

# Speciation and Mobility of Selected Heavy Metals in Sediments of the Nun River System, Bayelsa State, Nigeria

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## Abstract

The speciated fractions of some selected environmentally toxic heavy metals (Pb, Cu, Cr, Cd, Zn, Fe and Ni) were assessed in the bottom sediments of the Nun river system. The concentrations (mg/kg) of the selected heavy metals per fraction were analysed using the GBC AVANTA PM A6600 FAAS. Chemical speciation study applying the five-stage sequential extraction scheme revealed the prevalent fractions where the selected heavy metals were bound: Pb, Cu, Cr, Cd, Zn and Fe were prevalent in the residual fractions while Ni was mainly bound to the Fe-Mn oxide fraction. The mobility factor indices of the metals depicted the following trends: Pb>Cr>Zn>Cd>Ni>Cu>Fe and Pb>Cr>Cd>Ni>Zn>Fe>Cu for the samples and control points respectively. Mobility factor indices showed highest lability for Pb and Cr across the sample and control points, while the least lability and mobility was observed for Fe and Cu across all sampling points of the river. The sediments of the Nun river system revealed a high mobility and bioavailability for Pb and Cr. The two-way ANOVA statistical analysis of data showed significant variation ( $P<0.05$ ) between metal fractions and the spatial distribution of sediment samples across the river system except for Pb which revealed the highest mobility and tendency for bioavailability.

**Keywords:** Heavy metals; Speciation; Mobility factor; Lability; River Nun

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## Introduction

Elemental speciation is a key to identifying and quantifying metal species with respect to their affinity, mobility, bioavailability and environmental toxicity in the ecosystem. The standard analytical test protocol of one sequence extraction which is currently practicable for heavy metals quantification, and also forms the basis of our environmental guidelines and standard limitations for metals in the ecosystem, rather considers trace/heavy metals as bulk constituents of a sediment matrix rather than fractional isolates of individual metal species that depict the associated ecological risk of heavy metals.

Pollution of the ecosystem is affecting environmental sustainability [1-6]. Sediments contaminated with metals may act as a secondary pollution source for aquatic ecosystem, and study of metal concentration in sediment is useful for the estimation of pollution trends [7]. In a country like Nigeria, where the emission

and disposal of all sorts of wastes into the environment is not monitored, the contribution of heavy metals pollutants to the environment by anthropogenic sources is overwhelming, hence, repeated evaluation of the pollution status of the environment especially the soil is imperative [8].

Heavy metals are associated with various soil components in different ways and these associations determine their mobility and availability [9]. In a river system, sediments serve as heavy metals repository, however alterations in ecosystem conditions 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 [10,11].

The use of sequential extractions, although more time consuming, furnishes detailed information about the origin,

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mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals [12].

The aim of the present study is to investigate the different speciated chemical fractions of selected heavy metals (Pb, Cu, Cr, Cd, Zn, Fe and Ni) in the Nun river sediments as well as determine their mobility factor indices.

## Materials and Methods

### Study area

The River Nun is one of the major navigable channels of the Niger Delta which leaves the main course of the Niger River to split into two, forming the Nun and Forcados rivers. The Nun River flows for about 160 km south to the Gulf of Guinea, a wide inlet of the Atlantic Ocean at Akassa. The river course flows through thinly settled areas and swamps [13]. The main course of the river lies between the coordinates of latitude 5.298847°N and longitude 6.414350°E. The river was most extensively used for trade in the 19<sup>th</sup> century before the silting in the bar at the mouth of the river impeded access. The discovery of petroleum along the Nun River in 1963 and subsequent completion of the Trans-Niger pipeline in 1965 has increased the economic importance of the river. Over the years, substantial oil and gas exploration activities as well as other anthropogenic input along the course of the river may have substantially influenced the environment. The Nun flows through sparsely settled zones of fresh water, mangrove swamps and coastal sand ridges. The river system is characterized by large wetlands, a network of underwater oil pipelines which are sometimes prone to being vandalized, leaving surrounding mudflats and grassy lakes intermittently covered by oil sheen depending on the water tide. The predominant occupation of the inhabitants is majorly fishing and farming, the study area and sample locations are as shown in (Figure 1).

### Field sampling

Sediment samples were collected in a manner that reflected the oil and gas activities within the river. 12 sample and 2 control points were established in a random manner along the river course. An Eckman grab was deployed to collect bottom sediments and each sampling point was geo-referenced with a hand-held Garmin Etrex model GPS. Duplicate samples were collected for each sampling point and transferred into pre-cleaned polyethylene bags before being stored in an ice chest.

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

Sediment samples were air-dried at room temperature, homogenized by grinding and sieved through a 2 mm 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 working standard solution of 100 mg/l was prepared from the stock standard solution of each test metal; this was prepared by diluting known volumes of the stock solution in a calibrated volumetric flask using distilled water. 1000 mg/l of an AccuStandard, USA stock solution of each metal was diluted accordingly to prepare a series of intermediate standard

solutions which were used for the calibration of the FAAS. During analysis, method blanks and standard solutions were analysed 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, Cu=324.7 nm, Cr=357.9 nm, Cd=228.8 nm, Zn=213.9 nm, Fe=372.0 nm, Ni=232.0 nm.

