

## Seasonal Diagenetic Changes in Trace Metals Levels of a Brackish Water System in the Niger Delta, Nigeria

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**Abstract:** The concentrations of mercury, lead, nickel, vanadium and cadmium of a brackish water system in the Niger Delta were assessed in order to determine seasonal diagenetic changes and how such changes affect their correlations with water quality parameters. Nine locations were sampled at two monthly intervals for a period of one year. Solvent extraction using ammonium pyrrolidine dithiocarbamate (APDC) and methyl isobutyl ketone (MIBK) was employed for the extraction of trace metals. Buck scientific model 200A Atomic Absorption Spectrophotometer and air-acetylene flame were used for their analyses, except for mercury, which was analyzed by cold vapour technique. Water quality parameters were determined using appropriate meters and various standard methods. The results of the analyses showed ranges of concentrations (ppb) of trace metals as follows: Hg (BDL-1.25), Pb (0.13-131.13), Ni (0.28-246.80), V (BDL-1.18) and Cd (0.28-24.63). There were significant ( $p < 0.05$ ) seasonal differences for Pb and Cd. Two-way analysis of variance also showed significant ( $p < 0.05$ ) spatial variations in both dry and wet seasons. Total alkalinity (TA),  $Mg^{2+}$ ,  $K^+$ , and  $Na^+$  revealed significant ( $p < 0.05$ ) seasonal variations with respect to higher values in the wet season. Significant ( $p < 0.05$ ) correlation coefficients between  $PO_4^{3-}$  and Pb, V and Cd in the dry season, an indication that these metals were probably in their phosphates and as particulates, was observed, but the observation in the wet season was different, suggesting seasonal diagenetic differences. Also, apart from direct discharge of industrial and domestic wastes, the immense volume of storm water runoff and river waters entering this water system may have played major roles in transporting metals originating from wastes discharge on land and in small streams, especially during the rains. This phenomenon may have resulted in elevated levels of lead and cadmium in the water column in wet season.

**BDL:** Below Detection Limit

**Keywords:** seasonal diagenetic differences, solvent extraction, correlation coefficients, brackish water system, Niger Delta

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### I. Introduction

Trace metals are among the most common environmental pollutants, and their occurrence in waters and biota is in most cases, an implication for natural or anthropogenic sources. The main natural sources of metals in waters are chemical weathering of minerals and soil leaching. The anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm, water runoff, landfill leachate, mining of coal and ore, atmospheric sources and inputs from rural areas (Kabata-Pendias and Pendias, 1992; Biney et. al., 1994; Zarazua et. al., 2006).

The existence of trace metals in aquatic environments has led to serious concerns about their influence on plant and animal life. Exposure to elevated concentrations can cause organisms to die. Metals such as Pb, Cd, etc., exhibit extreme toxicity even at trace levels (Nicolau et. al., 2006). The concentrations at which metals are considered important vary as some are essential at low concentrations and toxic at higher levels.

The behaviour of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry (Osmond et. al., 1995). During their transport, the trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Dassenakis et. al., 1997; Akcay et. al., 2003) which affect their behaviour and bioavailability (Nicolau et. al., 2006).

Trace metals may be sensitive indicators for monitoring changes in the water environment, and with increasing public concern regarding environmental contamination by them, there is also a growing need to monitor, manage and remediate ecological damage (Jarup, 2003, Silva et. al., 2005). The concentration of metals in surface water depends on several factors like soil dust, local point sources, natural presence in bedrock and soils, and airborne contribution from long range transport (Frank and Cross, 1974; Pan and Brugam, 1997). In addition, conditions in the catchments and lake are important for the mobility and availability of metals in the water. Rivers and lakes are exposed to atmospheric deposition of anthropogenically derived trace elements. This can create harmful effects on environmental condition and human health due to their toxicity and

bioaccumulation in various environmental compartments (Boyd and Tucker, 1998; Jarup, 2003, Silva et. al., 2005).

There are also quite a number of studies on the physicochemical quality of river waters in literature (Okoye, 1991; Otokunefor and Obiukwu 2005; Sithik et. al., 2009; Garg et. al., 2010). Disposal of untreated wastes, discharge of chemicals, uncontrolled land use and agricultural activities are examples of water quality deterioration. Other activities concerning hydrological, hydrogeological and hydraulic activities (e.g. construction of dams, ground-water over pumping) also result in long-term environmental degradation. In addition to anthropogenic influences on water quality degradation, natural events (e.g. mud flow, hurricanes, torrential rainfall) can lead to deterioration of the aquatic environment. Rainfall in particular, is often the largest single variable affecting the quantity of water; although it normally undergoes only a low level of treatment, it may occasionally over-load the entire system (UNEP, 1992).

Reports on temporal changes, especially seasonal variations, in trace metal concentrations in river waters have been of interest in recent times (Iwashita and Shimamura, 2003). This is one of such attempts to obtain information on the variations of seasonal characteristics in order describe seasonal diagenetic changes in the relationship between water quality parameters and the levels of Hg, Pb, Ni, V and Cd in the water column of Bonny River and creeks around Okrika, a brackish water system.

