### Assessment of Heavy Metal Pollution in Surface Water of the Qua Iboe River, Akwa Ibom State, Nigeria

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Received 05 March 2020/Accepted 30 April 2020/Published online: 10 April 2020

Abstract Concentrations of Cd, Pb, Cr, Co, Cu, Se and Ni ions in Qua Iboe River system were assessed by analysing water samples collected from the river at Iwuochang, Mkpanak, Ukpenekang, Atabong, Eketai, and Marina stations. The results obtained indicate that the overall mean concentrations for Cd. Pb, Cr, Co, Cu, Se and Ni ions in the samples were 39.78±34.24. 44.22±44.71. 24.75±21.15, 48.64±42.19, 64±62.33, 1.15±0.40 and 55.39±68.07 µg/L, respectively. These concentrations were higher than NESREA's limits for surface waters. On comparing these values with the WHO standard for potable water, it was observed that the mean concentrations were higher than the acceptable limits. The coefficient of variations of the metals were also high with high degree of fluctuations in metal concentrations from station to station. Findings from this study show that Qua Iboe River, at the time of the present study, was polluted especially with respect to cadmium, lead and nickel. Copper was the most abundant metal ion while selenium had the lowest score. Highest concentrations of all the heavy metal ions were observed at Atabong and the general trend was The Cu>Ni>Co>Cd>Cr>Pb>Se. conclusion deduced from the present study that the pollution load of the Qua Iboe River system is on the increase corroborates previous reports on the river. This state of affairs portends serious threat to the health of this aquatic ecosystem and humans within the catchment f the river who depend on the river for conford

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heavy metal ions

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### 1.0 Introduction

The presence of heavy metals above tolerance concentrations in most of the water bodies has become a major threat to plants, animals and humans due to their toxicity and bioaccumulation tendencies and subsequent transfer of the metals to higher organisms through the food chain (Abu and Egenonu, 2008; Ademoroti, 1996; Nduka et al., 2008; Odukuma and Okpokwasili, 1997; Rim-Rukeh et al., 2006; Udotong et al., 2008). Water is vital for our daily living and for several domestic and industrial purposes. However, one of the greatest environmental challenges is the demand for good quality water, which is free from contaminations from natural, anthropogenic and industrial sources (Obafemi, et al., 2012; Onojake et al., 2011). In view of the need for portable water supply to meet all areas of domestic and industrial needs, the need for routine analysis of water from different sources in our environment should be emphasized. Contamination of water body can be point source and non-point source. Point source pollution is most severe in stagnant waters but its effect can be transported to great distances in moving water bodies such as rivers, seas, etc. The

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impact other components of the environment. The river system can be affected by point source and non-point source pollutants, indicating that there exist dynamic changes in the quality of the river system due to changes in season, industrialization, urbanization, natural processes and other factors (Abdul *et al.*, 2019;Eddy *et al*, ,2004,2005; Eddy and Ukpong, 2004,2005). Water bodies can be assessed in terms of physicochemical parameters, organoleptic properties, pesticides and heavy metals (Davies et al., 2006). However, heavy metal status of water bodies should be routinely investigated because they are non-biodegradable and most heavy metals are toxic above certain concentrations. They can be accumulated in an organism for a long time and can therefore be transferred from lower to higher organisms through the food chain (Odoemelam and Eddy, 2009; Sikoki et al., 2015). In view of the importance of establishing the pollution status of a river system, several rivers have monitored for heavy metal been levels. Shanbehzadeh, et al., (2024) studied levels of heavy metal pollution in Temi River in Iran and found that concentrations of Cd, Cr, Cu, Fe, Pb, Ni and Zn ions were higher at downstream sampling stations than upstream sampling stations. Eddy et al. (2004) and Eddy and Ukpong (2005) studied levels and distributions of heavy metals in the Cross River at Calabar and Oron. Comparative examination of the two sets of results they obtained indicated that lower concentrations were mostly recorded at the lower arm of the river except where pollution was majorly of anthropogenic or industrial origin. In the Qua Iboe River system, some studies have been reported. For example, Odiongenyi (2017) reported relatively high concentration of lead, cadmium, nickel and vanadium in Ibeno section of the Oua Iboe River and attributed it to industrial activities from Mobile Nigeria Plc and some anthropogenic activities. (2004) reported Ebong *et al*. significant concentrations of Pb, Ni, V, Fe, Cu and Cd ions in some sections of the Qua Iboe River Estuary and indicated that the Estuary system was polluted with reference to nickel and lead ions. They reported that wet season concentrations were higher than dry season concentrations. However, in their study, Dan et al. (2014) reported that during wet season, Cd, Cu, Fe, Pb and Zn showed minor surface enrichments while Cr and Ni showed no enrichment. During dry season, Cd, Fe and Zn were moderately enriched in surface water while Cr, Cu, Pb and Ni were not enriched. In view of the fact that concentration of heavy metals in a river system (including Qua Iboe River) is not static but dynamic thus changing continually, it is pertinent to always have routine estimation of the heavy metal concentrations at different points of the river system. Some previous studies on Qua Iboe River indicate that the pollution load on the river is constantly increasing (Ebong et



