# Spatial Distribution and Pollution Assessment of Some Metals in Intertidal Sediment of Sambreiro River in Rivers State, Nigeria

Millicent Uzoamaka Ibezim-Ezeani<sup>1,2</sup>, Owhonda Chikeru Ihunwo<sup>2\*</sup>

<sup>1</sup>(Department of Pure and Industrial Chemistry, University of Port Harcourt, P. M. B. 5323, Choba. Rivers State, Nigeria)

<sup>2</sup>(Niger Delta Aqua Research Group, Department of Biochemistry and Chemistry Technology, School of Science Laboratory Technology, University of Port Harcourt, P. M. B. 5323, Choba. Rivers State, Nigeria)

#### Abstract:

The spatial distribution and pollution associated with Cd, Cr, Fe, Ni and Pb metals between latitudes of 4°48'52.8"N and 4°47'02.9"N and longitudes of 7°02'46.7"E and 7°03'37.2"E respectively; situated along the Sambreiro river which flows intertidally from Woji and Elelenwo Creeks (downstream) to Opkoka River in lowtide, and vice versa in hightide were assessed. The mean concentration of heavy metals (Cd, Cr, Fe, Ni and Pb) in sediment samples collected weekly between January and May, 2020 from ten stations (St1 – St10) along Sambreiro River were analysed with Atomic Absorption Spectrophotometer (AAS), and the data evaluated with pollution indices such as Contamination factor (CF), Enrichment factor (EF) and Geoaccumulation index ( $I_{geo}$ ). The trend for the highest mean concentration (mg/kg) of heavy metals is: St2(3111.7) Fe > St2(136.6) Cr > St3(13.97) Pb > St2(5.286) Cd > St2(0.955) Ni, and that of CF is: St2(151.0) Cd > St3(10.5) Pb > St2(3.9) Cr > St2(0.48) Ni > St2(0.32) Fe; apparently facilitated by the influence of metal works along St2 and St3 axes. The order of maximum  $I_{geo}$  is: Cd (6.65) > Pb (2.81) > Cr (1.38) > Ni (-1.65) > Fe (-2.24); with Fe and Ni recording  $I_{geo} < 0$ , which signify unpolluted along all stations.

Key Word: Intertidal sediment, Heavy metal, Sambreiro River, Pollution indices, Multivariate statistics

Date of Submission: 15-01-2021

Date of Acceptance: 31-01-2021

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### I. Introduction

Natural and anthropogenic activities within and along coastal regions lead to the deposition of heavy metal elements in sediment causing contamination and possible pollution of sediment<sup>1,2</sup>. Some anthropogenic influences through which metallic-waste or metallic-pollutants enter rivers, creeks and other water bodies originate partly from the progressive pace of transformation from pre-industrial to industrial state, growth in economic output, coastal tourism, development of technologies, integration of acquired skills, reclamation of wasteland, increased utilization of agrochemicals, advances in construction works, disposal of urban sewage, corrosion of metallic parts, metal fabrication, etc.; while some natural effects include weathering of rocks, leaching of minerals by rainfall, heavy metal percolating through sediments, processes forming geogenic materials, etc.<sup>3,4</sup>.

The sediment which functions as sink and source of heavy metals to the water column, harbors the heavy metals as either solids or solutions<sup>5</sup>. In the solution phase, they are soluble (or partially soluble), fluidic, available and exhibit toxic properties; while in the solid phase, they are immovable, not readily reacting and unharmful<sup>6</sup>. However, the availability of heavy metals in the component phases is possible through the biological, physical and chemical disturbances to change sediment properties (such as cationic forms, pH, hydrological regime, oxidation-reduction potential or degradation of organic matter, etc.)<sup>7,8</sup>; as well as the periodic changes associated with tidal forces and wave motion. These disturbances and forces disrupt the water environment condition; and thus, the dynamic equilibrium ecological balance of the sediment-water interface is destroyed. The heavy metals in the sediment will then be transferred and transformed with the help of processes such as ion exchange, dissolution and desorption; and released to the overlaying water which will lead to the secondary effect of pollution on water quality<sup>5</sup>.

To assess the level of change due to anthropogenic input into the sediment, factors that compare metal concentration in sediment to pre-anthropogenic or background levels, or pristine condition have been developed. Enrichment Factor (EF) first compared metal concentration in sediment fine fraction and mean metal concentration in mudstone<sup>9</sup>. This was later developed to assess anthropogenic impact by normalising the metal concentration in sediment with a normalising element such as aluminium (Al) or Iron (Fe)<sup>9</sup>. Hakanson<sup>10</sup> first calculate the overall contamination factor based on seven metals and one organic contaminant by comparing the metan concentration of the target metal to their background concentrations. Furthermore, geoaccumulation index

 $(I_{\text{geo}})$  compares measured concentration of metal to the geochemical background concentration of the element applying a possible variation factor of background values due to lithogenic effect<sup>11,12</sup>.