## II. Materials And Methods

### Study Area

The studied area is in Okrika Local Government Area of Rivers State, Nigeria. It is a riverine and intertidal wetland which lies on the north bank of the Bonny River, about 35 miles (56 km) upstream from the Bight of Benin in the Eastern Niger Delta of Nigeria. A maze of rivers and winding creeks intersect it, and within it are, stretches of marshy land having mangrove trees with thickets of tangled roots as the vegetation. The tidal amplitude of the eastern Niger Delta is between 1.5 to 2 m in normal tide, and the water level increases and decreases depending on the lunar cycle (Chindah et. al., 2004).

Rainfall in the coastal belt of the area, of which Okrika is a major part, usually starts from March, reaching the peak between June/August and ending in November. It is usually heavy due to the closeness of the Delta region to the equator. Between December and February, there are usually occasional showers. Annual rainfall totals vary from 2400 to over 4000 cubic meters. Consequently, the river banks and beaches are constantly eroded by perennial flooding, the scouring of the sea due to natural causes, and marine or navigation activities; there has also been severe loss of land and so, flood control measures have been very minimal.

There is also salt water intrusions from sea water into the rivers with the result that to obtain portable water; boreholes must be sunk to a depth of several hundred feet to avoid the possibility of picking salt-water interface (Abam, 1999). Nine sampling locations as described in table 1 and figure below, chosen for the study all of which are tributaries of Bonny River, are also connected to the Port Harcourt Refinery Outfall making thus the area a potential recipient of process wastewater from the company.

**Table 1:** Description of sample locations and their codes

| S/N | Location | Description                 |
|-----|----------|-----------------------------|
| 1   | EKC      | Ekerekana Creek             |
| 2   | OKC      | Okochiri Creek              |
| 3   | OOC      | Okari/Okpaku creek          |
| 4   | OBR      | Okrika/Bonny River          |
| 5   | OGR      | Ogoloma River               |
| 6   | GAC      | George Ama Creek            |
| 7   | IBC      | Ibaka Creek                 |
| 8   | OTR      | Okpoka-Toru or Okpoka River |
| 9   | OAC      | Oba Ama Creek               |



#### Samples collection, treatment and analysis

Water samples were collected below the surface film with pre-rinsed 1-litre plastic containers for the analysis of physicochemical parameters and trace metals. Deep-freezing was used as the method of sample preservation since it allows only the least changes in the sample during storage.

Samples for trace metals analyses in water were treated with 2 ml conc. nitric acid prior to storage in order to maintain stable oxidation states of the metals in frozen condition, and also to avoid adsorption of metals on the container, before laboratory analysis (APHA, 1992). Those for biological oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD) and dissolved oxygen (DO) were collected in 250 ml glass stoppered reagent bottles. The BOD<sub>5</sub> samples were carefully filled without trapping in air and the bottles wrapped with dark polythene bags and incubated for 5 days, to exclude all light, the presence of which is capable of producing DO by autotrophes (algae) presumably present in the sample. Dissolved oxygen (DO) samples were fixed up on the spot with Winkler solutions I and II. The COD samples were acidified with tetraoxosulphate (VI) acid (APHA, 1998).

Solvent extraction using ammonium pyrrolidine dithiocarbamate (APDC) and methyl isobutyl ketone (MIBK) was employed for preparation of water samples for trace metals. The water samples for analysis of the major cations were prepared by acid digestion using 1:3:1 mixture of HClO<sub>4</sub>, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> acids. Buck Scientific atomic absorption spectrophotometer model 200A and air-acetylene flame were used for all trace metal analyses, except for mercury which was by the cold vapour method using sodium borohydride (NaBH<sub>4</sub>) in a mercury kit and vapour allowed to go into the AAS instrument without flame.

#### Water quality parameters

Water pH was determined using a multi parameter HARCH sensor 156, temperature by dipping a mercury in glass thermometer (British standard BS593), salinity using a Hanna membrane millimeter digital scan meter (H8314mmmodel), conductivity using a scan conductivity meter, model 1560, total hardness by complexometric titration, Total alkalinity by titration with HCl, COD (Titrimetry), DO, BOD<sub>5</sub>, by Winkler's method, Total suspended solids and Total dissolved solids by Gravimetry, Turbidity, silicate and nitrate by colorimetric method, sulphate by turbidimetric method phosphate by stannous chloride method, calcium and magnesium by EDTA titrimetry, and sodium and potassium by flame photometry (APHA, 1998; ASTM, 2005).

III. Results And Discussion

Results

Trace metal levels (ppb) in the unfiltered surface water samples are presented in Table 2.