### Reagents and chemicals

The reagents and chemicals used are of analytical grade, some of which include: 37% hydrochloric acid (Sigma-Aldrich, Germany), 65% nitric acid, 30% hydrogen peroxide and 39%-43% hydrofluoric acid (BDH – Poole, UK). All standard solutions were prepared using distilled water; working standards of the seven metals under study were prepared by diluting different known volumes of their stock solutions of 1,000 mgdm<sup>-3</sup>.

### Sequential extraction of heavy metals

The five-stage sequential extraction scheme reported by Rauret et al. was used. 1.0 g of air-dried sediment was sequentially extracted as follows [14]:

**Fraction 1 (Exchangeable metals):** 1 ± 0.0001 g duplicate portion of finely divided sample was weighed into a plastic centrifuge, 8 ml of 1 M MgCl<sub>2</sub>.6H<sub>2</sub>O (pH=7) was added and the sediment solution was extracted at room temperature for 1 hour with continuous agitation before being centrifuged at 2500 rpm for 20 minutes. After centrifugation, the mixture was filtered and the supernatant was stored.

**Fraction 2 (Metals bound to carbonates):** 8 ml of 1 M sodium acetate (pH=5, using acetic acid) was added to the recovered residue from fraction 1 at room temperature and under continuous agitation for 5 hours. Mixture was further centrifuged at 2500 rpm for 20 minutes before storing the supernatant.

**Fraction 3 (Metals bound to Fe-Mn oxide):** To the residue obtained from fraction 2 was added 20 ml of 0.04 M hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) in 25% v/v acetic acid. Solution was heated in a water bath at 96°C for 6 hours. Afterwards, mixture was centrifuged at 2500 rpm for 20 minutes and supernatant stored.

**Fraction 4 (Metals bound to organic matter):** 3 ml of 0.02 M nitric acid (HNO<sub>3</sub>) and 5 ml of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (pH=2, using nitric acid) was added to the residue obtained from fraction 3. Mixture was heated in a water bath at 85°C for 3 hours and cooled, a further 5 ml of 1.2 M ammonium acetate in 20% v/v nitric acid (HNO<sub>3</sub>) was added and diluted to 20 ml with distilled water, mixture was intermittently agitated for 30 minutes prior to a 20 minute centrifugation at 2500 rpm before storing the supernatant.

**Fraction 5 (Residual metals):** Residue from fraction 4 was transferred into Teflon beakers with minimum amount of distilled water before adding 2 ml HCl, 6 ml HNO<sub>3</sub> and 3 ml of 30% H<sub>2</sub>O<sub>2</sub>. Mixture was digested on a hotplate (in a fume cupboard) until almost dry. Further volumes of HNO<sub>3</sub>, HF and 30% H<sub>2</sub>O<sub>2</sub> were added and digested on a hot plate to near-dryness. 20 ml of distilled water was added and digested on a hotplate to about 15 ml volume. The extract was diluted to 25 ml with distilled water

and centrifuged at 2500 rpm for 20 minutes, filtered and the supernatant stored.

#### Mobility factor

The relative index of metal mobility was calculated as a mobility factor (MF) [15,16] by applying the equation:

$$MF = \left\{ \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \times 100 \right\}$$

#### Definition of variables:

F1=Exchangeable metal fraction

F2=Carbonate bound metal fraction

F3=Fe-Mn oxide bound metal fraction

F4=Organic matter bound metal fraction

F5=Residual metal fraction.

#### Statistical analysis of data

SPSS software was used to carry out the biostatistical analysis. The data were expressed as Mean  $\pm$  standard deviation. A two-way analysis of variance was carried out at  $P=0.05$ , and Duncan multiple range test statistics was used to determine the source of the observed variation. Fractionated heavy metals were correlated using Spearman's rho correlation matrix. The heavy metal concentration in each fraction was determined by using a GBC Avanta PM A6600 FAAS.

## Results and Discussion

### Concentration of heavy metals in sediment

The results of the spatial distribution of heavy metals in sediments from the Nun river system (**Table 1**) shows that lead (Pb) concentrations ranged from 3.66 mg/kg-7.18 mg/kg and 5.08 mg/kg-5.28 mg/kg with mean values of  $5.83 \pm 7.02$  mg/kg and  $5.18 \pm 7.38$  mg/kg for the sample and control points respectively. The mean levels of Pb in the Nun River were higher in the mobile fractions of sample points than in the control points (**Figure 2**). The levels of Pb from this study agree with levels reported in previous work [17].

