

METAL SPECIES, MOBILITY AND BIOAVAILABILITY IN AN OIL IMPACTED SOIL FROM IKOKU AND ALAOJI AUTOMOBILE SPARE PARTS MARKETS, NIGER-DELTA NIGERIA.

OSU CHARLES I.^a* E.C. OGOKO^b AND EMEZIEM D.^b

^a Department of Pure and industrial chemistry, University of Port Harcourt, PMB, 5323, Port Harcourt, Rivers State. Nigeria.

^b Department of Chemistry, National Open University of Nigeria, 14 – 16 Ahmadu Bello way. P.M.B. 80067, Victoria Island, Lagos, Nigeria.

* Corresponding Author: Phone: +2348037783246; E-mail: charsike@yahoo.com

Abstract. The species, distribution, mobility and bioavailability of heavy metals (Pb, Cd, Zn, Cu, and Cr) were investigated by the determination of chemical forms of the heavy metals in soil from automobile spare parts markets in Alaoji and Ikoku, Niger Delta, Nigeria. Sequential extraction was used to fractionate heavy metals from the samples into five operationally defined groups; exchangeable fraction, fraction bound to carbonate, Fe/Mn oxide bound fraction, fraction bound to organic matter and residual fraction. Moreover, the heavy metal labilities in soils were evaluated by extraction with EDTA. Analysis of the metals was carried out by UNICAM SOLAAR 32 atomic absorption spectrophotometer. Zn and Cr are mostly abundant bound to Iron and Manganese oxides with results ranging from 42.210 to 37.300 % and 50.260 to 54.780 % respectively. Cd and Pb are distributed more at the exchangeable phase in the entire sample with the fractions that ranges from; 58.809 to 61.670 %, Cd and 39.600 to 40.760 %, Pb .. The results were interpreted in terms of the environmental mobility and bioavailability of the metals. The results of this study suggest that the mobility and availability of the metals are in the following order: Cd > Pb > Cr > Zn > Cu. This potential availability of the heavy metals indicates that metals have contamination risk in Alaoji and Ikoku environment which can contaminate water supplies and transferred to food chain.

Key words: bioavailability, metal species, lability, pollution.

INTRODUCTION

Some portion of the total quantity of pollutant present in soil is potentially available for uptake by organisms. This concept is referred to as the biological availability (or bioavailability) of a chemical (Kendell et al., 2001). Bioavailable fraction is defined as the fraction of the total amount of a chemical present in a specific environment within a given time span, is either available or can be made available for uptake by organisms or plants, or

by ingestion of food (Peijnenburg and Jager, 2003). Kelly et al., (2002) have defined 'bioavailable fraction' as the extent to which a chemical can be absorbed by a living organism and reach the systemic circulation.

Metal bioavailability in soil is largely dependent on the partition of the metals between the solid and solution phases. Various species of the metals can exist in solution either as free ions or as complexes associated with organic (i.e functional groups such as carboxyl and phenolic) or inorganic (examples anions such as OH^- , CO_3^{2-} , SO_4^{2-} , NO_3^- or Cl^-) ligands. Examples of such complexes include cadmium chloride (CdCl^-), methylmercury (CH_3Hg^+), and lead bicarbonate (PbHCO_3^+). The metal ions in polluted soils are tie up as coordinate compounds by the naturally occurring ligands and chelating agents such as humic substances, sulfide, pesticide, and EDTA. These metals coordinates interactions would affect the biogeochemical pathways taken by the metal such as its bioavailability and toxicity to organisms, and adsorption/desorption reactions on suspended materials.

Less fixation of metal in soil (e.g. low pH, low organic matter content) lead to greater bioavailability to living organisms. Influential soil properties include pH, organic matter content, cation exchange capacity, redox conditions, the presence of hydrous hydroxides, and other ions. Metal content in soil increased markedly as the pH decreased below pH 5. Yang et al., (2006) studied the effect of pH on Pb^{2+} bioavailability in two variable charge soils (one developed from arenaceous rock, RAR; and the other derived from quaternary red earth, REQ). They observed that an acidic environment ($\text{pH} < 5$) was favourable for Pb^{2+} desorption and the desorptability of Pb^{2+} decreased with increasing solution pH.