Table 2 Mean seasonal values (n=6) of trace metals (ppb) in the brackish water system

| Metal | Dry Season                  | Wet Season                    |
|-------|-----------------------------|-------------------------------|
| Hg    | BDL                         | BDL                           |
| Pb    | (0.73-76.00) 16.45 ± 23.49  | (0.98 – 131.13) 27.51 ± 34.01 |
| Ni    | (0.50-246.80) 46.48 ± 68.19 | (0.28 – 210.50) 31.8 ± 53.69  |
| V*    | (0.28 – 1.00) 0.11 ± 0.24   | (0.28 – 1.18) 0.20 ± 0.34     |
| Cd    | (0.23 – 20.25) 1.87 ± 3.52  | (0.28 – 24.63) 7.03 ± 7.57    |

BDL: Below detection limits. Levels are ranges and means ± sd. \* Detectable values only

The table shows that mercury was not detectable in both seasons. Vanadium was however, only detectable in six samples from six different locations in the dry season, representing about 20 % of the total number of samples collected in that season. In the wet season, it was detectable in ten samples also from six different locations, and this represents about 33.33 % of the total number of samples analyzed in the season. Lead, nickel and cadmium were on the other hand, detectable in all samples from the nine locations during the two seasons. Results of recovery analysis using Standard Material (CASS-4) for the trace metals are as follows: cadmium (76.92%), lead (79.59 %), nickel (96.82 %), and vanadium (94.75 %). These could be considered favourable for trace metals analysis in water. The detection limits (ppm) for all the trace metals are as follows: lead (0.05), nickel (0.02), vanadium (0.2) and cadmium (0.002).

All the metals show higher mean values in the wet season, except nickel, which was lower in the same season. Two-way analysis of variance also showed significant (p<0.05) spatial variations in concentrations in both dry and wet seasons, while correlation coefficients of only the pair of Ni and Pb is significant (p<0.05) as shown in Table 3, suggesting that the two metals have a common source.

Table 3 Correlations matrices for the combined trace metals data of the brackish water system

|    | Hg   | Pb        | Ni       | V        | Cd |
|----|------|-----------|----------|----------|----|
| Hg | 1    |           |          |          |    |
| Pb | -1** | 1         |          |          |    |
| Ni | 1    | 0.259122* | 1        |          |    |
| V  | .    | 0.118662  | -0.14344 | 1        |    |
| Cd | 1**  | 0.227965  | 0.037272 | -0.01078 | 1  |

. \*\*Correlation is significant at the 0.01 level (2-tailed) \*Correlation is significant at the 0.05 level (2-tailed).

Tables 4a and 4b present average seasonal values of physicochemical parameters

Table 4a Mean levels of physico-chemical parameters of the brackish water system in the dry season

| Sample Location | Parameters  |                  |                               |                      |                                    |                                 |
|-----------------|-------------|------------------|-------------------------------|----------------------|------------------------------------|---------------------------------|
|                 | pH          | Temperature (°C) | Total Dissolved Solids (mg/L) | Salinity (mg/L)      | Conductivity (µscm <sup>-1</sup> ) | Total Hardness (Ca + Mg) (mg/L) |
| EKC             | 7.15 ± 0.10 | 27.93 ± 0.64     | 17,036.67 ± 309.89            | 8,400.00 ± 229.13    | 33,473.33 ± 1314.58                | 118.06 ± 79.19                  |
| OKC             | 7.40 ± 0.08 | 27.37 ± 0.40     | 32,885.00 ± 248.34            | 16,150.00 ± 975.96   | 63,100.00 ± 1997.50                | 149.63 ± 7.76                   |
| OOC             | 7.50 ± 0.06 | 27.03 ± 0.42     | 35,016.67 ± 1,027.54          | 17,250.00 ± 409.27   | 66,510.00 ± 704.50                 | 169.65 ± 2.44                   |
| OBR             | 7.57 ± 0.05 | 26.63 ± 0.23     | 32,968.33 ± 237.19            | 16,116.67 ± 857.81   | 63,566.67 ± 2157.16                | 170.89 ± 9.94                   |
| OGR             | 7.55 ± 0.06 | 27.03 ± 0.21     | 35,166.67 ± 611.01            | 17,066.67 ± 152.75   | 65,900.00 ± 2722.13                | 172.39 ± 16.91                  |
| GAC             | 7.71 ± 0.04 | 27.20 ± 0.62     | 34,066.67 ± 1,006.64          | 16,866.67 ± 208.17   | 65,280.00 ± 769.22                 | 139.08 ± 31.28                  |
| IBC             | 7.56 ± 0.05 | 26.83 ± 0.31     | 33,066.67 ± 351.19            | 16,383.33 ± 381.88   | 64,083.33 ± 225.46                 | 167.47 ± 10.38                  |
| OTR             | 7.72 ± 0.03 | 26.90 ± 0.36     | 33,266.67 ± 288.68            | 16,566.67 ± 305.51   | 65,026.67 ± 328.84                 | 169.21 ± 12.41                  |
| OAC             | 2.29 ± 0.02 | 26.33 ± 0.25     | 25,816.67 ± 768.66            | 13,050.00 ± 1,033.20 | 47,566.67 ± 1075.98                | 155.95 ± 13.39                  |
| Range           | (7.05-7.75) | (26.50-28.60)    | (445-35,700)                  | (226-17,600)         | (789-67,900)                       | (9.12-191.10)                   |
| Ov.mean±Sd      | 7.47 ± 0.19 | 27.18 ± 0.62     | 27,975.67 ± 10,786.48         | 13,791.47 ± 5,333.83 | 53,532.50 ± 20,657.89              | 145.45 ± 54.25                  |