Earlier study carried out along Woji Creek assessed the concentrations of Cd, Ni, Fe, Pb and Cu<sup>13</sup>, noted high metal concentrations in the sediment which was associated with the activities taking place along the creek. Thus, this study evaluates the level of accumulation and pollution of Cd, Cr, Fe, Ni and Pb metals in the sediment along Sambreiro River, Rivers State, in the Niger Delta Region of Nigeria; by applying various pollution indices such as Contamination factor (CF), Enrichment factor (EF) and Geoaccumulation index ( $I_{geo}$ ).

### **II.** Materials and Methods

Study area The Global Positioning System (GPS) location, name, community, river order and river width are presented in Table 1. St1- St5 of the study area is known as Woji Creek, St6 – St8 is Elelenwo Creek and St9 and St10 are the Opkoka River. There is a general trend of increasing river width downstream from 67.29 m in St1 to 568.95 m in St10.

# Table 1: Stations and corresponding GPS in the communities with creek name, river order and river width

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Station Identity	Latitude	Longitude	Name	Community	River order	River width (m)	
St1	4°48'52.8"N	7°02'46.7"E	Woji Creek	Woji	1st order	67.29	
St2	4°48'46.4"N	7°03'14.6"E	Woji Creek	Woji	1st order	119.51	
St3	4°48'25.8"N	7°03'36.4"E	Woji Creek	Woji	3rd order	160.59	
St4	4°48'11.3"N	7°03'55.5"E	Woji Creek	Okuruama	3rd order	232.87	
St5	4°47'47.8"N	7°04'07.5"E	Woji Creek	Okuruama	4th order	195.33	
St6	4°48'52.5"N	7°04'28.3"E	Elelenwo Creek	Elelenwo	2nd order	310.61	
St7	4°48'15.4"N	7°04'27.2"E	Elelenwo Creek	Akpajo	3rd order	327.12	
St8	4°47'45.2"N	7°04'22.7"E	Elelenwo Creek	Okujagu	3rd order	195.84	
St9	4°47'39.6"N	7°03'49.2"E	Okpoka River	Okuruama	4th order	282.48	
St10	4°47'02.9"N	7°03'37.2"E	Okpoka River	Okuruama	4th order	568.95	
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St1 is under the Woji bridge in Port Harcourt, there are several identifiable point source pollutions, e.g., the Port Harcourt Zoo, Slaughter market (abattoir), abandoned scrap metals, boats and barges, etc. St2 and St3 are close to large boat maintenance and fabrication companies; St4 and St5 do not have any activities taking place around. St6 is located after a bridge, and boat maintenance and fabrication companies. St7 and St8 are downstream away from community settlement and other anthropogenic activities; while St9 and St10 are beside fishing communities (Okujagu and Okuruama communities respectively) (Fig. 1).

This study river is intertidal, flowing from St1 and St6 downstream to St10 in low tide; and from St10 to St1 and St6 in high tide. There are three major points of mixing: St 3, St 5 and St7. St3 has a tributary of the Woji Creek north-west which carries water and mixes with the larger creek before St3. In low tide, water flowing downstream from St1 and St6 mixes close to St5. North-east of the study area flows another creek which joins the Elelenwo creek just below St6 but above St7.



Figure 1: Map of Rivers State, Nigeria, and the ten stations sampled

## Sample collection and analysis

Vertical grab samples of sediment were collected using a stainless steel Van Veen grab sediment sampler with the aid of a boat. At each station, four samples were collected (two from each side of the river) at low tide (i.e., while the river flowed from St1 and St6 upstream to St10 downstream). Samples collected were put into properly labelled plastic bags and put into a cooler. Ice packs were placed on top of the samples and each cooler used was sealed and transported to the laboratory for analysis. Samples were collected weekly for five months, from January to May 2020.

Samples collected were air-dried in the laboratory, fragments found in the sediments were removed and uniformly mixed by pulverization. Sediments were sieved through a 2 mm pore size sieve to remove coarse particles. From each sample, 0.5 g of sample was sieved and put into an acid-washed glass beaker and digested using the standard methodology ASTM D4698<sup>14</sup>. Thereafter, metals (Cd, Cr, Fe, Ni, Pb) levels were resolved using AAS<sup>15</sup>, and the mean concentration of four samples taken from each station representing the concentration of metal at each station.

## Quality assurance and quality control

AAS Certified Reference Materials (CFMs) for each metal was used; Cd, Cr, Fe, Ni and Pb standards for AAS TraceCERT: 1000 ppm of each metal in nitric acid. Before analyses, the standard material was serially diluted into 2, 4 and 6 ppm, and blank samples were analysed alongside to manage error; every sample was analysed in triplicate. The GBC SensAA Atomic Absorption Spectrophotometer was used to analyse the samples, this equipment has a detection limit of 0.001 and involves the use of a flame lamp for each metal

analysed. Percentage recovery (% R) for metals were calculated to be: Cd- 100%, Cr- 98.3%, Fe – 96.7%, Ni- 98.9% and Pb- 98.7%.

#### Data analysis

Analysis of variance, ordinary least squares regression and multivariate linear regression were analysed using PAST Statistics<sup>16</sup>.

