute for surface manganese in mixed valence Mn oxides. Exchangeable nickel varied from 7.52% to 50.17% with an average of 18.67% while carbonate fraction nickel varied from 10.12% to 27.84% with an average of 16.44%. Similar levels of nickel in carbonate fraction were reported by Horsfall and Spiff, (2005). Residual fraction contained the predominant species of manganese. The levels varied from 14.96% to 39.71% with an average of 24.43%. Relatively high level of manganese in residual fraction has been reported (Iwegbue, 2007; Horsfall and Spiff, 2005). The association of manganese with residual fraction implies partitioning into trioctahedral clay and/or crystalline oxides (Ryan *et al.*, 2002). Mn^{3+} and Mn^{4+} are insoluble ions which

form oxides such as MnO_2 , $MnOOH$ and Mn_3O_4 or become incorporated into silicates (McBride, 1997).

The carbonate fraction forms the second most important species of manganese in the soil matrix. The levels of manganese in this fraction varied from 15.26% to 32.76% with an average of 20.21%. Similar results were reported by Horsfall and Spiff, (2005) who observed an average manganese level of 19.07% in sediments of Diobu River in Port Harcourt. Iwegbue, (2007) reported an average of 22.6% manganese in carbonate fraction, in Ase River sediments in Niger Delta. These results corroborated observation of Pizzaro *et al.*, 2003) who reported 13-25% of total manganese with carbonate fraction for Rapel reservoir (Chile) sediment. Abeh *et al.*, (2007) reported an average of 20.33% carbonate manganese in street dust in Jos, Plateau State of Nigeria.

The percentage of total manganese in the Fe-Mn oxide fraction ranged from 13.24% of 31.77% with an average of 19.38%. Abeh *et al.*, (2007), reported manganese level in the range of 19.95% and 34.10% with an average of 24.72% while Iwegbue, 2007 reported the range from 13.38% to 55.06% of manganese in this fraction. The association of manganese may be attributed to its interference in the crystal of Fe oxide precipitate leading to its less occlusion (Abeh *et al.*, 2007). Though, this fraction may be considered relatively stable, it becomes more soluble under acidic conditions and less so under oxidizing conditions (Carot *et al.* 2002; Graham and Stangoulis, 2003).

Organic fraction contained manganese in the range from 13.36 to 23.91% with an average of 19.38%. Similar results were reported by Horsfall and Spiff, 2005, and Abeh *et al.*, (2007).

The exchangeable fraction of manganese ranged from 13.15% to 18.07% with an average of 15.56%. Similar association of manganese with exchangeable fraction has been reported (Pizzaro *et al.*, 2003; Iwegbue, 2007; Abeh *et al.*, 2007). The relative percentage ranges in exchangeable and carbonate fractions suggest that manganese is (1) available on the exchange sites (2) possibly also present in the soluble carbonates such as cholemites which may occur in trace amounts and dissolve during the HOAc extraction (Iwegbue 2007). The Mn^{2+} ion is very soluble in water at pH less than 7 (Brooklin 1988; McBride, 1997) and given the pH range of these soils (4.9-7.4), soluble exchangeable Mn^{2+} is likely.

The accuracy of the sequential extraction procedure was evaluated by comparing for the samples, the total metal content with the sum of the metal fractions extracted in the five fractions (Table 6). The values are in close agreement showing some degree of accuracy in the sequential procedure used.