Copper (Cu) levels across the Nun river sediments ranged between 0.25 mg/kg-14.64 mg/kg and 0.64 mg/kg-3.04 mg/kg with mean values of  $2.90 \pm 6.68$  mg/kg and  $1.84 \pm 2.68$  mg/kg for the sample and control points respectively (**Table 2**). The mean levels of Cu signify a higher retention of the element in the mobile fractions of sample points than in the control points (**Figure 3**). The levels of Cu in this study were similar to levels reported in previous works [17,18]. The concentration of chromium (Cr) as shown in **Table 2**, ranged between 7.04 mg/kg-15.38 mg/kg and 7.19 mg/kg-10.31 mg/kg with mean values of  $9.62 \pm 11.81$  mg/kg and  $8.75 \pm 10.61$  mg/kg for the sample and control points respectively. The mean levels of Cr in the mobile fractions of sample points were similar to those in the control points (**Figure 4**); this shows similarities in the Cr contamination across the Nun River irrespective of sampling point. Cr levels obtained in this study were higher than levels earlier reported [19].

The cadmium levels of the Nun river sediments ranged from 0.25 mg/kg-0.91 mg/kg for the sample points and 0.18 mg/kg-0.65 mg/kg for the control points with mean values of  $0.55 \pm 0.91$  mg/kg for the sample points and  $0.41 \pm 0.81$  mg/kg for the control points respectively (**Table 2**). The mean cadmium levels in the mobile fractions of control points exceed that observed in the sediment sample points (**Figure 5**). Cd levels reported in this study were similar to earlier findings [20]. Current study showed higher Cd levels compared with earlier findings by Ideriah et al.

Zinc (Zn) levels across the Nun river sediments ranged between 11.57 mg/kg-33.67 mg/kg and 9.65 mg/kg-15.71 mg/kg with mean values of  $17.56 \pm 16.91$  mg/kg and  $12.68 \pm 10.83$  mg/kg for the sample and control points respectively (**Table 2**). The mean levels of Zn reveals a higher retention of the element in the mobile fractions of sample points than in the control points (**Figure 6**). The levels of Zn obtained in this study were comparable with levels earlier reported in previous work by Osakwe et al., while comparatively higher and lower Zn levels were reported in earlier works by Horsfall et al. and Leizou et al. respectively.

The concentration of iron (Fe) ranged between 441.48 mg/kg-6,674.34 mg/kg and 495.95 mg/kg-503.12 mg/kg with mean values of  $3,393.11 \pm 4,283.22$  mg/kg and  $499.53 \pm 676.12$  mg/kg for the sample and control points respectively (**Table 2**). The mean levels of Fe in the mobile fractions of control points significantly exceeded those found in the sample points (**Figure 7**). This shows comparatively higher Fe contamination levels in the sediments of sample points. Fe levels obtained in this study were found to be slightly higher than those earlier reported by Osakwe et al., while the levels were far higher than levels obtained in earlier works of Leizou et al.

The nickel (Ni) levels of the Nun river sediments ranged from 8.63 mg/kg-88.29 mg/kg for the sample points and 8.96 mg/kg-10.68 mg/kg for the control points with mean values of  $17.78 \pm 43.52$  mg/kg for the sample points and  $9.82 \pm 10.12$  mg/kg for the control points (**Table 2**). The mean levels of Ni in the mobile fractions of control points exceeded that observed in the sediment sample points. Ni levels reported in this study were similar to the levels earlier reported by Horsfall et al. On the other hand, current study showed higher Ni levels when compared to earlier findings by Ideriah et al. and Osakwe et al.

The speciation patterns of the different metals studied in the Nun river sediment sample points are described below:

In general, the results obtained from this study revealed that lead (Pb) was predominant in the residual and exchangeable fractions at mean levels of 50.70% and 43.85% respectively (**Figure 2**). This is consistent with the results of Leizou et al. The high percentage of Pb in the exchangeable fraction depicts its bioavailability in the Nun river system.

The predominant speciation fraction of copper (Cu) in the sediments were the residual and organic matter bound fractions with mean levels of 52.10% and 35.93% respectively (**Figure 3**). This was similar to previous findings of Horsfall et al., Osakwe et al., Leizou et al. and Tamunobereton-ari et al. [21]. The retention of a higher percentage of copper (Cu) in the residual fraction means that copper will not be easily released to the water

**Table 1** Different fractions of heavy metals in the Nun River sediment.

Fractions	Pb, mg/kg	Cu, mg/kg	Cr, mg/kg	Cd, mg/kg	Zn, mg/kg	Fe, mg/kg	Ni, mg/kg
F1	13.14 ± 3.50b	1.03 ± 2.01a	12.47 ± 2.56b	0.50 ± 0.24b	13.97 ± 6.05b	110.78 ± 96.70a	5.92 ± 1.26a
F2	0.39 ± 1.06a	0.12 ± 0.17a	2.43 ± 1.98a	0.06 ± 0.16a	3.79 ± 4.38a	67.73 ± 98.61a	5.11 ± 2.53a
F3	0.41 ± 1.16a	0.70 ± 1.34a	3.63 ± 2.96a	0.02 ± 0.09a	24.88 ± 8.24c	3488.73 ± 1790.76b	30.49 ± 85.63b
F4	0.67 ± 2.14a	4.81 ± 8.79b	0.76 ± 1.50a	0.00 ± 0.00a	13.68 ± 11.77b	3466.94 ± 4654.66b	12.52 ± 21.52ab
F5	14.09 ± 4.68b	7.09 ± 8.97b	28.21 ± 11.60c	2.05 ± 0.91c	27.98 ± 26.54c	7764.53 ± 4474.11c	29.15 ± 4.54b