Table 4a Mean levels of physico-chemical parameters of the brackish water system in the dry season-contd

| Sample Location | Total Alkalinity (mg/L) | Biological Oxygen Demand (mg/L) | Chemical Oxygen Demand (mg/L) | Dissolved Oxygen (mg/L) | Total Suspended Solids (mg/L) | Turbidity (NTU) | SiO <sub>2</sub> <sup>2-</sup> (mg/L) |
|-----------------|-------------------------|---------------------------------|-------------------------------|-------------------------|-------------------------------|-----------------|---------------------------------------|
| EKC             | 88.07 ± 18.18           | 76.67 ± 4.98                    | 100.97 ± 2.29                 | 3.23 ± 0.01             | 26.63 ± 3.80                  | 18.40 ± 2.00    | 2.39 ± 0.53                           |
| OKC             | 98.00 ± 26.85           | 39.57 ± 0.57                    | 49.70 ± 4.58                  | 3.23 ± 1.00             | 28.33 ± 1.70                  | 21.77 ± 1.11    | 2.69 ± 0.09                           |
| OOC             | 125.27 ± 5.83           | 38.00 ± 5.41                    | 46.50 ± 1.21                  | 3.40 ± 0.93             | 34.27 ± 3.91                  | 18.70 ± 0.56    | 3.00 ± 0.38                           |
| OBR             | 98.10 ± 13.78           | 43.17 ± 10.90                   | 51.60 ± 1.37                  | 3.98 ± 0.81             | 20.10 ± 10.15                 | 9.50 ± 0.98     | 2.87 ± 0.08                           |
| OGR             | 45.57 ± 56.67           | 32.90 ± 0.96                    | 35.70 ± 3.84                  | 3.74 ± 0.33             | 12.83 ± 2.10                  | 15.50 ± 3.00    | 2.57 ± 0.60                           |
| GAC             | 108.90 ± 7.91           | 25.20 ± 5.29                    | 25.77 ± 1.68                  | 4.01 ± 0.65             | 11.63 ± 1.53                  | 14.13 ± 0.95    | 2.66 ± 0.29                           |
| IBC             | 127.20 ± 1.39           | 20.40 ± 0.70                    | 26.33 ± 2.53                  | 4.04 ± 0.24             | 5.93 ± 3.20                   | 7.50 ± 1.85     | 2.57 ± 0.26                           |
| OTR             | 80.47 ± 56.70           | 20.53 ± 2.01                    | 25.40 ± 1.32                  | 4.15 ± 0.40             | 3.47 ± 0.76                   | 6.63 ± 0.80     | 3.14 ± 0.07                           |
| OAC             | 92.77 ± 15.00           | 11.37 ± 0.86                    | 18.23 ± 2.06                  | 3.78 ± 0.65             | 5.10 ± 1.11                   | 3.87 ± 0.59     | 2.85 ± 0.13                           |
| Range           | (6.90-132.00)           | (10.60-77.30)                   | (16.10-102.80)                | (2.28-4.72)             | (2.80-38.59)                  | (3.20-22.80)    | (0.01-3.25)                           |
| Ov.mean±Sd      | 89.81 ± 39.53           | 37.35 ± 20.20                   | 45.43 ± 24.92                 | 3.70 ± 0.64             | 16.14 ± 10.83                 | 13.04 ± 5.58    | 2.48 ± 0.87                           |