Heavy metals in natural environment are present in various chemical forms and exhibits different behavior in term of chemical interactions, mobility, biological availability and potential toxicity.

Heavy metal speciation, in this context is taken to mean the fraction of the total content in exchangeable (bound to exchangeable site of clay minerals), acid extractable (bound to carbonates and hydroxides), reducible (bound to Fe/Mn oxides), oxidizable (bound to organic matter/sulfides) and residual form (bound to clay minerals). In this study, the bioavailability, distribution and chemical speciation of heavy metals (Pb, Cd, Zn, Cu and Cr) in soils of automobile spare parts markets in Alaoji (Aba) and Ikoku (Port Harcourt) in Niger Delta Nigeria were determined. The mobility factors were also determined.

MATERIAL AND METHODS

Sample collection and Preparation.

Soil samples were randomly collected from different locations of mgbuka area of the automobile spare parts markets in Alaoji(Aba) and Ikoku (Port Harcourt) at 0 to 20 cm depth using soil augar in August, 2013. The samples were air dried and grounded to fairly uniform size and sieved with 2 mm sieve. The representative samples were stored in a clean polyethene bag and labeled Alaoji and Ikoku.

The determination of the total metal concentrations

Acid digestion in a microwave oven was chosen as the dissolution procedure. Sample aliquots of 100 mg were treated with a mixture of 5 ml of aqua regia and 2 ml of hydrofluoric acid in tetrafluoromethoxyl (TFM) bombs. Four heating steps of 5 min each (250, 400, 600, 250 W power respectively), followed by a ventilation step of 25 min, were applied. Then 0.7 g of boric acid were added, and the bombs were further heated for 5 min at 250 W and again

cooled by a ventilation step of 15 min. At the end of the full treatment, the samples appeared completely dissolved. Finally the resulting solutions were diluted to 100 ml with HPW. The solutions were directly employed for the AAS analysis (Abollino et al., 2002; Sheldrick and Wang, 1993).

Single extraction.

The single extraction method was adopted after MAFF (1986). 5 g sample was extracted with 50 ml water and 0.05M EDTA (pH 7.0), respectively in a shaker for one hour at 25^oC and centrifuged. The supernatants were carefully transferred to plastic bottles and analyzed for metal contents using Flame Atomic Absorption Spectrometry (FAAS). UNICAM SOLAAR 32.

Heavy metal Geochemical fractionation.

The conventional method developed by Tessier, et al., (1979) was followed for the sequential extraction. The sequential extraction process was accomplished in five steps.

Sequential extraction procedure:

Extractions were carried out on 1.0 g aliquots of soil and involved the five following steps (Tessier et al., 1979, Tessier et al., 1980, Abu-Kukati, 2001):

1. Exchangeable fraction: the sample was placed in contact with a high ionic strength solution, in order to release the so-called exchangeable fraction of metal traces by altering the sorption-desorption superficial processes. In this step 8 ml of 1 N MgCl₂ were added to the sample and the suspension was shaken for 1 h.
2. Fraction bound to carbonates: the fraction of metal traces bound to carbonates, present in the sample, may be selectively labilised by varying the pH of the sample itself with a slightly acidic extraction solution. 8 ml of 1 M of CH₃COONa, plus CH₃COOH (pH 5) were added to the residue obtained from the first extraction, and the suspension was shaken for 5 h.
3. Fraction bound to iron and manganese oxides: this fraction may be labilised in anoxic reducing conditions. Therefore, 20 ml of 0.04 M NH₂OH/ HCl in 25% CH₃COOH were added to the residue and the suspension was shaken for 6 h at the temperature of 96 ± 3 °C.
4. Fraction bound to organic matter and to sulphides: this fraction can be released by treating the sample with an oxidising agent. 3 ml of 0.02 N HNO₃ and 5 ml of 30% H₂O₂ were added to the residue obtained from the third extraction, and the suspension was shaken for 5 h at the temperature of 85 ± 2 °C. After cooling, 5 ml of 3.2 M CH₃COONH₄ were added to the suspension, which was diluted to 20 ml with HPW and shaken for 30 min.
5. Residual fraction: it is the metal fraction present as scatter within the crystal lattice of the rocks and minerals that constitute the soil. Residue from fraction 4 was oven dried at 105°C. Digestion was carried out with a mixture of 5ml conc. HNO₃ (HNO₃, 70% w/w), 10ml of hydrofluoric acid (HF, 40% w/w) and 10ml of perchloric acid (HClO₄, 60% w/w) in Teflon beakers.

