



# **Chemical Speciation and Fractionation Study of Heavy Metals in Top Sediment Deposit of Owena River, Nigeria**

**Kolawole Rasheed<sup>1\*</sup>, Akinnawo Solomon<sup>2</sup> and Ademola Aiyesanmi<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Federal University of Technology, P.M.B 704, Akure, Nigeria.*

<sup>2</sup>*Department of Chemical Sciences, Ondo State University of Science and Technology, P.M.B 353, Okitipupa, Nigeria.*

## **Authors' contributions**

*This work was carried out in collaboration among all authors. Authors AA, KR and AS designed the study, wrote the protocol, and wrote the first draft of the manuscript. Authors KR and AS managed the literature searches, analyses of the study performed the spectroscopy analysis. All authors read and approved the final manuscript.*

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## **ABSTRACT**

This study investigates the chemical speciation and fractionation of heavy metals (Cd, Cr, Cu, Ni and Pb) in relation to their levels of pollution from six different locations along the course of Owena River during the dry and wet season of 2015. The top sediment deposit was subjected to sequential extraction and the heavy metals were identified and quantified using atomic absorption spectrophotometer. The concentration of the analyzed heavy metals in the top sediment deposit were found to occur below the maximum permissible limit of the Dutch reference standard for soil/sediment, thereby the sediment collected from Owena river is not contaminated with the analyzed heavy metals. The overall results of this research suggest that the mobility and bioavailability of heavy metals in sediment collected from Owena River decreases in the following order: Cu > Pb > Cr > Cd > Ni.

*Keywords: Chemical speciation; fractionation; heavy metals; sediment; bioavailability.*

\*Corresponding author: E-mail: [seunangel@gmail.com](mailto:seunangel@gmail.com);

## 1. INTRODUCTION

Heavy metals are by definition metals having densities higher than  $5\text{gmL}^{-1}$  or a molecular mass greater than  $5\text{gcm}^{-3}$  which is distinctly higher than the average particle density of soils ( $2.65\text{gcm}^{-3}$ ). Approximately fifty three of the ninety naturally occurring elements are called heavy metals and many of these, such as Cu, Mn, Fe, and Zn, are essential micronutrients, but can become toxic at concentrations higher than the amount required for normal growth. Other heavy metals, such as Cd, Hg, and Pb, have so far unknown roles in living organisms, and are toxic even at very low concentrations [1-4]. Heavy metals occur naturally in all ecosystems, but with large variations in concentration moving between atmosphere, hydrosphere, lithosphere, and biosphere, it is widely accepted that heavy metal contamination in sediment, soil, and groundwater is one of the largest threats to environmental and human health [5-7]. Heavy metals constitute a major threat to humans and the ecosystem due to the fact that they are stable, non biodegradable and persistent environmental contaminants since they cannot be biologically and chemically degraded or destroyed unlike many other organic toxic pollutants [8,9,10,11].

Heavy metals existed in the environment through natural process and human activities. The variation of natural sources such as acidification, erosion and weathering process are common ways of heavy metals brought into the environment [12]. Human activities such as industrial processes, domestic wastes, agricultural activities and emissions from vehicles and factory plants are the main sources of some heavy metals enters and deposited into the environment. These activities continuously accumulated and increased the metal particles in the various environmental systems. All of these anthropogenic sources contribute the negative impact to the surroundings. Sediment plays a major role in determining the pollution pattern of marine ecosystem [11,12]. Aquatic sediments are the ultimate sinks of pollutants in the marine environment and it constitutes an important medium for scientific research. Like soils in the terrestrial environment, aquatic sediments in the aquatic ecosystem are the sources of substrate nutrients and become the basis of support to living aquatic organisms, Heavy metals accumulate in sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix

and the properties of the adsorbed compounds,, Several processes enhance the association of heavy metals with solid phase such as direct adsorption by fine grained inorganic particles of clays, adsorption of hydrous ferric and magnetic oxides which may in turn be associated with clays, adsorption on natural organic substances, which may also be associated with inorganic particles and direct precipitation as new solid phases [13-15]. Heavy metals naturally occurred in all agricultural soils and lake sediments most of them are either essential or beneficial to all living organisms. However they can become toxic, if accumulated in excess amount in the food chains. Its harmful effects could cause dangerous situations sometimes affecting the ecological balance of these ecosystems. Soil pollution by heavy metals is a significant environmental problem worldwide. In particular, heavy metal pollution of surface soils due to intense industrialization and urbanization has become a serious concern in many developing countries [16-18]. Multi-elemental analysis of sediment may reveal the presence of heavy metals which are contaminants and may have toxic influence on ground water and surface water and also on plants, animals and humans [19]. Accumulation of trace metals occur in upper sediment in aquatic environment by biological and geochemical mechanisms may become toxic to sediment dwelling organisms and fish, resulting in death, reduced growth, or impaired reproduction and lower species diversity [20].

