

Spatio-temporal Variations in Heavy Metal Concentrations in Sediment of Qua Iboe River Estuary, Nigeria

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Abstract—The concentrations of heavy metals in sediments of Qua Iboe River Estuary (QIRE) were monitored at four different sampling locations in wet and dry seasons. A preliminary survey to determine the four sampling stations along the river continuum showed that the area spanned between <0.1‰ salinity at the control station and 21.5‰ at the fourth station along the river continuum. A preliminary survey to determine the four sampling locations along the river estuary showed variations in salinity and other physicochemical parameters. The estuary was found to be polluted with heavy metals from point and nonpoint sources at varying degrees. Mean values of 7.80 mg/kg, 4.97 mg/kg and 2.80 mg/kg of nickel were obtained for sediment samples from Douglas creek, Qua Iboe and Atlantic sampling locations, respectively in the dry season. The wet season nickel concentrations were however lower. The entire study area was grossly contaminated by iron. At Douglas creek, the concentration of iron in sediment was 9274 ± 9.54 mg/kg while copper, nickel, lead and vanadium were <0.5 mg/kg each as compared to iron. Bioaccumulation was therefore suspected within the study area as values of 31.00 ± 0.79 , 36.00 ± 0.10 and 55.00 ± 0.05 mg/kg of zinc were recorded in sediment at Douglas creek, Atlantic and the control sampling locations. The results from this study showed that the source of these heavy metals were from point sources like the corrosion of metal steel pipes from old bridges as well as oily sludge wastes from the Qua Iboe Terminal / tank farm located within the vicinity of the study area.

Keywords—Heavy metal, Qua Iboe River Estuary, seasonal variations, sediment.

I. INTRODUCTION

ENVIRONMENTAL problems associated with heavy metals in aquatic ecosystem have been of concern for many years now. These include the impact on nontarget organisms, bioaccumulation and persistence in the natural environment [1]. Today, human / industrial activities introduce toxic substances either deliberately or inadvertently into the environment which may affect the physical, biological and chemical properties of the environment [2]. As a result of inadequate legislation, poor enforcement, and limited research and monitoring facilities, most countries of the world and their people are susceptible to the consequences of the incorrect

handling and disposal of undesirable synthetic compounds, metal pollutants and a wide variety of other pollutants. Petroleum exploration and production (E & P) activities have been identified as one of the major activities that pollute the aquatic environment and resources. The wastes generated from the production activities have been evaluated [3] and components identified include heavy metals.

The Qua Iboe River estuary is currently hosting some industries whose wastes, if not properly managed, could impact the environment adversely. The operational base of Mobil Producing Nigeria Unlimited (MPNU), Nigeria's largest oil producer and the largest condensate producer in Africa is located in Qua Iboe Terminal (QIT) and the offshore areas of Ibendo Local Government Area of Akwa Ibom State [3]. The production platforms (PP) of MPNU are located along Akwa Ibom State coastal waters stretching from Oron and Mbo Local Government Areas to Ikot Abasi Local Government coastal waters [4]. Apart from the PP, flowstations, pipelines, tankers, a loading jetty and gas flare stations are also located in this area.

It is reported that in a crude oil producing field, the volume of water produced with crude oil can be more than ten times the volume of hydrocarbon produced [5]. Consequently, MPNU having produced over three billion barrels of crude oil in their over three decades of existence, may have produced and discharged into the environment more than 30 billion barrels of produced water. This and the total volumes of other oily wastes dumped into the environment from the early seventies when oil production started till date have caused damages to our environment. These wastes introduce heavy metals into the aquatic ecosystem.

Although there are no empirical data to show annual catches and values of harvesting of fish, fluctuation in captures and decreasing sizes of fish, personal communications with fisherfolks however give evidences of declining stocks from habitat degradation. Some studies have been carried out on the incidence of accidental oil spillages and subsequent contamination of the biota in the coastal waters of Rivers, Delta, Imo and Edo States [6], levels of toxic metal in parts of Akwa Ibom State [7], variations in oxygen and related pollution parameters in Itu [8] and toxicity of heavy metals and insecticide in the cross river system in Oku Iboku [9]. Little or no work has been done to monitor the distribution of the heavy metals in sediment of the Qua Iboe River estuary. This research was undertaken to evaluate the

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heavy metals concentrations of the sediment in the Qua Iboe River Estuary.

