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Monitoring and Assessment of Heavy Metals Contamination in Surface Water and Sediments in Bonny Estuary, Niger Delta

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Abstract: ***The study of heavy metals contamination on surface water, and sediment in the Upper Bonny Estuary was investigated. Samples of surface water, and sediment were collected at 5 selected stations namely: Okochiri River (S1), Ekerekana Creek (POD, S2), Okari-Ama River (S3), Ogoloma Creek (S4) and Bonny Estuary (Control, S5). Physico-chemical parameters (pH, temperature, DO, conductivity, salinity, TDS, TOC, and THC) were analyzed according to standard procedures for surface water (APHA), while heavy metal parameters (As, Cd., Cr, Pb, Hg, V and Zn) were analyzed for water, and sediment using Atomic Absorption Spectrophotometer. The results obtained indicated that the physico-chemical parameters varied significantly (P < 0.05). These parameters such as pH, temperature, conductivity, salinity, TDS and TOC were higher in the dry season while, THC was higher in content it presents above the permissible limit of 20 mg / l (FMEnv) at the point of effluent discharge (Ekerekana Creek S2) during the wet season and TDS in all sampled measured were above permissible limit. However, DO were values below FMEnv of 5.0 mg / l in most sampled stations in both seasons. Heavy metals (As, Cd, Cr, Pb, Hg, V and Zn) analysed were below detectable limit in water. Total metal content in sediment were higher than the levels recorded in water. The mean concentration in sediment was in the order Zn >Pb> Ni > V> Cd. As and Hg were not detected in the study. The degree of contamination in sediment revealed that the Contamination Factor of the studied metals in both seasons were all <1 except Pb during the dry season in (S4) and (S5) which were (1.07 mg/kg and 1.05 mg / kg) respectively. Further indices using Pollution Load Index (PLI) and Geo-accumulation Index (Igeo) revealed <1 in all the stations in both seasons. Comparison with USEPA (SQG) and WHO (SQG), proved that the levels of heavy metals were below permissible limit in the sampled stations.***

Keywords: Heavy metals, Monitoring, Assessment and Contamination

1. Introduction

The pollution of atmosphere from traffic and industrial activities in urban areas became severer and severer with the rapid urbanization and the accelerated development of the social economy over the world in the last twenty years (Han et al, 2007; Fenger, 1999; Ferguson and Kim, 1991). Aerosols of the atmospheric have the potential to play an important factor in modifying and or altering climate, water cycles and the characteristics of physical, chemical and biological parameters of the atmosphere (Koçak et al, 2009). Many studies were published on the health effects of metals pollution has focused on atmospheric particulate matter, soil, water plants and sediments have been conducted in several parts of the world (Abdul-Wahab and Yaghi, 2004; Al-Khashman, 2004; Arditsoglou and Samara, 2005; Al-Khashman and Shawabkeh, 2006; Pereira et al, 2007). The pollution of metals in surface water, river water and sediments is the major environmental issues especially in the industrialized areas during last decade (Ozmen et al. 2004; Fernandes et al. 2008). The pollution of heavy metal of river water and surface sediments becomes the major problems in fast urbanized cities since water and sediment quality maintenance and hygiene structure do not grow along with population and urbanization (Ahmad et al. 2010). Many studies prove that the both activities (natural and anthropogenic) are largely liable for the metal abundance in the environment (Wilson and Pyatt 2007; Khan et al. 2008).

2. Study Area

The sampling sites were established along Okrika Creek in Okrika Local Government Area and stretched up to the Upper Bonny Estuary of Rivers State, Niger Delta. The river is a brackish mangrove swamp with intertidal mud flats, and influenced by semi-diurnal tidal regime. The vegetation consists of *Rhizophora racemosa, Laguncularia racemosa, R. mangle, Nypa frutican,* and *Avicennia nitida* which line the shores of the creek. The creek is tidal in both wet and dry seasons. Anthropogenic activities along the stretch of Upper Bonny Estuary include discharge of industrial effluents, sand mining, dredging, fishing, navigation, washing, bathing and recreational activities. A major industrial outfit which is situated in station 2 (Ekerekana) is the Port Harcourt Refinery Company (PHRC) [a subsidiary of the Nigerian National Petroleum Corporation (NNPC)], which generates several volumes of effluents that are channeled into the creek via a drainage system (Anaero-Nweke *et al.,* 2016). These activities may influence the natural balance of the aquatic ecosystem and consequently its biota, such as plankton, benthos and fish. Okrika River is a highly urbanized brackish ecosystem impacted mainly by anthropogenic municipal and industrial activities that have significantly increased in the past decades.

