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# SPATIAL DISTRIBUTION AND CHEMICAL FRACTIONATION OF SOME HEAVY METALS IN CRUDE OIL SPILL SOIL

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## ABSTRACT

Soil contamination by heavy metals is consequently the most critical environmental problems as it poses significant impacts to human health and the ecosystem. The heavy metals may infiltrate deep into the layer of underground waters and pollute the groundwater and the surface water or are washed into nearby rivers and may pose great risk to the surrounding environment as a source of drinking water. This study was carried out to investigate the spatial distribution and chemical fractionation of some heavy metals in crude oil spill soil. An *ex-situ* experiment was carried out in the Department of Biochemistry, University of Benin laboratory on crude oil spill soil from Ubeji Community in Delta State, Nigeria. The physicochemical properties and total concentration of Pb, Zn and Cu of the aggregate soil sample were determined according to standard methods and the metals analytically determined using atomic absorption spectrophotometry. Descriptive statistics and analysis of variance were employed to statistically analyze data that were obtained. The result indicates high concentration of Cu, Pb and Zn. Total values of approximately 6mg/kg Cu, 5mg/kg Pb and 50mg/kg Zn were obtained in the representative soil samples. These values were below the threshold values reported for contaminated soil. The chemical fractionation of metals on the soil samples showed that 0.00-31.50% Cu, 0.00-56.25% Pb and 0.00-32.50% Zn were relatively mobile and potentially bioavailable in the crude oil spill soil. The results obtained suggest that remediation measures should be taken to prevent accumulation of heavy metals.

**Keywords:** Contamination, Crude oil, Fractionation, Heavy metals, Soil, Spatial distribution

## INTRODUCTION

Pollution is increasingly creating environmental stressors as industrialization increases. Environmental soil contamination by petroleum hydrocarbons is becoming prevalent in the world (Abioye, 2011; Olubodun and Eriyamremu, 2015). This is probably due to heavy dependence on petroleum as a major source of energy in the world and complete disregard for the environmental health. The amount of natural crude oil seepage was estimated to be 600,000 metric tons per year with a range of uncertainty of 200,000 metric tons per year (Kvenvolden and Cooper, 2003). Release of hydrocarbons into the environment either accidentally or as a result of human activities is a cause of water and soil pollution (Holliger *et al*, 1997). These hydrocarbon pollutants usually caused disruptions of natural equilibrium between the living species and their natural environment. Hydrocarbon components have been known to belong to the family of carcinogens and neurotoxic organic pollutants (Das and Chandran, 2010).

Heavy metals contaminated soil from industrial waste and other sources on the other hand, poses serious threat to both man and animals in the environment if not properly remediated to the innocuous level (Abioye, 2011). Environmental pollution by heavy metals which are released into the environment through various anthropogenic activities such as energy and fuel production, electroplating, wastewater sludge treatment, mining and agriculture is one of the world's major environmental problem. Heavy metals or trace metals refer to a large group of trace elements which are both industrially and biologically important (Abioye, 2011). Initially, heavy metals are naturally present in soils as natural components but the presence of heavy metals in the environment has increased due to human activities. This is a widespread problem around the world where excessive concentration of heavy metals such as lead (Pb), zinc (Zn), chromium (Cr), copper (Cu), cadmium (Cd) and arsenic (As) can be found in soils (Abioye, 2011; Olubodun and Eriyamremu, 2015).

Soil contamination by heavy metals is consequently the most critical environmental problems as it poses significant impacts to the human health as well as the ecosystems. The contaminants are able to infiltrate deep into the layer of underground waters and pollute the groundwater as well as the surface water. Heavy metals in the soil subsequently enter the human food web through plants and they constitute risk to the ecosystem as they tend to bio-accumulate and can be transferred from one food chain to another. Heavy metals are discovered in various food chains where the results are usually detrimental to microorganisms, plants (Olubodun and Eriyamremu, 2016), animals (Olubodun and Osagie, 2016; Olubodun *et al.*, 2016) and humans.

The specific type of metal contamination found in a contaminated soil is directly related to the operation that occurred at the site. The range of contaminant concentrations and the physical and chemical fractionation of contaminants will also depend on activities and disposal patterns for contaminated wastes on the site. Other factors that may influence the fractionation, concentration, and distribution of metal contaminants may include soil and ground-water chemistry and local transport mechanisms (Wuana and Okieimen, 2011). Metals occur in both the solid and aqueous phases in the soil environment but as free ions or complexes associated with organic/inorganic ligands in solutions. Heavy metals can be retained in organic/inorganic soil components by different sorption mechanisms in the solid phase. It may also exist as minerals or be co-precipitated with other minerals (Bernhard and Neff, 2001).