Centrifugation at 200 rpm for 15 min was done for separation after each extraction and supernatant was taken for analysis by Flame Atomic Absorption Spectrometry (FAAS) UNICAM SOLAAR 32.

RESULTS AND DISCUSSION

Table 1. Concentration of total heavy metals (mg kg^{-1}) in soil from Ikoku and Alaoji.

| Heavy metals | Ikoku (mg kg^{-1}) | Alaoji (mg kg^{-1}) |
|--------------|-------------------------------|--------------------------------|
| Pb | 18.810 ± 0.010 | 39.360 ± 0.700 |
| Cd | 12.890 ± 0.002 | 17.800 ± 1.200 |
| Zn | 205.200 ± 1.800 | 312.500 ± 0.900 |
| Cu | 11.500 ± 0.003 | 18.200 ± 0.800 |
| Cr | 6.400 ± 0.400 | 4.800 ± 0.060 |

Results = mean \pm S.D of three determinations

Table 2. Concentration of heavy metal extracted from (Ikoku) soil by water and EDTA-single extraction.

| Heavy metals | Water extractable (mg kg^{-1}) | EDTA extractable (mg kg^{-1}) |
|--------------|---|--|
| Pb | 1.860 ± 0.100 | 3.360 ± 0.030 |
| Cd | 0.690 ± 0.002 | 1.800 ± 0.200 |
| Zn | 0.500 ± 0.001 | 8.500 ± 0.200 |
| Cu | 0.450 ± 0.003 | 2.200 ± 0.100 |
| Cr | 0.400 ± 0.070 | 1.300 ± 0.100 |

Results = mean \pm S.D of three determinations

Table 3. Concentration of heavy metal extracted from (Alaoji) soil by water and EDTA-single extraction.

| Heavy metals | Water extractable (mg kg^{-1}) | EDTA extractable (mg kg^{-1}) |
|--------------|---|--|
| Pb | 2.650 ± 0.010 | 4.300 ± 0.700 |
| Cd | 0.890 ± 0.002 | 2.100 ± 0.200 |
| Zn | 0.320 ± 0.001 | 11.800 ± 0.200 |
| Cu | 1.500 ± 0.003 | 3.200 ± 0.100 |
| Cr | 1.700 ± 0.100 | 2.800 ± 0.200 |

Results = mean \pm S.D of three determinations

Table 4. Percent of total heavy metal extracted from (Ikoku) soil by water and EDTA-single extraction.

| Heavy metals | Water extractable (%) | EDTA extractable (%) |
|--------------|-------------------------|------------------------|
| Pb | 9.890 | 17.863 |
| Cd | 5.353 | 13.964 |
| Zn | 0.243 | 4.142 |
| Cu | 3.913 | 19.130 |
| Cr | 6.250 | 20.313 |

Table 5. Percent of total heavy metal extracted from (Alaoji) soil by water and EDTA-single extraction.

| Heavy metals | Water extractable (%) | EDTA extractable (%) |
|--------------|-------------------------|------------------------|
| Pb | 6.732 | 10.925 |
| Cd | 5.000 | 11.798 |
| Zn | 0.102 | 3.776 |
| Cu | 8.242 | 17.582 |
| Cr | 35.417 | 58.333 |

Table 6. Fractionation of heavy metals (mg. Kg⁻¹) in different geochemical fractions of soil from Ikoku.

| Geochemical fractions | Heavy metals | | | | |
|-----------------------|--------------|----|----|----|----|
| | Pb | Cd | Zn | Cu | Cr |

| | | | | |
|-----------|--------------|--------------|---------------|--------------|
| F1 | 7.667 | 7.572 | 15.492 | 0.152 |
| | 1.925 | | | |
| F2 | 0.631 | 4.038 | 42.886 | 1.042 |
| 0.653 | | | | |
| F3 | 6.425 | 1.198 | 76.538 | 2.263 |
| 3.492 | | | | |
| F4 | 3.879 | ND | 53.659 | 6.945 |
| 0.049 | | | | |
| F5 | 0.208 | 0.068 | 16.621 | 1.078 |
| 0.256 | | | | |
| Sum | 18.810 | 12.876 | 205.196 | 11.480 |
| 6.375 | | | | |

F1=exchangeable, F2=carbonate bound, F3=Fe/Mn oxide bound, F4= bound to organic matter and sulphide, F5=residual fraction, ND = not detected.