The study area has been subjected to domestic, industrial and illegal bunkering activities over the past decades and waste-water from residential houses and communities. Along the shores of the creek are located several communities.

The communities are but not limited to Okochiri, Ekerekana, Okari-Ama, Oba-ama, Ogoloma, and Kalio-Ama. Along the stretch of the river, artisanal fishers mainly exploit the fisheries. The fisher folks use wooden and dug-out canoes ranging in size from 3m to 8m long. The canoes are either paddled or powered by small outboard engines, and manned by an average of two men. From these boats, the fisher folks operate their cast nets, hook and lines, gill net and crab pots.

However, over the past decades, several studies have revealed that the sampling stations serve as the ultimate sink for a number of pollutants and increasing array of waste types, including sewage, municipal, and industrial effluents among others from the effluents and runoff from the surrounding metropolis. Bonny Estuary is an important habitat for a wide array of fish and marine organisms, that serve as the major source of seafood to the people of Okrika and its environment, the contamination of this ecosystem is not only a major concern for the fish and wildlife resources but also for the human population.

2.1 Location of sampling

There are five (5) main sample collection stations were selected in the study area as shown in Fig 1 and described in Table 1.

These include;

1) Okochiri River as station 1 (S. 1): This represents the station 500 metres to the right of the point source of industrial effluent discharge.
2) Ekerekana Creek which serves as the Point Of Discharge into the river and is Station 2 (S.2)
3) Okari-Ama River as station 3 (S.3): Representing the Station 500 metres to the left of the Point source.
4) Ogoloma Creek as station 4 (S.4): Representing the entrance to a creeklet from the Bonny Estuary but a distance opposite the point source
5) Bonny Estuary (Control station) is about 700m away from Ogoloma Creek entrance

2.2 Description of Sampling Stations

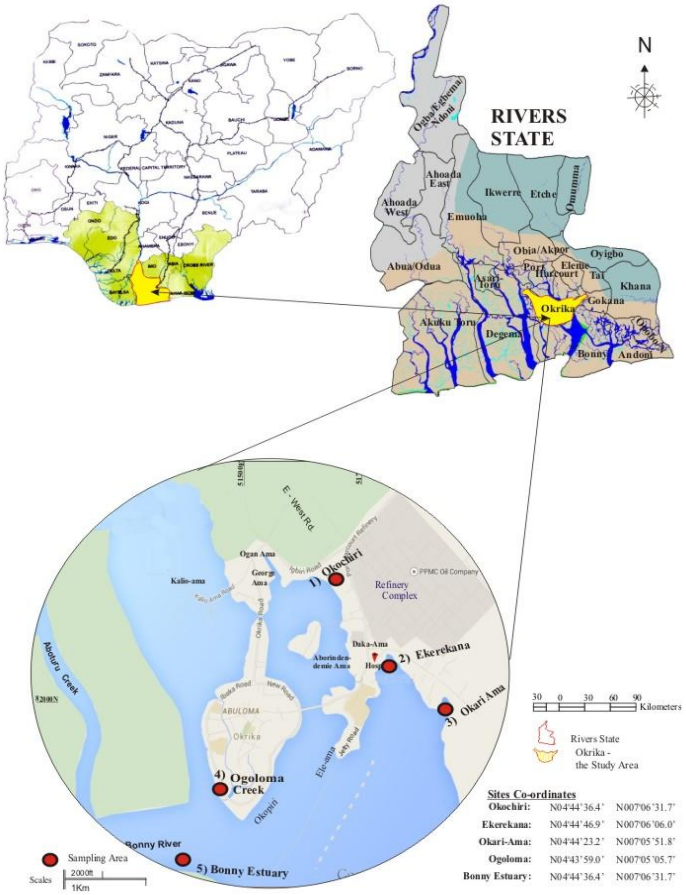

Figure 1: Location of studied area

3. Sampling and Methods of Analysis

3.1 Field Sampling Operations

Sampling of the investigated area includes surface water and sediments were collected from the designated sampling stations. The positions of the stations were accurately located by Global Positioning System (GPS). Accurate positioning was further facilitated by careful attention to permanent and semi-permanent structures at the stations. An open motorized fiber boat was used as a means of transportation with which sampling was carried out at each of the designated sampling stations. The sampling regime was carried out monthly for 12 months and the period was also dictated by the two hydrological seasons prevalent in the tropics which brought about significant differences in the physico-chemical conditions in the bodies of water.