To deduce CF, equation 1 was applied:

$$CF_i = \frac{c_i}{c_b} \tag{1}$$

Where  $CF_i$  is contamination factor for individual metal,  $C_i$  is the environmental concentration of individual metal in the sediment and  $C_b$  is the base concentration (mg/kg) of metal (Cd - 1.0, Cr - 35.0, Fe - 9800.0, Pb - 2.0, Ni - 7.0)<sup>17</sup>. To describe the level of contamination, the following terms were employed:  $CF_i < 1 - low$  contamination,  $1 \le CF_i < 3 - moderate$  contamination,  $3 \le CF_i < 6 - considerable$  contamination and  $CF_i \ge 6 - very$  high contamination.

EF was adopted as expressed in equation  $2^{18}$ :

$$EF = \frac{\left(\frac{C_i}{C_{Fe}}\right)}{\left(\frac{C_b}{C_{Fe-b}}\right)} \tag{2}$$

Where  $C_{Fe}$  and  $C_{Fe^-b}$  are the concentration of iron in the sediment and background concentration of iron respectively.

EF was characterised accordingly:  $EF \le 1 - no$  enrichment, 1 < EF < 3 - minor enrichment, 3 < EF < 5 - moderate enrichment, <math>5 < EF < 10 - moderate-to-severe enrichment, <math>10 < EF < 25 - severe enrichment, <math>25 < EF < 50 - very severe enrichment, EF > 50 - extremely severe enrichment<sup>19</sup>.

 $I_{\text{geo}}$  was deduced using equation 3:

$$I_{geo} = Log_2\left(\frac{C_i}{1.5C_b}\right) \tag{3}$$

Where 1.5 is the background matrix correction factor due to lithogenic effects<sup>20,21</sup>.

 $I_{geo}$  is characterised by the following:  $I_{geo} < 0$ : unpolluted,  $0 < I_{geo} < 1$ : unpolluted to moderately polluted,  $1 < I_{geo} < 2$ : moderately polluted,  $2 < I_{geo} < 3$ : moderately to strongly polluted,  $3 < I_{geo} < 4$ : strongly polluted,  $4 < I_{geo} < 5$ : strongly polluted,  $5 < I_{geo}$ : extremely polluted<sup>11,22</sup>.

#### **III. Results and Discussion**

#### **Concentration of metals in sediment** Trend of metal concentrations along the three locations were as follows: Woji Creek - Fe > Cr > Pb >Cd > Ni, Elelenwo Creek - Fe > Cd > Pb > Ni > Cr, Okpoka River - Fe > Cd > Pb > Ni > Cr. Along the stations, the metal concentrations were in the order: St2 > St4 > St1 > St5 > St9 > St8 > St6 > St7 > St3 > St10 (Cd), St2 > St7 > St5 > St9 > St4 > St6 > St8 > St3 > St10 (Cr), St2 > St1 > St3 > St5 > St4 > St6 > St7 > St8 > St9 > St10 (Fe), St2 > St1 > St5 > St4 > St6 > St7 > St3 > St8 > St10 > St9 (Ni) and St3 > St2 > St6 > St5 > St9 > St5 > St9 > St7 > SSt10 > St7 > St8 > St4 > St1 (Pb). Mean concentration of Cd was highest in St2 (5.286 ± 2.224 mg/kg) and lowest in St10 ( $0.042 \pm 0.099 \text{ mg/kg}$ ); ANOVA showed statistically significant difference in Cd concentration at St1, St4 and St9 (p < 0.05); and St2, St5 and St7 (p < 0.001). Highest mean concentration of Cr (136.6 ± 32.69 mg/kg – p < 0.001) was recorded in St2, and lowest concentration (0.004 ± 0.005 mg/kg) was found in St1. Fe yielded the highest concentration; St2 ( $3111.7 \pm 326.3 \text{ mg/kg}$ ) recording the highest mean concentration; while, St10 (129.8 $\pm$ 42.91 mg/kg) indicated the lowest mean concentration of Fe. ANOVA revealed a statistically significant difference in Fe concentration (p < 0.001) in St1 and St2. In St2, the highest mean concentration of Ni was recorded ( $0.955 \pm 0.522 \text{ mg/kg}$ ) and the lowest mean concentration was recorded in St9 ( $0.383 \pm 0.113$ mg/kg). ANOVA revealed statistically significant difference in St1 and St2 (p < 0.001), and St3, St4, St5 and St10 (p < 0.05). Highest concentration of Pb was recorded in St2 (13.97 $\pm$ 6.833 mg/kg), while the lowest concentration was recorded in St1 (0.034 $\pm$ 0.022 mg/kg). ANOVA indicated a statistically significant difference in Pb concentration in St3 (p < 0.001); and St2, St5 and St6 (p < 0.05) (Fig. 2).



Figure 2: Mean concentrations of Cd, Cr, Fe, Ni and Pb across sample stations (n = 20) Error bar = Standard deviation, (n = 32, \* = p < 0.05, \*\* = p < 0.001)

The concentration of metals studied were higher in Woji Creek (St1 – St5), compared to Elelenwo Creek (St6 – St8) and it was least in Okpoka River. The higher concentration of metals observed in Woji Creek can be related to the higher number of anthropogenic activities identified along the creek compared to the other parts of the study area<sup>2</sup>. Scrap metals were identified at several points along the Woji Creek, particularly at St1 and St2. Studies have associated scrap metals along fluvial systems to contamination in water, sediment and biota<sup>23,24,25</sup>.