Table 7. Fractionation of heavy metals (mg. Kg⁻¹) in different geochemical fractions of soil from Alaoji.

| Heavy metals Geochemical fractions | Pb | Cd | Zn | Cu | Cr |
|---------------------------------------|---------------|---------------|---------------|--------|--------------|
| F1 | 15.587 | 10.967 | 34.100 | | 0.307 |
| | 1.562 | | | | |
| F2 | 0.960 | 5.402 | 50.373 | | 1.484 |
| 0.516 | | | | | |
| F3 | 12.284 | 1.127 | 131.870 | 3.711 | 2.397 |
| F4 | 9.159 | ND | 75.935 | | 9.819 |
| 0.042 | | | | | |
| F5 | 1.370 | 0.286 | 20.187 | | 2.862 |
| 0.250 | | | | | |
| Sum | 39.36 | 17.782 | 312.465 | 18.183 | |
| 4.767 | | | | | |

F1=exchangeable, F2=carbonate bound, F3=Fe/Mn oxide bound, F4= bound to organic matter and sulphide, F5=residual fraction, ND = not detected.

Table 8. Fractionation of heavy metals (%) in different geochemical fractions of soils from Ikoku.

| Geochemical fractions | Heavy metals | | | | |
|-----------------------|--------------|--|--|--|--|
|-----------------------|--------------|--|--|--|--|

| | Pb | Cd | Zn | Cu | Cr |
|-----|-----------|-----------|-----------|-----------|-----------|
| F1 | 40.760 | 58.809 | 7.550 | 1.320 | |
| | 30.200 | | | | |
| F2 | 3.355 | 31.361 | 20.900 | 9.080 | |
| | 10.238 | | | | |
| F3 | 34.157 | 9.301 | 37.300 | 19.71 | |
| | 54.780 | | | | |
| F4 | 20.622 | 0 | 26.150 | 60.500 | |
| | 0.762 | | | | |
| F5 | 1.106 | 0.529 | 8.100 | 9.390 | |
| | 4.010 | | | | |
| Sum | | | | | |

F1=exchangeable, F2=carbonate bound, F3=Fe/Mn oxide bound, F4= bound to organic matter and sulphide, F5=residual fraction.

Table 9. Fractionation of heavy metals (%) in different geochemical fractions of soils from Alaoji.

| Geochemical fractions | Heavy metals | | | | |
|------------------------------|---------------------|---------------|---------------|--------------|-----------|
| | Pb | Cd | Zn | Cu | Cr |
| F1 | 39.600 | 61.670 | 10.920 | 1.690 | |
| | 32.750 | | | | |
| F2 | 2.440 | 30.380 | 16.120 | 8.160 | |
| | 10.810 | | | | |
| F3 | 31.210 | 6.340 | 42.200 | 20.410 | |
| | 50.260 | | | | |
| F4 | 23.270 | 0 | 24.300 | 54.010 | |
| | 0.880 | | | | |
| F5 | 3.480 | 1.610 | 6.460 | 15.740 | |
| | 5.300 | | | | |
| Sum | | | | | |

F1=exchangeable, F2=carbonate bound, F3=Fe/Mn oxide bound, F4= bound to organic matter and sulphide, F5=residual fraction.

Table 10. Mobility factor (%) and pH for the metals studied.

| Location | Heavy metals | | | | | pH |
|----------|--------------|----|----|----|----|----|
| | Pb | Cd | Zn | Cu | Cr | |
| | | | | | | |

| | | | | | | |
|--------|--------|--------|-------|-------|-------|------|
| Ikoku | 98.894 | 99.471 | 91.80 | 90.61 | 95.98 | 6.30 |
| Alaoji | 96.52 | 98.39 | 93.54 | 84.27 | 94.70 | 5.60 |