Physico-chemical parameters were including (pH, Temperature, DO, Conductivity, Total Dissolved Solids, Turbidity and Salinity). The surface water was collected at low tide with a 2-literplastic Hydrobios sample bottle below water surface by lowering the bottle to a depth of 10 – 20cm and allowing it to fill to over flow and also a 250 ml borosilicate glass bottle for Total Hydrocarbon Content.

Surface water samples for heavy metals (50 mls) were acidified with 2 drops of concentrated HNO_3 (APHA, 1998). All samples were transported cool (4^oC) in an ice chest to the laboratory where the samples were transferred to a refrigerator until further processing before analysis. However, the sediments samples were collected using an Eckman's grab from each station and placed in pre-cleaned labelled polythene bag for preservation, and transported cool in an ice chest to the laboratory where the samples were transferred to a refrigerator prior to chemical analysis.

3.2 Sediment Sample Analysis

Sediment samples were air dried for two to three weeks under room temperature. After drying, the samples were then disaggregated; visible remains of organisms and debris were removed. The dried sample was further crushed in a mortar, sieved through a 200µm sieve to normalize particle size and homogenized in a porcelain mortar, sieved (using a 2-mm mesh) and stored in plastic container for further analysis.

3.3 Heavy Metals

The sediment sample was air dried for two to three weeks under room temperature. After drying, the dried sample was crushed in a mortar, sieved through a 200µm sieve to normalize particle size and homogenized in a porcelain mortar, sieved (using a 2-mm mesh size) and stored in a plastic container for further analysis. Approximately 0.25g of dried sieved sediment sample was placed in a Teflon tube and 5ml aqua regia (HCl: HNO_3 in a ratio of 3:1) added for digestion. The mixture was left over night for cold extraction in a fume hood before digestion. Sealed containers was placed in a closed vessel Microwave digestion system (CEM –MARS 6- USA) and heated according to the digestion program (One touch US EPA-3051) following the procedure of Rahman *et al.* (2013). After digestion, sample solution was cooled to room temperature then transferred to a 50ml centrifuge tube and made up to 50ml using deionized water with a resistivity of 18:2 MΩ $cm^{-}1$ (Millipore, USA). Three blank digest and three control samples of NIST SRMs (Standard Reference Material® 2711) were also analysed the same way. The resulting digest was cooled and filtered (10mls) using Agilent filters (0.45µm) into a beaker. The metal content of the digest was determined by Atomic Absorption Spectrophotometer Model GBC by Avanta 2.02.

4. Statistical Analysis

Analysis and presentation of results was done using Microsoft excel, SPSS version 17. Analysis of Variance (ANOVA) was used to determine their relationships and levels of significance. Other analysis includes:

4.1 Evaluation of Risk Associated with Heavy Metals in Sediments

To determine the degree of contamination in the sediments three ecological pollution indices were used. Contamination Factor (CF), Pollution Load Index (PLI) and Geo-Accumulation Index (Igeo). Data were compared with international sediment quality guidelines to determine levels of pollution (Surva *et al.*, 2005).

4.2 Contamination Factor (CF)

The level of contamination of sediment by metals is expressed in terms of a Contamination Factor (CF) calculated as:
$CF = C_m$ sample/C_m background
Where, Cm, Sample is the concentration of a given metal in sediment
Cm Background is the value of the metal equals to the average shale value (ASV) given by Turekian and Wedepohl (1961) in mg / kg as (Cr (90), Zn (95), Pb (20) and Ni (68), Cd (0.3), As (103) which are considered as the background values.

4.3 Pollution Load Index (PLI)

Pollution load index (PLI), is a means of assessing the quality of sediment in the study area with respect to heavy metals contamination which was evaluated following the method of Tomlinson *et al.* (1980).
$PLI = (CF1x\ CF2\ xCF3x\ \ldots..\ CFn)^{1/n}$
Where, n is the number of metals
CF is the contamination factor of individual metals
CF = Metal concentration in sediment / Background values of the metal.
According to Chakravarty and Patgiri (2009) the PLI value > 1 indicates pollution while PLI value < 1 indicates no pollution.