TABLE 5: Percentage Metals in Various Geochemical Fractions of the Soil

| Sites | A | B | C | D | E | F | |
|-----------------------------|-------|-------|-------|-------|-------|-------|---------|
| Metal Fractions | | | | | | | AVERAGE |
| Fe | | | | | | | |
| F ₁ Exchangeable | 13.18 | 9.68 | 9.93 | 12.96 | 12.05 | 11.85 | 11.61 |
| F ₂ Carbonate | 19.95 | 10.54 | 12.33 | 13.85 | 14.24 | 10.53 | 13.57 |
| F ₃ Fe-Mn oxide | 22.36 | 22.50 | 12.90 | 13.64 | 24.76 | 16.93 | 18.52 |
| F ₄ Organic | 30.58 | 34.39 | 35.64 | 31.34 | 24.80 | 23.93 | 28.45 |
| F ₅ Residual | 33.98 | 22.89 | 29.21 | 28.21 | 24.15 | 36.76 | 29.20 |
| Co | | | | | | | |
| F ₁ Exchangeable | 27.40 | 53.10 | 28.90 | 44.35 | 14.43 | 68.97 | 39.53 |
| F ₂ Carbonate | 0.68 | 0.00 | 23.12 | 2.02 | 18.96 | 0.00 | 7.46 |
| F ₃ Fe-Mn oxide | 3.42 | 12.39 | 31.79 | 4.84 | 28.36 | 4.31 | 14.19 |
| F ₄ Organic | 24.66 | 5.31 | 11.56 | 6.05 | 14.7 | 8.62 | 11.86 |
| F ₅ Residual | 43.84 | 29.20 | 4.62 | 42.74 | 23.49 | 18.10 | 27.00 |
| Ni | | | | | | | |
| F ₁ Exchangeable | 14.71 | 11.95 | 18.78 | 50.17 | 8.88 | 7.52 | 18.67 |
| F ₂ Carbonate | 14.71 | 13.94 | 18.54 | 10.12 | 13.49 | 27.84 | 16.44 |
| F ₃ Fe-Mn oxide | 32.35 | 10.36 | 15.73 | 12.73 | 29.61 | 17.76 | 19.67 |
| F ₄ Organic | 20.59 | 29.88 | 35.21 | 16.86 | 13.65 | 21.67 | 22.97 |
| F ₅ Residual | 17.65 | 33.86 | 11.74 | 10.12 | 34.38 | 25.71 | 22.24 |
| Mn | | | | | | | |
| F ₁ Exchangeable | 17.28 | 13.15 | 15.17 | 16.46 | 18.07 | 13.24 | 15.56 |
| F ₂ Carbonate | 19.82 | 15.26 | 16.64 | 16.79 | 32.76 | 20.46 | 20.21 |
| F ₃ Fe-Mn oxide | 19.05 | 18.09 | 31.77 | 17.90 | 16.26 | 13.24 | 19.38 |
| F ₄ Organic | 20.45 | 21.03 | 15.34 | 23.91 | 17.95 | 13.36 | 19.38 |
| F ₅ Residual | 23.42 | 32.47 | 21.08 | 24.94 | 14.96 | 39.71 | 24.43 |

Table 3: Concentrations (mgkg⁻¹) of Nickel in geochemical fractions of the soil

| SITES | Depth (cm) | F ₁ | F ₂ | F ₃ | F ₄ | F ₅ |
|-------|------------|----------------|----------------|----------------|----------------|----------------|
| A | 0-15 | 0.02 | 0.03 | 0.06 | 0.03 | 0.00 |
| | 15-30 | 0.02 | 0.01 | 0.04 | 0.03 | 0.02 |
| | 30-45 | 0.01 | 0.01 | 0.01 | 0.01 | 0.04 |
| B | 0-15 | 0.02 | 0.02 | 0.02 | 0.08 | 0.05 |
| | 15-30 | 0.03 | 0.02 | 0.012 | 0.02 | 0.04 |
| | 30-45 | 0.01 | 0.03 | 0.02 | 0.05 | 0.08 |
| C | 0-15 | 0.01 | 0.03 | 0.012 | 0.09 | 0.01 |
| | 15-30 | 0.05 | 0.04 | 0.015 | 0.03 | 0.01 |
| | 30-45 | 0.02 | 0.009 | 0.05 | 0.03 | 0.03 |
| D | 0-15 | 0.52 | 0.03 | 0.031 | 0.08 | 0.02 |
| | 15-30 | 0.034 | 0.06 | 0.04 | 0.08 | 0.04 |
| | 30-45 | 0.041 | 0.03 | 0.08 | 0.04 | 0.06 |
| E | 0-15 | 0.022 | 0.031 | 0.066 | 0.024 | 0.073 |
| | 15-30 | 0.018 | 0.022 | 0.063 | 0.041 | 0.096 |
| | 30-45 | 0.014 | 0.029 | 0.051 | 0.018 | 0.04 |
| F | 0-15 | 0.066 | 0.049 | 0.144 | 0.38 | 0.231 |
| | 15-30 | 0.038 | 0.022 | 0.097 | 0.016 | 0.149 |
| | 30-45 | 0.041 | 0.025 | 0.092 | 0.022 | 0.166 |