The investigation of sediments from the water bodies is of great interest in aquatic systems research, metals tend to become incorporated into the underlying sediments hence sediments are good indicators of metal contamination levels. Sediments reflect the current quality of the system as well as providing information on the impact of pollution sources [21]. The pollution of aquatic environment has become a worldwide problem in recent years, because of its toxic effects on living organisms. Among environmental pollutants, heavy metals are of particular concern, due to their potential toxic effect and ability to bio accumulate in the ecosystem [22]. Heavy metals pollution in the natural environment is a worldwide problem because they are not removed from water as a result of self purification but they can accumulate in reservoirs by biological and geochemical mechanisms and enter the biological chain. In recent decade, many environmental and geochemical researchers have used sediment quality guidelines (SQGs) as useful tool to

assess the sediment chemistry with toxicity testing and biological effects [23].

Heavy metals are present in surface water and agrochemicals in various forms, which can be classified as soluble (compounds or free ions) and particulate (colloidal or adsorbed to suspended solids). Different forms of the metals exhibit different biological toxicities and environmental behaviors. The free (hydrated) ions of many metals cause chronic toxicity in aquatic organisms. Suspended solids are the dominant carriers of heavy metals in surface waters, and are responsible for 60%–97% of the total metal concentrations [24]. Concern over the possible ecological effect of the increasing accumulation of metallic contaminants in the environment is growing. For this reason, the investigation of heavy metals in soil is essential since even slight changes in their concentration above the acceptable levels, whether due to natural or anthropogenic factors, can result in serious environmental and subsequent health problems [25]. Speciation can be defined as identification and quantification of the different species or forms of phases in which elements occur. It is generally recognized that information about the physicochemical forms of the elements is required for understanding their mobility, pathways and bioavailability. Studies on the distribution and speciation of heavy metals in sediments can provide not only information on the degree of pollution, but specially the actual environmental impact, metal bioavailability as well as their origin [26,27]. A report on the Owena dam in 2012 shows that the distribution pattern of heavy metals levels in the water column suggests more of lithological origin with possible contribution from anthropogenic influences through runoff into the water body [28]. Contamination profile of pollutants such as heavy metals has been reported in Owena River, which reveals that the water and sediment is contaminated with cadmium [29]. The aim of this research is to investigate the chemical speciation and environmental pollution risk of selected heavy metals (Cd, Cr, Pb, Ni and Cu) in the sediment from Owena River.

## 2. MATERIALS AND METHODS

### 2.1 The Study Area

The Owena River is located on latitude 6°33'55.3" and longitude 5°8'24.83" of Ondo State, Nigeria. The estimate terrain elevation above sea level is 10 meters. Owen River is a major source of domestic water supply to the

people of Akure and the neighboring towns. The Owen dam, which is a major dam in Ondo State, is constructed as a result of damming the Owena River. Fishing and farming and domestic activities takes place in the vicinity of the Owena River rendering it prone to environmental contamination.

### 2.2 Sampling Treatment and Analysis

The top sediment samples (0-15cm) were collected from 6 different locations along the Owena River channel during the dry and wet season of 2015 using a GPS (Global Position System) to ensure consistency. Sediment samples were collected using hand auger, and stored in a polythene bag prior to analysis. The samples were air dried in the laboratory for two weeks, and later pulverized using laboratory mortar and pestle and sieved with 2mm mesh size sieve. The pH of the sediment was determined using a pH meter, the organic carbon was determined using the wet oxidation method of Walkley and Black [30], while the particle size and texture was determined by the hydrometer method described by Shedrick and Wang [31]. The sediment samples were subjected to a multi-sequential extraction step [32] as stated below;

**Fraction 1 (Exchangeable metal fraction):** The sample was extracted with 8 ml 1 M MgCl<sub>2</sub> at pH 7.0 for 1 h with continuous agitation, at room temperature.

**Fraction 2 (Carbonate bound metal fractions):** The residue from F<sub>1</sub> was leached for 5 h with 8 ml 1 M sodium acetate adjusted to pH 5.0 with acetic acid, at room temperature and with agitation.

**Fraction 3 (Elements associated with Fe-Mn oxide metal fraction):** The residue from F<sub>2</sub> was extracted with 20 ml of 0.04 M hydroxylamine hydrochloride in 25% acetic acid for 5 h in boiling water bath and with periodic agitation.

**Fraction 4 (Organic and sulfide metal fractions):** The residue from F<sub>3</sub> was extracted with 3 ml 0.02M HNO<sub>3</sub> and 8 ml 30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 2.0 with HNO<sub>3</sub> for 5 h at 85°C with occasional agitation and then at room temperature with 5 ml 3.2 M ammonium acetate in 20% HNO<sub>3</sub>.

**Fraction 5 (Inert fraction):** Residue from fraction 4 was oven dried at 105°C. Digestion was carried out with a mixture of 5ml conc. HNO<sub>3</sub> (HNO<sub>3</sub>, 70% w/w), 10ml of hydrofluoric acid (HF,

40% w/w) and 10ml of perchloric acid ( $\text{HClO}_4$ , 60%w/w).

The extract of each fraction was decanted and subjected to elemental analysis using atomic absorption spectrometer (AAS). Blanks were also used for correction of background and other sources of error.