4.4 Geo-accumulation Index (Igeo)

Geo-accumulation index (1geo) compares current concentration of heavy metals with preindustrial level. The geo-accumulation index (1geo) values were calculated for the different metals using the equation of Muller (1969).
Igeo = Log 2 (Cn / 1.5 Bn).
Where Cn = Measured concentration of element in the sediments sample
Bn = Geochemical background for the element n.

The factor 1.5 is used to compensate for possible variations with respect to background lithological variations. Muller (1969) proposed seven classes of the Igeo-accumulations index. Class 6 is an open class and comprises all values of the index higher than class 5. 1geo of 6 indicates almost 100 fold enrichment above background value. In these computations. Average shale value (ASV) by Turekian and Wedepohl (1961) in mg/kg (Cr (90), Zn (95), Pb (20) and Ni (50), Cd (0.3), As (103) was considered as the background values to estimate Igeo.

4.5 Sediment Quality Guideline (SQG)

The sediment Quality Guideline (SQG) of respective international bodies has been adopted as an informal tool to evaluate sediment chemical data in relation to possible adverse effects on aquatic biota. These (ISQG. USEPA SQG and SQUIRT by NOAA) are basically defined parameters and thresholds based in field and laboratory studies.

5. Results and discussion

5.1 Physico-chemical Parameters in Surface Water

The physico-chemical analysis of the surface water samples from the Upper Reaches of the Bonny Estuary revealed variations across the stations and sampling months, though the variability was not season dependent for most parameters. The pH of an aquatic system is an index of the water quality and the extent of pollution in the watershed (Jonnalagadda and Mhere, 2001). pH has been previously reported to affect the solubility and availability of nutrients and how they can be utilized by aquatic animals (Kusemiju, 2010). Acidification of running water has been reported to result in an aggravating reduction of species composition (Adakole and Amune, 2003; Emere and Nasiru, 2007).

pH of the water influences the solubility of metals and this in turn can affect their ability to settle on the sediment. In the present study, the monthly pH showed a significant longitudinal gradient of mild acidity to near alkaline that was fairly constant throughout the study period. The pH values recorded throughout the study period fell within the acceptable range (6.5-9) as suitable for aquatic life by FMEnv (1999) and also within the range previously reported in the Niger Delta environment (Hart and Zabbey, 2005). There was no significant difference ($P<0.05$) of pH recorded in the dry and wet season. The slightly acidic nature of all the sampling stations in the surface water may be due to the changes from humic to acidic form, which is formed from decaying organic matter. Changes in pH may also affect health of aquatic organisms since most of their metabolic activities are pH dependent (Morgan and McManhon, 1982; Chen and Lin, 1995), Conductivity showed significant increase in the sampled stations. The significant increases may be an indication that pollutants might have entered the water which could have negative impacts on the survival of aquatic animals and increase the level of toxicity measured by other parameters (Anaero-Nweke, 2013). Every creek has a baseline conductivity depending on the local geology and soils. Higher conductivity values will result from the presence of various ions including nitrates, phosphates and sodium (Sharon, 1997). Turbidity values however were seen to be below permissible limits as specified by FMEnv (1999). Pearson's correlation revealed a weak negative relationship with pH, temperature and conductivity which means that when there is an increase in turbidity values there is a decrease in pH, temperature and conductivity values but at a lower rate the values were significantly correlated ($P<0.05$).

The salinity values recorded in this study is an indication of estuarine and brackish water and is in agreement with the findings of McLusky (1989) whereby inflowing tidal water is diluted upstream due to mixing with out-flowing fresh water and land derived runoffs.

The range of temperatures measured (26.83 ^{o}C – 28.28^{o}C) were in accordance with (FMEnv, 1999) effluent permissible limit of < 40^{0}C and also considered normal with reference to the creek location in the humid equatorial Niger Delta (Alabaster and Lioyd 1980, NEDECO, 1980). Observed high peaks of temperature coincided with the dry season periods. Pearson correlation co-efficient revealed that a positive correlation existed between temperature and salinity, pH, Conductivity, TDS and DO ($P< 0.05$). This means that increase in temperature influenced positively in the concentration of these parameters (salinity, pH, conductivity, TOC and Dissolved Oxygen) in the ecosystem. Cluster Analysis further showed clusters between pH, salinity and DO which were likely due to type, volume, mixing and redistribution of materials brought about by physical and chemical phenomena including seasons and proximity to pollution source.