Table 2 showed the concentration of metals from sediment sampled from other locations across the world. Cd and Cr measured in Karnaphuli River in Chittagong City of Bangladesh were higher than those measured in sediment collected from our study area. Pb was similar to those measured along Woji Creek but lower than other locations in the study area<sup>26</sup>. Fe, Cr and Pb recorded in St1 and St2 were highest, this could be directly related to the abandoned boats and scrap metals identified along these stations<sup>27</sup>. The concentration of Fe in these stations fall within the range measured in Voghji River in Southeast Armenia<sup>28</sup>. Mean concentration

of all metals analysed across all stations exceeded those measured in Abereke, Awoye and Ayetoro in Ondo State, Nigeria<sup>29</sup>.

Country	Region	River	Metal	Concentration	Reference
				21.98 -73.42 <sup>a</sup>	
Bangladesh	Chittagong City	Karnaphuli River	Cr	37.23 - 160.32 <sup>a</sup>	26
			Pb	21.98 - 73.42 <sup>a</sup>	
			Fe	2053 - 20018 <sup>a</sup>	
			Cd	0.09 - 0.97 <sup>a</sup>	
Armenia	Southeast	Voghji River	Cr	1.95 - 11.8 <sup>a</sup>	28
			Ni	3.22 - 18.80 <sup>a</sup>	
			Pb	40.50 - 3052 <sup>a</sup>	
			Cd	5821.8 - 12808 <sup>a</sup>	
		Kienké watershed (Abiete)	Ni	8.37 - 48.6 <sup>a</sup>	
~	Abiete - Toko gold	(101010)	Pb	0.02 - 0.231 <sup>a</sup>	20
Cameroon	district	Tchangué watershed	Cd	7250.7 - 12120 <sup>a</sup>	- 30
			Ni	15.2 - 32.2 <sup>a</sup>	
		(1000)	Pb	0.068 - 0.139 <sup>a</sup>	
	The Egyptian Mediterranean Sea		Cd	0.04 - 0.47 <sup>a</sup> (0.22 <sup>b</sup> )	
			Cr	4.08 - 297.95 <sup>a</sup> (82.74 <sup>b</sup> )	
Egypt			Fe	234 - 38045 <sup>a</sup> (13256 <sup>b</sup> )	31
			Ni	1.65 - 60.25 <sup>a</sup> (25.98 <sup>b</sup> )	
			Pb	3.34 - 53.67 <sup>a</sup> (13.17 <sup>a</sup> )	
			Cd	$*0.55 \pm 0.10^{ c}$	
Nigeria			Cr	$*0.520 \pm 0.20^{c}$	
		Abereke	Fe	$*369.34 \pm 80.04^{c}$	
			Ni	$*7.345 \pm 1.78^{c}$	
			Pb	$*0.67 \pm 0.12$ <sup>c</sup>	
			Cd	$*0.845 \pm 0.23$ °	
			Cr	$*0.74 \pm 0.11$ <sup>c</sup>	
	Ondo State	Awoye	Fe	$*286.17 \pm 65.21$ <sup>c</sup>	29
			Ni	$*7.84 \pm 1.43$ <sup>c</sup>	
			Pb	$*2.065 \pm 1.10^{\circ}$	
			Cd	$*0.315 \pm 0.12$ °	
			Cr	$*0.235 \pm 0.10^{\circ}$	
		Ayetoro	Fe	$*417.50\pm89.87^{\rm \ c}$	
			Ni	$*3.73 \pm 1.52$ °	
			Pb	$*0.075 \pm 0.03$ <sup>c</sup>	

<b>Table 2: Concentration</b>	in mg/kg of some	metals in sediment	from selected r	ivers around the world

\*-  $\mu g/g$ ; a- range; b- mean; c- mean  $\pm$  standard deviation

### **Contamination factor (CF)**

 $\begin{array}{l} \mbox{Contamination factor for cadmium (Cd-CF) ranged from 1.2-151.0 with the trend St2 > St4 > St1 > \\ \mbox{St5 > St9 > St8 > St6 > St7 > St3 > St10; St3 and St10 indicated moderate contamination due to Cd, while other stations with CF > 6 indicated very high contamination due to Cd. Cr-CF ranged from 0.00011 - 3.9 with the \\ \end{array}$ 

trend St2 > St7 > St5 > St9 > St4 > St6 > St8 > St3 > St10 > St1; except for St2 with CF > 3 indicating considerable contamination, other stations had CF > 1 indicating low contamination. Fe-CF ranged from 0.013 – 0.32 with the trend St2 > St1 > St3 > St5 > St4 > St6 > St7 > St8 > St9 > St10; St1 – St10 indicated low contamination. Ni-CF ranged from 0.19 – 0.48 with the trend St2 > St1 > St5 > St4 > St6 > St7 > St8 > St4 > St6 > St7 > St8 > St9 > St10; St1 – St10 indicated low contamination. Ni-CF ranged from 0.19 – 0.48 with the trend St2 > St1 > St5 > St4 > St6 > St7 > St8 > St9 > St10; all stations sampled indicated low contamination due to Ni in the sediment. Pb-CF ranged from 0.0049 – 10.5 with trend St3 > St2 > St6 > St5 > St9 > St10 > St7 > St8 > St4 > St1; CF in St3 indicated very high contamination (CF > 6), St7 indicated moderate contamination and other stations indicated low contamination (Fig. 3).