Heavy metal contamination levels in the soil is however not adequate as criteria for determining the potential effect of the soil contamination as this will imply that all the forms of a given metal have equal impact on the environment. Since heavy metals are associated with different components in various ways, their associations determine mobility and availability (Kabala and Bal, 2001). The spatial distribution and chemical fractionation in which heavy metals exist in soils is essential to develop viable and cost effective remediation strategies for prediction of availability and mobility. The aim of the study was to assess the spatial distribution and chemical fractionation of some heavy metals in crude oil spill soil (COSS).

## MATERIALS AND METHODS

### *Study Location*

The *ex situ* study was carried out in the Department of Biochemistry, University of Benin, Benin City, Edo State, Nigeria. The soil from an uncultivated land with no known crude oil contamination as well as soil where there was crude oil spill was collected from Ubeji, Delta State, Nigeria.

### *Soil Sampling, Preparation and Characterization*

Ten grab samples were collected from ten different locations within a crude oil spill site in Ubeji, Delta State, Nigeria. Holes were dug at ten different points within the land to a depth of about twenty centimetres (20 cm using plastic spade), representing top soil. Ten soil samples were air-dried at ambient temperature (28 - 31°C) in the laboratory, crushed in a porcelain mortar and sieved through a 2-mm sieve. The experimental tests were performed on aggregate samples prepared by mixing thoroughly equal amount of each of the 10 soil samples collected by coning to make three replicate samples.

The physicochemical properties and total concentration of Pb, Zn and Cu of the aggregate sample were determined according to standard methods (IITA, 1982). Cation exchange capacity was estimated by summing the exchangeable cations determined by flame photometric method while the exchangeable acidity was determined by titration method (Jackson, 1960). The soil pH was determined using a 1:2 soil weight/water volume ratio by a Suntex digital pH meter (Folson *et al*, 1981). Particle size was done according to Bouyoucous method (Bouyoucous, 1962). Total organic carbon was determined by the Walkley-Black rapid oxidation method (Nelson and Sommer, 1982), while available phosphorus was determined by the Bray and Kurtz method (1945). Total concentration of Pb, Zn and Cu in the contaminated soil was determined by digesting 1g sample with 5mL concentrated nitric acid and 1mL perchloric acid. The resultant supernatant was then analysed by atomic adsorption spectrophotometer (AAS) [Buck scientific VGP 210].

### *Soil Fractionation*

1g of the aggregate soil samples was used for total heavy metal determination and sequential extraction. Sequential extraction was performed based on the method described by Tessier *et al.* (1979) with slight modification.

**(i) Exchangeable fraction:** This fraction extracts trace elements which are affected by sorption-desorption processes caused by changes in water ionic composition. The soil was extracted at room temperature for 1hr with 8ml of 1M magnesium chloride solution (pH7.0)

**(ii) Carbonates bound metals fraction:** This fraction specifically address the adsorbed and surface occluded trace elements fractions of the soil with 5% m/n carbonates and it is susceptible to pH changes. The residue from (i) was extracted at room temperature with 8ml of 1M sodium acetate adjusted to pH5.0 with acetic acid. The mixture was agitated for 5hrs.

**(iii) Fe-Mn oxides bound metals fraction:** This fraction extracts the iron and magnesium oxides fractions of the soil which exist as nodules, concentrations, cement between particles or simply as coatings on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions. The residue from (ii) was extracted with 20ml of 0.04M hydroxylamine hydrochloride in 25% acetic acid. Extraction was performed at 96 ± $3^oC$ with occasional agitation for 6hrs.

**(iv) Organic matter bound metals fraction:** This fraction extracts trace elements which are bounded to various forms of organic matter, living organisms, detritus, coatings on mineral particles, etc. which are bio-accumulated by complexation and peptization properties of natural organic matter. To the residue from (iii), 3ml of 0.02M trioxonitrate (v) acid and 5 ml of 30% hydrogen peroxide was added and adjusted to pH 2 with trioxonitrate (v) acid. The mixture was heated to 85 ± $2^oC$ for 2hrs with occasional agitation. An additional 3ml aliquot of the acidified 30% hydrogen peroxide was added and the mixture was heated at 85 ± $2^oC$ for 3hrs with intermittent agitation. 5ml of 3.2M ammonium acetate in 20% trioxonitrate (v) acid was added to the cooled mixture and the sample was diluted to 20ml and stirred continuously for 30mins.

