

Assessment of Spatial Variations of Heavy Metals in Superficial Sediments of Ikpoba River and Comparison with Sediment Quality Guidelines

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Abstract

Superficial sediment samples were collected from seven stations of Ikpoba River. Heavy metals (Pb, Ni, Cu, Fe and Cd) were determined in the sediments using Atomic Absorption Spectrophotometer. In this study, Fe had the highest mean concentrations followed by Cu, Pb and Ni. Generally, heavy metal concentration in the sediments of Ikpoba River showed an elevated concentration of all the metals at station 7 (Guinness Brewery). This can be attributed to the release of effluents from the Brewery. The values for Pb, Ni, Fe and Cd were well below threshold effects concentrations (TEC). For Cu, 66.77% of the values were below TEC while 33.33% of the values exceeded threshold probable effects concentrations (PEC). This implies that if pollution of station 4 with Cu continues, the toxicological potentials of the sediment with respect to Cu pollution may be severe. It affects various blood parameters, growth, behaviour, enzyme activity, and reproduction. Continuous monitoring of Ikpoba River is recommended.

Keywords: Metal, Aquatic, Sediment, Contamination, Atomic Absorption Spectrophotometer

INTRODUCTION

Sediments are free particles of soil found at the bottom of a water body, whether it be clay, sand, organic material, or silt. They originate from both erosion and decomposition of natural elements, animals, and plants. In aquatic ecosystems, sediments play important roles in the growth, evolution, and establishment of aquatic organisms (Enuneku *et al.*, 2018). Hence they are an integral part of the aquatic environment. Sediments are sinks for pollutants and the main receptacles in surface waters for contaminants from industrial discharges (He *et al.* 2016; Li *et al.* 2016; Nguyen *et al.* 2016; Peng *et al.* 2017). This inclination is as a result of adsorption, precipitation, diffusion processes, chemical reactions, biological activity and a combination of these phenomena (Ramirez *et al.*, 2005). The environmental conditions of a river system particularly sediment changes with the invasion of uncontrolled contaminants such as heavy metals. Thus, the presence of these metals in sediment can have adverse effects on aquatic life as well as man. This is because of the ecological dynamics of sediment which can be altered at any slight change in pH or redox potential. This property of sediments makes them to be considered as indicators of heavy metal pollution (Maroj and Padhy, 2014). Since sediments play a very important role in physicochemical and ecological dynamics, any change in toxic concentrations of heavy metal residues on the sediments will affect the natural aquatic life support systems. Pollution of aquatic ecosystem with heavy metals is ecologically significant because they cannot be totally eliminated from the reservoir even in the process of self-purification (Sharma, 2006, Imiuwa *et*

al., 2014). It is therefore imperative to assess sediment quality in order to understand heavy metal behavior and partitioning in the sediment matrix.

Before the 1980s, the contamination level of sediments was determined by comparing the concentration of a chemical in sampled sediments to “background” or reference values. This approach did not account for the types of biological resources in an aquatic environment or the concentration at which an adverse response would be observed in these organisms (Ingersoll and Wenning 2002). Sediment quality guidelines were then developed for use in assessing sediment quality, meaning contaminant concentrations that cause adverse effects. Sediment Quality Guidelines (SQGs) generally outline two concentration thresholds, one in which a toxic response is unlikely and one for which a toxic response is likely. The TEL is a sediment contamination concentration at which a toxic response has started to be observed in benthic organisms. The PEL is the concentration at which a large percentage of the benthic population shows a toxic response.

MATERIALS AND METHODS

Study area

Ikpoba River is centered at Lat 6.5°N and Long 5.8°E in Benin City, Edo State in South Nigeria. The study area is situated within the western littoral hydrological area of Nigeria (Akintola, 1986). Its headwater originates from North West of Benin City and flows north to south through the city (Benka-Coker and Ojior, 1995). The vegetation of Ikpoba River consists of rainforest which is secondary in nature and has been greatly subjected to deforestation and other anthropogenic influences. The study area is composed essentially of the secondary rainforest vegetation type and majorly composed of grasses, shrubs, epiphytic ferns, water hyacinth (*Eichornia carssipes*) palm trees (*Elaeis guinenses*), bamboo trees (*Bambusa bambusa*), and rubber tree (Ibezute *et al.*, 2016). The riparian communities are sparsely populated and their main activities are farming, fishing and palm-wine tapping. Industrial wastes and water from drainage channel are discharged into the river at several points especially at the Benin City storm water discharge point. Station 1 (6.4532°N, 5.6095°E) was at the Iguosa Stretch of the River, Station 2 (6.4513°N, 5.6162°E) was at Ewomore, Station 3 (6.4105°N, 5.6372°E) was at Ekosodin axis, Station 4 (6.4049°N, 5.6389°E) was at the Capitol directly under the bridge at the University of Benin, Station 5 (6.3761°N, 5.6461°E) was at Upper Lawani (storm water discharge point), station 6 (6.3517°N, 5.6467°E) was at the slaughter house and station 7 (6.3343°N, 5.6636°E) was at the Guinness Brewery.