Data are expressed as mean ± standard deviation (n=28); different letters (a, b, c) along the column indicate significance variation (P<0.05) according to Duncan multiple range test statistics

**Table 2** Spatial distribution of heavy metals in the Nun River sediment.

Locations	Pb, mg/kg	Cu, mg/kg	Cr, mg/kg	Cd, mg/kg	Zn, mg/kg	Fe, mg/kg	Ni, mg/kg
SED 1	6.13 ± 6.70a	14.64 ± 18.55b	7.19 ± 7.13a	0.91 ± 1.26e	26.60 ± 15.33bc	4198.67 ± 3990.69bc	14.97 ± 12.56a
SED 2	7.18 ± 6.61b	2.67 ± 3.12a	7.15 ± 8.49a	0.74 ± 1.17cde	14.64 ± 5.28ab	5027.61 ± 5248.43cd	11.08 ± 11.13a
SED 3	5.09 ± 5.00a	1.97 ± 2.41a	8.47 ± 9.66a	0.34 ± 0.51abc	11.57 ± 4.27a	1933.45 ± 1952.78ab	10.64 ± 8.18a
SED 4	5.08 ± 7.67a	2.22 ± 2.22a	8.38 ± 8.24a	0.25 ± 0.40ab	16.01 ± 9.04ab	3987.24 ± 3575.01bc	9.54 ± 10.84a
SED 5	6.78 ± 7.54b	1.99 ± 3.95a	15.38 ± 18.24c	0.36 ± 0.44abc	18.99 ± 10.77ab	6674.34 ± 6568.25d	11.69 ± 11.43a
SED 6	3.66 ± 5.06a	1.63 ± 1.73a	7.92 ± 7.95a	0.51 ± 0.85abcde	13.25 ± 7.86ab	2280.83 ± 2612.26ab	8.63 ± 11.56a
SED 7	5.55 ± 6.84ab	2.03 ± 2.48a	13.73 ± 18.89bc	0.54 ± 0.73abcde	19.15 ± 13.33ab	5107.06 ± 5575.53cd	10.38 ± 9.71a
SED 8	4.96 ± 6.62ab	1.41 ± 0.51a	11.51 ± 16.36abc	0.46 ± 0.91abcd	13.51 ± 9.66ab	3357.43 ± 5263.14bc	12.11 ± 11.95a
SED 9	6.47 ± 8.58ab	0.25 ± 3.27a	10.99 ± 15.67abc	0.54 ± 0.90abcde	13.13 ± 9.66ab	2487.28 ± 3652.66ab	10.36 ± 12.14a
SED 10	6.27 ± 8.17ab	2.86 ± 2.81a	9.51 ± 10.51ab	0.49 ± 0.88abcd	13.54 ± 7.73ab	2430.80 ± 3515.19ab	9.09 ± 9.36a
SED 11	7.10 ± 9.99ab	1.57 ± 2.10a	7.04 ± 6.67a	0.87 ± 1.58de	33.67 ± 46.05c	441.48 ± 624.68a	16.53 ± 14.22a
SED 12	5.75 ± 7.53b	1.61 ± 1.05a	8.22 ± 7.03a	0.57 ± 0.85abcde	16.62 ± 12.89ab	2791.10 ± 3548.52abc	88.29 ± 132.46b
SED C1	5.08 ± 8.28ab	3.04 ± 3.27a	10.31 ± 13.06abc	0.18 ± 0.23a	15.71 ± 13.63ab	503.12 ± 690.54a	10.68 ± 10.62a
SED C2	5.28 ± 6.82ab	0.64 ± 1.17a	7.19 ± 7.86a	0.65 ± 1.09abcde	9.65 ± 6.39a	495.95 ± 698.70a	8.96 ± 10.69a

Data are expressed as mean ± standard deviation (n=10); different letters (a, b, c, d, e) along the column indicate significance variation (P<0.05) according to Duncan multiple range test statistics

column and shows less bioavailability to the aquatic organisms in the Nun river.

The results obtained from this study revealed that chromium (Cr) was predominant in the residual and exchangeable fractions at mean levels of 58.34% and 26.67% respectively (**Figure 4**). This is consistent with the findings of Ideriah et al. However, the relatively high percentage of chromium (Cr) in the residual fraction may depict its less bioavailability to aquatic organisms in the river.

Cadmium (Cd) showed strong affinity for the residual fraction with a mean level of 79.18% (**Figure 5**). This was a clear indication that cadmium (Cd) will not be easily released to the water column and so will depict less bioavailability to aquatic organisms in the river. This result was consistent with earlier findings of Horsfall et al.