DO concentration in natural waters is dependent on the physical, chemical and biochemical activities in the water body. The values of DO recorded in the dry season were moderately higher than the values in the wet season. However, DO was lower than FMENV permissible limit of 5.0mg/l in Okochiri River, Ekerekana Creek and Okari-Ama River in the dry and wet season with values of 3.85 $\pm$ 0.60 mg / l, 4.32 $\pm$ 0.55 mg / l, 4.35 $\pm$ 0.52 mg / l and 3.85 $\pm$ 0.70 mg / l, 3.78 $\pm$ 0.89 mg / l and 4.21 $\pm$ 0.38 mg / l respectively and these are areas close to the effluent discharge points. Pearson's correlation revealed that DO have a very strong positive relationship with pH ($P<0.05$). The depletion of DO at the lower stations could also be due to enormous amount of organic loads which require high levels of oxygen for chemical oxidation, decomposition or breakdown and high temperature during the dry season. Also higher DO recorded in the wet season could be due to the tidal influence resulting in the mixing of the water due to high run-offs occurring during the rainy season.

Amongst the sampled stations. Total Hydrocarbon Content in water at the Point of Discharge (POD) was 37.97±92.87mg/l higher than other stations in the wet season. This concentration was above maximum permissible limit of 20 mg/l (FMEnv, 1999). In effect, the water quality at the point of effluent discharge POD may be considered to be similar to an improperly treated effluent in need of further treatment action in order to reduce the contaminant concentration to acceptable levels (Anaero-Nweke *et al.*, 2016). THC have been observed to be toxic to aquatic life. Cluster Analysis showed that there was clusters between THC, turbidity and TOC in all the sampled stations except at the point of discharge (Ekerekana Creek), the values were not significant ($P<0.05$).

Furthermore, THC was also above permissible limit of 20mg/kg Fmenv (1999), in all stations except in Ogoloma Creek which was relatively lower than the permissible limit (FMEnv, 1999) The high total hydrocarbon content could be traced to anthropogenic activities (illegal bunkering activities) in the river and a major industrial effluent discharge point (Ekerekana Creek) could account for very

high THC values and also be responsible for the reduction of fishes and other aquatic life in Ekerekana Creek. Interview from local fishermen during the study clearly indicated that the area around the point of discharge of industrial effluent (Ekerekana Creek) was devoid of fishes and hence lower / No fishing activity is carried out there anymore (Anaero-Nweke *et al.*, 2016). TOC levels were generally low irrespective of the prevalent season.

5.2 Heavy Metal Concentration in Surface Water

All heavy metals measurement (Cd, Cr, V, Ni, Zn, As, Hg) at different stations in the surface water were below detectable limit.

5.3 Heavy Metal Concentration in Sediment

These heavy metals (As, Cd, Cr, Hg, Ni, V, and Zn) were detected in measurable but varied concentrations during the wet and dry seasons in sediments, however As and Hg were not found. The temporal variations in the level of the heavy metals were characterized by irregular fluctuations. The observed low concentrations of these metals analysed (Cd, Cr, V, Ni, and Zn) in this study are consistent with the finding of Anaero-Nweke *et al*., (2016) in Ekerekana Creek, Obire *et al.*,(2003) on Elechi Creek but contrary to the reports of Chindah and Braide (2003) who recorded higher values of Cd and Pb on the same Elechi Creek.

The levels of observed heavy metals in sediments were significantly higher than those of surface water. The concentration of metals recorded in sediment can be attributed to the ability of sediment to act as a sink of influx of metals into the water body and their ultimate removal from the water column into the sediment that has been reported from previous studies (Ogbeibu *et al.,* 2014).

According to Odiete (1999), sediment is the major sink of metals, in some cases holding more than 99% of the total amount of a metal present in the aquatic system. Sediment unlike water is usually employed as a pollution indicator by contaminants (Ogbeibu *et al.,* 2014). According to Yau and Gray (2005) and Ogbeibu *et al.,* (2014), heavy metals analysed in sediments can provide a deeper insight into the long-term pollution state of the aquatic environment.

The ecological implication of the findings is that all edible biota is constantly exposed to varying sublethal metal concentrations irrespective of location, season or point of entry.

According to Oyewo (1998), the reason for the lack of regular seasonal variations are not clear but may be attributed to high variability over large areas of sampling and the restriction of number of samples imposed by a number of constraints. Moreover, no form of As and Hg was detected in water, sediment or even the biota analysed.

The mean concentrations of heavy metals in the sediments along the stretch of upper Bonny Estuary evaluated against some international set standards did not exceed the WHO (2004), CCME (1999) and the USEPA (1999) guidelines.

