

# Effects of Spatial, temporal and pH changes on fractionated heavy metals in sediments of the Middleton River, Bayelsa State, Nigeria

## Abstract

The chemical fractions and mobilities of heavy metal micropollutants (Cu, Mn, Co and Cd) were evaluated and their relationship with sediment acidity was established in order to account for the vulnerability of the Middleton river system to anthropogenic activities within and around its estuaries. The GBC Avanta FAAS was used to determine the fractional concentrations of heavy metals of interest. Results obtained for bottom sediments reported the most important fraction of manganese, cobalt and cadmium to be the readily mobile water-soluble fraction. Copper was the only metal which was prevalently affiliated to the immobile organic matter-bound fraction of the sediment matrix. The low levels of most of the metals in the residual fractions suggests that the bioavailable heavy metals may not have emanated from the natural environment but from anthropogenic activities releasing them within the environment (most notably is cobalt which may have resulted from activities of oil bunkers and faulty oil equipment). In addition, an increase in acidic conditions of the sediment environment was found to have increased the mobility and solubility of other heavy metals except copper. The acidity and potential mobility of sediments was greater in the dry season when compared to the wet season and this could be attributed to dilution effects from the increased tidal movement of water. On the other hand, the limited mobility of copper within the environment may have resulted from its chelation to organic matter.

**Keywords:** chemical fractions, mobility, bioavailability, Middleton River

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## Introduction

Any metallic element possessing relatively high density and toxicity even at lower concentrations is referred to as heavy metal.<sup>1</sup> Heavy metals occur naturally as a composition of the earth's crust and inundate the aquatic ecosystem via weathering and washing of bedrock and solid mineral materials, aerial downpour from volcanic discharge as well as anthropogenic inputs which include effluent discharges emanating from nearby industries, offshore equipment or installations and vehicular or boat transportation emissions). Heavy metals introduced in the marine ecosystem are mostly concentrated in coastal areas, near densely populated and industrialized regions. Heavy metals are usually associated to particles. These particles are often very small, and can therefore stay in solution for a very long time. Nevertheless they will end up in the sediments. Therefore concentrations in the sediments are often 10 to 100 times higher than those in solution. In the sediments, these particles may form important secondary source of contamination, even after the primary source has disappeared.<sup>2</sup> Heavy metal fractionation is the identification of the volumetric amounts and specific species (or forms) which makes up an element within a given environment. Hence, heavy metal fractionation helps to identify the environmental toxicity potential of a metal on the basis of its biogeochemistry. The total metal concentration is usually measured to quantify the elemental burden in sediment and soils.<sup>3</sup> Metal speciation includes the chemical form of the metal in the soil solution, either as a free ion or complexed to a ligand, in the gaseous phase and distributed amongst solid phases within the soil. However, the long-term bioavailability of metals to humans and other organisms is determined by the re-supply of the metal to the mobile pool (soil solution) from more stable phases (metals in and associated with solid species).<sup>4</sup>

It is extensively demonstrated that increasing heavy metal pollution from various industries constitutes environmental hazard for humans and other living things.<sup>5</sup> A number of events affecting water quality have resulted in increased public concern about surface water quality.<sup>6</sup> Such events as increased domestic wastes generation and indiscriminate disposal and discharge of untreated and poorly treated industrial wastes into surface water bodies impact negatively on water quality and lead to water quality deterioration.<sup>7,8</sup> Heavy metals associated with crude oil include Pb, Cd, Cu, Zn, Ni, V and Cr amongst others.<sup>9</sup> Diseases and pathological conditions related to heavy metal contaminants have been recently reviewed by Izah and Srivastav.<sup>6</sup> The level of pH is a very important factor which determines how heavy metals are retained or released in an aquatic environment. Hydrogen ion possesses the tendency to be strongly attached to surface negative charges and possess the power to replace most other cations.<sup>10</sup> Metal mobility tends to increase at lower pH and decreases at higher pH.<sup>11</sup> Mobility of metals in soil with low pH has been reported to decrease in the order: Cd > Ni > Zn > Mn > Pb, even though the effect of pH on mobility of elements in soil is highly variable depending on the content and type of organic matter.<sup>12</sup> The physicochemical properties of aquatic ecosystems are characterized by a number of independent parameters. Factors such as temperature, oxygen content and pH of a water body can alter the solubility of the salts in it, the forms of occurrence of particular species, as well as their bioavailability and toxicity. Thus, it is necessary to determine the various species of metals present in the different compartments of the aquatic ecosystem.<sup>13</sup> pH is known to have significant effect on metal dynamics because it controls adsorption and precipitation, which are the main mechanism of metal retention in soils.<sup>14</sup> Cd sorption by an acid sandy soil has been found to double for each 0.5 unit increase in