Mobility Factors of the Metals in the Soil Profile

The operationally defined extraction sequence fractionates the heavy metals in the soil in order of decreasing solubility. As a result, the exchangeable and carbonate (F₁ + F₂) fractions which are the early fractions, capture the most reactive and presumably the most mobile and bioavailable fractions (Kersten and Forstner, 1989).

The relative index of metal mobility was calculated as a mobility factor (MF) (Salbu et al, 1998; Narwal et al, 1999; Kabala and Singh, 2001) on the basis of the following equation.

$$MF = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times 100$$

Where F₁ = Exchangeable metal content fraction
F₂ = Metal content bound to carbonate fractions

F₃ = Metal content bound to Fe-Mn oxide fraction
 F₄ = Metals content bound to organic matter fraction
 F₅ = Residual metal content fraction

biological availability (Karczewska 1996; Ma and Rao 1997; Ahumuda *et al.* 1999; Narwal *et al.* 1999; Kabala and Singh 2001).

A high MF value for heavy metals in soil has been interpreted as evidence of relatively high lability and

The mobility factors (MF) of the metals for all the sites and soil depths are presented on Table 7

Fig. 6. Total concentrations of Fe, Co, Ni and Mn and the sum of fractions obtained by sequential extraction procedures

| Metal Total Concentrations (mgkg ⁻¹) | | | | | | Sum of the Fractions F ₁ to F ₅ (mgkg ⁻¹) | | | |
|--|-----------------|---------|-------|-------|-------|---|-------|-------|-------|
| Sites | Soil Depth (cm) | Fe | Co | Ni | Mn | Fe | Co | Ni | Mn |
| A | 0-15 | 2111.6 | 0.073 | 0.16 | 12.71 | 2071.2 | 0.70 | 0.14 | 15.46 |
| | 15-30 | 2897.00 | 0.028 | 0.13 | 8.67 | 2894.2 | 0.022 | 0.12 | 12.61 |
| | 30-45 | 768.30 | 0.060 | 0.084 | 12.30 | 760.0 | 0.054 | 0.08 | 8.61 |
| B | 0-15 | 2670.0 | 0.150 | 0.195 | 18.67 | 2669.8 | 0.011 | 0.14 | 15.46 |
| | 15-30 | 2852.00 | 0.038 | 0.129 | 17.16 | 2849.6 | 0.058 | 0.12 | 12.61 |
| | 30-45 | 2341.00 | 0.047 | 0.211 | 11.54 | 2336.0 | 0.044 | 0.08 | 8.61 |
| C | 0-15 | 1938.0 | 0.048 | 0.128 | 9.77 | 1932.8 | 0.045 | 0.152 | 8.98 |
| | 15-30 | 1931.0 | 0.099 | 0.147 | 10.26 | 1929.1 | 0.095 | 0.145 | 10.20 |
| | 30-45 | 1933.0 | 0.036 | 0.131 | 9.47 | 1925.0 | 0.033 | 0.129 | 9.43 |
| D | 0-15 | 2262.0 | 0.022 | 0.219 | 19.59 | 2259.5 | 0.01 | 0.681 | 19.53 |
| | 15-30 | 2118.0 | 0.101 | 0.258 | 17.31 | 2109.3 | 0.099 | 0.254 | 17.27 |
| | 30-45 | 1888.0 | 0.051 | 0.257 | 17.48 | 1883.4 | 0.049 | 0.251 | 17.45 |
| E | 0-15 | 2486.0 | 2.42 | 0.231 | 19.92 | 2481.7 | 2.34 | 0.216 | 19.89 |
| | 15-30 | 2465.0 | 2.16 | 0.254 | 11.69 | 2460.6 | 2.00 | 0.240 | 11.66 |
| | 30-45 | 1577.0 | 1.65 | 0.155 | 8.31 | 1567.6 | 1.62 | 0.152 | 8.29 |
| F | 0-15 | 1849.0 | 0.058 | 0.512 | 3.87 | 1844.7 | 0.054 | 1.311 | 3.84 |
| | 15-30 | 1776.0 | 0.036 | 0.338 | 1.78 | 1774.2 | 0.032 | 0.322 | 1.79 |
| | 30-45 | 1687.0 | 0.050 | 0.296 | 2.69 | 1682.0 | 0.030 | 0.296 | 2.68 |

