Available online at www.elixirpublishers.com (Elixir International Journal)

Applied Chemistry

Elixir Appl. Chem. 126 (2019) 52543-52548

ISSN: 2229-712X

Chemical Speciation and Mobility of Heavy Metal (Pb, Cd, Zn, Mn) Pollutants in Crude Oil Contaminated Soils of Niger Delta, Nigeria

Aigberua, Ayobami Omozemoje* and Inengite, Azibaola Kesiye
Department of Chemical Sciences, Faculty of Science, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria.

ARTICLE INFO

Article history:
Received: 3 December 2018;
Received in revised form:
07 January 2019;
Accepted: 19 January 2019;

Keywords
Chemical speciation,
Mobility,
Bioavailability,
Bdere community,
Ogoniland.

ABSTRACT

Chemical speciation and mobility factor indices of Pb, Cd, Zn and Mn were assessed in a crude oil contaminated soil and compared with control (uncontaminated) soil. The assessment was done to evaluate the impact of crude oil contamination on the bioavailability of metals in a soil matrix. Soil was collected in triplicate from four locations (three reflecting the crude oil impacted area and one uncontaminated soil as control). Soil was collected around a crude oil transfer pipeline within Bdere community in Ogoniland, Nigeria, within the month of August 2017. Fractional concentration of metals was determined using a GBC Avanta PM6600 atomic absorption spectrophotometer. In the oil contaminated soil, Zn (41.13%) and Mn (77.54%) were predominantly associated to the residual fractions while Pb (29.45%) and Cd (25.53%) were prevalent in the amorphous Fe-oxide and plant available fractions respectively. Similarly, the uncontaminated soil depicted the residual fractions of Zn (49.43%) and Mn (48.63%) to be the most important while Pb (56.17%) and Cd (62.16%) were both predominantly affiliated to plant available fractions. Heavy metal mobility factor indices reflected the order: (Zn>Cd>Pb>Mn) and (Cd>Mn>Zn>Pb) for crude oil impacted and uncontaminated soils respectively. Despite the prevalence of heavy metals to the inert fractions, the significant affiliation of metals to the readily mobile fractions of crude oil contaminated soil reflected the order: Pb (10.71%), Cd (25.53%), Zn (40.22%) and Mn (3.52%) which further suggested that these metals may have emanated from the introduction of crude oil into the soil matrix.

1.0 Introduction

Bdere is one of the vastly oil polluted communities in Ogoniland. Generally, Ogoniland which is situated in the Niger Delta has been classified as one of the world's most crude oil polluted regions. Many reports have implicated Shell Petroleum Development Company as a major culprit in the events of oil spills within the region. Shell on their part has blamed the crisis on third party sabotage and security challenges in the Niger Delta. In all of this, the inhabitants continue to suffer loss of their means of livelihood (SPDC, 1996). Most of the indigenous people of Bdere community are farmers and fishermen. However, the devastating effects of spilt crude oil on farmlands, water ways and even mangrove forests has led to the destruction of the means of livelihood of the people. Mangrove forests are particularly vulnerable to oil spills, because the soil soaks up the oil like a sponge and re-releases it every rainy season. Water contamination of local water supply has led to fish kills and ruinous effects on farmland (Manby, 1999). Industrial revolution, especially in the oil and gas sector has increased the release of heavy metal into the environment. Most metals are stable and cannot be degraded or destroyed, and therefore tend to accumulate in soil and sediment (Anderson, 2003).

Generally, oil spill incidence and causes have been widely reported by (Nwilo and Badejo, 2005; Iniaghe *et al*., 2013; Aigberua *et al*., 2017a). Accidental oil spills are resulting consequences of crude oil exploration and production, these activities include leaking or ruptured pipelines, sabotage to well head line and manifolds, overpressure, failure, overflow of process equipment components or blow out of well (Awobajo, 1991; Adelana *et al*., 2011; Aigberua *et al*., 2017a). Generally, oil spills are a big threat to the environment in producing regions (Kadafa, 2012). For instance, Oil spills could cause fire and lead to loss of wildlife, vegetation, loss of fertile soil, pollution of air and drinking water, degradation of farmland and damage to aquatic ecosystems (Ogbeibu and Iyobosa, 2013). Several heavy metals are associated with crude oil including lead, cadmium, copper, zinc, nickel and vanadium (Osuji *et al*., 2006; Fatoba *et al*., 2015; Aigberua *et al*., 2017a). These elements are found naturally in soils and rocks at different concentrations. They are also components of ground, surface waters and sediments (Izah *et al*., 2016; Asimiea and Lawal, 2017; Aigberua *et al*., 2017a, b), fisheries (Izah and Angaye, 2016; Aigberua and Tarawou, 2017).