Figure 3: Spatial distribution of contamination factor across the study area (n = 20)

Except for St3 and St1 with lower Cd-CF, other stations in the present study have lower values compared to those measured in surface sediments of the Bay of Bengal Coast<sup>32</sup>. Although other stations recorded Pb-CF lower than those from Bengal Coast, St2 has similar values; while St3 had an exceeded value. Ni-CF and Fe-CF values in the present study all fell below those from the Bay of Bengal Coast<sup>32</sup>. The average CF values of heavy metals in the sediments from the Lishui River Watershed, Southern China were as follows: 0.86, 0.79 and 1.35 for Cr, Ni and Pb respectively<sup>33</sup>. Except for St3, Cr-CF in the present study fell below the mean value measured in Lishui River; values measured in all stations for Ni-CF and Pb-CF were below the

average CF values for Ni and Pb in Lishui River. The highest contributor to contamination in the studied river is Cd, St1 - St5 (Woji Creek) were the most contaminated for all the CF values of metals studied, while St10 was the least contaminated, i.e., the contamination reduces downstream.

## **Enrichment factor (EF)**

The trend observed for enrichment factor for Cd (Cd-EF) was as follows: St9 > St8 > St4 > St6 > St7 > St5 > St1 > St2 > St10 > St3; except for St3 indicating severe enrichment of Cd, St1, St2, St4 – St10 indicated very severe enrichment of Cd. Trend for enrichment of Cr (Cr-EF) in sediment was St2 > St7 > St9 > St5 > St8 > St10 > St6 > St4 > St3 > St1, with all stations revealing no enrichment of Cr except St2 which indicates severe enrichment. Ni-EF in sediment was in the trend St10 > St9 > St8 > St7 > St6 > St4 > St3 > St1 > St2. EF in St1, St2 and St3 showed minor enrichment, St4 revealed moderate enrichment, St5 - St9 indicate moderate-to-severe enrichment and St10 indicates severe enrichment of Ni. Pb-EF trended as follows: St3 > St6 > St10 > St9 > St2 > St5 > St8 > St7 > St8 > St10 > St9 > St2 > St5 > St8 > St7 > St8 > St10 > St9 > St2 > St5 > St7 > St8 > St4 > St1 = St2 = St5 > St7 > St8 > St4 > St1 = St2 = St5 > St7 > St8 > St4 > St1 = St2 = St5 > St7 > St8 > St4 > St1 = St2 = St5 > St7 > St8 > St4 > St1 = St2 = St5 > St7 > St8 > St4 > St1 = St2 = St5 > St7 > St8 > St4 > St1 = St2 = St5 > St7 > St8 > St4 > St1 = St2 = St5 = St7 > St8 > St4 > St1 = St2 = St5 = St7 > St8 > St4 > St1 = St2 = St5 = St7 > St8 > St4 > St1 = St2 = St5 = St7 = St8 > St4 > St1 = St2 = St5 = St7 = St8 > St4 > St1 = St2 = St5 = St7 = St8 > St4 > St1 = St2 = St5 = St7 = St8 > St4 > St1 = St2 = St5 = St7 = St8 > St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St2 = St5 = St7 = St8 = St4 = St1 = St4 = St1 = St4 = St



Figure 4: Spatial distribution of enrichment factor across the study area (n = 20)

## Geoaccumulation index $(I_{geo})$

The  $I_{geo}$  for the metals ranged from -0.32 to 6.65, -13.68 to 1.38, -6.82 to -2.24, -2.29 to -1.65 and -8.27 to 2.81 for Cd, Cr, Fe, Ni and Pb respectively. Fe and Ni with  $I_{geo} < 0$  indicated unpolluted along all stations. Except for St2 (unpolluted to moderately polluted) and St3 (moderately to strongly polluted); Pb -  $I_{geo}$  calculated for other stations revealed unpolluted in relation to Pb in the sediment. Cr -  $I_{geo}$  indicated moderately polluted in St2; while St1, St3 to St10 indicated unpolluted. Cd -  $I_{geo}$  extremely polluted due to Cd input in the sediment in St2, St4, St5, St6, St7, St8 and St9; St 3 revealed unpolluted to moderately polluted, while St10 indicated unpolluted (Fig. 5).



**Figure 5: Spatial distribution of geoaccumulation factor across the study area (n = 20)** 

In a study carried out on spatial variations of heavy metals contamination in sediments from Odiel river (Southwest Spain)<sup>34</sup>; except for Area IV with Fe -  $I_{geo} = 0.1$ , other areas had values < 1 similar to the present study area. Similarly, except for St2, all stations in the present study also had Cd -  $I_{geo} < 1$  as those from Odiel river. Furthermore, except for St10 with Cd -  $I_{geo} < 1$ , all stations in the present study had values far exceeding those in Katerniaghat, Colonelganji, Ayodhya, Dohrighat and Chhapra in Ghaghara river sediment in Northern India<sup>21</sup>. St10 is the only station which is unpolluted with reference to the metals studied, while Cd had an effect on all stations except for St10; and Ni and Fe have no pollution effect on the stations sampled.