Table 7: Mobility factors of the metals in the samples

| SITES | Soil Depth (cm) | Fe | Co | Ni | Mn |
|-------|-----------------|-------|-------|-------|-------|
| A | 0-15 | 26.93 | 28.57 | 35.71 | 37.45 |
| | 15-30 | 27.96 | 45.45 | 25.00 | 40.44 |
| | 30-45 | 29.33 | 20.37 | 25.00 | 31.59 |
| B | 0-15 | 16.49 | 90.90 | 21.05 | 28.47 |
| | 15-30 | 24.48 | 34.48 | 40.98 | 25.50 |
| | 30-45 | 19.27 | 68.18 | 21.05 | 32.76 |
| C | 0-15 | 20.00 | 0.00 | 26.32 | 26.17 |
| | 15-30 | 20.09 | 73.68 | 62.07 | 37.94 |
| | 30-45 | 26.70 | 60.61 | 22.48 | 30.54 |
| D | 0-15 | 27.54 | 53.00 | 80.76 | 32.62 |
| | 15-30 | 29.13 | 63.27 | 37.01 | 35.90 |
| | 30-45 | 23.33 | 63.27 | 28.29 | 31.35 |
| E | 0-15 | 32.13 | 37.18 | 24.54 | 60.43 |
| | 15-30 | 24.90 | 28.00 | 15.83 | 41.51 |
| | 30-45 | 19.25 | 34.57 | 20.29 | 40.89 |
| F | 0-15 | 23.25 | 74.07 | 42.42 | 33.33 |
| | 15-30 | 18.41 | 62.50 | 18.63 | 34.64 |
| | 30-45 | 25.81 | 66.67 | 22.30 | 33.58 |

High mobility factor values were observed for cobalt at some soil depths in sites B, C, D and F and for nickel at site C (15-30cm depth) and D (0-15cm depth). The mobility factor (MF) values of the metals in all the sites and profiles follow the order Co > Ni > Mn > Fe. These values do not follow any particular trend with respect to soil depth. Similar observation

was reported by Osakwe and Egharevba (2008). The relatively high mobility factor observed for cobalt is quite in agreement with the high percentage of exchangeable fraction of cobalt recorded from the chemical fractionation results.

Conclusion: The chemical fractionation of the metals

studied revealed the geochemical nature of the four heavy metals and their probable association with different chemical forms in the soils around the automobile waste dumpsites. The results showed that the heavy metal concentrations found in the residual fraction was higher than those observed in any of the preceding extractions except in the case of cobalt where exchangeable fraction predominated and closely followed by residual fraction. The heavy metal fractionation results gave an overall picture that high percentage of the metals were found to be strongly bound to soil matrix i.e. in a form not readily available for introduction into the food chain except cobalt. This overwhelming importance of the residual fraction in this study illustrates clearly the difficulty of distinguishing between background and anomalous levels of heavy metal contamination when only total metal analyses are performed. The relatively high mobility factor observed in cobalt confirms the high liability, and biological availability of cobalt in some of the soils studied. The present study indicates that the metals studied do not pose environmental risks since the total metal concentration of cobalt which showed high liability and biological availability in this study was very low. Consequently the government can be encouraged to reclaim and utilize the sites for agricultural, residential, commercial or industrial purposes.

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