The poor solubility of lead minerals means that lead migrates into the environment far less intensively than cadmium or zinc. Even so, contamination by this element is unfortunately quite common. Lead can enter the natural waters from industrial waste waters, corrosion of tanks and piping, as well as materials made from lead (Kabata-Pendias and Pendias, 2000). Manganese is usually associated with the residual fractions and is usually immobile and less toxic in the environment (Osakwe, 2010).

Tele:
E-mail address: ozedee101@gmail.com

Elemental speciation can be used to determine the toxicity of metals and their tendency to pose immediate or potential risk to the environment. Hence, this sequential extraction protocol depicts a diagnostic potential in terms of its ability to qualitatively identify and quantitatively estimate metal species in the environment. The nine stage sequential extraction procedure (Olutona *et al*., 2012; Aigberua *et al*., 2018) was adopted during laboratory preparation of sample.

This study is aimed at applying sequential extraction procedure to investigate the effect of crude oil contamination on the bioavailability and potential toxicity of heavy metal micropollutants (lead, cadmium, zinc and manganese). Also, it is aimed at determining the impact of crude oil contamination on the level of plant available metal fractions in the soil, while also aiding the identification of possible sources of heavy metals (that is, anthropogenic (via oil spill) or from the natural environment).

2.0 Materials and Methods

2.1 Study Area

The crude oil impacted site in Bdere community is located within a seasonal swamp characterized by loose soil along an SPDC operation right of way about 2 to 3 kilometers distance from nearest human habitation. The study area lies between the coordinates of latitude N04.69130 and longitude E007.25437. The field of study was along a Shell Petroleum Development Company (SPDC) crude oil transfer line. The field area is characterized by a network of crude oil pipelines which are sometimes prone to being vandalized. Also, crude oil spills or leakages have been reportedly attributed to faulty pipeline joints (Aigberua *et al*., 2017a). Over the years, substantial oil and gas exploration and transportation activities as well as other anthropogenic input within the Bdere field may have significantly impacted the environment. The indigenous people are predominantly farmers and fishermen. Hence, they rely on a sustainable natural ecosystem to earn a living. Plate 1 depicts a cross-section of the affected oil pipeline in the crude oil contaminated field.

Plate 1. Cross-section of the affected crude oil pipeline in Bdere community.

2.2 Field Sampling

Soil samples were randomly collected at depths of 0 - 15 cm from three (3) locations across the oil impacted site while one (1) control point with no trace of crude oil contamination was established at about 100 m distance from entrance to crude oil contaminated field area. Soil auger was used to collect surface soil around the excavated portion of the affected pipeline and each sampling point was geo-referenced with a hand-held Garmin Etrex model GPS. The recorded latitude and longitudes were (SS1-N04.69050, E007.25407; SS2–N04.69048, E007.25437 and SS3–N04.69084, E007.25435) for the crude oil affected soils and (CS1–N04.69130, E007.25430) for the unaffected field area. Triplicate samples were collected for each sampling point and transferred into pre-cleaned polyethylene bags before been stored in an ice chest.

2.3 Sample Preparation, Analytical Validation and Quality Control Procedure

Soil samples were air-dried at room temperature, homogenized by grinding and sieved through a 2 mm mesh size sieve before being transferred into plastic vials. Glassware was acid-washed and copiously rinsed under tap water, further rinsed 3 to 4 times with distilled water. Thereafter, they were air-dried at room temperature and kept in designated storage area. Reagent blank was prepared for each fraction of the sequential extraction. Working standard solutions of 100 mg/l was prepared from an AccuStandard-USA stock standard solution (1,000 mg/l) of each test metal. Immediately after instrument calibration, method blanks were analyzed as quality control at the start, midpoint and end of run of each fractional species. The following wavelengths were applicable for the analysis of study metals: Pb (217.0 nm), Cd (228.8 nm), Zn (213.9 nm) and Mn (279.5 nm).

2.4 Reagents and Chemicals

The reagents and chemicals used were of analytical grade, some of which included: ammonium nitrate (Analytical Reagent, Yueqiao chemicals, China), ammonium nitrate (Analytical Reagent, Yueqiao chemicals, China), 96% glacial acetic acid (Riedel-De Haen, Germany), hydroxylamine hydrochloride (Analytical Reagent, Guangdong Guanghua Sci-Tech Co., Ltd Shantou, China), EDTA Disodium salt (Analytical Reagent, Interchem Europe (UK) Ltd), ammonium oxalate (LabTech Chemicals, India), ascorbic acid (BDH Chemicals Ltd, Poole England), hydrofluoric acid (BDH Chemicals Ltd, Poole England), Hydrofluoric acid (BDH Chemicals Ltd, Poole England), 65% nitric acid (Riedel-De Haen, Germany), 37% hydrochloric acid (Sigma-Aldrich Chemicals, USA), sodium hexametaphosphate (Analytical Reagents – Cartivalues Scientific Enterprises, (Singapore) PTE. Ltd), potassium dichromate (Analytical Reagent, Kermel - Colmar, France), sulphuric acid (BDH Chemicals Ltd, Poole England), 1,10-phenanthroline hydrate (Hopkins & Williams, Chadwell Health Essex, UK) and ferrous sulphate (Analytical Reagent, Kermel – Colmar, France). All standard solutions were prepared in distilled water, the working standards of the four (4) study metals were prepared by diluting different known volumes of heavy metal stock solutions (1,000 mg/l).