Sample Collection and Analysis

Collection of Sediment Samples

Twenty-one (21) superficial sediment samples (0-5cm) were collected using a Van Veen Grab from October to December 2018. They were collected from seven stations of the river beginning from the source downwards as it traverses the city. The sampling stations were chosen based on the prevailing stresses including the Benin City storm water discharge point.

Chemical Analysis

Chemicals and reagents

All chemicals and reagents were analytical grade. Materials and reagents were used including 72% HNO₃ (BDH), 37% HCl (JHD). In order to construct the calibration curves, working standard

solutions for Cd, Pb, Cu, Ni, Fe and Zn were freshly prepared by diluting an appropriate aliquot of standard solutions containing 1000ppm with serial concentrations for each element using 0.1% HNO₃. Glassware and polyethylene containers were cleaned and soaked in 10% HNO₃ for 48 hours and then rinsed thoroughly with deionized water.

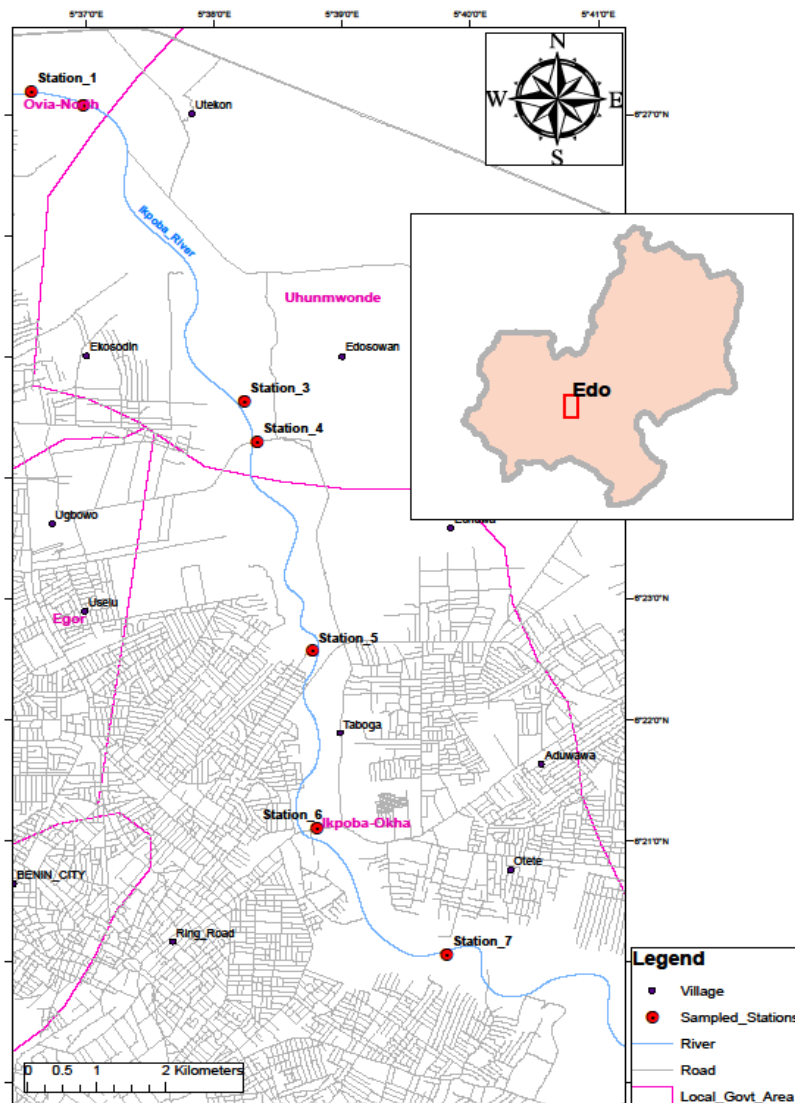


Figure 1: Map Showing Study Area

Sample digestion and heavy metal analysis

In the laboratory, the soil samples were air dried for 48 hours and grounded with ceramic mortar and pestle. Digestion of soil samples was carried out after the modified method of Likuku *et al.* 2013 and Massadeh *et al.* 2017). Then 1g of sample was digested in 10ml freshly prepared aqua regia (3:1, HNO₃ : HCl) in a hot sand bath on a hot plate for 45 minutes. It was allowed to cool. Twenty (20) ml of distilled water was then added. Then it was filtered through a whatman filter paper (110mm) into a 100ml standard flask. It was made up to mark with distilled water. Samples

were then analysed for heavy metals using atomic absorption spectrophotometer (Buck Scientific, 210 VGP).