### 2.3 Data Analysis

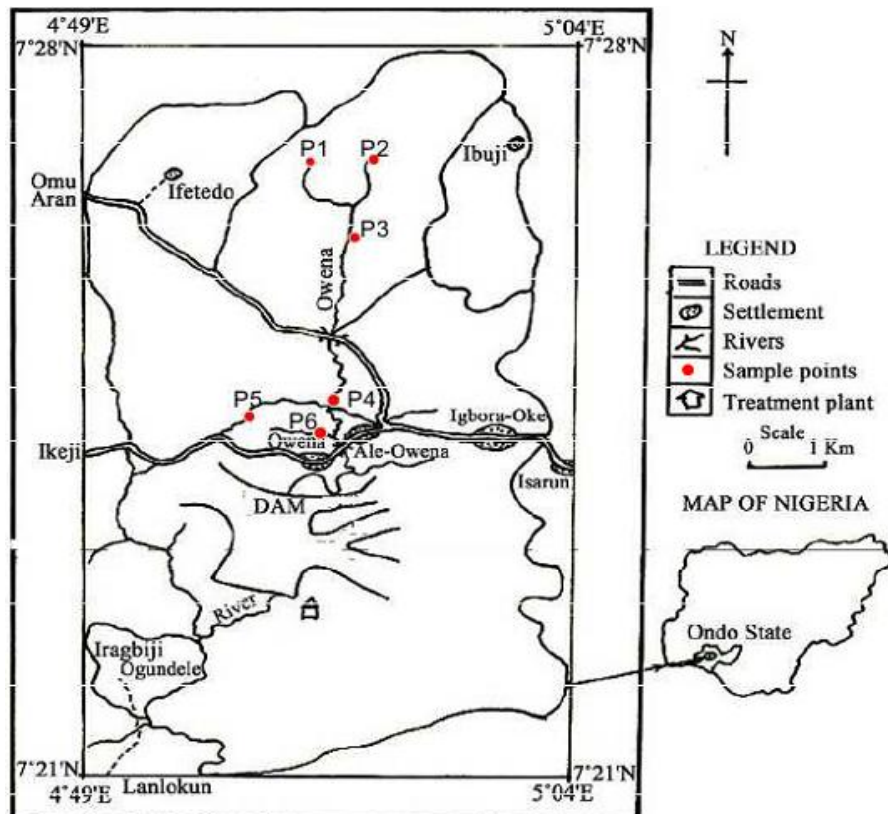
Data generated on concentrations of each metal were analyzed for spatial variation using one way analysis of variance (ANOVA) with SPSS package version 20. One level of significance ( $p < 0.05$ ) was considered in the results interpretation.

### 3. RESULTS AND DISCUSSION

The speciation of heavy metals in the sediment samples was carried by the Tessier sequential extraction method. Table 2-6 shows the results of the speciation and the seasonal variation of

heavy metals in the top sediment deposit of Owena River at six different sampling sites.

The pH of the sediment falls with the range of 5.04-7.23 during the dry and wet season, this present a slight acidic to alkaline condition [33]. The mobility and solubility of trace metals in contaminated soil/sediment are greatly influenced by the effect of pH. An alkaline soil may not favor metal mobility due to high sorption of these metals in them while Acidic condition (low pH) may enhance metal solubility and facilitate the leaching and mobility of trace metals in soil/sediment into water column, thereby render the metals bioavailable in the aquatic environment. The high acidity of soil/sediment has been attributed to possible combination of the oxidation of pyrite ( $\text{FeS}_2$ ) to sulphuric acid, depletion of calcium level or increased in the level of aluminium concentration in the soil/sediment matrix [34].



**Fig. 1. Map of Owena river showing the six sampling sites**

Point 1: Elev (323M) ZIN (0722187) UTM (0818970), Point 2: Elev (323M) ZIN (0722267) UTM (0818909)  
 Point 3: Elev (326M) ZIN (0722220) UTM (0818926), Point 4: Elev (327M) ZIN (0722198) UTM (0818949)  
 Point 5: Elev (327M) ZIN (0722239) UTM (0818898), Point 6: Elev (328M) ZIN (0722274) UTM (0818846)

The total organic carbon and total organic matter in the sediment samples during the dry and wet seasons ranges from 0.22 - 2.77 % and 0.38 – 4.80 % during the dry and wet season, while slit, clay and sand in the sediment during the dry and wet seasons ranges from 0.024 – 5.136 %, 7.590

– 9.256 % and 85.24 – 92.38 % respectively. TOC/TOM and clay in sediments regulates the behavior of other chemical species such as metals, it affects biogeochemical processes, nutrient cycling, biological availability, chemical transport and interactions [35,36].