al., 2004; Uwah et al., 2013; Dan et al., 2014;

Odiongenyi, 2017). Therefore, the present work was designed to assess the status of heavy metal concentrations at Iwuochang, Mkpanak, Ukpenekang, Atabong, Eketai, and Marina, which are sections close to some point source pollution. Knowledge of point source pollution can guide the prediction of the overall quality of the river system because pollution loads are always heavier at point source than non-point source (Carpenter et al., 1998).

### 2.0 Materials and Methods 2.1 Study area

Qua Iboe River is a confluence of rivers from different sources rising from Umuahia in Abia State. and flowing through many communities including Eket and Ibeno in Akwa Ibom State into the Gulf of Guinea (Atlantic Ocean). The river receives inputs of municipal wastes, municipal/urban runoff, untreated industrial discharges from food processing industries, as well as other solid wastes. The river system serves as a major source of water for the predominantly rural population of the area whose major occupation is commercial fish farming. The Eket/Ibeno community plays host to the multinational oil giant, Exxon-Mobil. The study area lies between latitudes 4°32' N and 4°39' N, and longitudes 7°55'E and 7°59'E. Six (6) stations were selected for the study, these include: Iwuochang (4°34'N, 7°58'E), Mkpanak (4°32'N, 7°59'E), Ukpenekang (4°34'N, 7°58'E), Atabong (4°39'N, 7°55'E), Eketai (4°36'N, 7°56'E) and Marina (4°37'N, 7°55'E). The map of the study area is shown in Fig. 1.

## Fig. 1; Map of the study area showing sampling stations along Qua Iboe River

### 2.3 Sampling

The water samples were collected between April 2018 and March 2019 from six (6) different locations along the Qua Iboe River. Water samples were collected with polyethylene plastic bottles which were pre-washed and soaked with 0.1M HNO<sub>3</sub> solution for nine (9) hours. Samples were placed in an iced-chest and taken to the laboratory. In the laboratory they were filtered and preserved by adding 2.0 ml of 0.1 M HNO<sub>3</sub> solution and kept at <  $4^{\circ}$ C in a refrigerator until time for analysis. Metal ion concentrations were estimated with Atomic

Absorption Spectrophotometer (AAS) equipped with hollow cathode lamp and graphite furnace (Greenberge *et al.*, 1992).

### **3.0** Results and Discussion

Mean concentrations of Cd, Pb, Cr, Co, Cu, Se and Ni ions in water samples from Iwuchang, Mkpanak, Ukpenekan, Atabong, Eketai and Marina are recorded in Table 1. Mean concentrations of cadmium ions scaled through the least value of 4.83  $\mu$ g/l (at Mkpanak), to 5.17  $\mu$ g/l (at Ukpenekang), 7.00  $\mu$ g/l (at Eketai), 57.50  $\mu$ g/l (at Marina), 93.50  $\mu$ g/l (at Iwuochang) and highest at Atabong (97.3 3  $\mu$ g/l.). The WHO standard for cadmium in water is 10  $\mu$ g/L, therefore water samples from Marina, Iwuochang and Atabong were polluted with reference to cadmium ions.