II. MATERIALS AND METHODS

A. Description of Study Area

The study area is an extensive coastal area situated at the extreme south of Akwa Ibom State (Southern Nigeria). The Qua Iboe river empties into the South East Atlantic Ocean [3]. The estuary lies within latitude 40 30' to 40 45' N and longitude 70 30' to 80 00' E on the South Eastern Nigerian coastline. It is a mesotidal estuary having a tidal amplitude of 1m and 3m at neap and spring phases respectively [10].

Four sampling stations were chosen for this study and were approximately equidistant from each other. The stations were chosen to show the gradation of physical and chemical characteristics of the river estuary in order to reflect the concept of river continuum. To choose the sampling stations, a series of preliminary investigations were carried out to determine the suitability of the stations in line with the objectives of the study. The four sampling stations and their coordinates are shown in Table I.

TABLE I
DESCRIPTION OF THE FOUR SAMPLING STATIONS

S/N	Sample Station	Description of location	GPS Coordinates
1	I	Douglas Creek	N 04' 33' 182" E 008' 00' 152"
2	II	Douglas creek/ Qua Iboe River mouth	N 04' 33' 107" E 007' 59' 366"
3	III	Atlantic Ocean/ Mouth of Qua Iboe River	N 04' 32' 712" E 007' 59' 358"
4	IV (Control)	Qua Iboe River at Eket-Ikot Abasi bridge head	N 04' 38' 371" E 007' 54' 891"

For convenience sampling locations II and III will be referred to as Qua Iboe and Atlantic, respectively

B. Physicochemical Characterization of Sampling Sites

The physicochemical parameters of Qua Iboe River (QIR) estuary water samples at the four designated sampling stations studied were pH (hydrogen ions concentration), total dissolved solids (TDS), dissolved oxygen (DO), salinity, temperature, conductivity and turbidity. These parameters were determined *in situ* using a portable sensitive water quality checker (PHOX system LTD, UK PATENT N 999, 909, type N903 system).

C. Sediment Samples Collection and Preparation

Mangrove sediment samples were collected as in [11]. The sediment samples were collected at each of the designated stations using Eckman grab sampler and subsampled into labeled polythene bags and transported to the laboratory. In the laboratory the sediment samples were dried and ground to pass 0.22µm sieve. This was digested according to [12].

The digests were aspirated into the atomic absorption spectrophotometer (AAS) with appropriate cathode lamps for each metal after adjusting the instrument to appropriate wavelength at zero reading point in each case. The results of the analysis were recorded as R values in the readout columns of the instrument and later converted to mg L⁻¹ (ppm) using

the formula $\text{mg L}^{-1} (\text{ppm}) = \frac{R \times D \times V}{Wt}$ where D is the dilution factor, V is the volume of the digest prepared and Wt is the dry weight of the sediment originally taken for digestion.

III. RESULTS AND DISCUSSION

A. Physicochemical Characteristics of Sampling Sites

The physicochemical parameters of water from the sampling site are as shown in Table II [13]. Whereas the temperature of the water from Douglas Creek and Qua Iboe River was 30.8°C, the temperature of water at Atlantic was 31.0°C. The temperature of 28.4°C was recorded at the control station. There was much variation in the concentrations of total dissolved solids (TDS). The value at Douglas creek was 1,412 mg/L while a higher value (1507 mg/L) was obtained at the Atlantic Ocean and a very minimal value of 7.5mg/L was obtained at the control site. Dissolved oxygen was highest at the control site (7.1 mg/L) whereas DO of range 6.3 – 6.5 mg/L was obtained for Douglas creek, Qua Iboe river and Atlantic. The pH was slightly acidic at the control site (6.35) and slightly alkaline (7.75) at Douglas creek while it was much more alkaline at Qua Iboe river and Atlantic (8.2 and 8.3 respectively). The turbidity was less at control site (30 FTU), least at Douglas creek (16 FTU) and highest at Atlantic Ocean (110 FTU). The conductivity was only 11 µs/cm at the control site, 15,500 µs/cm at Douglas creek, double the value at Atlantic (33,200 µs/cm) and 2,800 µs/cm at the Qua Iboe river. Salinity was least at the control site (<0.1 per cent) and increased progressively towards the Atlantic with values of 9.0, 13.0 and 21.5 for Douglas creek, Qua Iboe river and Atlantic respectively. The above results showed that each of the four (4) sampling stations had different physicochemical characteristics.