Sediment quality guidelines (SQGs)

The consensus-based sediment quality guidelines (SQGs) were used in this study to assess the possible risk that would arise from heavy metal contamination in the area studied. Globally, several researchers have used SQGs as powerful tools for the assessment of sediment contamination by heavy metals (Varol *et al.*, 2011, Niu *et al.*, 2015). They are used to screen sediment contamination by comparing sediment contamination concentrations with the corresponding sediment quality guidelines. The comparison of metal concentrations in sediments with SQGs is necessary for estimating the likelihood that such sediments would be toxic to sediment fauna. Two types of SQGs developed for freshwater ecosystems (MacDonald *et al.*, 2000) were adopted in this study to assess the expected incidence of toxicity by heavy metals concentrations in sediments: (a) the threshold effects concentrations (TECs) below which harmful effects are unlikely to be observed and (b) the probable effects concentrations (PECs) above which harmful effects are likely to be observed.

RESULTS AND DISCUSSION

Figures 2a,b,c,d show the mean concentrations of Pb, Ni, Fe and Cu from September to October, 2018. The highest concentrations in these months were found in station 7 for Pb, Ni and Fe. The highest concentration of Cu was found in November and in station 4 (Figure 2d).

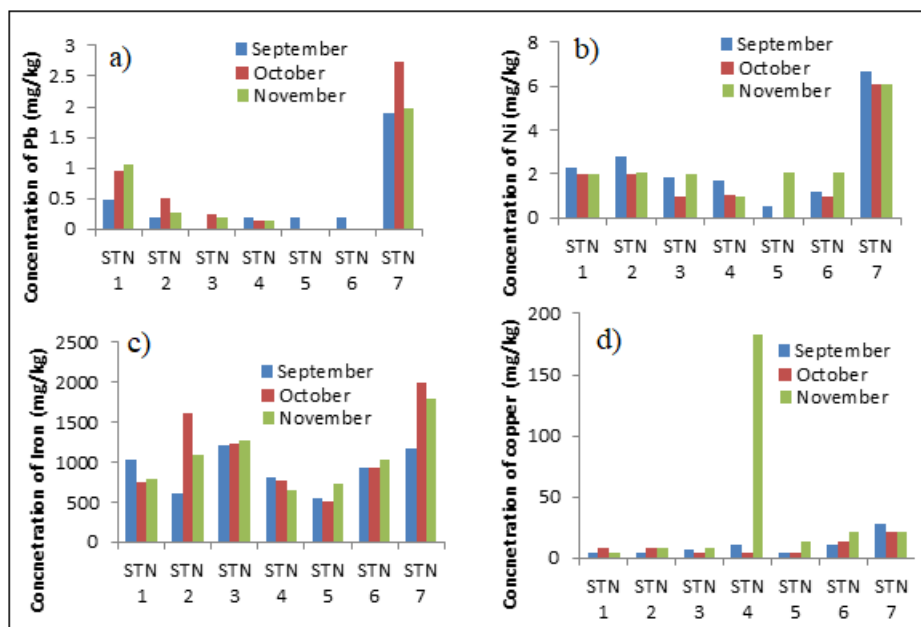


Figure 2: Spatial variation of a) Pb, b) Ni, c) Iron, and d) Copper in sediment of Ikpoba River between September and October 2018.

The mean \pm SD and range of heavy metals in the sediment of Ikpoba River are presented in Table 1. The highest mean concentration of Lead was in station 7 (2.20 mg/kg) while the lowest concentration was in station 5. The highest concentration of Ni was recorded in station 2 while the lowest was recorded in station 7. The highest concentration of iron (1651.85 mg/kg) was recorded in station 7 while the lowest (594.06 mg/kg) was in station 5. The highest concentration of Cu (66.17 mg/kg) was observed in station 4 while the lowest (5.81 mg/kg) was observed in station 1.

Cadmium was not observed in stations 1 to station 6. Mean cadmium concentration of 0.007 mg/kg was observed in station 7.