The results of concentration of metals in soil samples were presented in Table 1. The total concentration of heavy metals studied ranged between 18.810 ± 0.010 to 39.360 ± 0.700 , 12.890 ± 0.002 to 17.800 ± 1.200 , 205.200 ± 1.800 to 312.500 ± 0.900 , 11.500 ± 0.003 to 18.200 ± 0.800 and 6.400 ± 0.400 to 4.800 ± 0.060 for lead, cadmium, zinc, copper and chromium respectively. The concentration pattern was observed as: $Zn > Pb > Cd > Cu > Cr$. Alaoji had the highest concentration of metals (39.360 ± 0.700 , Pb; 17.800 ± 1.200 , Cd; 312.500 ± 0.900 , Zn and 18.200 ± 0.800 , Cu) compared to Ikoku (18.810 ± 0.010 , Pb; 12.890 ± 0.002 , Cd; 205.200 ± 1.800 , Zn; and 11.500 ± 0.003 , Cu). The high level of Pb in these samples indicates the disposal of Pb batteries, chemicals from dumped old spare parts, Pb-based paints and pipes at the site (Mor, et al., 2005).

Water and EDTA extractable metals and their percentage extractable metals were presented in table 2 to 5. Water extractable phase contains most mobile and bio-available metals (Bhupander Kumar *et al*, 2011; Ure, 1996), whereas EDTA is capable of extracting metals in non-silicate bound phase. The percentage of water extractable fraction of metals was less with the range of 9.890 to 6.732 %, Pb; 5.353 to 5.000 %, Cd; 0.243 to 0.102 %, Zn; 8.242 to 3.913 %, Cu; and 6.250 to 35.417 %, Cr. EDTA extracts higher percentage of metals from soils compared to water and ranged from 17.863 to 10.925 %, 13.964 to 11.798 %, 4.142 to 3.776 %, 19.130 to 17.582 % and 20.313 to 58.333 % for Pb, Cd, Zn, Cu and Cr respectively. Bhupander Kumar *et al*, (2011) and Mehra *et al.*, (1999) reported that water is less capable in extraction of metals, but the presence of chelating agents (such as soluble organic species) increase the metals extractability and their bioavailability. Results of present study are similar to results obtained by Bhupander Kumar *et al*, (2011) and Mehra *et al.*, (1999).

Geo-Chemical partitioning of heavy metals were reported in table 6 to 9, which provides information on the partitioning of metals into different sediment fractions and can be useful in the understanding of mobility and bioavailability. The study of the distribution of the metals revealed that all the metals are associated with different phase. Zn and Cr are mostly abundant bound to Iron and Manganese oxides with results ranging from 42.210 to 37.300 % and 50.260 to 54.780 % respectively (table 8 and 9). The percent fractions for other metals ranged from 6.340 to 9.301 %, Cd; 19.71 to 20.410 %, Cu and 31.210 to 34.157 %, Pb. This is in agreement with Zerbe *et al.*, (1999), Osu *et al.*, (2013) and Fagbote and Olanipekun (2010). Fe-Mn oxide minerals have relatively large area and surface site density (Forstner, and Wittmann, 1983). The Fe-Mn oxide, the reducible phase of the soil under oxidizing conditions is a significant sink for the heavy metals. The association of higher concentration of metals with this fraction is caused by adsorption of these metals by the Fe-Mn mineral surface (Ma and Rao, 1997).

The results of sequential extraction in this study revealed that copper is mostly (54.010 to 60.500 %) abundantly bound to organic matters. Other metals have percent fraction that ranged from 0.762 to 0.880 %, Cr; 20.622 to 23.270%, Pb; 24.30 to 26.150 %, Zn and Zero percent for Cd. Copper can easily complex with organic matters because of high formation of organic-Cu compounds (Haung *et al.*, 2007). Heavy metals with high abundance in the phase bound to Organic matter are more available than heavy metals in the residual fraction. The organic phase is relatively stable in nature but can be mobilized under strong oxidizing

conditions due to degradation of organic matter (Tessier et al., 1979; Haung et al., 2007). Organic matter plays an important role in the distribution and dispersion of metals by mechanisms of chelating and cation exchange. In this phase a reaction between a metal ion and an organic ligand leading to a species which can either precipitate directly or be adsorbed on soil materials. Carboxyl, phenolic, hydroxyl and carbonyl functional groups are assumed to be primarily responsible for metal binding (Bhupander Kumar *et al*, 2011; Wilber, and Hunter, 1979). Metal humic complexes are reversible, and metals can be desorbed by salting out or by hydrogen ion competition. The organic fraction of metals is not considered very mobile or available because of its association with high molecular weight stable humic substances.