**(v) Residual fraction:** This fraction extracts primary and secondary minerals which hold trace metals within their crystal lattices. The residue from (iv) was digested with 5ml of aqua regia and 1ml of perchloric acid and diluted to 100ml with distilled water.

After each successive extraction phase, the residue was washed with 8ml of deionised water. The supernatant and 4ml aqua regia were added and diluted to 100ml.

The selective extractions were conducted in centrifuge tubes to minimise losses of the solid material. The concentrations of Pb, Cu and Zn in every extract were measured by atomic absorption spectrophotometer.

To ensure accuracy and reliability of the results, all reagents used for the analyses were of analytical grades (BDH or Sigma). All glasses and plastics were acid-washed. Buck scientific standard solutions were used to calibrate the Atomic Absorption Spectrophotometer. Procedural blank samples were subjected to similar extraction method using the same amounts of reagents and all experiments were done in triplicate.

***Statistical Analysis***

The result of the study was expressed as mean ± standard error of mean (SEM). Analysis of variance was used to test for differences in the groups, while Duncan's multiple comparisons test was used to determine significant differences between means. The Instat-Graphpad software, San Diego, California, USA, was used for this analysis. A $P < 0.05$ was considered statistically significant

## RESULTS AND DISCUSSION

The physicochemical composition of the crude oil spill soil (COSS) is presented in Table 1. Results obtained showed that electrical conductivity, cation exchange capacity, total organic carbon, and total organic matter were significantly higher ($P < 0.05$) in the crude oil contaminated soil when compared to control soil. However, pH was significantly lower ($P < 0.05$) in the crude oil contaminated soil when compared to control soil. The low pH indicates that the soils were slightly acidic. Similar pH values have been reported for Niger Delta soils, some soils in other parts of Nigeria and soils with cassava processing effluents (Iwegbue *et al.*, 2013). However, it is at variance with pH values reported for dumpsites (Obasi *et al.* 2013). The observed pH values in the soils may have altered the physicochemical compositions of the soil as well as the chemical fractionation (Obasi *et al.,* 2012).

The electrical conductivity of the control soil was found to be lower than that of COSS (0.04±0.01). The high conductivity value of the COSS may be attributed to the presence of metals that are soluble salts in the soil (Obasi *et. al.*, 2012).

Cation exchange capacity (CEC) of the control soil was found to be lower than that of the COSS.

Table 1: Physico-chemical compositions of crude oil spill soils (dry weight)

| Parameter/Sample | Control | COSS |
|---|---|---|
| pH($H_2O$) | 6.44±0.03$^a$ | 6.74±0.01$^b$ |
| $PO_4^{3-}$(mg/kg) | 63.58±0.02$^a$ | 8.83±0.02$^b$ |
| $Na^+$ (Cmol/kg) | 0.43±0.01$^a$ | 0.34±0.05$^b$ |
| $K^+$ (Cmol/kg) | 0.31±0.01$^a$ | 0.18±0.02$^b$ |
| $Ca^{2+}$ (Cmol/kg) | 2.90±0.02$^a$ | 4.00±0.05$^b$ |
| $Mg^{2+}$ (Cmol/kg) | 2.20±0.02$^a$ | 2.40±0.03$^a$ |
| Cation Exchange Capacity (Cmol/kg) | 7.08±0.01$^a$ | 9.98±0.02$^b$ |
| Total Hydrocarbon (mg/kg) | 0.00±0.01$^a$ | 74.88±0.01$^b$ |
| Total Organic Carbon (%) | 1.26±0.01$^a$ | 3.89±0.01$^b$ |
| Total Organic Matter (%) | 2.17±0.02$^a$ | 5.41±0.02$^b$ |
| Clay | 26.68 | 16.28 |
| Silt | 10.30 | 10.70 |
| Sand | 63.02 | 73.02 |

Values are mean of three (n=3) replicates ± standard error of mean. COSS = Crude Oil Spill Soil. $PO_4^{3-}$ = Phosphate. Cmol/kg (centimoles of charge per kg soil = meq/100 g). Means of the same row carrying different notations are statistically different at $P<0.05$ using Instat graphpad.