pH when adjusted in the laboratory.<sup>15</sup> The relationship between pH and the bioavailability of many elements exist, apart from plants, in many aquatic organisms, that is, fish in acid lakes contained higher concentrations of Al, Cd, Hg and Pb than in neighbouring lakes with higher pH.<sup>11</sup>

The Middleton River estuary is situated in Southern-Ijaw local government area of Azuzuama community in Bayelsa state, Nigeria. It is a major oil producing zone in the heart of the Niger Delta region and as such plays host to oil installations and under-water crude oil pipelines and manifolds which serve as transfer lines to well heads within and around its environ. The river is tidal and sometimes overflows; driving spilt crude oil into surrounding freshwater, mangrove swamps, mudflats, hence, the aquatic environment intermittently reflects oil sheen. In addition, other forms of indiscriminate and uncontrolled municipal discharges negatively impact on the overall quality of the aquatic environment. The environmental significance of elemental speciation on the Middleton river system is enormous due to the economic importance of this river as one of the many oil producing areas in the Niger Delta region of Nigeria. The socio-economic impact of oil pollution on the water ways and the attendant adverse environmental impact on the bottom sediments of the river system of host communities in the Niger Delta have led to far reaching devastations such as incessant forfeiture of arable agricultural farmlands, the consequential absence of habitable fresh water and loss of aquatic organisms, poor economic activities, intrusion of contaminants into surrounding groundwater resources and associated adverse health impacts. The nine-stage multi-step extraction procedure previously applied by Olutona et al.<sup>16</sup> was adopted for the present study. The extraction scheme aided a better understanding of the concept of bioavailability and mobility of elements in the environment. The hazard and chemical response of metals and their systemic availability in an aquatic habitat can lead to the qualification and quantification of different species of the metal ions. The present study was targeted towards identifying the effect of pH, point of sample collection and sampling season on metal fractions that are retained in sediments of the Middleton River.

## Materials and methods

### Sampling

Sediment samples were collected in triplicate from seven locations (five were within the vicinity of oil installations and two were controls; collected at about 1km upstream (C1) and 2km downstream (C2) distances from areas where the oil installations were situated). Sampling was done in the dry and wet months of March and August 2017 respectively. The geographical coordinates of the sampling points across the Middleton River were obtained with a hand-held Garmin Etrex model GPS; the coordinates were recorded as: A (N04° 41' 48.1", E005° 55' 20.0"), B (N04° 42' 40.2", E005° 55' 18.4"), C (N04° 42' 00.3", E005° 56' 38.0"), D (N04° 42' 51.3", E005° 56' 27.9"), E (N04° 43' 09.0", E005° 56' 11.2"), Control 1 (N04° 43' 58.3", E005° 56' 41.5") and Control 2 (N04° 40' .068", E005° 53' .018"). An Eckmann grab was deployed to collect triplicate samples of sediment at each sample location. Samples were transferred into pre-cleaned polyethylene bags before been stored in an ice chest for preservation prior to delivery in the laboratory.

### Sample preparation, analytical validation and quality control procedure

Sediment samples were air-dried at room temperature, homogenized by grinding and sieved through a 2mm mesh size sieve before being further sub sampled and labelled in plastic vials. Glassware was properly cleaned, oven-dried and cooled in a desiccator. Reagent blank was prepared for each fraction of the sequential extraction. A series of working standard solutions of 0.5, 1, 2, 5, 10 and 100 mg/l were prepared from the stock standard solution of each test metal; this was done by diluting known volumes of the stock solution in 100 ml volumetric flasks using distilled water. 1000 mg/l of an AccuStandard (USA) metal stock solution of each metal was diluted accordingly to prepare a series of intermediate standard solutions which were used for the calibration of the Flame Atomic Absorption Spectrophotometer (FAAS). During analysis, method blanks and standard solutions were aspirated at the start, midpoint and end of each metal run. The following were the working wavelengths were: Cu (324.7 nm), Cd (228.8 nm), Co (240.7nm) and Mn (279.5nm). In addition, pH was read electrometrically using an HANNA HI8314 model pH meter dipped in a 1:1 sediment solution of 20g air-dried sediment and 20 ml distilled water.