According to USEPA (1999) and WHO (2004) guidelines, the sediments were unpolluted by heavy metals because the measured concentrations were lower than the permissible limits.

Results obtained from ecological risk indices (PLI, Igeo, and CF) showed that the heavy metal Pb is a major contributor to ecological risks associated with heavy metals in the sediments along the stretch of Upper Bonny Estuary in the dry and wet seasons. The area therefore can be said to be relatively unpolluted. The Contamination Factor (CF), Pollution Load Index (PLI) and the Geo-Accumulation Index (Igeo) are used extensively in the assessment of sediment pollution by heavy metals (Priju and Narayana, 2007; Akan *et al.,* 2010; Iwoha *et al.,* 2012). The results of the present study revealed that the sediment along the stretch of Upper Reaches of Bonny Estuary is unpolluted by the studied heavy metals, the computed Contamination Factor (CF) revealed low contamination in other metals except by Pb in Ogoloma Creek (S4) and Bonny Estuaryin the dry season which revealed moderate degree of contamination. Cummulatively, even where there is moderate contamination from Pb during the dry season, the PLI for all the studied metals in all stations in both seasons (wet and dry) were less than 1. Thus indicating a practically uncontaminated condition. The results by implication may be due to the type of anthropogenic activities going on in and around the Upper Reaches of Bonny Estuary and the potential for self-purification from high tidal flushing within the ecosystem. Thus the sediments along the stretch of Upper Reaches of Bonny Estuary can be said to be unpolluted for the assessed heavy metals.

Table 1: Mean Physico-chemical Parameters in Surface Water during the Wet Seasons

Parameters	Okochiri (S1)	Ekerkana (POD, S2)	Okari-Ama (S3)	Ogoloma (S4)	Bonny Estuary (Control, S5)	FMEnv (1999)limit
pH	6.53 ± 0.43	6.54 ± 0.57	6.80 ± 0.33	6.91 ± 0.22	6.91 ± 0.30	6-9
Temp (^{0}C)	27.28 ± 0.39	27.48 ± 0.32	27.42 ± 0.69	26.80 ± 0.43	27.22 ± 0.15	<40
Conductivity	12283.33 ± 3996.21	12158.33 ± 1437.27	13460.00 ± 2190.93	20881.67 ± 5026.62	20298.33 ± 4871.59	NS
Turbidity	2.22 ± 1.38	1.44 ± 1.77	0.90 ± 0.54	0.52 ± 0.25	1.59 ± 0.93	10 NTU
TDS	5027.33 ± 3329.05	8011.33 ± 2658.16	10806.33 ± 4248.77	10729.00 ± 2182.78	13251.83 ± 1659.10	2000mg/l
DO	3.85 ± 0.70	3.78 ± 0.89	4.21 ± 0.38	6.88 ± 1.51	6.21 ± 0.33	5.0mg/l
Salinity (ppt)	7.11 ± 1.01	6.11 ± 0.94	8.66 ± 1.21	11.19 ± 2.45	10.82 ± 2.71	NS
TOC (%)	0.006 ±0.005	0.006 ± 0.004	0.007 ± 0.004	0.004 ± 0.003	0.006 ±0.004	
THC	0.28 ± 0.20	72.60 ± 126.87	0.75 ± 0.25	0.61 ± 0.72	0.46 ± 0.34	20mg/l

Table 2: Mean Physico-chemical Parameters in RiverWater during the Dry Seasons

Parameters	Okochiri (S1)	Ekerkana (POD, S2)	Okari-Ama (S3)	Ogoloma (S4)	Bonny Estuary (Control, S5)	FMEnv (1999)limit
pH	6.56± 0.17	6.76± 0.14	6.67± 0.26	6.96± 0.35	6.92± 0.25	6-9
Temp (^{0}C)	26.37± 2.35	29.07± 2.46	28.13± 1.49	28.93± 1.38	28.43±1.30	<40
Conductivity	12648.33 ±12624.73	12416.00±9817.93	15383.33± 10091.07	26583.33±3435.94	29200.00±2016.93	NS
Turbidity (NTU)	2.57± 1.23	0.46±0.39	1.27± 0.27	0.58± 0.30	1.22± 1.05	10 NTU
TDS	7538.83±7030.66	4888.00±3840.82	17383.33 ±1064.74	16066.67± 2158.39	16016.67± 1604.27	2000mg/l
DO	3.85 ± 0.70	3.78 ± 0.89	4.21 ± 0.38	6.88 ± 1.51	6.21 ± 0.33	5.0mg/l
Salinity (ppt)	12.00±3.57	2.41±2.45	12.78±3.41	13.68±3.03	12.98±3.92	NS
TOC (%)	0.007±0.006	0.004± 0.002	0.006± 0.004	0.007± 0.005	0.009± 0.005	
THC	0.65± 0.37	3.35± 1.22	0.59± 0.26	0.99± 0.96	2.25± 1.36	20mg/l

