



## Evaluation of Heavy Metal Species in Bottom Sediments from Imo River System, Southeastern Nigeria

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### Abstract

Total metal concentrations and five-stage sequential extraction schemes were employed to investigate the potential environmental risk of six important metals in sediments from the upper reaches of Imo River system in Southeastern Nigeria. The concentrations of trace metals in each fraction were determined using AANALYST 400 Perkin-Elmer AAS. The average concentrations (mg/kg) for the six metals in dry season sediment samples were  $0.30 \pm 0.09$  (Cd),  $2.28 \pm 1.20$  (Cu),  $12.35 \pm 8.97$  (Zn),  $1.79 \pm 0.74$  (Ni),  $3.52 \pm 1.68$  (Pb), and  $2025.72 \pm 304.43$  (Fe), while the mean metal concentrations (mg/kg) in wet season samples were  $0.29 \pm 0.05$  (Cd),  $2.06 \pm 0.74$  (Zn),  $24.57 \pm 5.78$  (Cu),  $5.79 \pm 1.67$  (Ni),  $6.26 \pm 3.73$  (Pb), and  $2534 \pm 476.98$  (Fe) respectively. Fe and Pb content in river sediments exceed the Federal Environmental Protection Agency (FEPA) regulatory Standards for soil. Chemical speciation study applying the five-stage sequential extraction schemes revealed that Cd in sediment prevails mostly in exchangeable fractions. Cu, Pb and Fe were more prevalent in residual fractions, while Zn and Ni were found more in carbonate, organic and residual fractions. Eco-toxicological assessment of the river sediments using the mobility factor indices reveals the following sequence: nickel > zinc > cadmium > copper > lead > iron in dry season and cadmium > nickel > zinc > lead > copper > iron in wet seasons respectively. Mobility factor indices for sediment metals revealed a high environmental contamination risk for nickel and cadmium, which indicate an environmental threat to the river ecosystem.

**Key words:** Chemical speciation, eco-toxicology, trace metals, Imo River, sequential extraction.

### Introduction

The evaluation of elemental speciation in environmental compartment is a significant step to understanding the potential environmental risk, mobility and bioavailability of pollutants. Elemental speciation helps in the identification and quantification of the different fractions in which an element exists in the environment. In elemental speciation studies, sequential extractions are usually carried out by means of various chemical reagents in an increasing order of extraction strength<sup>1-3</sup>. The total metal concentration is usually measured to quantify the elemental burden in sediments and soils<sup>4,5</sup>. Since the total metal concentration does not provide a signal on the potential availability of elemental species and their possible mobility in an aquatic ecosystem, various single-extraction schemes are usually employed in order to estimate the bioavailability of elements in sediments or soils<sup>6</sup>, while their mobility in sediment and soil are assessed by sequential extraction procedures<sup>7</sup>. There are three-stage<sup>8</sup>, four-stage<sup>9</sup>, five-stage<sup>10</sup> and nine-stage<sup>11</sup> extraction procedures usually employed in chemical speciation studies to explore the bioavailability or mobility of elements in the environment. These investigations provide valuable data on the fate, chemical behavior or

mechanism of elements in sediments or soils. Tessier and co-workers<sup>12</sup> developed the five-stage sequential extraction scheme, while the nine-stage sequential procedure was a modification<sup>13</sup> of the Tessier five-stage procedure.

The behavior of metals and their availability in the environment is a consequence of their chemical speciation<sup>13</sup>. It is therefore indispensable to make available data on the probable availability of elemental species in the environment<sup>14</sup>.

In river system, sediments serve as heavy metals repository, however alterations in ecosystem circumstances such as tidal currents, wind energies and turbulent dynamics, water pH, redox potential, seasonal flooding and storms may cause periodic remobilization of contaminated surface and bottom sediments, thereby making bottom sediments a potential source by releasing heavy metals into the overlying water column<sup>15,16</sup>.

Horsfall and Spiff<sup>17</sup> reported high concentration risk of metals in Diobu River as the metals were in potentially available forms.

Imo River is constantly impacted with enormous urban runoffs, aerial depositions and intensive sand mining. These activities

may lead to accumulation, re-suspension and bioavailability of toxic materials over a period of time. The significance of this research is that, there is no relevant literature on heavy metal speciation studies of the Imo River system in Southeastern Nigeria and therefore becomes indispensable to institute a study that will provide the data bank for heavy metals in the sediment for evaluating the eco-toxicological potential of the river system.