2.5 Sequential Extraction of Heavy Metals

The nine-stage sequential extraction scheme for metal fractionation reported by (Olutona *et al*., 2012; Aigberua *et al*., 2018) was adopted. This fractionation scheme depicted two more important factors; water soluble and plant available fractions. In this scheme, heavy metals were separated into nine operationally defined fractions (F): water soluble (F1), exchangeable (F2), bound to carbonate (F3), plant available (F4), bound to Mn (F5), bound to amorphous Fe oxide (F6), bound to crystalline oxide (F7), bound to organic matter (F8), and residual fraction (F9).

One gram of each sediment sample was weighed and sequentially extracted using different selective extraction solutions as applicable for each speciation protocol. Distilled water was used to wash the residues after each extraction to ensure selective dissolution and avoid cross-contamination between extraction fluids. All samples were run in triplicate; the analytical protocol used is detailed below:

Fraction 1: Water soluble metals

Water soluble metals were extracted with a solution of 50 ml distilled water at pH 7.0 and at 28°C for 2 h.

Fraction 2: Exchangeable metals

The residue from (water soluble metals) was extracted with 25 ml of 1.0 M NH_4COOCH_3 (pH = 7.0). The suspension was agitated for 30 min at 28°C.

Fraction 3: Metals bound to carbonate

The residue from (exchangeable metals) was extracted with 3 M sodium acetate solution (CH_3COONa) adjusted to pH 5.0 with acetic acid (CH_3COOH). The suspension was agitated for 5 h.

Fraction 4: Plant available metals

The residue from (metals bound to carbonate) was extracted by shaking with a solution mixture consisting 50 ml of 0.025 M HCI + 0.05 M H_2SO_4 for 30 min at 28°C.

Fraction 5: Metals bound to Mn-oxide

The residue from (plant available metals) was shaken for 30 min at 28°C with a solution of 25 ml 0.1 M hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25% acetic acid (CH_3COOH) (pH 2 to 3).

Fraction 6: Metals bound to amorphous Fe-oxide

The residue from (Mn-oxide bound metals) was extracted with 25 ml of 0.2 M Ammonium oxalate [$(NH_4)_2C_2O_4$] (pH 3.0) for 30 min at 50°C using a water bath with occasional stirring.

Fraction 7: Metals bound to crystalline Fe-oxide

The residue from (amorphous Fe-oxide bound metals) was extracted using a mixture of 0.2 M Ammonium oxalate [$(NH_4)_2C_2O_4$] and 0.1 M ascorbic acid (pH 3.25) and it was heated in a water bath with occasional stirring at 100°C for 30 min.

Fraction 8: Metals bound to organic matter

The residue from (crystalline Fe-oxide bound metals) was extracted with 10 ml of 0.02 M HNO_3 and 15 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3). The mixture was then heated to 85°C for 5 h with occasional agitation. A second 15 ml of 30% H_2O_2 (pH 2 with HNO_3) was added and the mixture was heated again to 85°C for 3 h with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4COOCH_3 in 20% (v/v) HNO_3 was added and the samples diluted to 20 ml and agitated continuously for 30 min.

Fraction 9: Residual metals

The residue from (organic matter bound metals) was digested with a mixture of concentrated HF, HNO_3 and $HCIO_4$ for 8 h (Olutona *et al.*, 2012; Aigberua *et al.*, 2018).

3.0 Results and Discussion

3.1 Concentration of Heavy Metals in Sediment

Result of the spatial distribution of heavy metals in crude oil contaminated soil depicted the following range and mean values: Pb (<0.001-3.74 mg/kg; 0.55±1.02 mg/kg), Cd (<0.001-0.12 mg/kg; 0.02±0.03 mg/kg), Zn (<0.001-8.15 mg/kg; 1.66±2.39 mg/kg) and Mn (<0.001-5.12 mg/kg; 0.45±1.11 mg/kg) while the uncontaminated soil recorded range and mean concentrations of Pb (<0.001-2.14 mg/kg; 0.42±0.77 mg/kg), Cd (<0.001-0.23 mg/kg; 0.04±0.08 mg/kg), Zn (<0.001-6.47 mg/kg; 1.45±2.06 mg.kg) and Mn (<0.001-9.41 mg/kg; 2.15±3.41 mg/kg). Apart from Mn which is a soil micronutrient, mean concentrations of all other heavy metals were reportedly higher in the crude oil contaminated site when compared to the unaffected soil. This can be attributed to the introduction of metals associated with crude oil. This agreed with the findings of Aigberua *et al.* (2017a) where heavy metal concentrations were reported to be relatively higher in crude oil contaminated soils.