Cd and Pb are distributed more at the exchangeable phase in the entire sample with the fractions that ranges from; 58.809 to 61.670 %, Cd and 39.600 to 40.760 %, Pb . Other metals have a lower percent of range: 7.550 to 10.920 %, Zn; 1.320 to 1.690 %, Cu and 30.200 to 32.750 %, Cr (table 8 and 9). High levels in the exchangeable, acid soluble and easily reducible fractions may indicate pollution from anthropogenic origin (Mesuere et al., 1991; Hung et al., 1993). Heavy metals in the exchangeable fraction held by electrostatic adsorption represent the most mobile and readily available for biological uptake in the environment, thus this fraction can be regarded as a pollution indicator (Zakir, et al. 2008). The concentration of metals in this phase indicates the environmental impact. In this study, the Zn and Cu associated with this fraction are the least. Therefore, we conclude that the exchangeable fraction of Zn and Cu is least bioavailable and on the other hand Pb, Cd and Cr show health risks because of high percent in the exchangeable or dissolved fraction.

These heavy metals, as shown in table 8 and 9 had the lowest abundance in the Residual fraction as follows: Cd –1.100 to 3.480 %, Pb – 0.527 to 1.610 %, Zn – 6.460 to 8.100 %, Cu – 9.390 to 15.740 %, and Cr – 4.010 to 5.300 % . This is in agreement with Osu et al. (2013). Metals present in the Residual fraction are a measure of the degree of environmental pollution. The higher the metals present in this fraction, the lower the degree of pollution and verse versa (Banat, 2001). In this study it was found that the percentage of these metals present in the residual fraction is the lowest which indicate that the samples are highly polluted with the metals. It also concerned with the most stable and least bioavailable of all the chemical fractions of the soil and sediments, since it is believed that metals are occluded within the crystal lattice of silicates and well crystallized oxide minerals (Horsfall Jr and Ayebaemi, 2005; Bhupander Kumar et al., 2011). The residual phase represents metal largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh considerations. The residual fraction is a major carrier of metals in most environmental systems. The relatively small amount of heavy metals in this fraction indicates their high mobility and therefore high environmental contamination risk to auto mobile spare parts markets soils in Niger Delta region of Nigeria. The speciation pattern of the carbonate fraction suggests greater environmental risks of Cd with fraction ranging from 30.380 to 31.361 %.

Mobility of Cd, Cu, Pb, Zn and Cr in the studied samples were assessed on the basis of absolute and relative content of fraction weakly bound to soil components (Kabala and Singh, 2001). The potential mobility of a metal can be assessed by adding up the results of the Exchangeable phase, Carbonate phase, Fe-Mn oxide phase and organic phase of that metal (Haung et al., 2007). The results showed that most fractions of all the investigated heavy metals were found in the potentially available form. The mobility factor gave values that ranged from 96.52 to 98.894 %, Pb; 98.39 to 99.471%, Cd; 91.80 to 93.54 %, Zn; 84.27 to 90.61 %, Cu and 94.70 to 95.98 % (table 10), which signified high stability and as a result of

relatively high liability and biological availability of the metals in the samples. The results of this study suggest that the mobility and availability of the metals are in the following order: Cd > Pb > Cr > Zn > Cu. This potential availability of the heavy metals indicates that metals have contamination risk in Alaoji and Ikoku environment which can contaminate water supplies and transferred to food chain.

CONCLUSION

The speciation of heavy metals with selective extracting agents gives additional information about the fundamental reactions governing the behaviors of the metals in the soils. Single extraction study shows that heavy metals except Cr were not readily available as indicated by the water extraction experiment, but the presence of chelating agents can render the metals more bioavailable. The distribution of the metals in the various fractions confirms differences in mobility. Of the metals studied, Cd and Pb appeared to be the most readily solubilized, thus, making the metal the most potentially bioavailable. This may posed a threat as Cd and Pb are transferred into the food chain from soil contaminated by cadmium.

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