The predominant speciation fraction of zinc (Zn) in the sediment

was the residual and Fe-Mn oxide bound fractions with mean levels of 33.34% and 28.14% respectively (**Figure 6**). This further reflects the previous results of Horsfall et al., Leizou et al. The retention of a higher percentage of zinc (Zn) in the residual and Fe-Mn oxide fraction means that zinc will not be easily released to the water column and shows less bioavailability to the aquatic organisms in the river system.

The results obtained for iron (Fe) revealed its prevalence in the residual and organic matter bound fractions showing mean levels of 52.20% and 23.75% respectively (**Figure 7**). This is consistent with the findings of Osakwe [22] and also Osakwe et al. Leizou et al. However, the relatively higher percentage of iron (Fe) in the residual fraction may depict its less bioavailability to aquatic organisms of the Nun River.

The predominant speciation fraction of nickel (Ni) in the sediments were the Fe-Mn oxide and residual bound fractions

**Table 3** Spearman's rho correlation matrix of the heavy metal parameters studied.

Parameters	Pb	Cu	Cr	Cd	Zn	Fe	Ni
Pb	1.000						
Cu	0.330**	1.000					
Cr	0.786**	0.314**	1.000				
Cd	0.881**	0.427**	0.842**	1.000			
Zn	0.338**	0.401**	0.358**	0.329**	1.000		
Fe	0.216*	0.468**	0.269**	0.281**	0.639**	1.000	
Ni	0.447**	0.507**	0.538**	0.537**	0.625**	0.425**	1.000

\*\* . Correlation is significant at the 0.01 level (2-tailed)

\* . Correlation is significant at the 0.05 level (2-tailed)

N=140

**Table 4** P-value (significance level) for the heavy metals studied.

Parameters	Model	Location	Fractions
Pb, mg/kg	0.000	0.303	0.000
Cu, mg/kg	0.000	0.000	0.000
Cr, mg/kg	0.000	0.005	0.000
Cd, mg/kg	0.000	0.001	0.000
Zn, mg/kg	0.000	0.008	0.000
Fe, mg/kg	0.000	0.000	0.000
Ni, mg/kg	0.000	0.000	0.012

Note: Any metal with value less than 0.05 indicate a significant difference

**Table 5** Mobility factors of heavy metals in sediment.

Mobility Factor (s) (%)	Sample points	Control points
Lead, Pb	48.99	34.83
Copper, Cu	5.91	1.55
Chromium, Cr	31.29	31.91
Cadmium, Cd	20.92	23.88
Zinc, Zn	21.92	14.07
Iron, Fe	1.12	4.21
Nickel, Ni	12.56	20.81

which revealed mean levels of 39.10% and 32.78% respectively (**Figure 8**). This further reflects previous findings of Horsfall et al., Osakwe et al. and Tamunobereton-ari et al. The predominance of inactive forms of nickel (Ni) in the Fe-Mn oxide and residual bound fraction implies that nickel will not be easily released to the water column and shows less bioavailability to the aquatic organisms in the river system.

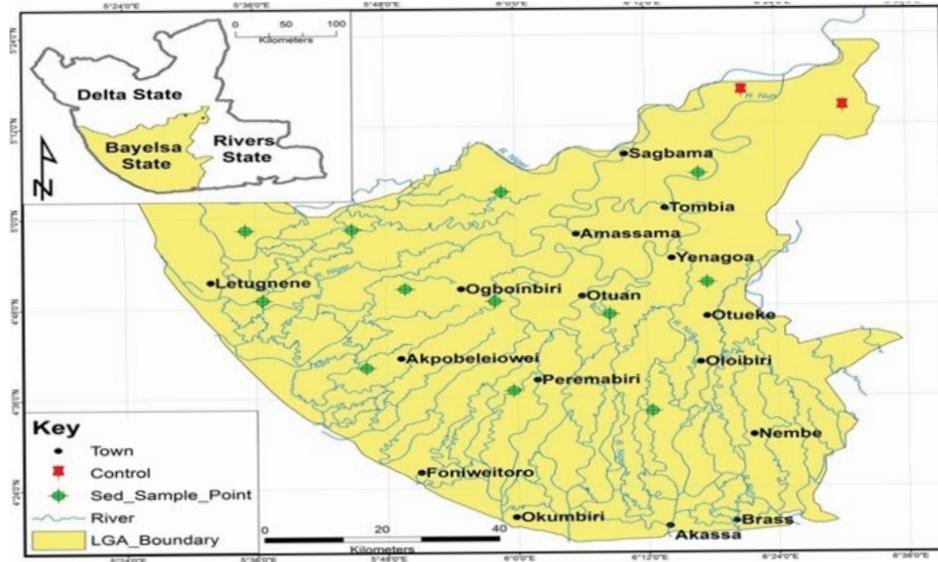
The speciation patterns of the different study metals in the Nun river control points revealed an almost similar trend to that obtained for the sample points. Lead (Pb) was present only in two fractions; the residual and exchangeable fractions at mean levels of 65.25% and 34.75% respectively (**Figure 2**). Copper was predominant in the residual, Fe-Mn oxide and organic matter found fractions at mean levels of 46.30%, 26.20% and 25.87% respectively (**Figure 3**). A similarly strong affinity for the residual and exchangeable fractions was observed with mean levels of 61.49% and 75.96% (residual fractions) with 26.60% and 24.04% (exchangeable fractions) for chromium (Cr) and cadmium (Cd) respectively (**Figures 4 and 5**).