3.2 Heavy metal speciation of oil impacted and uncontaminated Bdere soil

The obtained data shows the heavy metal species or ions that characterize the oil-contaminated and uncontaminated soils of Bdere community in Ogoniland, Rivers State. The essential and non-essential metal species studied includes: Pb, Cd, Zn and Mn. The metal species being studied represent the mobile and immobile fractions which can either become bioavailable or inert within the soil environment. Metal fractions were quantified across different sampling locations (crude oil impacted and control sites) within the same field location. Sampling was carried out in the month of August 2017 to reflect the wet season. This is because the field location is a seasonally flooded swamp area. A total of twelve (12) soil samples were sampled and analyzed using multi-step extraction procedures as adopted by (Olutona *et al.*, 2012; Aigberua *et al.*, 2018). The results are presented in Figures for the oil-contaminated and uncontaminated soil for fractions 1 (F1) to 9 (F9).

In general, the results obtained from this study revealed that all metals were prevalent in the poorly mobile and immobile fractions (Figure). In the oil contaminated soil, Zn (41.13%) and Mn (77.54%) were predominantly associated to the residual fractions while Pb (29.45%) and Cd (25.53%) were prevalent in the amorphous Fe-oxide and plant available fractions respectively. Similarly, the uncontaminated soil depicted the residual fractions of Zn (49.43%) and Mn (48.63%) to be the most important while Pb (56.17%) and Cd (62.16%) were both predominantly affiliated to plant available fractions (Figures 1 to 4).

Despite the relative prevalence of metals to the inert fractions, the oil impacted site revealed the significant affiliation of Pb to the easily available exchangeable fractions (9.97%), while Cd was potentially more available than Pb as it was present in the easily mobile fractions of water soluble (6.38%), exchangeable (10.64%) and carbonate-bound (8.51%) fractions. Also, Zinc depicted the most affiliation to the readily and easily available fractions as its most important fractions were the water soluble (13.44%), exchangeable (19.22%) and carbonate-bound (7.56%) fractions. Manganese revealed the least association to the easily available fractions as its most significant association was found in the water soluble (3.52%) fractions. Overall, the total percentage affiliation of metals to the potentially bioavailable fractions are reported as Pb (10.71%), Cd (25.53%), Zn (40.22%) and Mn (3.52%) (Figures 1 to 4). Hence, the metals being studied depicted the following potential for toxicity: Zn>Cd>Pb>Mn. The impact of crude oil retention in soil may have rendered Mn immobile in soil, while the presence of Zn, Cd and Pb as crude oil constituents may have resulted to their adsorption on soil colloids and potential availability.

On the other hand, the uncontaminated soil depicted Pb (1.05%) in the carbonate-bound fractions, Cd (10.81%) in the exchangeable fractions, Zn (4.20%) in the carbonate-bound fractions and Mn (3.82% and 2.22%) in the water soluble and exchangeable fractions respectively. Overall, the total percentage affiliation of metals to the potentially bioavailable fractions are reported as Pb (1.05%), Cd (10.81%), Zn (4.20%) and Mn (6.04%) (Figures 1 to 4).

Therefore, potential for metal toxicity in the uncontaminated soil depicted Cd>Mn>Zn>Pb. Mn is an essential soil mineral which may be responsible for its bioavailability in the uncontaminated (control) soil. The increased Mn level may have come from agrochemical production, growing vegetation or run-off from neighboring farmlands within study location. Mn was reportedly more mobile in uncontaminated soil as compared to the oil impacted soil.

Except for Mn, results obtained from this study agreed with the findings of Ideriah *et al*. (2013) that the exchangeable fractions of oil contaminated soils of Ola-1 oil spill site at Umuola in Abara community, Etche local government area of Rivers State depicted Pb (22.27%), Cd (37.78%), Zn (22.43%) and Mn (21.43%). It was consistent with the findings of Osakwe (2010) where Mn in soils around automobile waste dumpsites in Northern Niger Delta was reported to be majorly associated with residual fractions (24.43%).