### 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 using distilled water; working standards of the ten (10) metals to be determined were prepared by diluting different known volumes of their stock solutions (1,000mg/l).

### Sequential extraction of heavy metals

The nine-stage sequential extraction scheme for metal fractionation reported by Olutona et al.<sup>16</sup> 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 following after each extraction. This was done to ensure selective dissolution and to avoid cross-contamination between extraction fluids. All samples were run in triplicate; the detailed analytical protocol adopted is as follows (Figure 1):



**Figure 1** Insertion of sample extracts into test tube holding compartments of the centrifuge.

**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  $\text{NH}_4\text{COOCH}_3$  (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 ( $\text{CH}_3\text{COONa}$ ) adjusted to pH 5.0 with acetic acid ( $\text{CH}_3\text{COOH}$ ). 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 HCl + 0.05 M  $\text{H}_2\text{SO}_4$  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 ( $\text{NH}_2\text{OH.HCl}$ ) in 25% acetic acid ( $\text{CH}_3\text{COOH}$ ) (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 [ $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ] (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 [ $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ] 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  $\text{HNO}_3$  and 15 ml of 30%  $\text{H}_2\text{O}_2$  (adjusted to pH 2 with  $\text{HNO}_3$ ). The mixture was then heated to 85°C for 5 h with occasional agitation. A second 15 ml of 30%  $\text{H}_2\text{O}_2$  (pH 2 with  $\text{HNO}_3$ ) was added and the mixture was heated again to 85°C for 3h with intermittent agitation. After cooling, 5ml of 3.2M  $\text{NH}_4\text{COOCH}_3$  in 20% (v/v)  $\text{HNO}_3$  was added and the samples diluted to 20ml 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,  $\text{HNO}_3$  and  $\text{HClO}_4$  for 8h.

**Results and discussion**

**Heavy metal fractionation of bottom sediment**

The obtained data shows the heavy metal species or fractions that characterize the sediments of the Middleton River. The heavy metal species include: Cu, Mn, Co and Cd. The available metal species represents the inert and mobile metal fractions which can either become immobile or bioavailable within the aquatic ecosystem, depending on the prevailing metal fractions that are found within the bottom sediments. Metal fractions were quantified across different sampling locations (impacted and control sites) along the Middleton River. The effect of seasonal and spatial variation was also determined. The result is presented in Table 1 as percentage metal species or fractions (F1 to F9) in sediment. Fractionation pattern of heavy metals in the different fractions (F1 - F9)

**Table 1** Percentage fractionation of heavy metals in sediment

Heavy metal fractions	Dry season				Wet season			
	%fraction (Cu)	%fraction (Mn)	%fraction (Co)	%fraction (Cd)	%fraction (Cu)	%fraction (Mn)	%fraction (Co)	%fraction (Cd)
Water-soluble (F1)	5.6	49.4	40.8	62.5	0.6	19.3	15.4	20.0
Exchangeable (F2)	1.0	18.9	17.2	16.7	4.4	25.2	14.6	50.0
Carbonate-bound (F3)	5.1	3.7	2.5	0.0	6.2	5.5	2.5	0.0
Plant available (F4)	1.4	1.3	1.4	0.0	2.3	18.2	5.5	0.0
Mn-oxide (F5)	2.9	0.9	3.3	20.8	12.9	6.3	3.7	30.0
Amorphous Fe-oxide (F6)	19.3	0.7	0.8	0.0	27.4	3.6	5.7	0.0
Crystalline Fe-oxide (F7)	8.7	2.5	2.3	0.0	4.2	5.1	3.6	0.0
Organic bound (F8)	34.1	10.6	5.3	0.0	23.8	7.8	2.9	0.0
Residual (F9)	21.9	12.1	26.6	0.0	18.3	9.1	46.1	0.0