Table 1: Summary Table for heavy metal concentration in sediments of Ikpoba River between September and November, 2018.

Stations	Heavy metals (mg/kg)				
	Pb	Ni	Fe	Cu	Cd
Station 1					
Mean ± SD	0.83±0.30 ^b	2.10±0.16 ^b	857.82±159.45 ^{ab}	5.81±2.52	BDL
Min	0.48	2.00	748.66	4.36	
Max	1.05	2.28	1040.80	8.72	
Station 2					
Mean ± SD	0.32±0.16 ^a	2.29±0.44 ^b	1104.76±501.01 ^b	7.27±2.52	BDL
Min	0.19	2.02	613.90	4.36	
Max	0.50	2.80	1615.34	8.72	
Station 3					
Mean ± SD	0.15±0.13 ^a	1.61±0.54 ^{ab}	1236.28±29.64 ^{bc}	6.63±2.19	BDL
Min	0.00	1.00	1208.80	4.36	
Max	0.25	2.02	1267.69	8.72	
Station 4					
Mean ± SD	0.17±0.03 ^a	1.23±0.39 ^{ab}	746.53±81.11 ^{ab}	66.17±101.36	BDL
Min	0.15	1.00	654.38	4.36	
Max	0.20	1.68	807.10	183.14	
Station 5					
Mean ± SD	0.06±0.11 ^a	0.87±1.10 ^a	594.06±115.49 ^a	7.27±5.03	BDL
Min	0.00	0.00	507.08	4.36	
Max	0.19	2.10	725.09	13.08	
Station 6					
Mean ± SD	0.07±0.12 ^a	0.57±0.33 ^{ab}	965.97±62.76 ^{bc}	15.29±5.73	BDL
Min	0.00	1.00	922.30	11.00	
Max	0.20	2.07	1037.89	21.80	
Station 7					
Mean ± SD	2.20±0.46 ^c	0.35±0.20 ^c	1651.85±426.97 ^c	23.87±3.58	0.007±0.01
Min	1.90	6.07	1171.00	21.80	0.00
Max	2.73	6.68	1986.55	28.00	0.02
P value	p < 0.001	p < 0.001	p < 0.05	p > 0.05	

P < 0.001 highly significant, p < 0.05 significant. Similar superscripts indicates no significant difference based on DMR test

Comparison of the heavy metal concentration with the sediment quality guidelines are depicted in table 2. Table 2 shows that the values for Pb, Ni, Fe and Cd were well below threshold effects concentrations (TEC). For Cu, 66.77% of the values were below TEC while 33.33% of the values exceeded threshold probable effects concentrations (PEC).

Sediments are the main repository of pollutants including heavy metals. The level of accumulation of heavy metals in water and sediments is a function of the source and type of pollutants being

discharged into the water body. Analyzing sediment concentrations of heavy metals give a deeper insight into the long-term pollution state of the aquatic environment (Yau and Gray, 2005).

Table 2: A comparison of threshold effects concentration (TEC) with probable effects concentration (PEC) with concentrations obtained in this study.

		Pb	Ni	Fe	Cu	Cd
SQGs	TEC	35.8	22.7	-	31.6	0.99
	PEC	128	48.6	-	4.98	4.98
Measured values in this study	Mean	0.54	2.26	1022.47	18.9	<DL
STN 1	<TEC	100%	100%	-	100%	0%
	>PEC	0%	0%	-	0%	0%
STN 2	<TEC	100%	100%	-	100%	0%
	>PEC	0%	0%	-	0%	0%
STN 3	<TEC	100%	100%	-	100%	0%
	>PEC	0%	0%	-	0%	0%
STN 4	<TEC	100%	100%	-	66.77%	0%
	>PEC	0%	0%	-	33.33%	0%
STN 5	<TEC	100%	100%	-	100%	0%
	>PEC	0%	0%	-	0%	0%
STN 6	<TEC	100%	100%	-	100%	0%
	>PEC	0%	0%	-	0%	0%
STN 7	<TEC	100%	100%	-	100%	0%
	>PEC	0%	0%	-	0%	0%

Percentage of samples above or below TEC or PEC

Lead (Pb) is a persistent heavy metal which has been characterized as a priority hazardous substance (Sfakianakis *et al.*, 2015). The concentration and bioavailability of Pb is mainly dependent on the absorption into the sediments and the natural organic matter content of the water as well as the pH, alkalinity and hardness (Mager, 2011, Sepe *et al.*, 2003). Pb concentrations in this study ranged between 0.00 mg/kg to 2.20 mg/kg with the lowest (0.06 mg/kg) and highest (2.20 mg/kg) mean concentrations observed in stations 5 (the storm water) and stations 7 (Guinness Brewery) respectively. A highly significant ($p < 0.001$) spatial variation was observed in the Pb concentration of the seven stations. *A posteriori*' DMR test revealed that stations 1 and 7 had significantly higher Pb concentrations than stations 2, 3, 4, 5 and 6 who had similar mean concentrations. A higher lead concentration of 3.95 mg/kg was reported for Pb in sediment from Bonny River, Nigeria by Bubu *et al.* (2017).