This research is therefore to investigate the elemental speciation of some metals in sediments from the upper reaches of Imo River system in Southeastern Nigeria using Tessier's<sup>12</sup> five-step sequential extraction schemes.

## Material and Methods

**Study Area.** Imo River (figure 1) with a length of 241 km is located in southeastern Nigeria. The source of the river is Abaigbo in Imo State and runs through Abia, Rivers, Akwa Ibom and flows through Opobo and finally empties into the Atlantic Ocean. Imo River estuary is around 40km wide, with an annual discharge of 4 km<sup>2</sup> within 26,000 hectares of wetland. The Imo River tributaries are the Rivers Otamiri and Oramirukwa. This place is situated in Ukwa-East, Abia, Nigeria; its geographical coordinates are 4° 53' 7" North and 7° 10' 25" East. The Imo River features two bridges at the crossing between Rivers State and Abia State (480 meters) and Akwa Ibom and Abia State (830 meter). The river serves as a source of water for domestic uses, fishery, recreational activities, sand mining and agricultural irrigation programs for more than five million people settled along the River.

**Reagents and Chemicals:** The reagents and chemicals used are of analytical grade. The reagents used are 65 % nitric acid, 30 % hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> and 70 % perchloric acid (BDH, Poole, UK). Working standards of the six metals were obtained by diluting 1000 mg dm<sup>-3</sup> stock solution with 0.25 mol dm<sup>-3</sup> HNO<sub>3</sub>. All plastic and glassware were acid-washed and thoroughly rinsed with deionised water.

**Sample Collection and Preparation:** Sediment sampling was carried out in January and March for Dry season and July and September for wet season in 2011 from five (5) points along the river using a stainless Eckman grab and placed in a pre-cleaned polythene bag. A 2mm mesh size sieve was used to sieve sediment samples after air drying.

**Sequential Extraction of Heavy Metals:** The five-stage sequential extraction scheme reported by Tessier and co-workers<sup>12</sup> was used. A 5.0 g of dried, homogenized and finely divided sediments samples were extracted sequentially as follows:

**Step 1:** To 5 ± 0.0001 g duplicate portion of finely divided sediment sample in a 50 ml extraction flask, 40 ml 1.0 M MgCl<sub>2</sub> solution at a pH of 7.0 was added. The mixture was extracted for five hours using a Stuart Flask Shaker at room temperature. At the end of the five hours, the mixture was filtered using 450 mm filter paper. The concentrations of cadmium, copper, zinc, nickel, lead and iron were immediately analyzed using Perkin Elmer Analyst 400 Atomic Absorption Spectrophotometer. This fraction represents metals bound to adsorptive and exchangeable fractions.