The higher values of CEC observed in the COSS when compared with control are comparable to values of CEC reported in soil that received cassava effluents in Benin City, Nigeria (Oviasogie and Ofomaja, 2007). The high CEC recorded in the COSS may be due to high calcium content in the soil. Total organic carbon (TOC) content was significantly higher in the contaminated soil when compared with control. The total mean percentages of total organic matter (TOM) ranged from 2.17±0.01 of control soil to 5.41±0.01%. The total organic carbon (TOC) and Total Organic Matter (TOM) values obtained in the results are comparable to those reported by Obasi *et al.* (2012). The levels of organic matter in soils affect the soil chemical and physical processes and acts as an indicator of the soils ability to hold plants (Obasi *et. al.*, 2012). Particle size shows that the soil in the contaminated samples is mainly sandy clay loam.

The concentration of some metals in the crude oil contaminated soil is presented in Table 2. The values of Pb, Cu and Zn for the contaminated soil were above the values of control soil but below those of 190%, 36%, and 140% intervention and target values for soils provided by Department of Petroleum Resources (DPR) guidelines (DPR, 2002).

The concentration of copper, lead and zinc ranged from 1.05±0.00 control to 6.00±0.02 mg/kg COSS; 0.08±0.00 control to 5.00±0.02 COSS and 10.00±0.03 control to 50.00±0.04mg/kg COSS respectively. The concentrations of all three metals analyzed were higher in the crude oil contaminated soil than the control (Table 2).

Table 2: Soil concentration, regulatory guidelines, target and intervention values of some metals in the crude oil contaminated soil and for standard soil (mg/kg soil dry weight)

| Metal/Sample | Control | COSS | Regulatory limits** | Target value | Intervention value |
|---|---|---|---|---|---|
| Lead (Pb) | 0.08±0.01$^a$ | 5.00±0.12$^b$ | 600.00 | 35.00 | 190 - 210.00 |
| Zinc(Zn) | 10.00±0.03$^a$ | 50.00±0.04$^b$ | 1,500.00 | ---- | ---- |
| Copper (Cu) | 1.05±0.02$^a$ | 6.00±0.02$^b$ | ---- | 0.30 | 10.00-36.00% |

Values are mean of three (n=3) replicates ± standard error of mean. COSS = Crude Oil Spill Soil. Means of the same row carrying different notations are statistically different at $P<0.05$ using Instat graphpad. ** (NJDEP, 1996; Wuana and Okieimen, 2011).

Other researchers also reported elevated levels of heavy metals in different types of contaminated soils (Iwegbue *et. al.*, 2013; Obasi *et al.*, 2012; Okoye and Okwute, 2014). The higher concentration of Cu, Pb and Zn in the COSS when compared with control even though from relatively same source, may be attributed to the crude oil present in the soil (Table 2).

The results of the chemical fractionation of the metals and their geochemical distribution in the COSS are shown in Table 3. The metals were categorized into five fractions namely: exchangeable phase, oxidizable phase (bound to organic matter), Acid soluble phase (bound to carbonate), reducible phase (bound to Fe-Mn oxides) and residual phase (bound to silicates and detrital materials).

Total extractable Pb ranged from 0.08 of the control to 4.16 mg kg$^{-1}$ of the COSS (Table 3). The levels of Pb in all the exchangeable, acid soluble, oxidizable, residual and reducible fractions of the control soil and the oxidizable fraction of the COSS was below detection limit but was found to be more concentrated in the residual fraction of the COSS.

Total extractable Zn ranged from 9.05 of the control to 51.07 mg kg$^{-1}$ of the COSS (Table 3). Zinc was found to be more concentrated in the residual fraction of the COSS (15.28 mg kg$^{-1}$) and less in the acid soluble fraction.

Total extractable Cu ranged from 0.17 of the control to 6.00 mg kg$^{-1}$ of the COSS (Table 3). Copper was found to be more concentrated in the residual fraction of the COSS (4.11 mg kg$^{-1}$). In the control soil and some of the COSS, Cu associated with exchangeable and acid soluble fractions were below detection limit. The results showed higher percentages (%) of the non-residual fraction for Pb and Zn and higher percentages (%) of the residual fraction for Cu.

Table 3: Fractionation of Cu, Pb and Zn in the COSS (mg/kg soil dry weight)