## **Regression analysis**

Ordinary Least Squares Regression for River Order-River width (m) revealed a positive correlation between both hydrological parameters (river width and river order) in the study area (r = 0.36, p = 0.07) (Fig. 6). This implies that as the river order increases, the river width also increases<sup>35</sup>. The increasing river order increases the volume of water; and hence, the width of the river to accommodate the quantity of water flowing through.





Applying linear regression to the variables studied show that, except for Pb -  $I_{geo}$ , Cd – EF and Ni – EF showing positive correlation to both river width and river order, and Pb – EF to river order; other variables showed a negative correlation to both river width and river order (Table 3). Therefore, the quantity of water flowing plays a role on the level of contaminants, contamination and pollution in the sediment.

There are more anthropogenic activities between St1 - St3 and St6; this was reflected in the concentration of metals measured in sediment sampled from these stations. Water flowing downstream from Woji creek and Elelenwo creek meet at St5; the meeting of these water causes an increase in the concentration of some metals and indices calculated. Hence, there is an initial spike in St5 due to pollutant mixing from both creeks downstream and a later dilution from St9 – St10 as confirmed by the regression analysis<sup>36,37</sup>.

Variable -	River width		River	River order	
variable	r	р	r	р	
Cd	-0.58	0.08	-0.45	0.19	
Cr	-0.32	0.37	-0.56	0.10	
Pb	-0.26	0.48	-0.02	0.95	
Ni	-0.62	0.06	-0.75	0.01	
Fe	-0.65	0.04	-0.78	0.01	
Cd - Igeo	-0.52	0.13	-0.37	0.29	
$\operatorname{Cr}$ - $I_{geo}$	-0.18	0.62	-0.18	0.61	
Pb - I <sub>geo</sub>	0.07	0.86	0.10	0.79	
Ni - I <sub>geo</sub>	-0.66	0.04	-0.75	0.01	
Fe - Igeo	-0.82	0.00	-0.74	0.02	
Cd - CF	-0.58	0.08	-0.45	0.19	
Cr - CF	-0.32	0.37	-0.56	0.10	
Pb- CF	-0.26	0.47	-0.02	0.95	

able 5. Multivariate inical regression statistica		Table 3:	<b>Multivariate</b>	linear	regression	statistics
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Ni - CF	-0.62	0.05	-0.76	0.01
Fe - CF	-0.65	0.04	-0.78	0.01
Cd - EF	0.04	0.90	0.30	0.41
Cr - EF	-0.31	0.39	-0.54	0.11
Pb - EF	-0.09	0.81	0.11	0.77
Ni - EF	0.92	0.00	0.62	0.06

#### **IV. Conclusion**

This study has assessed the spatial distribution and pollution associated with Cd, Cr, Fe, Ni and Pb metals in the intertidal sediment of Sambreiro River in Rivers State (Nigeria). The trend of metal concentrations along the three locations in Sambreiro River are in the order: Woji Creek - Fe > Cr > Pb > Cd > Ni, Elelenwo Creek - Fe > Cd > Pb > Ni > Cr, and Okpoka River - Fe > Cd > Pb > Ni > Cr. The range of CF values is in the order: Cd (1.2 - 151.0) > Pb (0.0049 - 10.5) > Cr (0.00011 - 3.9) > Ni (0.19 - 0.48) > Fe (0.013 - 0.32), which indicated that Cd was the highest contributor to contamination in the studied river. Many stations depicted different levels of EF for the metals, which suggested the likelihood of adsorption, complexation, flocculation, precipitation or sedimentation for their enrichment in the sediment. The range of  $I_{geo}$  values for Cd is -0.32 to 6.65, Cr is -13.68 to 1.38, Fe is -6.82 to -2.24, Ni is -2.97 to -1.65 and Pb is -8.27 to 2.81; with Fe and Ni ( $I_{geo} < 0$ ) indicating unpolluted along all stations. The study also revealed the effect of dilution of pollutant concentration with increasing river width. Results obtained in this study draws a direct connection between anthropogenic activities and pollution due to metals accumulated in the sediment in the study river. Thus, there is need for local and state authorities to carry out more extensive studies on possible ecological and human health risk and effect of these metals in the environment. Proper environmental management plans should also be implemented and enforced on the companies along the river.

#### Acknowledgments

The authors appreciate the support of field and laboratory personnel of the Niger Delta Aqua Research Group (P. C. Elenga, Mmedorenyi Okon and Mmedara Okon), Prof. P. C. Mmom (Dean, Faculty of Social Science, University of Port Harcourt), Assoc. Prof. Amalo-Ndu Dibofori-Orji (Dept. of Chemistry, Ignatius Ajuru University of Education, Port Harcourt, Nigeria), A. R. Shahabinia (Groupe de Recherche Interuniversitaire en Limnologie, Département des Sciences Biologiques, Université du Québecà Montréal) and Dr. M. O. Onyema (Dept. of Pure and Industrial Chemistry, University of Port Harcourt). Immense thanks to HRH Eze Amb. Sir Dr. E. G. Ihunwo (JP. FCAI, Paramount Ruler of Woji Community) for supporting the research in Woji community.