Results further revealed the predominance of inactive forms of zinc (Zn), iron (Fe) and nickel (Ni). Zinc was prevalent in the Fe-Mn oxide and residual fractions at mean levels of 40.97% and 31.90%

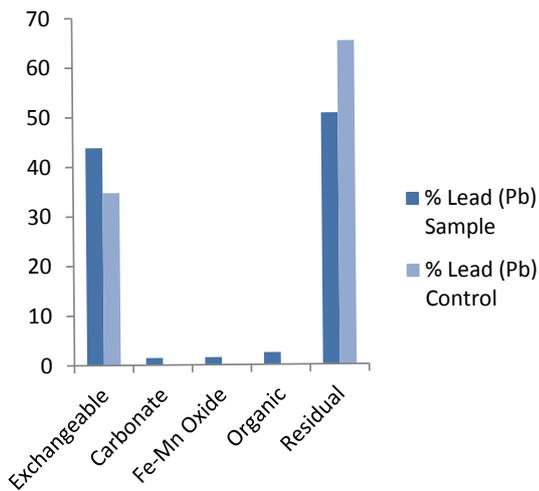
respectively. The residual and Fe-Mn oxide fractions retained the most significant concentration of iron (Fe) with mean levels of 48.58% and 43.67% respectively. Nickel (Ni) was mostly found in the residual phase with a mean level of 59.56% (**Figures 6, 7 and 8**). Therefore, the metals under investigation in the Nun river sediment control points resided in the inactive geochemical fractions and depict less bioavailability to the aquatic organisms.

The heavy metal concentrations based on different fractions and spatial distributions from the Nun river sediments were presented in **Tables 1 and 2** respectively. While the Spearman's rho correlation coefficient (r) matrices for the analysed heavy metals and p-value (significance level) of the statistics carried out were presented in **Tables 3 and 4** respectively. Lead concentration among the different fractions in all samples and control points ranged between 0.39 mg/kg-14.09 mg/kg (**Table 1**), being significantly different ( $P < 0.05$ ) (**Table 4**). Metals in fractions F2, F3 and F4 showed significant variations with those in fraction F1 and F5 ( $P < 0.05$ ). While the spatial distribution ranged from 3.66 mg/kg-7.18 mg/kg (**Table 2**), are not significantly different ( $P < 0.05$ ) (**Table 2**). Lead showed positive significant relationship with copper ( $r = 0.330$ ), chromium ( $r = 0.786$ ), cadmium ( $r = 0.881$ ), zinc ( $r = 0.338$ ) and nickel ( $r = 0.447$ ) at  $P < 0.01$  and iron ( $r = 0.216$ ) at  $P < 0.05$  (**Table 3**).

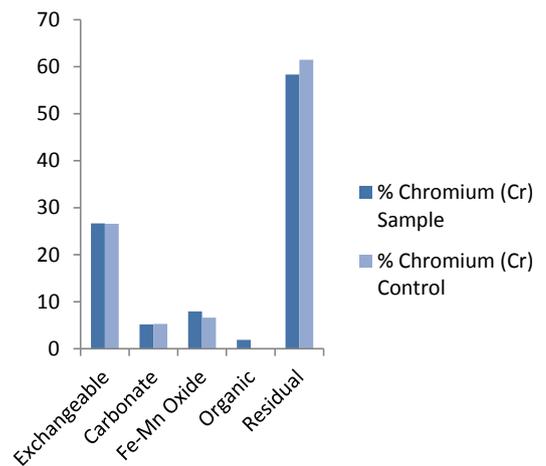
The concentration of copper among the various fractions ranged from 0.12 mg/kg-7.09 mg/kg (**Table 1**). Basically, there was significance difference ( $P < 0.05$ ) among the different fractions (**Table 1**). While the spatial distribution ranged from 0.25 mg/kg-14.64 mg/kg (**Table 2**), being significantly different ( $P < 0.05$ ) (**Table 4**). Metals in fraction F1, F2 and F3 showed significant variations with those in fractions F4 and F5 ( $P < 0.05$ ). Copper showed positive significant relationship with lead ( $r = 0.330$ ), chromium ( $r = 0.314$ ), cadmium ( $r = 0.427$ ), zinc ( $r = 0.401$ ), iron ( $r = 0.468$ ) and nickel ( $r = 0.507$ ) at  $P < 0.01$  (**Table 3**).