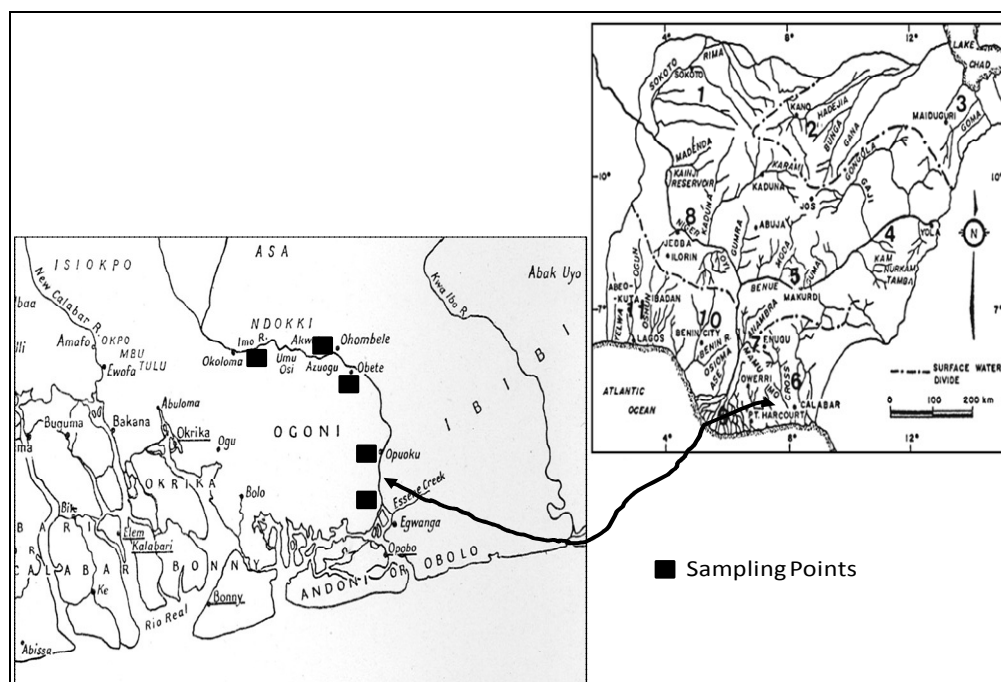


Figure-1  
Imo River showing the sampling stations

**Step 2:** To the separated solid phase from step 1, 40 ml 1.0 M sodium acetate was carefully added. The mixture was extracted, centrifuged, decanted, filtered and analyzed as in step 1. This fraction represents metals bound to reducible fractions.

**Step 3:** To the separated solid phase from step 2, 40ml 0.5 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  was added. The mixture was extracted (for six hours), centrifuged (25 min), decanted, filtered, and analyzed as in step 1. This fraction represents metals bound to oxidizable fractions.

**Step 4:** To the separated solid phase from step 3, 15 ml 0.02 M  $\text{HNO}_3$  and 25 ml 30%  $\text{H}_2\text{O}_2$  were added and heated for two hours at  $85^\circ\text{C}$ , followed by addition of 15ml 30%  $\text{H}_2\text{O}_2$  and few drops of conc.  $\text{HNO}_3$  and further heated at  $85^\circ\text{C}$  for several hours. After cooling, 25 ml 3.2 M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  was added to the mixture and shaken for 30 min at room temperature. The mixture was extracted (for six hours), centrifuged (25 min), decanted, filtered, and analyzed as in step 1. This fraction gave the metals bound to organic matter.

**Step 5:** To the separated solid phase from step 4, 100 ml 40% HF and 150 ml 60% HClO were added. The mixture was digested, followed by addition of 2 ml 60% HClO and further evaporated until white fumes emerged. 6 ml distilled water and 15 ml aqua regia were added to the residue and further digested for 8 min, thereafter, the residue was dissolved in 100 ml 3.0M HCl. The concentrations of cadmium, copper, zinc, nickel, lead and iron were analyzed as in step 1. This fraction represents the residual metals which are of detrital and lattice origin.

**Analytical Precision and Quality Control:** Care was taken during every sample collection and preservation. Glassware was properly cleaned and reagents were of analytical grade. Purity of analytical reagents and standard solutions were well tested prior to analysis. Reagent blanks and working standards/solutions were prepared by using freshly prepared double distilled water. The reliability of experimental results was obtained by replicate analysis of sediment samples. For metal analysis E-mark (AR grade, Germany) standard solutions ( $1000 \text{ mg mL}^{-1}$ ) were used for calibration and standardization of instrument. Intermediate solutions were prepared carefully by diluting stock standard solution ( $1000 \text{ mg mL}^{-1}$ ) with freshly prepared distilled water by using micropipette.

Each analytical process/batch was consisting of a method blank and standard solutions were analyzed after every 10 sample to check instrument performance. The  $R^2$  values were 0.9997, 0.9994, 0.9996, 0.9992, 0.9998, and 0.9997 for cadmium, copper, zinc, nickel, lead and iron respectively.

**Determination of Metal Concentrations in the Sample:** The concentrations of metal ions in the samples were determined by digestion. 2 g of sample in a glass container was added 10 ml conc.  $\text{HNO}_3$  covered with watch glass and left overnight. In the following day, the sample was heated to  $125^\circ\text{C}$  until clear liquor

is obtained. This was followed by the addition of  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{O}_2$  and HCl and heated to  $135^\circ\text{C}$  for one hour until the liquor becomes colourless. During the process, more  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  were added to ensure complete destruction of organic materials. The digest was cooled and dissolved in 5 ml 1.0 M  $\text{HNO}_3$  and diluted to 25 ml.

**Analysis and Quality Control:** The digested samples were sent to the Technical Quality Control Laboratory of Notore Chemical Industries Limited, Onne, Rivers State and analyzed in triplicate for metals using AANALYST 400 Perkin-Elmer AAS.

## Results and Discussion

The instrument was recalibrated after every set of sample has been run. For spike recovery, standard metal solutions were introduced into the sample already analyzed. The mixture was re-analyzed and metal recoveries obtained were 97.8% for Cd; 102.3% for Cu, 95.7% for Zn, 104.1% for Ni, 97.1% for Pb, and 99.2% for Fe. Blanks were used to correct all instrument reading before statistical calculation. Pearson correlation was employed to establish a relationship of heavy metal significance in sediment samples between dry and wet seasons, with values greater than 0.755 ( $n = 5$ ,  $\alpha = 0.05$ ) as being statistically significant. All results were expressed on the basis of dry sample weight.