**Table 1. Physicochemical properties, particle size and texture of sediment**

Point	pH		Slit (%)		Clay (%)		Sand (%)		TOC (%)		TOM (%)	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
1	6.14	6.26	0.136	0.106	8.696	7.884	91.168	92.01	2.25	1.36	3.89	2.34
2	5.84	5.89	5.136	0.904	9.624	8.056	85.24	91.04	2.77	0.90	4.80	1.55
3	6.43	6.35	0.064	0.024	8.696	7.590	91.24	92.38	1.50	1.0	2.58	1.72
4	5.04	6.59	2.920	0.920	8.912	8.050	88.17	91.03	1.00	0.42	1.72	0.72
5	6.72	7.23	2.104	0.608	8.856	9.256	89.04	90.136	0.44	0.22	0.76	0.38
6	5.81	7.13	2.104	0.608	8.856	7.840	92.04	91.55	0.90	0.90	1.55	1.55

**Table 2. Showing the fractionation of Cd (ppm) at different location during the dry and wet seasons**

Location and season	Fractions				
	F1	F2	F3	F4	F5
Point 1 dry	0.030±0.01 <sup>b</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.067±0.00 <sup>g</sup>	0.141±0.00 <sup>g</sup>
Point 1 wet	0.000±0.00 <sup>a</sup>	0.006±0.00 <sup>c</sup>	0.000±0.00	0.044±0.00 <sup>ef</sup>	0.046±0.00 <sup>a</sup>
Point 2 dry	0.030±0.01 <sup>b</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	0.159±0.00 <sup>h</sup>
Point 2 wet	0.000±0.00 <sup>a</sup>	0.010±0.00 <sup>d</sup>	0.000±0.00	0.034±0.00 <sup>c</sup>	0.056±0.00 <sup>b</sup>
Point 3 dry	0.033±0.01 <sup>b</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	0.132±0.00 <sup>e</sup>
Point 3 wet	0.000±0.00 <sup>a</sup>	0.004±0.00 <sup>c</sup>	0.000±0.00	0.046±0.00 <sup>f</sup>	0.073±0.00 <sup>d</sup>
Point 4 dry	0.023±0.00 <sup>b</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	0.144±0.00 <sup>g</sup>
Point 4 wet	0.000±0.00 <sup>a</sup>	0.005±0.00 <sup>c</sup>	0.001±0.00	0.027±0.00 <sup>b</sup>	0.057±0.00 <sup>b</sup>
Point 5 dry	0.000±0.00 <sup>a</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	0.141±0.00 <sup>g</sup>
Point 5 wet	0.000±0.00 <sup>a</sup>	0.002±0.00 <sup>b</sup>	0.000±0.00	0.042±0.00 <sup>e</sup>	0.138±0.00 <sup>e</sup>
Point 6 dry	0.001±0.00 <sup>a</sup>	0.000±0.00 <sup>a</sup>	0.001±0.00	0.000±0.00 <sup>a</sup>	0.159±0.00 <sup>h</sup>
Point 6 wet	0.000±0.00 <sup>a</sup>	0.005±0.00 <sup>c</sup>	0.000±0.00	0.038±0.00 <sup>d</sup>	0.068±0.00 <sup>c</sup>

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different (P<0.05)

**Table 3. Showing the fractionation of Cr (ppm) at different location during the dry and wet seasons**

Location and season	Fractions				
	F1	F2	F3	F4	F5
Point 1 dry	0.006±0.00 <sup>ab</sup>	0.000±0.00 <sup>a</sup>	0.432±0.01 <sup>d</sup>	0.323±0.02 <sup>abc</sup>	2.733±0.02 <sup>e</sup>
Point 1 wet	0.085±0.01 <sup>e</sup>	0.122±0.01 <sup>cd</sup>	0.358±0.01 <sup>b</sup>	0.355±0.02 <sup>bcd</sup>	1.261±0.02 <sup>c</sup>
Point 2 dry	0.013±0.00 <sup>ab</sup>	0.000±0.00 <sup>a</sup>	0.517±0.01 <sup>e</sup>	0.333±0.03 <sup>abc</sup>	1.587±0.02 <sup>d</sup>
Point 2 wet	0.000±0.00 <sup>a</sup>	0.127±0.01 <sup>cd</sup>	0.323±0.00 <sup>a</sup>	0.320±0.01 <sup>abc</sup>	1.140±0.02 <sup>b</sup>
Point 3 dry	0.028±0.00 <sup>cd</sup>	0.073±0.01 <sup>b</sup>	0.433±0.00 <sup>d</sup>	0.361±0.01 <sup>bcd</sup>	1.587±0.01 <sup>d</sup>
Point 3 wet	0.000±0.00 <sup>a</sup>	0.133±0.01 <sup>cd</sup>	0.380±0.00 <sup>bc</sup>	0.337±0.01 <sup>abc</sup>	2.807±0.01 <sup>f</sup>
Point 4 dry	0.017±0.01 <sup>bc</sup>	0.059±0.01 <sup>b</sup>	0.453±0.00 <sup>d</sup>	0.285±0.03 <sup>a</sup>	0.406±0.01 <sup>a</sup>
Point 4 wet	0.000±0.00 <sup>a</sup>	0.151±0.01 <sup>d</sup>	0.355±0.02 <sup>b</sup>	0.406±0.01 <sup>de</sup>	1.607±0.02 <sup>d</sup>
Point 5 dry	0.031±0.00 <sup>d</sup>	0.046±0.01 <sup>b</sup>	0.377±0.01 <sup>bc</sup>	0.404±0.03 <sup>de</sup>	1.636±0.02 <sup>d</sup>
Point 5 wet	0.000±0.00 <sup>a</sup>	0.153±0.01 <sup>d</sup>	0.374±0.01 <sup>bc</sup>	0.435±0.01 <sup>e</sup>	1.587±0.02 <sup>d</sup>
Point 6 dry	0.002±0.00 <sup>a</sup>	0.058±0.01 <sup>b</sup>	0.397±0.01 <sup>c</sup>	0.376±0.01 <sup>cde</sup>	2.733±0.02 <sup>e</sup>
Point 6 wet	0.000±0.00 <sup>a</sup>	0.107±0.01 <sup>c</sup>	0.399±0.01 <sup>c</sup>	0.304±0.02 <sup>ab</sup>	1.611±0.00 <sup>d</sup>