Definition of terms: OIS: oil impacted soil, CS: control soil,

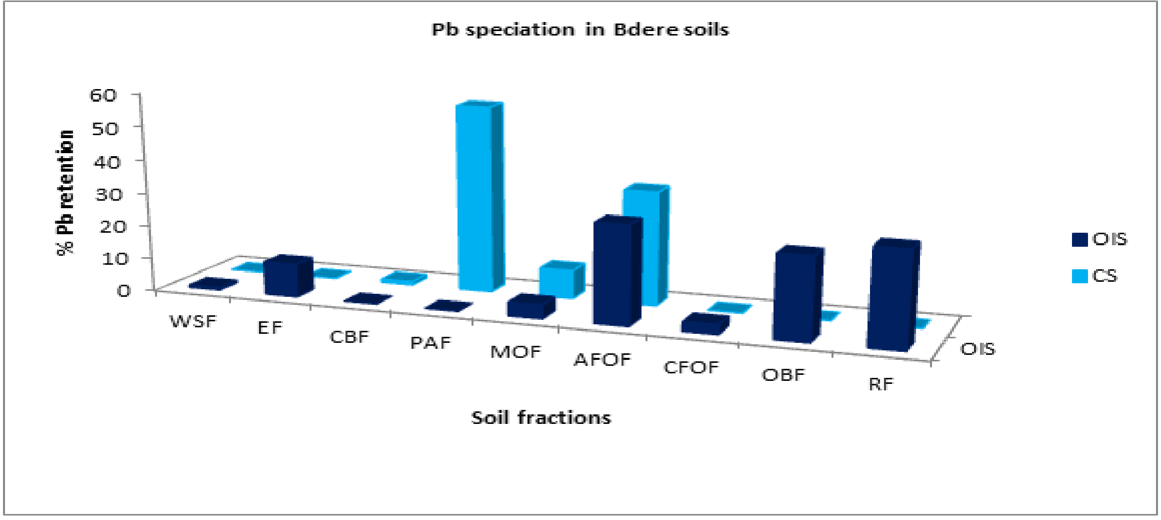

Figure 1. Speciation of lead in Bdere oil impacted and control soils.

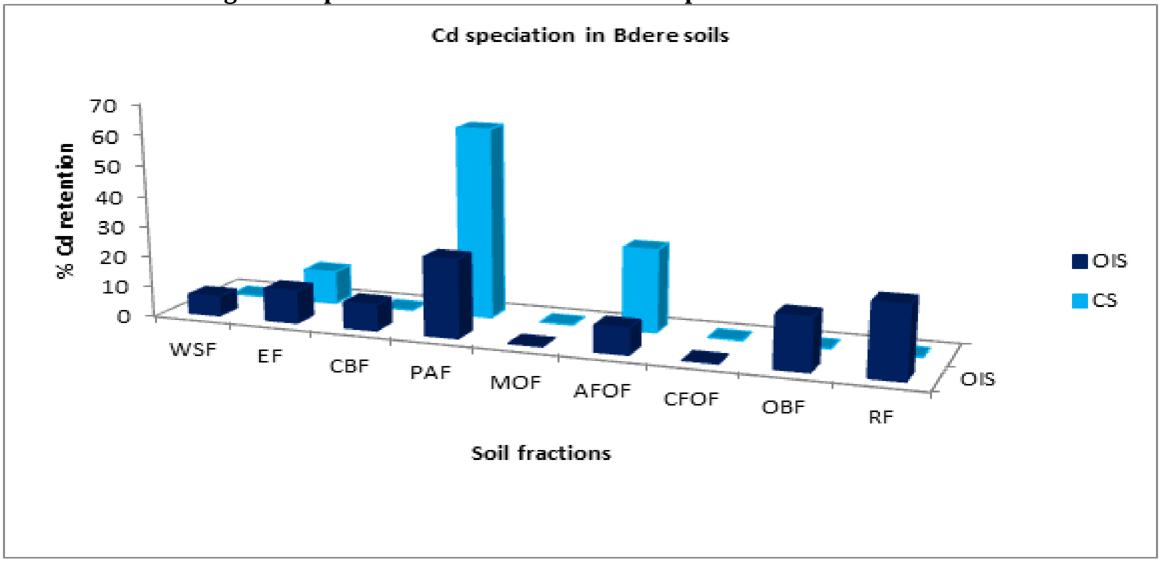

Figure 2. Speciation of cadmium in Bdere oil impacted and control soils.