## Copper

The distribution of copper revealed the organic matter bound fraction (34.1%) and residual fraction (21.9%), followed by the amorphous Fe-oxide fraction (19.3%) to be the prevalent fractions in the dry season. Wet season levels revealed the prevalence of the amorphous Fe-oxide fraction (27.4%) and organic matter bound fraction (23.8%), followed by the residual fraction (18.3%) (Table1). This suggests that copper posed no potential threat to the aquatic environment. This finding was in agreement with the report of Osakwe that reported the highest fraction of copper to be in the residual form within sediments of the Imo River. Iwegbue et al.<sup>17</sup> reported copper to be higher in the organic bound, residual and Fe-Mn oxide fractions. Horsfall et al.<sup>18</sup> reported the organic matter bound and sulphide fractions to be the most prevalent association of copper in the Okrika river system. Leizou et al.<sup>19</sup> reported copper to be found in the residual fractions of Pennington river sediments, while, Tamunobereton-ari et al.<sup>20</sup> had reported copper to be predominant in the residual fractions of the Okrika river system at a percentage of about 60-70%. The findings however disagreed with the earlier report of Olutona et al.<sup>16</sup> that reported copper to be associated with the exchangeable and carbonate fractions. Ideriah et al.<sup>21</sup> also observed copper to have its highest concentration in the exchangeable fractions of soils around Abara and Ozuzu oil wells. Therefore, copper exists in the form of insoluble fractions within the Middleton river system. Hence, activities leaching copper in aquatic ecosystems may not be prevalent in this vicinity.

## Manganese

During the dry season, manganese levels in the sediment showed that the water soluble (49.4%) and exchangeable (18.9%) were mostly prevalent, followed by residual fraction (12.1%). Similarly, the wet season depicted high levels of manganese in the exchangeable fraction (25.2%) and water soluble (19.3%), followed by plant available fractions (18.2%) (Table1). This was similar to the findings of Olutona et al.<sup>16</sup> where manganese was reported to be associated with the exchangeable and carbonate fractions. This result was also identical to the findings of Ideriah et al.<sup>21</sup> where the highest concentration of manganese was found in the exchangeable fractions of soils collected from around Abara and Ozuzu oil wells during the dry season. Awokunmi et al.<sup>22</sup> in their sequential extraction procedures observed manganese to be dominated in the non-residual phases. The presence of manganese in the underlying bottom sediments and overlying surface water could have emanated from municipal wastewater discharges, sewage sludge or the combustion of fossil fuels by oil bunkers; this is because most manganese salts are readily soluble in water (WHO, 2004).<sup>23</sup>

## Cobalt

The fractionation pattern of cobalt in the Middleton river sediment depicted that water soluble (40.8%) and residual (26.6%) were most predominant, followed by exchangeable (17.2%), this was during the dry season. However, the wet season showed that cobalt was dominated in the residual (46.1%) with concentrations in the water soluble and exchangeable fractions at (15.4%) and (14.6%) respectively (Table1). The dry season trend for this study agreed with the report of Awokunmi et al.<sup>22</sup> that cobalt was dominant in its non-residual phase. Leizou et al.<sup>19</sup> had also observed cobalt levels to be highest within the exchangeable fractions of Pennington river sediments in Bayelsa state. The result of this study portends a higher

potential bioavailability of cobalt in the dry season as compared to the wet season. Activities releasing cobalt ions may have occurred within the vicinity of the river or the effect of low water tide during the dry season and residual concentration effect due to typically high evaporation rate of the river water by which the dry season is characterized may have been responsible for the mobility of this metal. The other cobalt sources in surface waters may have resulted from the burning of fossil fuels (especially when oil bunkers apply crude or local means to cook or distil illegally tapped crude oil).

## Cadmium

During the dry season, the distribution of cadmium in the sediment revealed that the easily and readily mobile fractions were most associated to cadmium. The water soluble and Mn-oxide fractions were prevalent at 62.5% and 20.8% respectively, followed by the exchangeable fractions (16.7%). Similarly, the wet season depicted the prevalence of cadmium in the exchangeable fraction (50.0%) and Mn-oxide fraction (30.0%), followed by the water soluble fraction (20.0%) (Table1). The results of this study compared to Horsfall which had recorded cadmium to be mostly in the exchangeable fraction. Osakwe et al.<sup>24</sup> had revealed cadmium to be mostly associated to the exchangeable fractions of sediments of the Imo river system. Awokunmi et al.<sup>22</sup> found that the non-residual phases were the dominant fractions of cadmium. However, Iwegbue et al.<sup>17</sup> had reported cadmium to exist mostly in the residual and readily exchangeable fractions..