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different (P<0.05)

**Table 4. Showing the fractionation of Cu (ppm) at different location during the dry and wet seasons**

Location and season	Fractions				
	F1	F2	F3	F4	F5
Point 1 dry	0.023±0.00 <sup>ef</sup>	0.031±0.00 <sup>a</sup>	0.051±0.00 <sup>g</sup>	0.033±0.00 <sup>a</sup>	0.492±0.00 <sup>j</sup>
Point 1 wet	0.017±0.00 <sup>a</sup>	0.036±0.00 <sup>bc</sup>	0.035±0.00 <sup>c</sup>	0.102±0.00 <sup>e</sup>	0.165±0.00 <sup>c</sup>
Point 2 dry	0.022±0.00 <sup>cd</sup>	0.034±0.00 <sup>b</sup>	0.039±0.00 <sup>d</sup>	0.034±0.00 <sup>a</sup>	0.177±0.00 <sup>d</sup>
Point 2 wet	0.018±0.00 <sup>ab</sup>	0.036±0.00 <sup>cd</sup>	0.034±0.00 <sup>bc</sup>	0.101±0.00 <sup>e</sup>	0.126±0.00 <sup>a</sup>
Point 3 dry	0.024±0.00 <sup>f</sup>	0.036±0.00 <sup>cd</sup>	0.045±0.00 <sup>f</sup>	0.042±0.00 <sup>b</sup>	0.137±0.00 <sup>b</sup>
Point 3 wet	0.021±0.00 <sup>c</sup>	0.129±0.00 <sup>g</sup>	1.049±0.00 <sup>j</sup>	5.037±0.00 <sup>g</sup>	0.401±0.00 <sup>h</sup>
Point 4 dry	0.027±0.00 <sup>def</sup>	0.036±0.00 <sup>cd</sup>	0.032±0.00 <sup>b</sup>	0.032±0.00 <sup>a</sup>	0.196±0.00 <sup>e</sup>
Point 4 wet	0.021±0.00 <sup>c</sup>	0.044±0.00 <sup>e</sup>	0.081±0.00 <sup>h</sup>	0.093±0.00 <sup>d</sup>	0.224±0.00 <sup>g</sup>
Point 5 dry	0.023±0.00 <sup>ef</sup>	0.031±0.00 <sup>a</sup>	0.041±0.00 <sup>de</sup>	0.045±0.00 <sup>c</sup>	0.137±0.00 <sup>b</sup>
Point 5 wet	0.019±0.00 <sup>b</sup>	0.079±0.00 <sup>f</sup>	0.255±0.00 <sup>i</sup>	0.130±0.00 <sup>f</sup>	0.477±0.00 <sup>i</sup>
Point 6 dry	0.027±0.00 <sup>g</sup>	0.034±0.00 <sup>b</sup>	0.029±0.00 <sup>a</sup>	0.093±0.00 <sup>d</sup>	0.204±0.00 <sup>f</sup>
Point 6 wet	0.023±0.00 <sup>ef</sup>	0.038±0.00 <sup>d</sup>	0.042±0.00 <sup>e</sup>	0.093±0.00 <sup>d</sup>	0.204±0.00 <sup>f</sup>

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different (P<0.05)

**Table 5. Showing the fractionation of Ni (ppm) at different location during the dry and wet seasons**

Location and season	Fractions				
	F1	F2	F3	F4	F5
Point 1 dry	0.035±0.00 <sup>cd</sup>	0.043±0.00 <sup>b</sup>	0.000±0.00	0.008±0.00 <sup>a</sup>	1.421±0.01
Point 1 wet	0.046±0.01 <sup>de</sup>	0.031±0.01 <sup>b</sup>	0.000±0.00	0.022±0.00 <sup>b</sup>	0.622±0.01 <sup>bc</sup>
Point 2 dry	0.050±0.00 <sup>e</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	1.671±0.00 <sup>g</sup>
Point 2 wet	0.033±0.02 <sup>cd</sup>	0.041±0.01 <sup>b</sup>	0.000±0.00	0.031±0.01 <sup>b</sup>	0.490±0.00 <sup>a</sup>
Point 3 dry	0.039±0.00 <sup>cd</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	1.443±0.01 <sup>e</sup>
Point 3 wet	0.004±0.00 <sup>ab</sup>	0.033±0.01 <sup>b</sup>	0.000±0.00	0.028±0.00 <sup>b</sup>	0.701±0.00 <sup>c</sup>
Point 4 dry	0.052±0.00 <sup>e</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	1.334±0.09 <sup>d</sup>
Point 4 wet	0.000±0.00 <sup>a</sup>	0.036±0.01 <sup>b</sup>	0.000±0.00	0.033±0.01 <sup>c</sup>	0.586±0.01 <sup>f</sup>
Point 5 dry	0.027±0.00 <sup>cd</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	1.565±0.01 <sup>f</sup>
Point 5 wet	0.041±0.00 <sup>de</sup>	0.038±0.00 <sup>b</sup>	0.000±0.00	0.034±0.00 <sup>c</sup>	1.370±0.01 <sup>de</sup>
Point 6 dry	0.021±0.00 <sup>bc</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00	0.000±0.00 <sup>a</sup>	1.619±0.00 <sup>fg</sup>
Point 6 wet	0.005±0.00 <sup>ab</sup>	0.039±0.00 <sup>b</sup>	0.000±0.00	0.033±0.00 <sup>c</sup>	0.644±0.01 <sup>bc</sup>