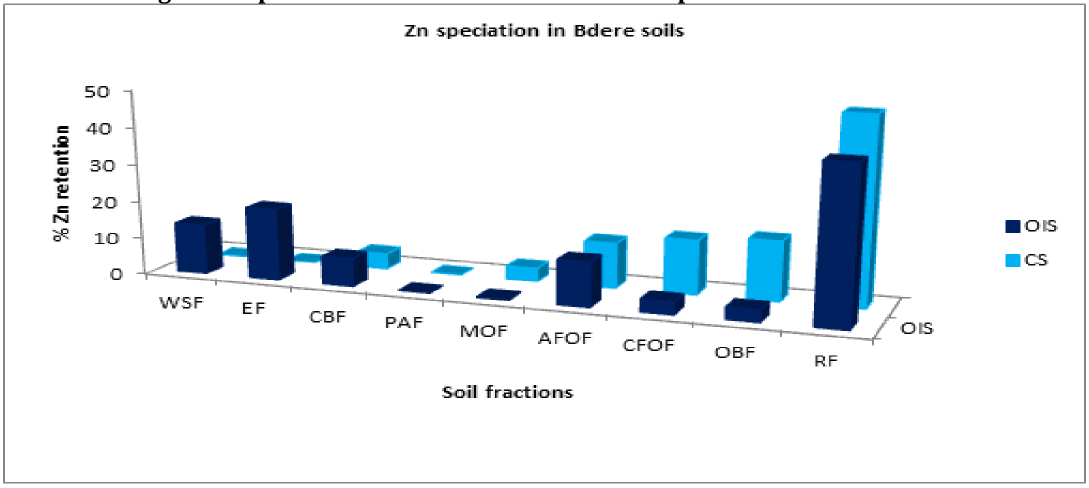

Figure 3. Speciation of zinc in Bdere oil impacted and control soils.

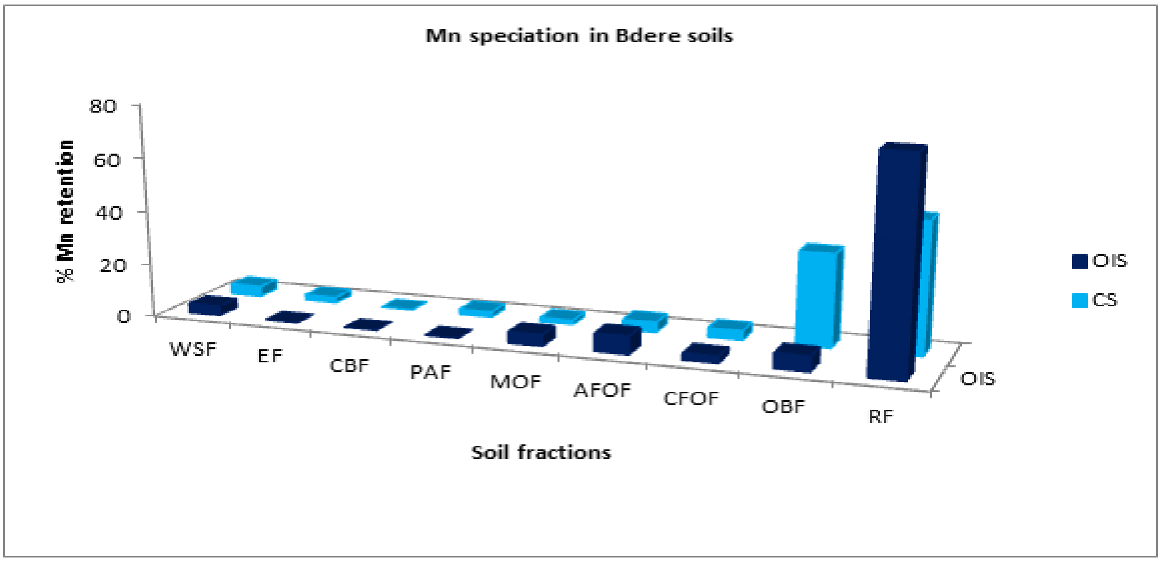

Figure 4. Speciation of manganese in Bdere oil impacted and control soils.

WSF: Water Soluble Fraction, EF: exchangeable fraction, CBF: carbonate bound fraction, PAF: plant available fraction, MOF: Mn-oxide fraction, AFOF: amorphous Fe-oxide fraction, CFOF: crystalline Fe-oxide fraction, OBF: organic bound fraction and RF: residual fraction.

3.3 Mobility Factors of Heavy Metals in Bdere soil

The fate of metal ions in soil is dependent on its mobility factor. Mobility factors (MF) of metals provide an indication of the bioavailability or non-bioavailability of the metal (as described in Aigberua et al., 2018). Heavy metals in soil are fractionated in the order of decreasing solubility, therefore, the water soluble, exchangeable and carbonate-bound (F1 + F2 + F3) fractions which are the free metal ion species with most solubility reflect the mobile and bioavailable forms (see table 1). The relative index of metal mobility was calculated as a mobility factor (MF) (Kabala and Singh, 2001) by applying the equation:

$$MF=\left\{\frac{F1+F2+F3}{F1+F2+F3+F4+F5+F6+F7+F8+F9}\right\}\ x\ 100$$

Definition of variables:

F1: water soluble metal fraction
F2: exchangeable metal fraction
F3: carbonate-bound metal fraction
F4: plant available metal fraction
F5: Mn-oxide bound metal fraction
F6: amorphous Fe-oxide bound metal fraction
F7: crystalline Fe-oxide bound metal fraction
F8: organic matter bound metal fraction
F9: residual metal fraction

A high mobility factor value of the heavy metals in the soil has been interpreted as evidence of relatively high potential for toxicity and biological availability (Kabala and Singh 2001; Fedotov and Miro, 2008; Aigberua *et al*., 2018) (see Table 1).