Mean concentrations of nickel ions in the water samples from Qua Iboe River ranged from  $8\pm2.45$  (at Eketai) to  $170.33\pm48.03 \ \mu\text{g/L}$  (measured at Atabong). Other mean concentrations determined were  $10.67\pm3.01 \ \mu\text{g/L}$  (Iwuochang),  $24.33\pm7.97 \ \mu\text{g/L}$  (Mkpanak),  $14.33\pm4.55 \ \mu\text{g/L}$  (Ukpenekang) and  $104.67\pm54.65 \ \mu\text{g/L}$  (Marina). Therefore, at the time of the present study, the Qua Iboe River was polluted with respect to nickel ions except at Eketai.

Table 1: Heavy metal ions in surface water from Qua Iboe River in µg/L

Station	Cd	Pb	Cr	Со	Cu	Se	Ni
Iwuochang	93.5±31.68	$15\pm6.60$	35.33±10.75	$13.50 \pm 6.47$	31.50±15.57	$1.22 \pm 0.29$	$10.67 \pm 3.01$
Mkpanak	4.83±1.47	$21.83 \pm 7.11$	$14.50 {\pm} 5.01$	40±16.05	41.17±12.59	$1.028 \pm 0.2$	24.33±7.97
						0	
Ukpenekang	$5.17 \pm 3.71$	$16.17 \pm 4.96$	$16.17 \pm 6.37$	27.17±13.24	30.67±10.56	$1.07 \pm 0.50$	$14.33 \pm 4.55$
Atabong	97.33±27.88	62±24.67	$95.83 \pm 30.91$	$105.33 \pm 37.18$	$176.33 \pm 65.95$	$1.24 \pm 0.36$	$170.33 \pm 48.03$
Eketai	7±3.16	6±4	28±34.65	15.17±17.55	$17.5 \pm 6.47$	$1.24 \pm 0.48$	8±2.45
Marina	57.5±17.85	27.5±8.87	$48.83 \pm 19.34$	90.67±29.11	86.83±26.47	$1.12 \pm 0.58$	$104.67 \pm 54.65$
Mean± SD	$44.22 \pm 44.71$	24.75±21.15	39.78±34.24	48.64±42.19	64±62.33.00	$1.15 \pm 0.40$	55.39±68.07
	(101.11)	(85.45)	(86.07)	(86.74)	(97.39)	(34.78)	(122.89)
Range	1-141	2-97	5-147	3-164	11-271	0.07-1.96	5-241
WHO(µg/L)	10	20	100	-	1300	50	20

As presented in Table 1, the concentration of lead ions determined from Qua Iboe River was lowest at Eketai (6.00±4.00 µg/l) and highest at Atabong  $(62.00\pm24.67 \mu g/l)$ . Mean lead ion concentrations at other stations were 21.83±7.11, 16.17±4.96 and 27.5±8.87µg/L at Mkpanank, Ukpenekang, and Marina, respectively. WHO standard for concentration of lead in water is 20 µg/L. Therefore, the water was polluted with respect to lead at all the stations except Eketai. The overall mean concentration still reflected lead pollution in all the stations sampled. This pollution status with respect to lead ion had earlier been observed by Ebong et al. (2004) and Odiongenyi (2017).