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different (P<0.05)

**Table 6. Showing the fractionation of Pb (ppm) at different location during the dry and wet seasons**

Location and season	Fractions				
	F1	F2	F3	F4	F5
Point 1 dry	0.013±0.00 <sup>c</sup>	0.010±0.00 <sup>a</sup>	0.313±0.00 <sup>bc</sup>	0.263±0.01 <sup>bc</sup>	0.000±0.00 <sup>a</sup>
Point 1 wet	0.000±0.00 <sup>a</sup>	0.000±0.00 <sup>a</sup>	0.353±0.01 <sup>c</sup>	0.000±0.00 <sup>a</sup>	0.247±0.00 <sup>b</sup>
Point 2 dry	0.010±0.00 <sup>b</sup>	0.000±0.00 <sup>a</sup>	0.307±0.00 <sup>bc</sup>	0.273±0.00 <sup>c</sup>	0.000±0.00 <sup>a</sup>
Point 2 wet	0.000±0.00 <sup>a</sup>	0.000±0.00 <sup>a</sup>	0.427±0.01 <sup>d</sup>	0.000±0.00 <sup>a</sup>	0.417±0.00 <sup>d</sup>
Point 3 dry	0.000±0.00 <sup>a</sup>	0.010±0.00 <sup>a</sup>	0.297±0.01 <sup>bc</sup>	0.247±0.00 <sup>b</sup>	0.000±0.00 <sup>a</sup>
Point 3 wet	0.000±0.00 <sup>a</sup>	0.270±0.03 <sup>d</sup>	0.847±0.01 <sup>g</sup>	0.000±0.00 <sup>a</sup>	1.060±0.01 <sup>f</sup>
Point 4 dry	0.000±0.00 <sup>a</sup>	0.057±0.00 <sup>b</sup>	0.273±0.01 <sup>b</sup>	0.297±0.01 <sup>d</sup>	0.000±0.00 <sup>a</sup>
Point 4 wet	0.010±0.00 <sup>b</sup>	0.820±0.01 <sup>e</sup>	1.397±0.00 <sup>h</sup>	0.000±0.00 <sup>a</sup>	0.320±0.01 <sup>c</sup>
Point 5 dry	0.010±0.00 <sup>b</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00 <sup>a</sup>	0.380±0.02 <sup>e</sup>	0.000±0.00 <sup>a</sup>
Point 5 wet	0.000±0.00 <sup>a</sup>	0.190±0.01 <sup>c</sup>	0.667±0.07 <sup>f</sup>	0.000±0.00 <sup>a</sup>	0.000±0.00 <sup>a</sup>
Point 6 dry	0.010±0.00 <sup>b</sup>	0.010±0.00 <sup>a</sup>	0.000±0.00 <sup>a</sup>	0.373±0.00 <sup>e</sup>	0.000±0.00 <sup>a</sup>
Point 6 wet	0.000±0.00 <sup>a</sup>	0.000±0.00 <sup>a</sup>	0.497±0.01 <sup>e</sup>	0.000±0.00 <sup>a</sup>	0.663±0.01 <sup>e</sup>

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different (P<0.05)

Metals such as Cd, Cu, Pb and Zn have been reported with high tendency of binding tenaciously to organic matter contained in soil, sediment and suspended particulate within the water column. Organically bound metals may dissociate as free ions and participate in cation exchange reactions with various minerals and living organism, depending on ambient pH, ionic strength and temperature. Soil organic matter had been reported to be a major soil property that greatly affects sorption of heavy metal because they contain functional groups that are capable of complexing metals. Thus, the organic matter of sediments is known to play a major role in determining the leaching and bioavailability of heavy metals [37,38].

Analysis of data reveals that the concentration of Cadmium in the chemical fraction follows the following order residual fraction (74%) > bound to organic matter (17%) > exchangeable fraction (7%) > bound to carbonate (2%), the concentration of Cadmium in the bond to iron and manganese fraction is negligible. This result shows that the environment is not polluted with Cadmium and that Cadmium cannot be leached into the water column because the metals is associated with the residual fraction, and this reveals that Cadmium is of a mainly of a lithogenic origin. This result agrees with the report on chemical fractionations and bioavailability of cadmium and zinc to Cole (*Brassica campestris* L.) grown in the multi-metals contaminated oasis Soil, Northwest of China [39].