The mobility factors for the oil impacted and uncontaminated soil locations are presented in table 2 for the month of August 2017 which represents the wet season. The observed trend for the mobility factors of metals was depicted as Zn>Cd>Pb>Mn and Cd>Mn>Zn>Pb for the oil impacted and uncontaminated (control) soils respectively. Consequently, manganese depicted the least mobility factor and bioavailability in the oil impacted soil thereby suggesting that they were majorly from natural sources. On the other hand, the poor mobility of lead in the uncontaminated (control) soil was an indication that lead had insignificant anthropogenic contribution (see Table 2).

Table 1. Operationally defined fraction and extracted components (Fedotov and Miro, 2008).

Defined Fraction	Extracted Components	Physicochemical mobility	Potential bioavailability
Water soluble	Free ions	Mobile	Easily available
Exchangeable	Exchangeable ions (metals retained by weak electrostatic interactions)	Mobile	Easily available
Acid soluble	Carbonates (for non-calcareous soils)	Easily mobilizable	Easily available
Easily reducible	Mn oxyhydroxides	Readily mobilizable	Readily available
Easily oxidizable	Metal-organic complexes	Readily mobilizable	Readily available
Moderately reducible	Amorphous Fe (and Al) oxyhydroxides	Poorly mobilizable	Poorly available
Moderately and poorly oxidizable	Refractory organic compounds and sulfides	Poorly mobilizable	Poorly available
Poorly reducible	Crystalline Fe and Al oxyhydroxides	Poorly mobilizable	Poorly available
Residual	Mineral lattice (metals retained within the crystal structure)	Immobile	Unavailable

Table 2. Mobility factors of heavy metals in Bdere soil.

Mobility Factor(s) (%)	Oil impacted Soil (sample)	Uncontaminated soil (control)
Lead, Pb	10.71	1.05
Cadmium, Cd	25.53	10.81
Zinc, Zn	40.21	4.20
Manganese, Mn	3.52	6.05

Apart from manganese which recorded higher mobility factor in uncontaminated (control) soil, the oil contaminated soils

depicted relatively higher mobility for lead, cadmium and zinc. This study was in agreement with Osakwe *et al*. (2014) that reported greater mobility factor indices for zinc and cadmium when compared to lead as depicted by the trend: (Ni > Zn > Cd > Cu > Pb > Fe) and (Cd > Ni > Zn > Pb > Cu > Fe) for bottom sediments of the Imo River system during the dry and wet seasons respectively.

4.0 Conclusion

Even though this study revealed the inert metal fractions to be the most important, the significant affiliation of zinc, cadmium and lead to the easily mobile and bioavailable fractions of oil impacted soil of Bdere rendered them potentially toxic and further suggested that these metals may have emanated from the introduction of crude oil into the soil. Also, mobility factor indices revealed manganese to possess higher mobility and reactivity in the uncontaminated (control) soil, the readily soluble nature of manganese makes it quite mobile and potentially bioavailable in the environment while the relatively poor mobility of manganese in the oil impacted site may have been due to retention of oil in the pore spaces of the polluted soil matrix.

References

Adelana, S. O., Adeosun, T. A., Adesina, A. O., Ojuroye, M. A. (2011). Environmental pollution and remediation: challenges and management of oil spillage in Nigerian coastal areas. *Am. J. Sci. Ind. Res, 2(6)*: 834-845.

Aigberua, A., Tarawou, T. (2017).Assessment of Heavy Metals in Muscle of Tilapia zilli from some Nun River Estuaries in the Niger Delta Region of Nigeria. *Academic Journal of Chemistry, 2(9)*: 96-101.

Aigberua, A. O., Ekubo, A. T., Inengite, A. K., Izah, S. C. (2017a). Assessment of some selected heavy metals and their pollution indices in an oil spill contaminated soil in the Niger Delta: a case of Rumuolukwu community. *Biotechnol Res, 3(1)*: 1-5.

Aigberua, A., Tarawou, T., Abasi, C. (2017b).Spatial and Seasonal Assessment of Heavy Metals in Surface Waters of the Middleton River in the Niger Delta, Nigeria. *International Journal of Natural Resource Ecology and Management, 2(5)*: 94-98.

Aigberua, A. O., Tarawou, J. T., Abasi, C. Y. (2018).Effect of Oxidation-Reduction Fluctuations on Metal Mobility of Speciated Metals and Arsenic in Bottom Sediments of Middleton River, Bayelsa State, Nigeria.*J. Appl. Sci. Environ. Manage, 22(9)*: 1511-1517.