#### References

- Nwajei GE, Dibofori-Orji AN, Iwegbue CMA, Ojuh BO. Distribution of trace elements in surface water and sediments from Crayford Creek in Warri, Delta State of Nigeria. Academic Research International. 2014;5(4):123–134.
- [2]. Dibofori-Orji AN, Ihunwo O, Udo KS, Shahabinia AR, Onyema MO, Mmom PC. Spatial and temporal distribution and contamination assessment of heavy metal in Woji Creek. Environmental Research Communications. 2019;1(11):1–10. doi: 10.1088/2515-7620/ab4a8c.
- [3]. El-Sorogy AS, Youssef M, Al-Kahtany K, Saleh MM. Distribution, source, contamination, and ecological risk status of heavy metals in the Red Sea-Gulf of Aqaba coastal sediments, Saudi Arabia. Marine Pollution Bulletin. 2020;158:111411. doi: <u>https://doi.org/10.1016/j.marpolbul.2020.111411</u>.
- [4]. Xu M, Wang R, Yang X, Yang, H. Spatial distribution and ecological risk assessment of heavy metal pollution in surface sediments from shallow lakes in East China. Journal of Geochemical Exploration. 2020;213:106490. doi: https://doi.org/10.1016/j.gexplo.2020.106490.
- [5]. Zhang H, Walker TR, Davis E, Ma G. Ecological risk assessment of metals in small craft harbour sediments in Nova Scotia, Canada. Marine Pollution Bulletin. 2019;146:466–475. Doi: <u>https://doi.org/10.1016/j.marpolbul.2019.06.068</u>.
- [6]. Ogundiran MB, Osibanjo O. Mobility and speciation of heavy metals in soils impacted by hazardous waste. Chemical Speciation & Bioavailability. 2009;21(2):59–69. doi: 10.3184/095422909X449481.
- [7]. Liu B, Wang J, Xu M, Zhao L, Wang Z. Spatial distribution, source apportionment and ecological risk assessment of heavy metals in the sediments of Haizhou Bay national ocean park, China. Marine Pollution Bulletin. 2019;149:110651. doi: <u>https://doi.org/10.1016/j.marpolbul.2019.110651</u>.
- [8]. Varol M. Environmental, ecological and health risks of trace metals in sediments of a large reservoir on the Euphrates River (Turkey). Environmental Research. 2020;187:109664. doi: <u>https://doi.org/10.1016/j.envres.2020.109664</u>.
- [9]. Buat-Menard P. Influence de la retombee atmospherique sur la chimie des metaux en trace dans la matiere en suspension de l'Atlantique Nord. University of Paris. 1979.
- [10]. Hakanson L. An ecological risk index for aquatic pollution control.a sedimentological approach. Water Research. 1980;14(8):975– 1001. doi: <u>https://doi.org/10.1016/0043-1354(80)90143-8</u>.
- [11]. Müller G. Schwermetallen in den Redimen des rheins. Umschau. 1979;79(24):778-783.
- [12]. Müller G. The heavy metal pollution of the sediments of neckars and its tributary: a stocktaking. Chemiker Zeitung. 1981;105:157–164.