**Total Trace metals in sediment:** Seasonal variations of the total metal concentrations in sediment samples from the upper reaches of Imo River System in Southeastern Nigeria obtained by direct dissolution of the sediment samples using aqua regia is presented in table-1.

The data shows that, concentration (mg/kg) of cadmium in sediments ranged from 0.19 - 0.42 with mean value of  $0.30 \pm 0.09$  during the dry season while it ranged from 0.22 - 0.35 ( $0.29 \pm 0.05$ ) in wet season. A comparative analysis between cadmium levels in Imo River and other rivers in the same region as reported in table-2<sup>18-21</sup> shows that, values of cadmium in this study were low. The result agreed with concentration of cadmium in natural environment<sup>21</sup>.

Concentration (in range, mean  $\pm$  standard deviation, mg/kg) for copper was 0.73 - 3.51 ( $2.28 \pm 1.20$ ) in dry season and 1.53 - 3.16 ( $2.06 \pm 0.74$ ). The result for copper levels in sediment of Imo River is similar to that of Ipo Stream as obtained by Kpee and co-workers<sup>18</sup> and were also low, when compared to levels in natural environment<sup>21</sup>.

Zinc levels in Imo River sediment samples were 4.66 - 27.33 ( $12.35 \pm 8.97$ ) mg/kg in dry season and 21.00 - 32.93 ( $24.57 \pm 5.78$ ) mg/kg for wet season. The result obtained in this study for zinc concentrations agreed with those reported by Horsfall and Spiff<sup>17</sup> from Diobu River in Port Harcourt, which are of the same geographical region with similar sources of contaminant input.

The concentration of nickel ranged between 1.09 – 2.82 1.09 mg/kg with an average of  $1.79 \pm 0.74$  mg/kg during the dry season while it ranged from 3.16 – 7.25 mg/kg in wet season with an average of  $5.79 \pm 1.67$  mg/kg. The values agreed with those of Ekeanyanwu and co-workers<sup>19</sup> from Okumeshi River. The levels were also lower when compared with levels in natural environment<sup>21</sup>.

The concentration of Pb ranged from 0.70 – 4.95 mg/kg with a mean ( $3.52 \pm 1.68$ ) mg/kg during the dry season while it ranged from .62 –12.52 mg/kg in wet season with a mean of  $6.26 \pm 3.73$  mg/kg. The values agreed with those of Obasohan and co-workers<sup>22</sup> from Ikpobar River.

The values (mg/kg) for iron (range, mean  $\pm$  std) in dry and wet seasons were (1558.38 - 2286.75,  $2025.72 \pm 304.43$ ) and

(2056.3 -3059.97,  $2534 \pm 476.98$ ) respectively. The levels of iron were lower when compared to levels in natural environment<sup>21</sup>.

In order to locate the internal composition not obtainable at a primary glimpse of the data in table-1, Pearson correlation matrix (PCM) was built (table-3) between the total metal concentrations of the dry and wet seasons. The PCM analysis provided a means of statistically ascertaining the association/correlation of one parameter with another. PCM analysis reveals a positive correlation between the metal ions in both seasons; this could indicate a common source for all the metals, however, very few of the metals are significantly correlated with each other. This behavior could indicate a non-point source.

**Table-1**  
Seasonal variations of total mean metal concentrations (mg/kg) in sediment of Imo River

Trace Metals	Dry season		Wet season	
	Range	Mean $\pm$ std	Range	Mean $\pm$ std
<b>Cd</b>	0.19- 0.42	$0.30 \pm 0.09$	0.22 – 0.35	$0.29 \pm 0.05$
<b>Cu</b>	0.73 – 3.31	$2.28 \pm 1.20$	1.53 – 3.16	$2.06 \pm 0.74$
<b>Zn</b>	4.66 –25.53	$12.35 \pm 8.97$	21.00 – 32.93	$24.57 \pm 5.78$
<b>Ni</b>	1.09 – 2.82	$1.79 \pm 0.74$	3.16 – 7.25	$5.79 \pm 1.67$
<b>Pb</b>	0.70 – 4.95	$3.52 \pm 1.68$	2.62 –12.52	$6.26 \pm 3.73$
<b>Fe</b>	1558.38 – 2286.75	$2025.72 \pm 304.43$	2056.3 -3059.97	$2534 \pm 476.98$