Table 3: Mean THC / Heavy metals in Sediments and Comparison with some Sediment Quality Guidelines for the Wet Season

Stations	Cd	Cr	Pb	Ni	Zn	V	THC	As	Hg
Okochiri (S1)	0.08 ± 0.10	5.51 ± 2.46	5.13 ± 6.75	2.39 ± 1.77	24.23 ± 24.20	0.13 ± 0.10	41.85±59. 41	-	
Ekerekana creek (POD,S2)	0.01 ± 0.02	5.48 ± 2.42	7.07 ± 10.97	2.31 ± 1.64	15.30 ± 4.43	0.12 ± 0.08	124.94± 186.97	-	
Okari-Ama River (S3)	0.09 ± 0.20	6.76 ± 0.86	8.40 ± 10.06	2.87 ±2.66	26.38 ± 15.08	0.15 ± 0.14	66.37 ± 88.33	-	
Ogoloma River (S4)	0.10 ± 0.09	4.32 ± 2.64	7.53 ± 11.13	1.22 ± 1.04	6.17 ± 5.06	0.05 ± 0.05	6.69 ± 5.40	-	
Bonny Estuary (Control S5)	0.023 ± 0.04	4.68 ± 3.28	8.68 ± 13.68	1.94 ± 2.11	15.74 ± 12.66	0.08± 0.11	76.49 ± 133.09	-	
ASV	0.3	90	20	50	95	103	-	-	
WHO (SQG)	6	25		20	123		-	-	
USEPA (SQG)	1	25	40	16	110		-	-	
CCME (SQG)	1	37	35		123				

* ASV – Average Shale Value (Turekian and Wedepohl, 1961)
* WHO, 2004, * USEPA, 1999 * CCME, "Canadian Water Quality Guidelines for Protection of Aquatic Life" (1999)
* SQG – Sediment Quality Guidelines

Table 4: Mean THC / Heavy metals in Sediments and Comparison with Sediment Quality Guidelines for the Dry Season

Stations	Cd	Cr	Pb	Ni	Zn	V	THC	As	Hg
Okochiri (S1)	0.12± 0.10	5.51 ± 2.46	10.58± 7.33	3.53 ± 2.91	42.11± 26.67	0.24± 0.13	59.87 ± 21.03	-	-
Ekerekana (POD,S2)	0.10 ± 0.16	5.48 ± 2.42	11.45± 5.52	3.77±1.78	49.07± 8.32	0.21± 0.08	96.37 ± 42.75	-	-
Okari-Ama (S3)	0.08± 0.05	6.76 ± 0.86	19.28± 11.58	4.51±2.73	41.98± 18.07	0.24±0.10	42.42 ± 27.31	-	-
Ogoloma (S4)	0.06± 0.07	4.32 ± 2.64	21.53 ±11.42	2.51± 1.24	11.57± 6.42	0.10 ± 0.07	24.25 ± 22.65	-	-
Bonny Estuary (Control S5)	0.04± 0.04	4.68 ± 3.28	21.00± 14.09	1.44 ± 2.07	10.24 ±7.45	0.08 ± 0.09	31.46 ± 25.51	-	-
ASV	0.3	90	20	50	95	103		-	-
WHO (SQG)	6	25		20	123		-	-	-
USEPA (SQG)	1	25	40	16	110		-	-	-
CCME (SQG)	1	37	35	35	123			-	

* ASV – Average Shale Value (Turekian and Wedepohl, 1961)
* WHO, 2004, * USEPA, 1999 * CCME, "Canadian Water Quality Guidelines for Protection of Aquatic Life" (1999)
* SQG – Sediment Quality Gaa

Table 5: Contamination Factor (CF), Pollution Load Index (PLI) and Cummulation of Heavy Metals in Sediment during the StudyPeriod.