Anderson, D. (2003)‘ Introduction to Heavy Metal Monitoring’. Centre for Ecology and Hydrology’. Available at:http://www.heavymetals.ceh.ac.uk/resources/CEH_hm_intro.PDF (Accessed: 2 March 2007).

Asimiea, A. O., Lawal, O. (2017).Investigation of relationship between sediment characteristics and heavy metals across seasons in the Lower Forcados River, Nigeria. *J. Appl. Sci. Environ. Manage, 2(1)*: 208-215.

Awobajo, S. A. (1991). Analysis of oil spill incidents in Nigeria, In proceeding of the seminar on the petroleum industry and Nigeria Environmental. NNPC/FMOWW and PTI Warri,Nigeria.

Fatoba, P. O., Ogunkunle, C. O., Ihazai, C. O. (2015). Assessment of Metal Pollution of Soil and Diagnostic Species Associated With Oil Spills in the Niger Delta, Nigeria. *Environmental Research, Engineering and Management, 71*: 13-22.

Fedotov, P. S., Miro, M. (2008).Fractionation and mobility of trace elements in soils and sediments, In Violante, A., Huang, P. M., and Gadd, G. M. (eds).Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments. *Wiley-Jupac Series Vol 1,* John Wiley & Sons, Hoboken, NY. pp: 467-520.

Ideriah, T. J. K., Ikpe, F. N., Nwanjoku, F. N. (2013). Distribution and Speciation of Heavy Metals in Crude Oil Contaminated Soils from Niger Delta, Nigeria. *World Environment, 3(1): 18-28.*

Ideriah, T. J. K., Ikpe, F. N., and Nwanjoku, F. N. (2013). Distribution and Speciation of Heavy Metals in Crude Oil Contaminated Soils from Niger Delta, Nigeria. *World Environment, 3*(1), 18–28.

Iniaghe, P. O., Tesi, G. O., Iniaghe, P. O. (2013) Environmental degradation and sustainable development in Nigeria’s Niger delta region. *Journal of Sustainable Development in Africa, 15(3)*: 51-78.

Izah, S. C., Angaye, T. C. N. (2016). "Heavy metal concentration in fishes from surface water in Nigeria: Potential sources of pollutants and mitigation measures. "*Sky Journal of Biochemistry Research, 5*: 31-47.

Izah, S. C., Chakrabarty, N., and Srivastav, A. L. (2016). A Review on Heavy Metal Concentration in Potable Water Sources in Nigeria: Human Health Effects and Mitigating Measures. *Exposure and Health, 8,* 285-304.

Kabala, C., Singh, B. R. (2001).Fractionation and Mobility of copper, lead and zinc in vicinity of copper smelter. *J. of Environ. Qual., 30:* 485-492.

Kabata-Pendias, A., Pendias, H. (2000).Trace Metals in Soils and Plants. 3rd Ed. CRC Press LLC, Boca Raton, New York, Washington, D.C.

Kadafa, A. A.(2012).Oil Exploration and Spillage in the Niger Delta of Nigeria. *Civil Environ. Res, 2(3)*: 38-51.

Manby, B. (1999)“The Price of Oil”.Human Rights Watch. Retrieved December 16, 2014.

Nwilo, C. P., Badejo, T.O. (2005) Impacts and Management of Oil Spill Pollution along the Nigerian Coastal Areas.

Ogbeibu, A. E., Iyobosa, S. E. (2013). Illegal crude oil bunker in Nigeria: proximate and ultimate factors. *Journal of Nigeria Environmental Society, 7(4)*: 1-18.

Olutona, G. E., Aribisala, O. G., Akintunde, E. A. (2012). A study of chemical speciation of metals in aquatic bottom sediment of Aiba reservoir, Iwo, Nigeria.*African Journal of Environmental Science and Technology 6(8)*: 312-321.

Osakwe, S. A. (2010).Chemical Speciation and Mobility of Some Heavy Metals in Soils around Automobile Waste Dumpsites in Northern Part of Niger Delta, South Central Nigeria. *J. Appl. Sci. Environ. Manage, 14(4)*: 123-130.

Osakwe, J. O., Adowei, P., Horsfall, M. J. (2014).Evaluation of Heavy Metal Species in Bottom Sediments from Imo River System, Southeastern Nigeria.*Res. J. Chem. Sci. 4(6)*: 23-30.

Osuji, L. C., Iniobong, D. I., Ojinnaka, C. M.(2006). Preliminary investigation of Mgbede-20 oil-polluted site in Niger Delta,Nigeria.*Chem. Biodiv.,3(5)*: 568-577.

Shell Petroleum Development Company (SPDC) (1996). People and the environment, annual report Lagos, SPDC press.