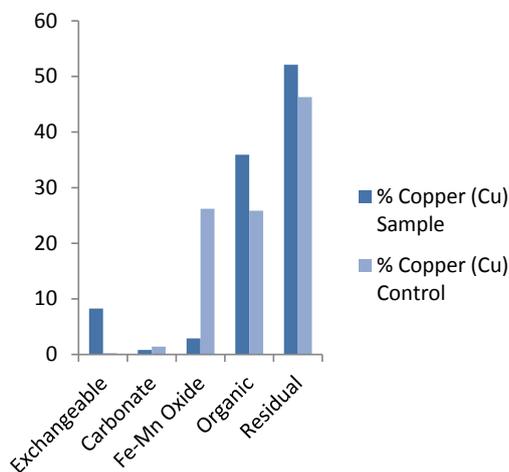
**Figure 1** Map of sediment sampling points on the Nun River.



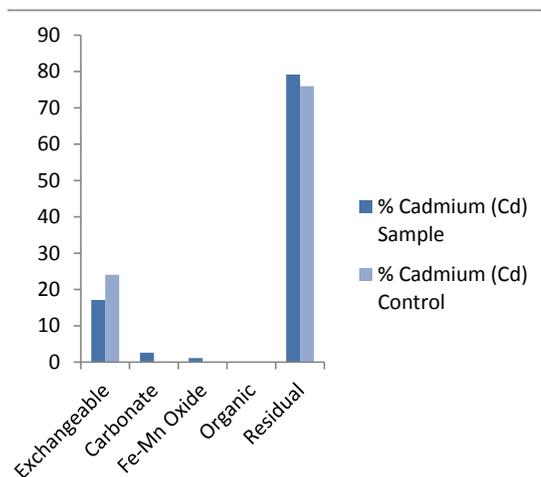
**Figure 2** Speciation pattern of lead.



**Figure 4** Speciation pattern of chromium.



**Figure 3** Speciation pattern of copper.



**Figure 5** Speciation pattern of cadmium.

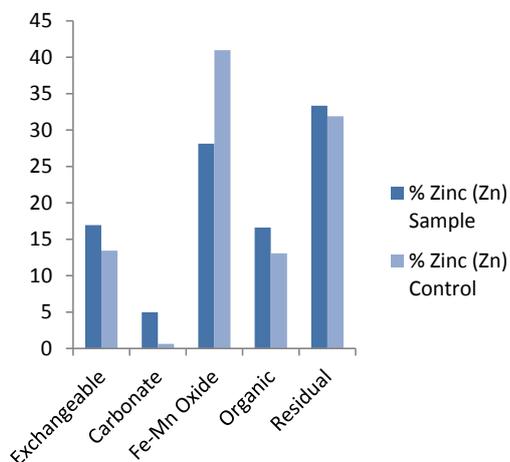


Figure 6 Speciation pattern of zinc.

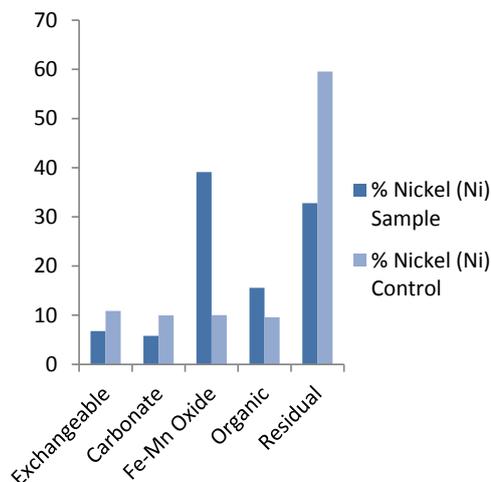


Figure 8 Speciation pattern of nickel.

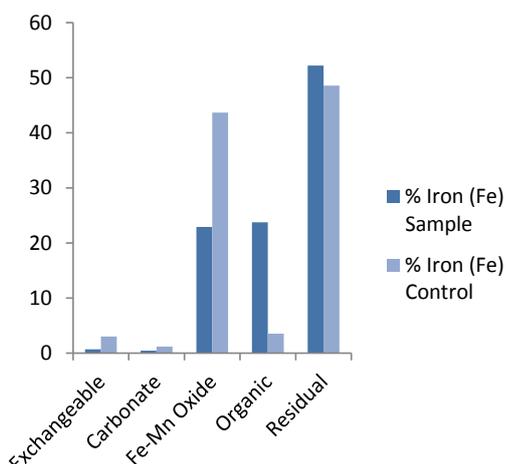


Figure 7 Speciation pattern of iron.

The concentration of chromium among the various fractions ranged from 0.76 mg/kg-28.21 mg/kg (Table 1). Basically, there was significant difference ( $P < 0.05$ ) among the different fractions (Table 4) apart from fractions F2, F3 and F4. While the spatial distribution ranged from 7.04 mg/kg-15.38 mg/kg (Table 2), being significantly different ( $P < 0.05$ ) (Table 4). The source of the variation is from station 10 (Table 2). Chromium showed positive significant relationship with lead ( $r = 0.786$ ), copper ( $r = 0.314$ ), cadmium ( $r = 0.842$ ), zinc ( $r = 0.358$ ), iron ( $r = 0.269$ ) and nickel ( $r = 0.538$ ) at  $P < 0.01$  (Table 3).