**Table 4a** Mean levels of physico-chemical parameters of the brackish water system in the dry season-contd

| Sample location | NO <sub>3</sub> <sup>-</sup> (mg/L) | SO <sub>4</sub> <sup>2-</sup> (mg/L) | PO <sub>4</sub> <sup>3-</sup> (mg/L) | Ca <sup>2+</sup> (mg/L) | Mg <sup>2+</sup> (mg/L) | Na <sup>+</sup> (ppm) | K <sup>+</sup> (mg/L) |
|-----------------|-------------------------------------|--------------------------------------|--------------------------------------|-------------------------|-------------------------|-----------------------|-----------------------|
| EKC             | 0.01 ± 0.00                         | 20.27 ± 3.37                         | 0.27 ± 0.35                          | 37.85 ± 1.53            | 2.92 ± 0.13             | 10.51 ± 1.04          | 5.76 ± 2.77           |
| OKC             | 0.84 ± 0.59                         | 25.20 ± 3.40                         | 0.19 ± 0.14                          | 54.42 ± 0.26            | 2.97 ± 0.14             | 9.89 ± 0.61           | 8.49 ± 0.35           |
| OOO             | 1.20 ± 0.76                         | 23.63 ± 0.50                         | 0.19 ± 0.02                          | 62.74 ± 0.70            | 2.95 ± 0.04             | 10.45 ± 0.12          | 8.45 ± 0.35           |
| OBR             | 1.17 ± 0.48                         | 25.17 ± 1.40                         | 0.21 ± 0.01                          | 57.44 ± 2.10            | 2.93 ± 0.04             | 10.05 ± 0.41          | 8.49 ± 0.61           |
| OGR             | 1.32 ± 0.14                         | 26.01 ± 2.94                         | 0.72 ± 0.93                          | 61.79 ± 0.24            | 2.59 ± 0.45             | 9.62 ± 0.29           | 8.66 ± 0.14           |
| GAC             | 1.18 ± 0.42                         | 23.20 ± 0.52                         | 0.87 ± 1.09                          | 51.78 ± 6.62            | 2.92 ± 0.05             | 10.66 ± 0.73          | 8.23 ± 0.34           |
| IBC             | 1.40 ± 0.20                         | 24.57 ± 0.59                         | 0.75 ± 0.83                          | 60.66 ± 0.54            | 2.81 ± 0.13             | 10.64 ± 0.53          | 8.47 ± 1.48           |
| OTR             | 1.48 ± 0.23                         | 26.27 ± 2.48                         | 0.33 ± 0.08                          | 60.11 ± 0.54            | 2.77 ± 0.23             | 10.05 ± 0.94          | 8.41 ± 0.66           |
| OAC             | 0.51 ± 0.02                         | 21.97 ± 0.64                         | 0.18 ± 0.02                          | 54.52 ± 0.56            | 2.90 ± 0.09             | 9.64 ± 0.66           | 8.41 ± 0.19           |
| Range           | (BDL-1.740)                         | (10.70-28.70)                        | (0.02-2.13)                          | (2.47-63.41)            | (1.52-3.12)             | (7.00-11.43)          | (2.14-9.97)           |
| Ov.mean±Sd      | 0.98 ± 0.55                         | 23.13 ± 3.83                         | 0.39 ± 0.52                          | 50.39 ± 17.74           | 2.78 ± 0.37             | 9.87 ± 1.08           | 7.58 ± 2.13           |

**Table 4b** Mean levels of physico-chemical parameters of the brackish water system in the wet season

| Sample Location | Parameters  |                  |                               |                      |                                    |                                 |
|-----------------|-------------|------------------|-------------------------------|----------------------|------------------------------------|---------------------------------|
|                 | pH          | Temperature (°C) | Total Dissolved Solids (mg/L) | Salinity (mg/L)      | Conductivity (µscm <sup>-1</sup> ) | Total Hardness (Ca + Mg) (mg/L) |
| EKC             | 6.87 ± 0.05 | 26.70 ± 0.46     | 15,415.00 ± 410.09            | 7,914.00 ± 255.91    | 30,578.00 ± 886.55                 | 70.30 ± 74.86                   |
| OKC             | 7.88 ± 0.07 | 27.17 ± 0.42     | 27,304.67 ± 870.10            | 13,466.67 ± 1,365.04 | 54,976.67 ± 297.38                 | 149.59 ± 1.59                   |
| OOO             | 7.62 ± 0.67 | 27.07 ± 0.47     | 27,777.33 ± 807.43            | 13,900.00 ± 360.56   | 54,273.33 ± 933.88                 | 174.41 ± 8.45                   |
| OBR             | 7.73 ± 0.06 | 26.87 ± 0.67     | 27,813.33 ± 1,036.60          | 14,033.33 ± 404.15   | 54,400.00 ± 2,137.76               | 177.48 ± 10.50                  |
| OGR             | 7.87 ± 0.15 | 27.23 ± 0.59     | 31,100.00 ± 5,200.00          | 14,000.00 ± 435.89   | 58,716.67 ± 5,833.17               | 166.32 ± 16.48                  |
| GAC             | 7.25 ± 0.28 | 27.37 ± 0.55     | 31,933.33 ± 5,063.92          | 17,200.00 ± 608.28   | 60,050.00 ± 8,463.30               | 155.55 ± 11.24                  |
| IBC             | 8.00 ± 0.17 | 27.10 ± 0.26     | 33,516.67 ± 4,417.11          | 16,700.00 ± 871.78   | 62,066.67 ± 3,807.01               | 174.68 ± 13.03                  |
| OTR             | 7.47 ± 0.42 | 26.80 ± 0.10     | 33,240.00 ± 1,566.14          | 16,583.33 ± 1,277.04 | 63,133.33 ± 3,894.01               | 169.28 ± 14.85                  |
| OAC             | 7.25 ± 0.28 | 27.40 ± 0.26     | 26,836.67 ± 1,565.58          | 13,900.00 ± 1,558.85 | 49,733.33 ± 5,115.99               | 163.75 ± 16.75                  |
| Range           | (6.42-8.20) | (26.10-27.90)    | (234-37,100)                  | (127-17,900)         | (430-67,300)                       | (8.42-189.60)                   |
| Ov.mean±Sd      | 7.44 ± 0.52 | 27.08 ± 0.43     | 24,702.87 ± 11,003.99         | 12,776.60 ± 5,032.70 | 48,837 ± 18,998.03                 | 144.18 ± 59.26                  |