WHO standard for chromium ion in water is 100  $\mu$ g/L. Mean concentration of chromium ions in all the reference stations were below this limit. Therefore, the river was not contaminated severely with reference to chromium ion at the time of this investigation. The highest mean concentration of chromium ion was recorded as 95.83  $\mu$ g/L at Atabong with a wide variability of 30.91. This variability was, however, higher than the mean concentrations observed at Mkpanak (14.50±5.01  $\mu$ g/L), Ukpenekang (16.17±6.37  $\mu$ g/L), Eketai (28±34.65  $\mu$ g/L). This implies that measured concentrations of chromium ions in the water



samples from these locations were widely distributed or spread from the mean, indicating strong positive skewness.

Mean concentrations of cobalt ion in water samples were  $13.50\pm6.47$ ,  $40\pm16.05$ ,  $27.17\pm13.24$ ,  $105.33\pm37.18$ ,  $15.17\pm17.55$  and  $90.67\pm29.11 \mu g/L$ for water samples from Iwuochang, Mkpanank, Ukpenekang, Atabong, Eketai and Marina, respectively. The highest mean concentration of cobalt ion was determined at Atabong and the lowest at Iwuochang. There is no strong regulations or standards that limits the concentration of cobalt ions at the present. Therefore, a categorical statement can not be pronounced about its toxicity in water.

The WHO standard for copper is 1300  $\mu$ g/L. The mean concentrations of copper ions in all the tested water samples were below this limit indicating that the water was not polluted with respect to copper ion. The highest concentration of copper was measured at Atabong (176.33±65.95  $\mu$ g/L) and least at Eketai (17.5±6.47  $\mu$ g/L). Other mean concentrations were 31.50±15.57, 41.17±12.59, 30.67±10.56 and 86.83±26.47  $\mu$ g/L at Iwuochang, Mkpanak, Ukpenekang and Marina, respectively.

Mean concentrations of selenium ion in the water samples from Qua Iboe River were  $1.22\pm0.29$ ,  $1.028\pm0.20$ ,  $1.07\pm0.50$ ,  $1.24\pm0.36$ ,  $1.24\pm0.48$  and 1.12±0.58 µg/L for water samples from Iwuochang, Mkpanak, Ukpennekang, Atabong, Ektai and Marina sampling stations, respectively. The highest mean concentration (1.24  $\mu$ g/L) was observed at both Atabong and Eketai stations while the least (1.028 µg/L) was observed at Mkpanak. Measured concentrations at all stations were below the WHO standard for water. Therefore, at present, selenium ion pollution is not a threat to the Qua Iboe River. The pollution of the Qua Iboe River system with nickel ion established in this work had earlier been confirmed by Ebong et al. (2004) and Odiongenyi attributed the (2017),who pollution to anthropogenic and industrial waste.

Table 2 presents values of inter-correlationship calculated for the mean concentrations of the heavy metal ions investigated.

# Table 2: Pearson correlation coefficients of tracemetals of surface water samples from Qua IboeRiver system

<i>(</i> <b>)</b> 1				
<i>C</i> 1				
60 1				
6 <sup>a</sup> 1				
.740 <sup>a</sup>	1			
8a .868a	.899ª	1		
05 0.248	0.059	0.144	1	
.783 <sup>a</sup>	.826ª	.867ª	0.165	1
_				Ra         .783a         .826a         .867a         0.165           s significant at the 0.05 level (2 tail)

Significant correlation relationships were observed between lead and all the heavy metal ions examined except Se. Cadmium correlated significantly with Cr and Cu. Similarly chromium correlated significantly with Co, Cu and Ni ions. Correlation between Cu and Ni ion was also positive and significant. The observed positive and significant correlations between some of these metals suggest that they might have been introduce from a common source where the metal ions coexisted together (Edori et al., 2019; Nnaji *et al.*, 2019)

### 4.0 Conclusions

The results of the study reveal that The Qua Iboe River was polluted with respect to lead, cadmium and nickel. The pollution status had long been established by earlier studies on the river system indicating that pollution load to the river was increasing. If adequate provision is not made to control discharge of waste from domestic and industrial sources, now and in future, this might pose serious health problem to the aquatic ecosystem and human beings within the catchment of Qua Iboe River through contamination of the food chain.

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