**Table-2**  
Comparison of mean metal concentrations (mg/kg) in sediments of Imo River and other rivers

	<b>Cd</b>	<b>Cu</b>	<b>Zn</b>	<b>Ni</b>	<b>Pb</b>	<b>Fe</b>	<b>Reference</b>
<b>Imo River (DS)</b>	$0.30 \pm 0.1$	$2.28 \pm 1.20$	$12.35 \pm 9.0$	$1.79 \pm 0.7$	$3.52 \pm 1.7$	$2025.72 \pm 304.4$	This Study
<b>Imo River (WS)</b>	$0.29 \pm 0.1$	$2.06 \pm 0.7$	$24.57 \pm 5.8$	$5.79 \pm 1.7$	$6.26 \pm 3.7$	$2534 \pm 476.9$	This Study
<b>IPO stream (W/DS)</b>	1.35	2.91	-	18.48	25.73		Ref 18
<b>Okumeshi River</b>	1.32	-	-	1.21	0.45	-	Ref 19
<b>Lagos Lagoon</b>	$1.15 \pm 0.09$	$0.60 \pm 0.27$	$0.73 \pm 0.34$	$0.87 \pm 0.08$	$0.45 \pm 0.60$	$19.39 \pm 6.65$	Ref. 20
<b>Ikpoba River</b>	-	10.35	7.41	0.57	6.67	-	Ref. 21

WS = wet season, DS = dry season, W/DS = wet/dry season

**Table-3**  
Pearson correlation matrix (PCM) between total heavy metal concentrations of Imo River Sediment samples in dry and seasons

	Dry Season						Wet Season						
	<b>Cd</b>	<b>Cu</b>	<b>Zn</b>	<b>Ni</b>	<b>Pb</b>	<b>Fe</b>	<b>Cd</b>	<b>Cu</b>	<b>Zn</b>	<b>Ni</b>	<b>Pb</b>	<b>Fe</b>	
<b>Cd</b>	1.00						<b>Cd</b>	1.00					
<b>Cu</b>	0.65	1.00					<b>Cu</b>	0.45	1.00				
<b>Zn</b>	0.01	0.55	1.00				<b>Zn</b>	0.11	0.37	1.00			
<b>Ni</b>	0.92	0.34	0.16	1.00			<b>Ni</b>	0.90	0.32	0.34	1.00		
<b>Pb</b>	0.65	0.68	0.22	0.38	1.00		<b>Pb</b>	0.02	0.31	0.89	0.12	1.00	
<b>Fe</b>	0.24	0.64	0.13	0.13	0.75	1.00	<b>Fe</b>	0.50	0.24	0.16	0.60	0.56	1.00

Speciation is the determination of the species or the physico-chemical types of an element that comprises its total concentrations in a sample. The chemical species for the six metals investigated in sediment samples of the upper reaches of Imo River system in Southeastern Nigeria was investigated in both dry and wet seasons and results are presented in figures 2-7 as percent fraction of metal species in the five geochemical phases.

Speciation patterns for cadmium in dry and wet seasons are shown in figure-2. The results indicate an occurrence of the highest cadmium percentage in exchangeable and Fe-Mn oxide fractions in both dry and wet seasons. The least percent of cadmium appeared in the organic and carbonates fractions. This is an indication that cadmium was biologically available in the river being investigated. Speciation pattern of copper in both seasons is presented in figure-3. The figure shows that copper had highest accumulation in residual fraction in both dry and wet seasons. It was however low in all the other easily mobilized fractions. This shows that there is little or no danger of copper bioavailability in the study area.

The accumulation of zinc did not follow any regular pattern as shown in figure-4. The highest accumulation was obtained in the carbonate fraction in both seasons, which could make zinc to be available in the water layer when the pH of the sediment changes. In figure-5, lead accumulated most in the residual fraction in both seasons followed by the other fractions. This means that lead will not be released easily to the water layers and so will be less bio-available to the organisms in the study area.

The speciation pattern of nickel in the sediment is presented in figure 6. Ni accumulated most in the carbonate fraction followed by organic, residual and exchangeable fractions. It had least accumulation in the Fe-Mn oxides fractions.

Figure-7 shows the speciation pattern of Fe. The lowest value of iron in the fractions was obtained in exchangeable fraction. The other geochemical fractions that contain low percent of iron are carbonate, organic and Fe-Mn oxide respectively. The highest value was obtained in the residual fraction in both seasons. This shows that iron is cannot be remobilized in the study area.