Nickel (Ni) is a ubiquitous trace metal and occurs in soil, water, air, and in the biosphere. Ni is released during Ni mining and by industries that convert scrap or new Ni into alloys or Ni compounds (Authman *et al.*, 2015). Mean Ni concentrations observed were 2.10 mg/kg in station 1, 2.29 mg/kg in station 2, 1.61 mg/kg in station 3, 1.23 mg/kg in station 4, 0.87 mg/kg in station 5, 0.57 mg/kg in station 6 and 0.35 mg/kg in station 7. Ni was below detectable limits in station 5

in October while maximum concentration was observed in station 7 in that same month showing highly significant ($p < 0.001$) spatial variation. *A posteriori*' DMR test revealed that stations 7 had significantly higher Ni concentrations than the other stations. Imiuwa *et al.*, (2014) reported the highest value of 0.19mg/kg for Ni in sediments of Ikpoba River.

The concentration of Fe in the seven stations showed significant spatial variation. *A posteriori*' DMR test revealed that stations 7 had significantly higher Fe concentrations than the other stations. Fe values ranged between 507.08 mg/kg to 1986.55 mg/kg with the highest (1651.85 mg/kg) and lowest (594.06 mg/kg) mean concentrations observed in station 7 and station 5 respectively. Fe is prevalent component of industrial and mining effluents that are often discharged into aquatic environments. Ighariemu *et al.* (2019) reported a higher mean of 2143.23 mg/kg for Fe in sediments of Ikoli Creek, Bayelsa state, Nigeria.

According to Zaki *et al.*, (2012) domestic sources are the main contributors of Cu element in the ecosystems. The highest mean Cu concentration of 66.17 mg/kg was observed in station 4 (capitol) while the lowest (6.63 mg/kg) was in station 2 (Evwomore). No significant spatial variation was observed in the mean Cu concentration. Imiuwa *et al.*, (2014) reported the highest mean value of 8.04 mg/kg for Cu in sediments of Ikpoba River. This means that there has likely been an elevation in Cu concentrations in Ikpobal River sediments over the last six years. Copper has been known to affect various blood parameters, growth, behaviour, enzyme activity, and reproduction in aquatic animals.

Cd is a non-essential and non-degradable cumulative pollutant capable of altering aquatic trophic levels for centuries (Sorenson, 1991, Authman *et al.*, 2015). Cd was below detectable limits in all the stations throughout the period of sampling except in station 7 where 0.02 mg/kg was recorded in September. However, Olatunde *et al.* (2014) reported a range of 0.03 and 0.66 mg/kg for Cd in sediments of Ogun River within Abeokuta, south-western Nigeria.

Generally, heavy metal concentration in the sediments of Ikpoba River revealed an elevated concentration of all the metals at station 7 (Guinness Brewery). This can be attributed to the release of effluents from the Brewery aligning with the reports of Imoobe and Okoye, (2011).

Results from this study were tested with threshold effect concentration (TEC) with probable effects concentration (PEC) to determine the toxicological potentials of the sediment to aquatic fauna. The values for Pb, Ni, Fe and Cd were well below TEC. For Cu, 66.77% of the values were below TEC while 33.33% of the values exceeded PEC. This implies that if pollution of station 4 with Cu continues, the toxicological potentials of the sediment with respect to Cu pollution may be severe.

CONCLUSION

In this study, varying concentrations of heavy metals occurred in the stations of Ikpoba River sampled. Heavy metal levels in the sediments of the river showed an elevated concentration of all the metals at station 7 (Guinness Brewery). This can be attributed to the release of effluents from the Brewery. Metal concentrations obtained were compared with the consensus-based sediment quality guidelines. The values for Pb, Ni, Fe and Cd were well below TEC. For Cu, 66.77% of the values were below TEC while 33.33% of the values exceeded PEC. This implies that if contamination of station 4 with Cu continues, the toxicological potentials of the sediment with

respect to Cu pollution may be severe as copper has been known to affect various blood parameters, growth, behaviour, enzyme activity, and reproduction in aquatic animals.

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