- [13]. Ibezim-Ezeani MU, Dibofori-Orji AN, Solomon UK, Ihunwo OC. Assessment of metal contamination in sediment from Woji Creek, Niger Delta Region of Nigeria. International Journal of Environmental Analytical Chemistry. 2020; doi: 10.1080/03067319.2020.1832482.
- [14]. ASTM. D4698-92 Standard practice for total digestion of sediment samples for chemical analysis of various metals, standards. West Conshohocken, PA. 2013; doi: 10.1520/D4698-92R13.
- [15]. APHA. Metals by flame atomic absorption spectrometry\*', in Arnold EG, Lenore SC, Andrew DE, Mary AHF. (eds) Standard methods: for the examination of water and wastewater. 18th edn. Washington, DC 20005: American Public Health Association, American Water Works Association, Water Environment Federation. 1999.
- [16]. Hammer Ø. PAST: PAleontological STatistics, reference manual. Oslo: Natural History Museum, University of Oslo. 2020; doi: 10.1093/cid/ciq238.
- [17]. Turekian KK, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. GSA Bulletin. 1961;72(2):175– 192. doi: 10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2.
- [18]. Ergin M, Saydam C, Baştürk Ö, Erdem E, Yörük R. Heavy metal concentrations in surface sediments from the two coastal inlets (Golden Horn Estuary and İzmit Bay) of the northeastern Sea of Marmara. Chemical Geology. 1991;91(3):269–285. doi: <u>https://doi.org/10.1016/0009-2541(91)90004-B</u>.
- [19]. Birch GF. A scheme for assessing human impacts on coastal aquatic environments using sediments, in CD, W. and RA, F. (eds) Coastal GIS: an integrated approach to Australian coastal issues. Wollongong: Wollongong University Papers in Center for Maritime Policy, 14, Australia. 2003.
- [20]. Zhang W, Feng H, Chang J, Qu J, Xie H, Yu L. Heavy metal contamination in surface sediments of Yangtze River intertidal zone: An assessment from different indexes. Environmental Pollution. 2009;157(5):1533–1543. doi: https://doi.org/10.1016/j.envpol.2009.01.007.
- [21]. Singh H, Pandey R, Singh SK, Shukla DN. Assessment of heavy metal contamination in the sediment of the River Ghaghara, a major tributary of the River Ganga in Northern India. Applied Water Science. 2017;7(7):4133–4149. doi: 10.1007/s13201-017-0572-y.
- [22]. Müller G. Die schwermetallbelastung der sedimenten des neckars und seiner nebenflüsse. Chemiker-Zeitung. 1981;6:157-164.
- [23]. Reddy MS, Basha S, Sravan KVG, Joshi HV, Ramachandraiah G. Distribution, enrichment and accumulation of heavy metals in coastal sediments of Alang–Sosiya ship scrapping yard, India. Marine Pollution Bulletin. 2004;48(11):1055–1059. doi: https://doi.org/10.1016/j.marpolbul.2003.12.011.
- [24]. Rahman MS, Hossain MB, Babu SMOF, Rahman M, Ahmed ASS, Jolly YN, Choudhury TR, Begum BA, Kabir J, Akter S. Source of metal contamination in sediment, their ecological risk, and phytoremediation ability of the studied mangrove plants in ship breaking area, Bangladesh. Marine Pollution Bulletin. 2019;141:137–146. doi: https://doi.org/10.1016/j.marpolbul.2019.02.032.
- [25]. Ibezim-Ezeani MU, Ihunwo OC. Assessment of Pb, Cd, Cr and Ni in water and water hyacinth (eichhornia crassipes). Journal of Applied Science and Environmental Management. 2020;24(4):719–727. doi: 10.4314/jasem.v24i4.26.
- [26]. Ali MM, Ali ML, Islam MS, Rahman MZ. Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh. Environmental Nanotechnology, Monitoring & Management. 2016;5:27–35. doi: https://doi.org/10.1016/j.enmm.2016.01.002.
- [27]. Turner A, Rees A. The environmental impacts and health hazards of abandoned boats in estuaries. Regional Studies in Marine Science. 2016;6:75–82. doi: https://doi.org/10.1016/j.rsma.2016.03.013.
- [28]. Gabrielyan AV, Shahnazaryan GA, Minasyan SH. Distribution and identification of sources of heavy metals in the voghji river basin impacted by mining activities (Armenia). Journal of Chemistry. 2018;1–9. doi: 10.1155/2018/7172426.
- [29]. Tunde OL, Oluwagbenga AP. Assessment of heavy metals contamination and sediment quality in Ondo coastal marine area, Nigeria. Journal of African Earth Sciences. 2020;170:103903. doi: 10.1016/j.jafrearsci.2020.103903.
- [30]. Mandeng EPB, Bidjeck LMB, Bessa AZE, Ntomb YD, Wadjou JW, Doumo EPE, Dieudonné LB. Contamination and risk assessment of heavy metals, and uranium of sediments in two watersheds in Abiete-Toko gold district, Southern Cameroon. Heliyon. 2019;5(10). doi: 10.1016/j.heliyon.2019.e02591.
- [31]. Soliman NF, Nasr SM, Okbah MA. Potential ecological risk of heavy metals in sediments from the Mediterranean coast, Egypt. Journal of Environmental Health Science and Engineering. 2015;70. doi: 10.1186/s40201-015-0223-x.
- [32]. Khan MZH, Hasan MR, Khan M, Aktar S, Fatema K. Distribution of heavy metals in surface sediments of the bay of bengal coast. 2017. https://doi.org/10.1155/2017/9235764
- [33]. Watershed R, Shen F, Mao L, Sun R, Du J, Tan Z, Ding M. Contamination evaluation and source identification of heavy metals in the sediments from the Lishui River watershed, Southern China. International Journal of Environmental Research and Public Health. 2019;16(336):1–14. doi: 10.3390/ijerph16030336.
- [34]. Santos BJC, Beltrán R, Gómez AJL. Spatial variations of heavy metals contamination in sediments from Odiel river (Southwest Spain). Environment International. 2003;29(1):69–77. doi: https://doi.org/10.1016/S0160-4120(02)00147-2.
- [35]. Downing JA, Cole JJ, Duarte CM, Middelburg JJ, Melack JM, Prairie YT, Kortelainen P. Global abundance and size distribution of streams and rivers. Inland Waters. 2012;2:229–239. doi: 10.5268/IW-2.4.502.
- [36]. Kachiashvili K, Gordeziani D, Lazarov R, Melikdzhanian D. Modeling and simulation of pollutants transport in rivers. Applied Mathematical Modelling. 2007;31(7):1371–1396. doi: https://doi.org/10.1016/j.apm.2006.02.015.
- [37]. Xin SZX. Pollutant source identification model for water pollution incidents in small straight rivers based on genetic algorithm. Applied Water Science. 2017;7(4):1955–1963. doi: 10.1007/s13201-015-0374-z.

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DOI: 10.9790/2402-1501021324