Stations	Cd			Cr			Ni			Pb			V			Zn			PLI		
	Dry	Wet	Cum.	Dry	Wet	Cum.	Dry	Wet	Cum	Dry	Wet	Cum	Dry	Wet	Cum.	Dry	Wet	Cum.	Dry	Wet	Cum.
Okochiri (S1)	0.4	0.26	0.30	0.08	0.06	0.07	0.05	0.04	0.05	0.53	0.25	0.39	2.33×10^{-03}	1.26×10^{-03}	1.84×10^{-03}	0.4	0.25	0.34	0. 10	0.06	0.08
Ekerekana (POD,S2)	0.34	0.03	0.16	0.06	0.06	0.06	0.05	0.04	0.06	0.57	0.35	0.46	2.03×10^{-03}	1.16×10^{-03}	1.65×10^{-03}	0.51	0.16	0.33	0. 12	0.04	0.07
Okari-Ama (S3)	0.25	0.30	0.26	0.07	0.07	0.07	0.06	0.05	0.07	0.96	0.42	0.69	2.33×10^{-03}	1.45×10^{-03}	1.94×10^{-03}	0.44	0.27	0.35	0.13	0.08	0.08
Ogoloma (S4)	0.19	0.33	0.23	0.04	0.04	0.04	0.04	0.02	0.03	1.07	0.37	0.72	9.70×10^{-04}	4.85×10^{-04}	7.76×10^{-04}	0.12	0.06	0.09	0.07	0.04	0.05
Bonny Estuary (Control S5)	0.13	0.06	0.10	0.05	0.05	0.03	0.02	0.03	0.03	1.05	0.43	0.74	7.76×10^{-04}	7.76×10^{-04}	7.76×10^{-04}	0.1	0.16	0.13	0.06	0.04	0.04

PL1=Pollution load index
Cf= Contamination factor
Cf =(Low contamination)
1 ≤ Cf (Moderate contamination)
13≤ Cf <6 (Considerable contamination)
Cf >6 (Very high contamination)

PL1 < 1 (No pollution)
PLI > 1 (Pollution/site deterioration)
PL1 = 1 (Baseline levels)

Table 6: Geo-accumulation Index (Igeo) and Cummulation of Heavy Metals in Sediment During the Study Period (Sept. 2016 to Aug. 2017)

Stations	Cd			Cr			Ni			Pb			V			Zn		
	Dry	Wet	Cum.	Dry	Wet	Cum.	Dry	Wet	Cum.	Dry	Wet	Cum.	Dry	Wet	Cum.	Dry	Wet	Cum.
Okochiri (S1)	2.64×10^{-04}	0.05	0.06	0.01	0.06	0.01	0.01	9.57×10^{-03}	0.01	0.10	0.05	0,07	4.66×10^{-04}	2.53×10^{-04}	3.67×10^{-04}	0.08	0.05	0.06
Ekerekana (POD,S2)	0.06	3.01×10^{-03}	0.03	0.01	0.06	0.01	0.01	9.27×10^{-03}	0.01	0.11	0.06	0.09	4.06×10^{-04}	2.33×10^{-04}	3.31×10^{-04}	0.1	0.03	0.06
Okari-Ama (S3)	0.05	0.06	0.05	0.01	0.07	0.01	0.01	0.01	0.01	0.19	0.08	0.13	4.66×10^{-04}	2.91×10^{-04}	3.88×10^{-04}	0.08	0.05	0.06
Ogoloma (S4)	0.03	0.06	0.04	9.63×10^{-03}	0.04	6.02×10^{-03}	9.03×10^{-03}	3.01×10^{-03}	7.46×10^{-03}	0.21	0.07	0.14	1.94×10^{-04}	9.63×10^{-05}	1.55×10^{-04}	0.02	0.01	0.01
Bonny Estuary (Control S5)	0.02	0.01	0.01	9.03×10^{-03}	0.05	6.02×10^{-03}	5.77×10^{-03}	6.02×10^{-03}	6.02×10^{-03}	0.21	0.08	0.14	1.55×10^{-04}	1.55×10^{-04}	1.55×10^{-04}	0.02	0.03	0.02

Igeo < O (Practically uncontaminated) = Igeo < 1 (Uncontaminated to) Pollution
I< Igeo< 2 (Moderately contaminated) (Moderate contamination)
3≤ Igeo < 4 (Heavily contaminated) 2< Igeo > 3 (Moderately to heavily (Very high contamination) contaminated
5 ≤ Igeo >6 (Extremely Contaminated) 4 < Igeo <5 (Heavily to extremely contaminated)

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