The concentration of cadmium among the various fractions ranged from 0.00 mg/kg-2.05 mg/kg (Table 1). Basically, there was significant difference ( $P < 0.05$ ) among the different fractions (Table 1) apart from fractions F2, F3 and F4. While the spatial distribution ranged from 0.18 mg/kg-0.91 mg/kg (Table 2), being significantly different ( $P < 0.05$ ) (Table 4). Cadmium showed positive significant relationship with lead ( $r = 0.881$ ), copper ( $r = 0.427$ ), chromium ( $r = 0.842$ ), zinc ( $r = 0.329$ ), iron ( $r = 0.281$ ) and nickel ( $r = 0.537$ ) at  $P < 0.01$  (Table 3).

The concentration of zinc among the various fractions ranged from 3.79 mg/kg-27.98 mg/kg (Table 1). There was significant difference ( $P < 0.05$ ) (Table 4). While the spatial distribution ranged from 9.65 mg/kg-33.67 mg/kg (Table 2), showing significant variation ( $P < 0.05$ ) (Table 2). Zinc showed positive significant relationship with lead ( $r = 0.338$ ), copper ( $r = 0.401$ ), chromium ( $r = 0.358$ ), cadmium ( $r = 0.329$ ), iron ( $r = 0.639$ ) and nickel ( $r = 0.625$ ) at  $P < 0.01$  (Table 3).

The concentration of iron among the various fractions ranged from 67.73 mg/kg-7,764.53 mg/kg (Table 1). There was significant difference ( $P < 0.05$ ) among the different fractions (Table 1). While the spatial distribution ranged from 441.48 mg/kg-6,674.34 mg/kg (Table 2), showing significant variation ( $P < 0.05$ ) (Table 4). Iron showed positive significant relationship with lead ( $r = 0.216$ ), copper ( $r = 0.468$ ), chromium ( $r = 0.269$ ), cadmium ( $r = 0.281$ ), zinc ( $r = 0.639$ ) and nickel ( $r = 0.425$ ) at  $P < 0.01$  (Table 3).

Similarly, the concentration of nickel among the various fractions ranged from 5.11 mg/kg-30.49 mg/kg (Table 1). There was significant difference ( $P < 0.05$ ) among the different fractions (Table 1). While the spatial distribution ranged from 9.65 mg/kg-33.67 mg/kg (Table 2), showing significant variation ( $P < 0.05$ ) (Table 4). Metals in fraction F1 and F2 showed significant variation with those in fractions F3, F4 and F5 ( $P < 0.05$ ). Nickel showed positive significant relationship with lead ( $r = 0.447$ ), copper ( $r = 0.507$ ), chromium ( $r = 0.538$ ), cadmium ( $r = 0.537$ ), zinc ( $r = 0.625$ ) and iron ( $r = 0.425$ ) at  $P < 0.01$  (Table 3).

The findings of this study suggest that there was no significant variation in the different heavy metal fractions and their spatial distributions apart from lead (Pb). There was also significant variation between all metals in the five fractions. The variation in lead may have resulted from the different levels of oil and gas activities across the Nun River. The significant variations in the different metal fractions may be attributed to the heavy metals different binding affinities that may have been due to the effect of environmental changes.

## Mobility factors of heavy metals in sediment

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 bioavailability or non-bioavailability of the metal as described by Osakwe et al. Heavy metals in sediment are fractionated in the order of decreasing solubility, therefore, the exchangeable and carbonate (F1+F2) fractions which are the free ion species with most solubility reflect the mobile and bioavailable forms [23]. A high MF value of the heavy metals in the sediment has been interpreted as evidence of relatively high lability and biological availability [24].

The mobility factors (MF) for all the sample and control points are presented in **Table 5**.

The mobility factors for the heavy metals studied show the following trend: Pb>Cr>Zn>Cd>Ni>Cu>Fe and Pb>Cr>Cd>Ni>Zn>Fe>Cu for the sample and control points respectively. The relatively high mobility factor of lead (Pb) and chromium (Cr) in the bottom sediments of the Nun river at both the sample and control points reflect the significant concentrations of lead (Pb) and chromium

(Cr) that were found in the exchangeable fraction (Refer to **Tables 1 and 5**). This trend confirms that lead (Pb) and chromium (Cr) possess high lability, bioavailability and may be considered as pollutants of the river system; on the other hand, iron (Fe) and copper (Cu) were observed to be the least mobile and possessing the least bioavailability, hence they posed no risk to the Nun river tributary.

## Conclusion

The single phase extraction scheme most commonly used for the quantitative estimation of heavy metals and as guide for environmental decision making may need to be used side by side with the multi-step and sequential qualitative approach in order to paint a vivid picture of the biogeochemical interactions that take place within an ecosystem with focus on identifying the free, labile and mobile metal ion species that become biologically available in such a way as to pose ecological risk. This study showed that heavy metals such as copper, cadmium, zinc, iron and nickel were significantly affiliated to the inert fractions of the sediment matrix which limited their mobility and reactivity while lead and chromium showed significant concentrations in the more labile and mobile exchangeable fractions of the sediment matrix.

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