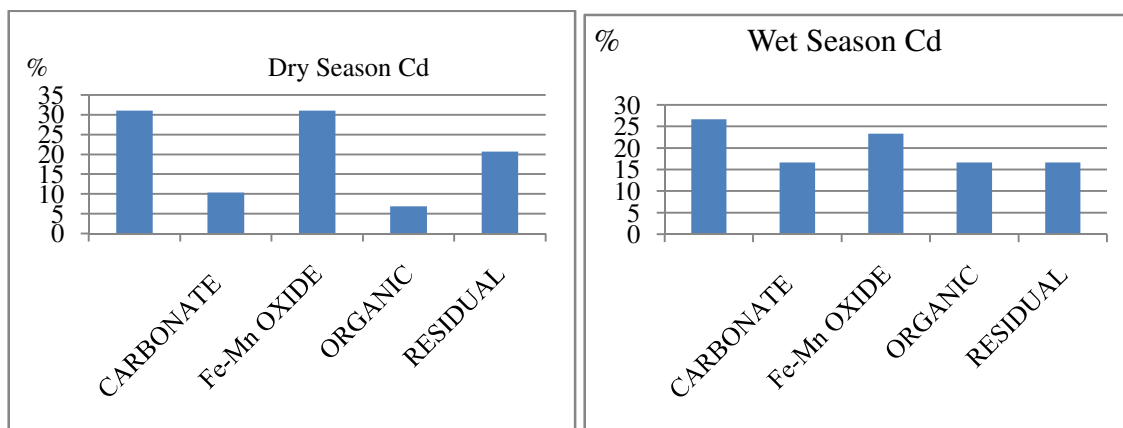


Figure-2  
 Dry and wet seasons speciation pattern of cadmium

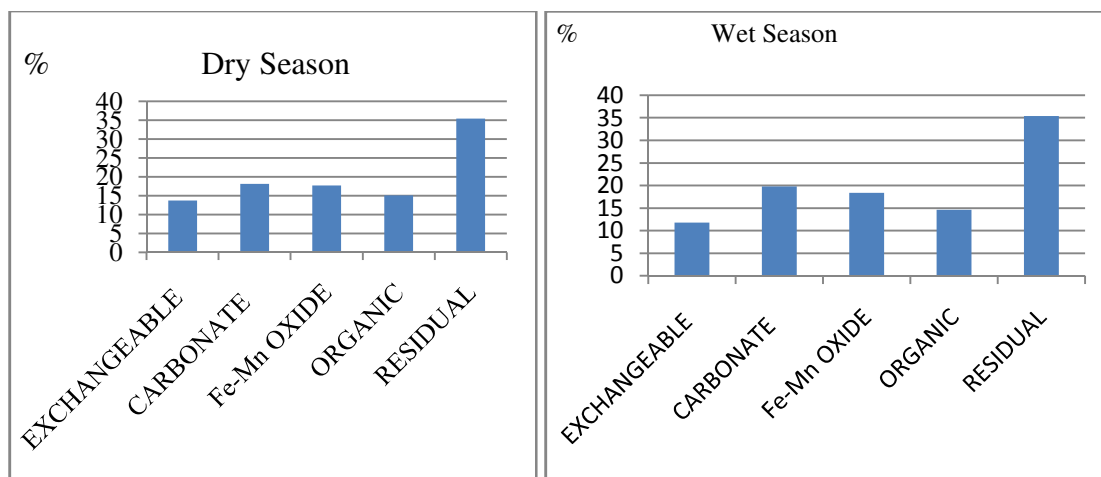
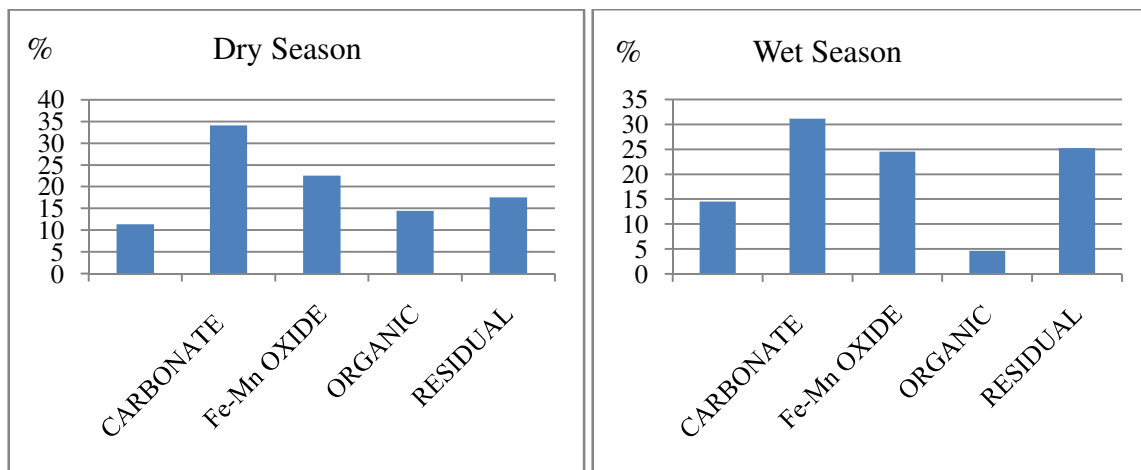