TABLE II
PHYSICOCHEMICAL PARAMETERS OF WATER FROM STUDY AREA

Sampling stations	TDS mg/L	Temp °C	DO Mg/L	pH	Turb FTU	Cond Us/cm	Sal ‰
Control	7.5	28.4	7.1	6.35	30	11	<0.1
DOUGLAS CREEK	1,412	30.8	6.5	7.75	16	15,500	9.0
QUA IBOE RIVER	1,117	30.8	6.4	8.2	47	2,800	13.0
ATLANTIC	1,507	31.0	6.3	8.3	110	33,200	21.5

ftu = formazin turbidity unit

B. Heavy Metal Concentration in Sediment from the Qua Iboe River Estuary

Results of heavy metal contents in sediment samples from the four designated sampling stations in the dry season are shown in Table III. The concentration of nickel in sediment of Douglas creek was 7.80 ± 0.20 mg/kg while zinc had the value of 31.00 ± 0.79 mg/kg and iron concentration was very high with a value of $8,700.00 \pm 4.36$ mg/kg. The concentrations of copper, lead and vanadium at Douglas creek were below detectable limit. The concentrations of heavy metals in sediment from the four sampling locations in the wet season were as summarized in Table IV. At Douglas creek location,

zinc was found to be present in the sediment at a concentration of 14.90 ± 0.53 mg/kg. Iron concentration on the other hand was $9,274 \pm 9.54$ mg/kg while copper, lead, nickel and vanadium was found to be below the detectable limit.

The result obtained at the Qua Iboe station in the dry season (Table III) showed that the concentration of nickel in the sediment was 4.97 ± 0.04 mg/kg. The value for zinc was 22.00 ± 1.00 mg/kg while iron was $15,390 \pm 4.00$ mg/kg. Copper, lead and vanadium were not detected in the samples. The heavy metal concentrations in the sediment at the Qua Iboe sampling stations in the wet season are shown in Table IV. Copper had a mean value of 1.00 ± 0.27 mg/kg while the concentration of nickel was 3.60 ± 0.46 mg/kg. The concentration of zinc was 27.10 ± 0.36 mg/kg while iron had a concentration of $2,179 \pm 7.94$ mg/kg. Lead and vanadium were however, below detectable limits.

At the Atlantic sampling site in the dry season (Table III), mean values of 2.80 ± 0.56 , 36.00 ± 0.10 and $22,200.00 \pm 19.00$ mg/kg were obtained in the sediment for nickel, zinc and iron. Copper, lead and vanadium concentrations were below detectable limits. In the wet season, the sediment concentrations of copper, nickel, zinc and iron were 4.00 ± 0.53 , 6.80 ± 0.56 , 33.6 ± 0.75 and $1,680 \pm 10.00$ mg/kg, respectively. Lead and vanadium were below detectable limits.

The results obtained for the control site in the dry season shown in Table III indicated that nickel in the sediment was 0.15 ± 0.05 mg/kg. Zinc was present at a concentration of 55.00 ± 0.05 mg/kg while iron was as high as $24,700.00 \pm 5.0$ mg/kg in the sediment at this site. Copper, lead and vanadium were below the detectable limits. In the wet season at the control sampling station (Table IV), zinc concentration was 40.1 ± 0.46 mg/kg while iron was seen to be $7,008 \pm 3.00$

mg/kg. Copper, lead, nickel and vanadium were below detectable limit in the control sediment.

Sediments have been used extensively as indicators of chronological pollution of coastal areas [14]. Recent studies in coastal wetlands have successfully developed chronologies of metal additions [15]. One of the consistent findings of many of these studies is the recent decrease in heavy metal concentrations in sediments [16]. The present study however reveals the concentrations of lead in the two seasons studied (wet and dry season) to be constantly low. Concentrations of metals in sediments showed a spread of values which were related to the different sampling locations. Generally, the area was found to be free from pollution regarding the presence of copper, lead and vanadium. Sublethal effects should however not be ruled out. These results are similar to levels of metals in Kuwait near shore sediments reported by [17] and within the range reported from sediments in many polluted areas of the world. From the results of this study, Qua Iboe river estuary can be said to be polluted by some heavy metals. Notable among them is nickel found to be high in the dry season sediment samples. While the mean values of 7.80 ± 0.02 mg/kg, 4.97 ± 0.04 mg/kg and 2.80 ± 0.56 mg/kg of nickel were obtained for Douglas creek, Qua Iboe and Atlantic, respectively in this work in the dry season, [18] recorded highest nickel level of 0.03mg/kg in the sediment of the lower Bonny estuary. Also, [19] recorded sediment nickel content of 14.8mg/kg, 135.3mg/kg and 76.7mg/kg for the minimum, maximum and mean values in the sampling sites along the Indus River in Pakistan. The order of pollution of these sediment samples would then be Indus river samples > Qua Iboe river estuary > lower Bonny river.