**Table 4b** Mean levels of physico-chemical parameters of the brackish water system in the wet season-contd.

| Sample Location | Total Alkalinity (mg/L) | Biological Oxygen Demand (mg/L) | Chemical Oxygen Demand (mg/L) | Dissolved Oxygen (mg/L) | Total Suspended Solids (mg/L) | Turbidity (NTU) | SiO <sub>2</sub> <sup>+</sup> (mg/L) |
|-----------------|-------------------------|---------------------------------|-------------------------------|-------------------------|-------------------------------|-----------------|--------------------------------------|
| EKC             | 93.50 ± 13.94           | 59.63 ± 9.50                    | 86.40 ± 8.18                  | 3.67 ± 0.50             | 24.13 ± 2.97                  | 15.50 ± 1.47    | 2.04 ± 0.60                          |
| OKC             | 114.77 ± 30.00          | 38.33 ± 1.90                    | 38.40 ± 5.07                  | 3.76 ± 0.54             | 23.67 ± 2.27                  | 14.63 ± 3.18    | 2.51 ± 0.12                          |
| OOO             | 128.30 ± 4.78           | 35.53 ± 0.75                    | 42.37 ± 3.88                  | 3.65 ± 0.99             | 29.67 ± 3.27                  | 16.70 ± 1.25    | 2.71 ± 0.26                          |
| OBR             | 103.73 ± 14.46          | 37.13 ± 6.03                    | 46.70 ± 2.86                  | 3.62 ± 0.19             | 10.13 ± 0.40                  | 7.37 ± 1.53     | 2.63 ± 0.56                          |
| OGR             | 78.60 ± 59.93           | 33.43 ± 5.17                    | 34.07 ± 3.31                  | 3.91 ± 0.78             | 17.80 ± 0.50                  | 11.40 ± 1.10    | 2.46 ± 0.45                          |
| GAC             | 112.87 ± 9.87           | 48.17 ± 13.71                   | 54.80 ± 39.03                 | 4.06 ± 0.51             | 13.00 ± 1.54                  | 7.70 ± 0.75     | 2.56 ± 0.39                          |
| IBC             | 123.57 ± 1.50           | 23.20 ± 6.43                    | 24.60 ± 4.13                  | 3.68 ± 0.47             | 9.23 ± 1.03                   | 13.83 ± 0.45    | 2.37 ± 0.54                          |
| OTR             | 138.47 ± 45.60          | 22.53 ± 1.68                    | 25.70 ± 2.52                  | 4.40 ± 0.49             | 4.67 ± 3.43                   | 5.20 ± 0.50     | 2.75 ± 0.13                          |
| OAC             | 92.27 ± 11.35           | 11.20 ± 1.65                    | 15.07 ± 1.27                  | 3.69 ± 0.77             | 3.70 ± 0.69                   | 2.90 ± 0.62     | 3.41 ± 0.65                          |
| Range           | (6.50-190.00)           | (10.10-69.30)                   | (10.40-95.70)                 | (2.53-4.75)             | (2.30-33.10)                  | (2.20-18.30)    | (0.11-3.97)                          |
| Ov.mean±Sd      | 104.72 ± 34.08          | 35.42 ± 14.72                   | 43.39 ± 23.21                 | 3.77 ± 0.57             | 14.70 ± 8.69                  | 10.67 ± 4.66    | 2.39 ± 0.83                          |