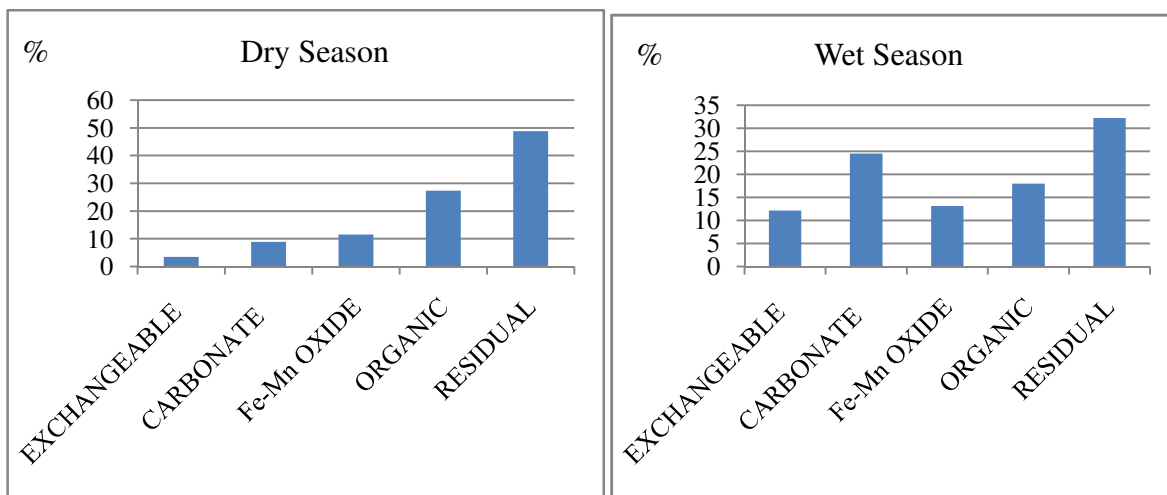


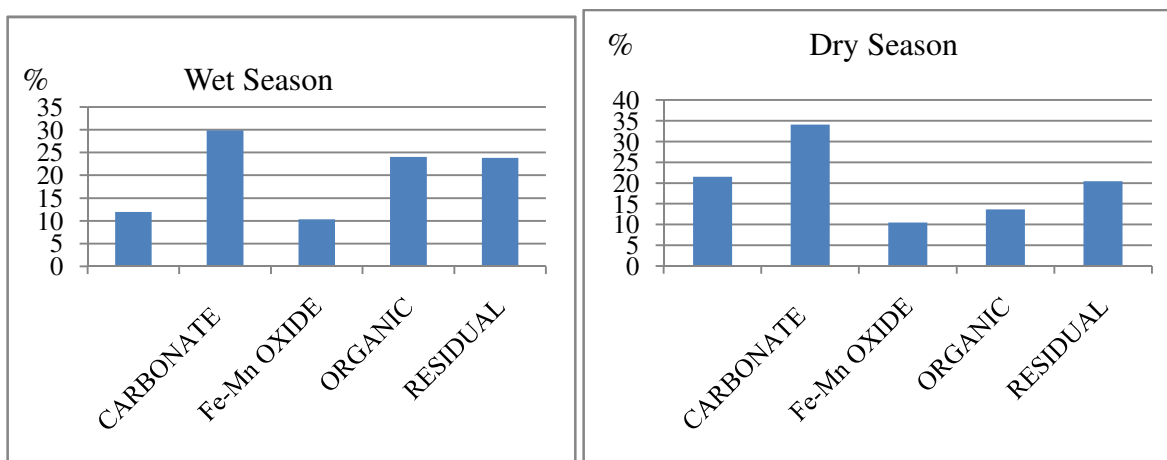
Figure-3  
 Dry and wet seasons speciation pattern of copper