TABLE III
HEAVY METAL CONTENT (MG/KG) OF SEDIMENT (DRY SEASON)

Sampling sites	Heavy Metals	1	2	3	Σx	Mean \pm SD
Douglas Creek 1	Cu	<0.05	<0.05	<0.05	—	—
	Pb	<1.00	<1.00	<1.00	—	—
	Ni	7.60	8.00	7.80	23.40	7.80 ± 0.20
	V	<0.001	<0.001	<0.001	—	—
	Zn	30.10	31.30	31.60	93.00	31.00 ± 0.79
	Fe	8,703.00	8,695.00	8,702.00	26,100.00	$8,700.00 \pm 4.36$
Qua Iboe 2	Cu	<0.05	<0.05	<0.05	—	—
	Pb	<1.00	<1.00	<1.00	—	—
	Ni	4.94	4.95	5.02	14.91	4.97 ± 0.04
	V	<0.001	<0.001	<0.001	—	—
	Zn	23.00	21.00	22.00	66.00	22.00 ± 1.00
	Fe	15,386.00	15,394.00	15,390.00	46,170.00	$15,390.00 \pm 4.00$
Atlantic 3	Cu	<0.05	<0.05	<0.05	—	—
	Pb	<1.00	<1.00	<1.00	—	—
	Ni	2.30	2.70	3.40	8.40	2.80 ± 0.56
	V	<0.001	<0.001	<0.001	—	—
	Zn	35.90	36.00	36.10	108.00	36.00 ± 0.10
	Fe	22,216.00	22,179.00	22,205.00	66,600.00	$22,200 \pm 19.00$
Control 4	Cu	<0.05	<0.05	<0.05	—	—
	Pb	<1.00	<1.00	<1.00	—	—
	Ni	0.20	0.10	0.15	0.45	0.15 ± 0.05
	V	<0.001	<0.001	<0.001	—	—
	Zn	54.80	55.10	55.10	165.00	55.00 ± 0.05
	Fe	24,705.00	24,695.00	24,700.00	74,100.00	$24,700.00 \pm 5.00$

TABLE IV
HEAVY METAL CONTENT (MG/KG) OF SEDIMENT FROM QUA IBOE RIVER ESTUARY (WET SEASON)

Sampling Station	Heavy Metals	Sediment			Σx	Mean \pm SD
		1	2	3		
Douglas Creek 1	Cu	<0.05	<0.05	<0.05	—	—
	Pb	<0.47	<0.47	<0.47	—	—
	Ni	<0.03	<0.03	<0.03	—	—
	V	<0.20	<0.20	<0.20	—	—
	Zn	15.30	14.30	15.10	44.70	14.90 \pm 0.53
	Fe	9,264.0	9,275.0	9,283.0	27,822.00	9,274.00 \pm 9.54
Qua Iboe 2	Cu	1.30	0.80	0.90	3.00	1.00 \pm 0.27
	Pb	<0.47	<0.47	<0.47	—	—
	Ni	4.00	3.10	3.70	10.80	3.60 \pm 0.46
	V	<0.20	<0.20	<0.20	—	—
	Zn	27.50	26.80	27.00	81.30	27.10 \pm 0.36
	Fe	2,170.0	2,185.0	2,182.0	6,537.00	2,179.00 \pm 7.94
Atlantic 3	Cu	3.60	3.80	4.60	12.00	4.00 \pm 0.53
	Pb	<0.47	<0.47	<0.47	—	—
	Ni	6.90	6.20	7.30	20.40	6.80 \pm 0.56
	V	<0.20	<0.20	<0.20	—	—
	Zn	32.80	33.70	34.30	100.80	33.6 \pm 0.75
	Fe	1,680.0	1,690.0	1,670.0	5,040.00	1,680 \pm 10.00
Control 4	Cu	<0.05	<0.05	<0.05	—	—
	Pb	<0.47	<0.47	<0.47	—	—
	Ni	<0.03	<0.03	<0.03	—	—
	V	<0.20	<0.20	<0.20	—	—
	Zn	40.20	4.50	39.60	120.30	40.1 \pm 0.46
	Fe	7,008.0	7,005.0	7,011.0	21,024.00	7,008.00 \pm 3.00