**Table 4b** Mean levels of physico-chemical parameters of the brackish water system in the wet season-contd.

| Sample location | NO <sub>3</sub> <sup>-</sup> (mg/L) | SO <sub>4</sub> <sup>2-</sup> (mg/L) | PO <sub>4</sub> <sup>3-</sup> (mg/L) | Ca <sup>2+</sup> (mg/L) | Mg <sup>2+</sup> (mg/L) | Na <sup>+</sup> (mg/L) | K <sup>+</sup> (mg/L) |
|-----------------|-------------------------------------|--------------------------------------|--------------------------------------|-------------------------|-------------------------|------------------------|-----------------------|
| EKC             | 0.02 ± 0.01                         | 18.47 ± 3.14                         | 0.48 ± 0.38                          | 24.78 ± 1.46            | 3.88 ± 1.88             | 13.92 ± 6.53           | 6.31 ± 0.24           |
| OKC             | 1.09 ± 0.58                         | 25.00 ± 0.89                         | 0.89 ± 1.16                          | 49.66 ± 13.17           | 6.58 ± 3.25             | 14.99 ± 4.71           | 12.91 ± 4.26          |
| OOO             | 1.07 ± 0.17                         | 23.60 ± 2.74                         | 0.20 ± 0.01                          | 57.56 ± 3.61            | 6.00 ± 2.70             | 14.61 ± 5.26           | 13.72 ± 4.40          |
| OBR             | 1.04 ± 0.15                         | 22.67 ± 0.40                         | 0.15 ± 0.05                          | 56.26 ± 3.68            | 6.16 ± 2.83             | 14.88 ± 5.05           | 13.82 ± 3.40          |
| OGR             | 1.24 ± 0.24                         | 23.30 ± 1.64                         | 0.38 ± 0.31                          | 56.81 ± 5.43            | 6.72 ± 3.14             | 15.94 ± 5.13           | 12.74 ± 5.80          |
| GAC             | 1.33 ± 0.61                         | 22.87 ± 1.16                         | 0.19 ± 0.05                          | 48.33 ± 14.17           | 6.15 ± 3.73             | 14.94 ± 5.08           | 12.13 ± 5.34          |
| IBC             | 1.11 ± 0.34                         | 20.93 ± 0.85                         | 0.38 ± 0.29                          | 57.66 ± 2.65            | 5.72 ± 3.56             | 14.79 ± 5.02           | 12.79 ± 5.88          |
| OTR             | 1.04 ± 0.37                         | 24.00 ± 1.01                         | 0.23 ± 0.05                          | 56.34 ± 3.82            | 5.37 ± 3.37             | 14.93 ± 5.96           | 12.66 ± 5.23          |
| OAC             | 0.55 ± 0.20                         | 23.47 ± 4.02                         | 0.18 ± 0.05                          | 56.36 ± 4.74            | 5.82 ± 3.08             | 14.36 ± 5.44           | 11.42 ± 4.63          |
| Range           | (BDL-1.96)                          | (10.70-27.70)                        | (0.04-2.23)                          | (1.57-60.74)            | (0.72-8.88)             | (6.01-18.93)           | (1.50-16.48)          |
| Ov.mean±Sd      | 0.88 ± 0.53                         | 21.7 ± 3.95                          | 0.34 ± 0.41                          | 46.59 ± 18.79           | 5.31 ± 2.99             | 14.36 ± 4.54           | 11.18 ± 4.99          |

Mean pH in the dry season was 7.47 ± 0.19. In the wet season, it was 6.42 - 8.20 and the overall mean was 744 ± 0.52. Salt intrusion at all stations was evident with very high levels of salinity, producing a brackish condition all over. Mean temperature was 27.18 ± 0.62 in the dry season, while in the wet season, it was 27.08 ± 0.43. There was no significant change in temperature (p>0.05). Total dissolved solids (TDS) ranged from 445 - 35,700 ppm in the dry season with an overall mean level of 27,797.67 ± 10,786.48. In the wet season, it was from 234 - 37,100 ppm with a mean level of 24,702.87 ± 11,003.99. Salinity levels ranged from 226 - 27,600 ppm with a mean level of 13,791.47 ± 5,333.83. In the wet season, the range was 127 - 17,900 ppm with a mean level of 12,776.60 ± 5,032.70. Conductivity levels in the dry season ranged from 789-67,900 µscm<sup>-1</sup> with a mean level of 53,532.50 ± 29,657.89. In the wet season the ranged was from 430 - 67,300 µscm<sup>-1</sup> with a mean level of 48,837 ± 18,998.03. Seasonal change was not significant (p>0.05).

Levels of hardness (Ca + Mg) ranged from 9.12 – 191.29 ppm with a mean level of  $145.45 \pm 54.25$  in the dry season. In the wet season, the range was 8.42 – 189.29 ppm with a mean level of  $144.18 \pm 59.26$ . Seasonal variation was insignificant ( $p > 0.05$ ) on the combined data of Ca and Mg. However, t-test on each of Ca and Mg data indicated Mg seasonally variable ( $p < 0.05$ ). Levels of total alkalinity in the dry season ranged from 6.90-132 ppm with a mean of  $89.81 \pm 39.53$ . In the wet season, it was from 6.50-190 ppm with a mean of  $104.72 \pm 34.08$ . Seasonal difference was significant ( $p < 0.05$ ). Levels of total suspended solids (TSS) ranged in the dry season from 2.90-38.59 ppm with a mean of  $16.14 \pm 10.83$ , whereas in the wet season, the range was 2.30-33.10 ppm with a mean of  $14.70 \pm 8.69$ . Seasonal difference was insignificant ( $p > 0.05$ ). Turbidity levels ranged from 3.20 – 22.80 NTU in the dry season with a mean level of  $13.04 \pm 5.84$ . In the wet season, it ranged from 2.20-18.30 NTU with a mean level of  $10.67 \pm 4.66$ . Seasonal variation was not significant ( $P > 0.05$ ).

Biological oxygen demand (BOD) levels ranged from 10.60 - 77.30 ppm with a mean of  $37.35 \pm 20.20$  in the dry season. In the wet season, the range was from 10.10 -69.30 ppm with a mean of  $35.42 \pm 14.72$ . Chemical oxygen demand (COD) ranged from 16.10 - 102.80 ppm with a mean level of  $45.43 \pm 24.92$  in the dry season. In the wet season, the range was from 10.40 - 95.70 ppm with a mean of  $43.39 \pm 23.21$ . Dissolved oxygen (DO) levels ranged in the dry season from 2.28 - 4.72 ppm with a mean of  $3.79 \pm 0.64$ . In the wet season, the range was from 2.53-4.75 ppm with a mean of  $3.77 \pm 0.57$ .