The fractionation pattern of chromium in sediment from Owena River was characterized by dominance in the residual fraction (67%), the contribution of chromium to the bound to organic matter (14%) and bound to iron and manganese (15%) fractions were of similar magnitude. The

contribution of chromium to the exchangeable and bound to carbonate fractions was minor and negligible. The occurrence of chromium in the sediment from Owena River is mainly lithogenic in origin and the possibility of chromium leaching into the water column is very low due to the dominance of chromium in the residual fraction and minor contribution in the exchangeable and bound to carbonate fractions. This result agrees with several reports on risk assessment and geochemical behavior of heavy metals in sediments [40-42].

Copper in the sediment from Owena River was found to have its highest concentration in the bound to organic matter fraction (52%), this is due to the association of copper to organic matter, the concentration of copper in the residual fraction (26%) was lower but higher than the concentration of copper in the bound to iron and manganese (15%) and carbonate (5%) fractions. The contribution of copper to the exchangeable fraction was 2%, which is very low and negligible. This result agrees with the report on metal speciation in surface sediments of the Vigo Ria [43]. The occurrence of copper in both residual and non residual fractions reveals that copper is of both lithogenic and anthropogenic origin, with the highest concentration in the non residual fraction shows that most of the copper detected in the sediment from Owena River is of anthropogenic origin. This result agrees with the report on speciation and pollution index of heavy metals in river Ala sediment, Akure, Nigeria [44].

Nickel in sediment from Owena River was mainly found in the residual fraction (94%), the contributions of nickel to exchangeable, bound to carbonate and bound to organic matter fractions was observed to be very low and negligible, nickel was not detected in the bound to iron and manganese fraction. Nickel cannot be leached

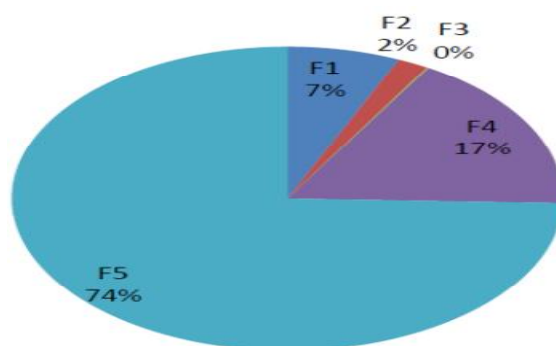


Fig. 2. Relative partitioning of Cd in chemical fractions (F=fraction)

into the water column of the Owena River because from the results, nickel is mostly associated with the residual fraction and nickel in the sediment of the river Owena is of lithogenic origin. This result agrees with the report on speciation of heavy metals pollutants and the vulnerability of groundwater resource in Okirika of Rivers State, Nigeria [45].

Lead in the sediment from Owena River was mainly found in the bound to iron and manganese (47%), residual fraction (24%),

bound to organic matter (16%), bound to carbonate (12%). The contribution of lead to the exchangeable fraction is negligible when compared to other chemical fractions associated with lead in the sediment from Owena River. This result agrees with the report on speciation of heavy metals in sediment deposit of lakes [46]. Lead could be possibly leached into the water column under a strong oxidizing condition because lead in the sediment from Owena River is mainly associated with the bound to organic matter fraction. The occurrence of lead in the

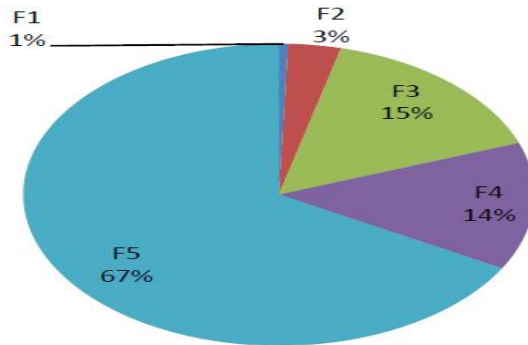


Fig. 3. Relative partitioning of Cr in chemical fractions (F=fraction)

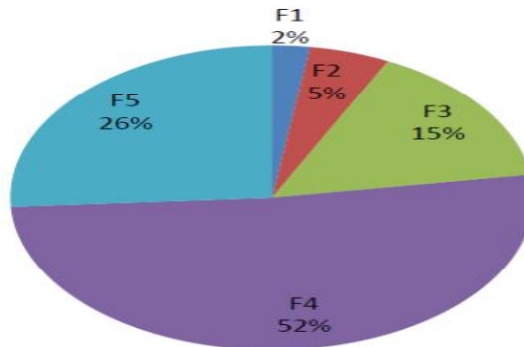


Fig. 4. Relative partitioning of Cu in chemical fractions (F=fraction)

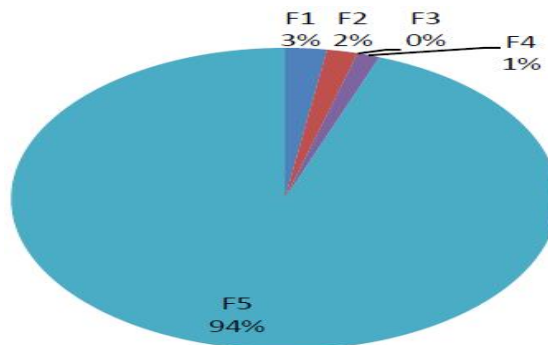


Fig. 5. Relative partitioning of Ni in chemical fractions (F=fraction)