The nickel concentration in the wet season sediment was however lower with maximum value of 6.80 ± 0.56 mg/kg recorded at Atlantic sampling station. The next value was 3.60 ± 0.46 mg/kg recorded for Qua Iboe sampling site while Douglas creek nickel concentration was below detectable limit. It is surprising to note that while the sediment at the Mobil Producing Nigeria Unlimited Douglas creek had little or no nickel in the wet season, the sediment recorded a high value (7.80 ± 0.20 mg/kg) for this metal in the dry season. The probable reason for this observation is the dilution effect during wet season. There was a progressive reduction of metals in the sediment along the sampling sites showing that there was also progressive settling with reduction in the flowing receiving water. In the wet season, the levels of the metals in the sediment increased from discharge point to where the water enters the Atlantic Ocean. There was also evidence of gross dilution at the effluent discharge point with progressive concentration of the metal in the sediment in downstream direction. The nickel concentration in the dry season control sediment was only 0.15 ± 0.05 mg/kg while that of the wet season was below the detectable limit. This was in order, as the control station received no heavy metal input from the effluents discharged into the estuary either directly or through tidal influence. This is evident by the salinity of the control station which was typical of a freshwater environment ($<1.0\text{‰}$).

The concentrations of zinc in the dry season sediment samples were 31.00 ± 0.79 mg/kg, 22.00 ± 1.00 mg/kg and 36.00 ± 0.10 mg/kg for the Douglas creek, Qua Iboe and Atlantic sampling stations, respectively. The high value of the metal at Douglas creek followed by a reduction at the next site (Qua Iboe) and a sharp rise in the sediment of the Atlantic sampling site suggests that either the sediment characteristics

or the metal speciation may have influenced the rate of settling of the metal in the sediment. Effluent dilution of heavy metals concentration in the sediment did not seem to play a role in the sediment zinc levels at the various sampling sites. In the wet season, zinc concentration was lowest at the Douglas creek site and increased in value downstream up to the Atlantic sampling site. Here, low salinity was not a major determinant of sediment heavy metals concentration but may have been due to the introduction and settling of heavy metal from non-point sources. The concentration of zinc was high at the control station (55.00 ± 0.05 mg/kg) even though this site received no input from the MPNU dumping activities (evident by low salinity of this site with a value of $< 1.0\text{‰}$). This strongly supports the presence of nonpoint (MPNU) heavy metal pollution. Another evidence of nonMPNU point source of metal in the study area is provided by the presence of copper in the sediment of Qua Iboe and Atlantic locations even though this metal was absent in sediment of Douglas creek and the control stations. The most noteworthy feature is the very high value of iron in the sediment of the control station ($24,700.00 \pm 5.00$ mg/kg). From this study, there is evidence of a point source of iron at the control sampling location as well as at Douglas creek sampling station.

IV. CONCLUSION

Generally, the entire study area is polluted by heavy metals which were site related. It is interesting to note that while activities of MPNU introduces huge amount of iron into the environment as evidenced by the concentration at Douglas creek, much more iron can be contributed unnoticed by metals in bridge. Bridges constructed over water thus have advantages and disadvantages and can constitute dangers to human health through contamination of sediment and hence

edible aquatic resources like tilapia fish obtained from such contaminated environment. It can therefore be concluded that heavy metals contamination of the Qua Iboe river estuary was from point and nonpoint sources.

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Tropics (E. N. Adinna, O.B. Ekop and V. I. Attah; Eds), Enugu, Nigeria, SN AAP Press Ltd, 2003; Microbiological and physicochemical studies of wetland soils in Eket, Nigeria. P. World Academy of Science, Engineering and Technology, 34, 837-842, 2008 and Effect of waste generation and management on outdoor air quality in Uyo metropolis, Akwa Ibom State, Nigeria. *Geosystems Engineering* (Taylor and Francis Group) 15 (4): 239-246, 2012. Her current research interest is the management of hospital waste. She has done some work on indoor air quality; heavy metal pollution of aquatic environment as well as public health surveys.

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