**Figure-4**  
 Dry and wet seasons speciation pattern of zinc



**Figure-5**  
 Dry and wet seasons speciation pattern of lead



**Figure-6**  
 Dry and wet seasons speciation pattern of nickel

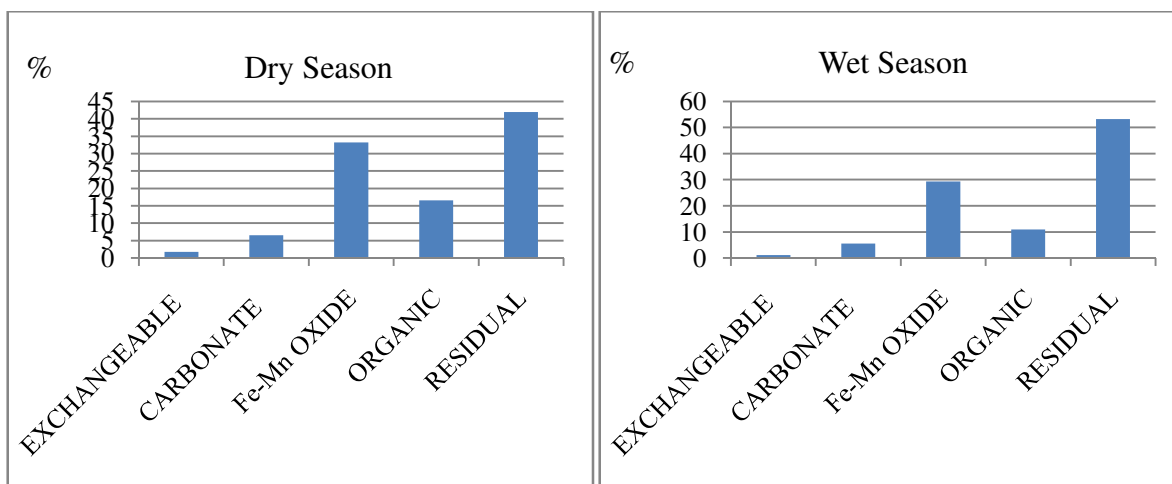


Figure-7

Dry and wet seasons speciation pattern of iron

**Mobility Factor of Metals:** The fate of metal ions in sediment of the overlying water column is dependent on its mobility factor. Mobility factors (MF) of metals provide an indication of the bio-availability or non-bioavailability of the metal. This may be assessed as a ratio of the concentrations of metal in easily remobilizable fractions to the combine concentrations in all the geochemical fractions. In a five-stage sequential extraction scheme, Salbu and co-workers<sup>23</sup> employed fraction 1 (F1) and fraction 2 (F2) to represent the easily remobilizables fractions. Based on their proposal, the mobility factor of metals may be obtained using equation-1.

$$MF = \frac{F1+F2}{F1+F2+F3+F4+F5} \times 100 \quad (1)$$

Where, F1 = adsorptive and exchangeable fraction; F2 = carbonate fraction; F3 = Fe-Mn oxide fraction; F4 = organic fraction and F5 = residual fraction.

Mobility factors (MF) of the metal ions in the Imo River system during dry and wet seasons are presented in table-4. According to the works of Narwal and co-workers<sup>24</sup> and Kabala and Singh<sup>25</sup> a high mobility factor (MF) value for metal in sediment is an indication of relatively high mobility and biological availability tendencies.

Table-4

Mobility factors of trace metals for dry and wet seasons in the sediment samples

Dry Season		Wet Season	
	MF		MF
Ni	55.50	Cd	43.33
Zn	44.04	Ni	41.80
Cd	41.38	Zn	38.38
Cu	31.86	Pb	36.68
Pb	12.03	Cu	31.60
Fe	8.31	Fe	6.54

## Conclusion

In the dry season, Ni had the highest mobility factor and was the most bio-available metal followed by zinc, cadmium and copper. Iron had the least followed by lead. In the wet season, cadmium had the highest mobility factor and was the most bio-available metal followed by nickel, zinc, lead, copper and finally iron. Of all the metals studied, the mobility factor of lead increased sharply from the level in the dry season to a high level in the wet season. This calls for concern considering that lead a highly toxic metal.

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