## Mobility factors of heavy metals in bottom sediments of the Middleton River

The operationally defined extraction sequence fractionates the heavy metals in the sediment in order of decreasing solubility. For a nine stage sequential extraction procedure, the water soluble, exchangeable and carbonate (F1+F2+F3) fractions which are the early fractions reflect the most reactive and presumably the most mobile and potentially bioavailable fractions (Table 2).<sup>25</sup>

The relative index of heavy metal mobility was calculated as a mobility factor (MF)<sup>26</sup> on the basis of the equation:

$$MF = \left[ \frac{(F1+F2+F3)}{(F1+F2+F3+F4+F5+F6+F7+F8+F9)} \right] \times 100$$

Where,	F1 = Water soluble fraction
	F2 = Exchangeable fraction
	F3 = Carbonate fraction
	F4 = Plant available fraction
	F5 = Mn-oxide fraction
	F6 = Amorphous Fe-oxide fraction
	F7 = Crystalline Fe-oxide fraction
	F8 = Organic matter bound fraction
	F9 = Residual fraction

A high mobility factor (MF) value for heavy metals in soil has been interpreted as evidence of relatively high lability and biological availability.<sup>26</sup>

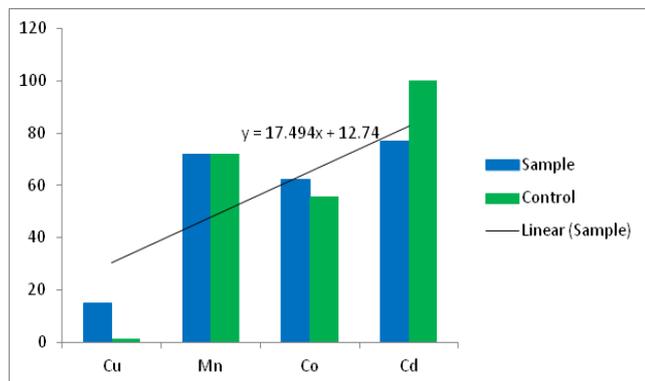
The mobility factors (MF) of the metals for all the sediment sampling points across the Middleton River were presented in Figures

2 & 3 for the dry and wet seasons respectively. The observed trend for the mobility factors of metals depicted  $Cd > Mn > Co > Cu$  for both sample and control locations respectively during the dry season. On the other hand, wet season data revealed the trends:  $Cd > Mn > Co > Cu$  and  $Mn > Co > Cu > Cd$  for both the sample and control locations respectively during the wet season. Consequently, copper depicted the least mobility factor and bioavailability across both seasons and sample locations except for the control locations during the wet season (Figure 3). Hence, the dry season showed comparatively higher mobility factor for cadmium. Cadmium has been reported to be more mobile in most natural environments.<sup>27</sup> This finding partly agreed

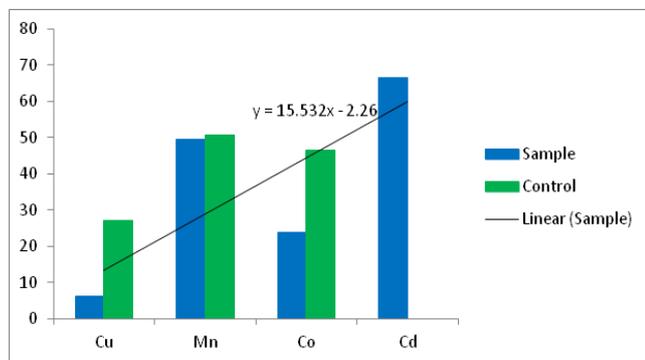
with that of Osakwe et al.<sup>24</sup> where he had reported a greater mobility factor indices for cadmium than copper as depicted by the trends  $(Ni > Zn > Cd > Cu > Pb > Fe)$  and  $(Cd > Ni > Zn > Pb > Cu > Fe)$  for bottom sediments of the Imo River system during the dry and wet seasons respectively. The readily soluble nature of manganese makes it quite mobile and potentially bioavailable in the environment. Manganese was observed to possess high mobility factor, closely following as the second most mobile heavy metal in the Middleton River (Figures 2&3) across the sample and control locations for both the dry and wet seasons respectively.