| Fraction /Sample | Copper (Cu) C | COSS | Lead (Pb) C | COSS | Zinc (Zn) C | COSS |
|---|---|---|---|---|---|---|
| Exchangeable | ND | 1.89±0.03 | ND | 1.34±0.03 | 0.28±0.01$^{a}$ | 8.85±0.03$^{b}$ |
| Oxidizable | 0.05±0.03 | ND | ND | ND | 03.38±0.06$^{a}$ | 10.11±0.03$^{b}$ |
| Acid soluble | W | ND | ND | 1.00±0.05 | 0.68±0.06$^{a}$ | 7.75±0.03$^{b}$ |
| Reducible | 0.04±0.03 | ND | ND | 0.24±0.02 | 03.35±0.03$^{a}$ | 9.08±0.05$^{b}$ |
| Residual | 0.08±0.03$^{a}$ | 4.11±0.03$^{b}$ | ND | 1.58±0.03 | 1.36±0.03$^{a}$ | 15.28±0.03$^{b}$ |
| TEMs | 0.17±0.07$^{a}$ | 6.00±0.05$^{b}$ | 0.00 | 4.16±0.11 | 09.05±0.07$^{a}$ | 51.07±0.06$^{b}$ |
| Sum of BF | 0.00 | 1.89 | 0.00 | 2.34 | 0.96 | 16.60 |
| Percent Bioavailable | 0.00 | 32.00 | 0.00 | 47.00 | 10.00 | 33.00 |
| Non-residual (%) | 52.94 | 37.00 | 0.00 | 62.02 | 84.97 | 70.08 |
| Residual (%) | 47.06 | 68.50 | 0.00 | 37.98 | 15.03 | 29.92 |
| Mobility Factor (%) | 0.00 | 31.50 | 0.00 | 56.25 | 10.61 | 32.50 |

Values are mean of three (n=3) replicates ± standard error of mean ND = Not Detectable. TEMs = total extractable metals, BF = bioavailable fraction. Means of the same row carrying different notations are statistically different at P<0.05

The highest concentrations of Cu, Pb and Zn were found in the residual fractions of the COSS. This may be as a result of the sandy nature of the soil, the presence of acid resistant minerals and/or the co-precipitation of the metals with various silicate species consequent to their adsorption into mineral lattice (Rahman *et al.*, 2004). Similar results were recorded by other researchers in different contaminated soils (Iwegbue *et al.*, 2013; Obasi *et al.*, 2012; Obasi *et al.*, 2013). The percent bioavailability of the metals in the COSS is relatively high since the mobile phase contains reasonable percent of total extractable fractions suggesting that the metals in the COSS are potentially more bioavailable for plant uptake (Obasi *et al.*, 2013). It was suggested that high mobility factor (MF) values are symptoms of relatively high lability and biological availability of heavy metals in soils (Fig. 1).

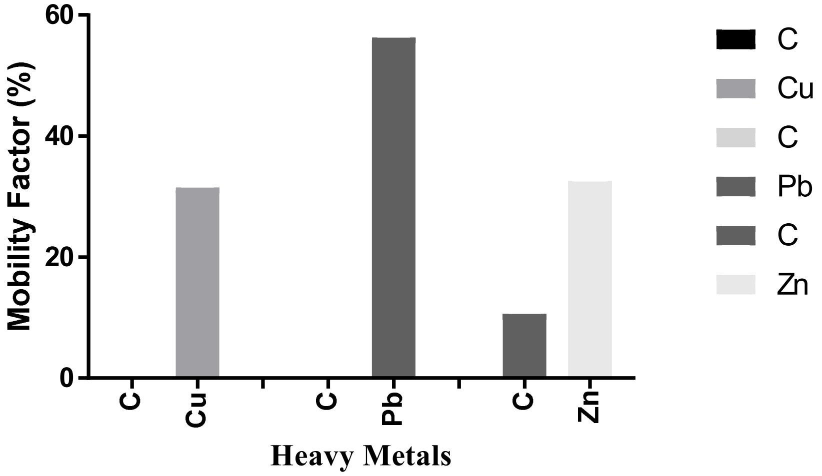

Fig. 1: Mobility factor of metals in crude oil spill soil

However, mobility factor describes the potential mobility of metal in soil. The mobility of metals in soil is calculated on the basis of absolute and relative content of fractions weakly bound to soil components. Mobility factor is expressed as the percentage ratio of the sum of the soil's mobile fraction (Water-soluble, Exchangeable, Bound to carbonate) to the sum of all fraction of the soil (Cezary and Bal, 2001). It is important to note that metals extracted bound to carbonate are relatively less mobile than those extracted by exchangeable and water soluble fractions. The mean percentage order of mobility and bioavailability of these metals were: Pb > Zn > Cu metals (Table 3; Fig. 1).

## CONCLUSION

Result from the study shows that the crude oil spill soil was relatively uncontaminated in terms of heavy metal contamination. Since heavy metals have the characteristics of persisting in the environment, continuous spill and other anthropogenic activities of humans, may lead to contamination of soil which may eventually pose risks to the ecosystem. The study suggests that remediation measures should be taken to prevent accumulation of heavy metals.

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