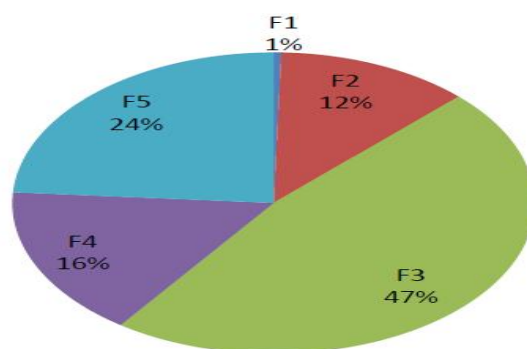


Fig. 6. Relative partitioning of Pb in chemical fractions (F=fraction)

Table 7. Total concentration (ppm) and permissible limit of heavy metals in sediment

Elements	Dry season	Wet season	*Target value of soil	**Intervention value of soil
Cadmium	0.152	0.15	0.8	12
Chromium	2.79	3.21	100	360
Copper	0.43	1.69	36	190
Lead	0.72	1.74	85	530
Nickel	1.68	0.93	35	210

Where \*Target values are specific to indicate desirable maximum levels of elements in unpolluted soils.

\*\*Intervention when remedial action is necessary, Source: Denneman and Robberse 1990[48] and Ministry of Housing, Netherland 1994 [49]

sediment from Owena River could be attributed to both lithogenic and anthropogenic origin due to the relationship of lead concentration existence in the residual and non residual chemical fractions of lead in the sediment [47].

**Cadmium (Cd):** The concentration of Cd in sediment ranges from 0.152 ppm during the dry season and 0.15 ppm during the wet season. These values are lower than the Dutch maximum permissible limit of 0.8 ppm. This result agrees with the report on Retention and mitigation of metals in sediment, soil, water, and plant of a newly constructed root-channel wetland (China) from slightly polluted source water [50].

**Chromium (Cr):** The Cr concentration in the sediment was found to range from 2.79 ppm during the dry season to 3.21 ppm during the wet season. These values were below the Dutch maximum permissible limit of 100 ppm, this result agrees with the report on the Assessment of Heavy Metal Contamination of Agricultural Soil around Dhaka Export Processing Zone (DEPZ), Bangladesh: Implication of Seasonal Variation and Indices [51].

**Copper (Cu):** The concentration of Cu in sediment ranges between 0.43 ppm during the dry season and 1.69 ppm during the wet season

respectively. These values are below the Dutch maximum permissible limit of 36 ppm set for sediment. This result agreed with the report on heavy metal content of agricultural soil in a Mediterranean semiarid are: the Segura River Valley (Alicante, Spain) [52].

**Lead (Pb):** The concentration of lead in sediment ranges from 0.72 ppm during the dry season to 1.74 ppm during the wet season. These values are below the Dutch maximum permissible limit of 85 ppm in sediment thereby rendering the rivers sediment unpolluted with lead. This result agrees with the report on heavy metals in surface water, sediment, fish and periwinkles of Lagos Lagoon [53].

**Nickel (Ni):** The concentration of Ni in sediment from Owena River ranges between 1.68 ppm during the dry season and 0.93 ppm during the wet season, this value is below the Dutch maximum permissible limit of 35 ppm in sediment thereby rendering the rivers sediment unpolluted with nickel. This result agrees with the report on accumulation of heavy metals in agricultural soils and spring seasonal plants, irrigated by industrial waste water [54].

Mobility and Bioavailability of heavy metals in sediment collected from Owena River.

Sequential extraction procedures provide useful information for risk assessment, since the amount of metals mobilized under different environmental conditions can be estimated. In the present study, it is reasonable to state that the mobility and bioavailability of the metals decrease approximately in the order of the extraction sequence from bioavailable to non bioavailable [55-57]. In a sequential extraction the mobile and bioavailable fraction are the  $F_1$  and  $F_2$  while  $F_3$ ,  $F_4$  and  $F_5$  and the fraction with low mobility and low bioavailability respectively [58-60].

The overall results of this research suggest that the mobility and bioavailability of heavy metals in sediment collected from Owena river decreases in the following order:  $Cu > Pb > Cr > Cd > Ni$ .

#### 4. CONCLUSION

The heavy metal content in the top sediment deposit of Owena River has been fractionated by sequential extraction procedure in order to determine the environmental fate of selected heavy metals (Cd, Cr, Cu, Ni and Pb). This study reveals that nickel, chromium and cadmium were mainly associated with the residual fraction and the minor contribution to exchangeable and bound to carbonate fractions reduces the possibility of nickel, chromium and cadmium leaching into the water column. Copper and lead has their major contribution in the bound to organic matter and bound to iron and manganese fractions respectively, therefore the probability of copper and lead in the sediment leaching into the river will mainly occur under a strong oxidizing or reducing condition respectively. The total concentration of the heavy metals when compared to the Dutch maximum permissible limit shows that the sediment of Owena River is not polluted with the analyzed heavy metals. This study also provides baseline information on the concentration of heavy metals in the top sediment deposit of Owena River, which can be used to evaluate future problems due to anthropogenic activities.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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