**Table 2** 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



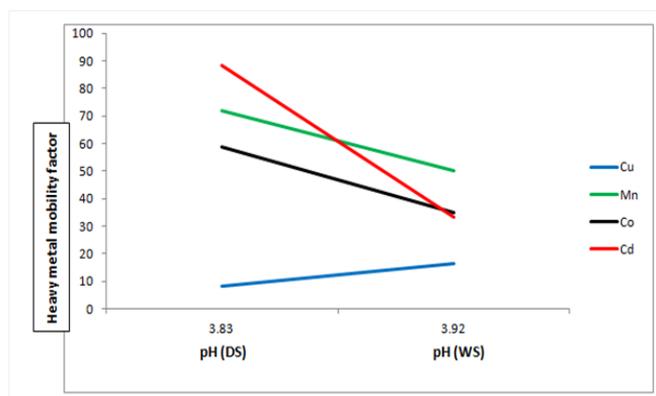
**Figure 2** Heavy metal mobility factors during the dry season.



**Figure 3** Heavy metal mobility factors during the wet season.

### Effect of pH on mobility factor of heavy metals in sediments

The effect of pH on the toxicity and mobility of fractionated metals in bottom sediments of the Middleton River is depicted in (Figure 4). Figure 4 above shows the linear relationship between [pH (DS); pH level in the dry season and pH (WS); pH level in the wet season] and the mobility factor indices of heavy metals within bottom sediments of the Middleton River. The pH level of bottom sediments was slightly higher in the wet season when compared to the dry season (Figure 4). This may have resulted from dilution effects during the tidal month of August. Even though, the bottom sediment was acidic on the whole, copper was readily mobile as pH increased. In addition, manganese, cobalt and cadmium revealed declining mobility factor with increasing pH, hence, the mobility of these metals in the sediment environment is favoured by increasing acidity. Also, cadmium was observed to depict the sharpest drop in mobility factor with reducing acidity of the sediment environment. Except for the case of copper, findings of this study was in agreement with Ideriah et al.<sup>21</sup> where they had attributed the potential bioavailability of heavy metals in oil contaminated soil to factors such as acid soils and the relatively low silt and clay contents. Also, findings from this study agreed with Baruah et al.<sup>28</sup> where cationic availability ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$ ) was observed to decrease with decreasing pH while both studies contradicted in terms of seasonal pH fluctuations as the same study had observed wet season soil samples to be more acidic than those obtained during the dry season. However, the justification that the observed trend in this earlier finding may have stemmed from greater leaching of soils during the rainy season may not apply to a typical sediment environment where the sediment is constantly overlaid by water column and soil-water interactions are continuous.



**Figure 4** Linear relationships between pH and heavy metal mobility factor.

## Conclusion

Results obtained from this study showed that even insignificant changes in environmental pH conditions can result in notable changes in the mobility and solubility of heavy metals. Consequently, manganese, cobalt and cadmium showed direct relationship with sediment acidity (hence, mobility rate increased with increasing acidity) while copper depicted an inverse relationship with sediment acidity (thereby revealing decreasing solubility with increasing acidity). The acidity level of sediments was greater in the dry season when compared to the wet season and this could be attributed to dilution effects from the increased tidal movement of water. Data obtained from heavy metal fractionation showed that the most important fraction of manganese, cobalt and cadmium was the water-soluble fraction. Hence, they possess the tendency to be readily bioavailable within the Middleton River system. Furthermore, the low levels of these metals in the immobile (or residual fractions) suggests that the bioavailable heavy metals may not have emanated from the natural environment but from anthropogenic activities releasing them within the environment. Most notably is cobalt which may have resulted from activities of oil bunkers who locally distil crude oil and release noxious gaseous emissions into the environment as well as leaving trails of run-off into the water body. Copper was the only metal which was prevalently affiliated to the inert organic matter-bound fraction of the sediment matrix. This limited its mobility and reactivity and may have been responsible for its inverse relationship with sediment pH. This is because the acidic level of the bottom sediments of the aquatic ecosystem may not have been sufficient enough to release its free metal ions from the strong organic matter bonding. Also, the rate of metal mobility was higher in the dry season when compared to the wet season, except for copper. Generally, sample locations (from point sources of oil contamination) within the field reflected relatively higher mobility for most of the heavy metals been studied when compared to control locations for both seasons. Overall, the environment was rich in acidic conditions which favoured the leaching and transportability of heavy metal micropollutants within the Middleton river system. Based on the foregoing, it is pertinent to note that adequate measures need to be taken by regulatory agencies to forestall the indiscriminate discharge of contaminants into the environment.

## Acknowledgments

None.

## Conflicts of interest

The author(s) declares that there is no conflicts of interest.

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