Levels of silicates in the dry season ranged from 0.01 – 3.25 ppm with a mean of  $2.48 \pm 0.87$ , while in the wet season, the range was from 0.11 – 3.97 ppm with a mean of  $2.39 \pm 0.83$ . Levels of nitrate in the dry season ranged from below detection limits (BDL) to 1.74 ppm with a mean of  $0.98 \pm 0.55$ . In the wet also, it ranged from BDL to 1.96 ppm with a mean of  $0.88 \pm 0.53$ . Sulphate levels in the dry season ranged from 10.70 – 28.70 ppm with a mean of  $23.13 \pm 3.83$ . In the wet season, the range was from 10.70 – 27.70 ppm with a mean of  $21.70 \pm 3.95$ . Phosphate levels in the dry season ranged from 0.02 – 2.13 ppm with a mean of  $0.39 \pm 0.52$ . In the wet season, the range was from 0.04 – 2.23 ppm with a mean of  $0.34 \pm 0.41$ . Seasonal levels of these nutrient were however comparable ( $p > 0.05$ ).

Sodium levels in the dry season ranged from 7.00 – 11.43 ppm with a mean of  $9.87 \pm 1.08$ . In the wet season, the range was from 6.01 – 18.93 ppm with a mean of  $14.36 \pm 4.54$ . Seasonal levels differed significantly ( $p < 0.05$ ) with higher levels in the wet season. Potassium levels in the dry season ranged from 2.14 – 9.97 ppm with a mean of  $7.58 \pm 2.13$ . In the wet season, the range was from 1.50 -16.48 ppm with a mean of  $11.18 \pm 4.99$ . Seasonal variation was significant ( $p < 0.05$ ). In summary, Total alkalinity (TA),  $Mg^{2+}$ ,  $K^+$ , and  $Na^+$  revealed significant ( $p < 0.05$ ) seasonal variations with respect to higher values in the wet season.

Tables 5a and 5b show the matrices of correlation coefficients between trace metals and physicochemical parameters measured in surface water of Bonny River and creeks around Okrika. Some significant correlation coefficients /r/ were seasonal.

**Table 5a** Correlation matrices: Trace metals versus physicochemical parameters in the dry season

|                                | Hg | Pb      | Ni     | V      | Cd     |
|--------------------------------|----|---------|--------|--------|--------|
| pH                             | -  | 0.099   | 0.114  | 0.544  | 0.097  |
| Temperature                    | -  | -0.411* | 0.236  | -0.088 | -0.219 |
| TDS                            | -  | 0.297   | -0.228 | 0.255  | 0.112  |
| Salinity                       | -  | 0.282   | -0.231 | 0.232  | 0.123  |
| Conductivity                   | -  | 0.243   | -0.212 | 0.227  | 0.130  |
| TH                             | -  | 0.353   | -0.261 | 0.314  | 0.119  |
| TA                             | -  | 0.419   | -0.241 | -0.048 | 0.153  |
| BOD <sub>5</sub>               | -  | -0.298* | -0.018 | -0.453 | -0.153 |
| COD                            | -  | -0.270  | -0.062 | -0.538 | -0.132 |
| DO                             | -  | 0.330   | 0.160  | 0.655  | 0.142  |
| TSS                            | -  | -0.117  | -0.348 | -0.627 | -0.223 |
| Turbidity                      | -  | -0.013  | -0.259 | -0.333 | -0.223 |
| SiO <sub>3</sub> <sup>2-</sup> | -  | 0.124   | -0.250 | 0.274  | 0.102  |
| NO <sub>3</sub> <sup>-</sup>   | -  | 0.364   | 0.007  | 0.271  | 0.238  |
| SO <sub>4</sub> <sup>2-</sup>  | -  | 0.020   | -0.044 | 0.257  | 0.127  |
| PO <sub>4</sub> <sup>3-</sup>  | -  | 0.621** | -0.238 | 0.819* | 0.409* |
| Ca <sup>2+</sup>               | -  | 0.231   | -0.183 | -0.012 | 0.136  |
| Mg <sup>2+</sup>               | -  | -0.137  | -0.251 | 0.002  | -0.022 |
| Na <sup>+</sup>                | -  | 0.044   | 0.021  | 0.214  | 0.177  |
| K <sup>+</sup>                 | -  | 0.174   | -0.237 | 0.150  | -0.028 |

\*  $p < 0.05$  \*\*  $p < 0.01$  • TA- total alkalinity • TH- total hardness In the dry season, significant correlation coefficients were those of Pb/temp; Pb/BOD; Pb/PO<sub>4</sub><sup>3-</sup>; V/PO<sub>4</sub><sup>3-</sup>; Cd/PO<sub>4</sub><sup>3-</sup> ( $p < 0.01, 0.01; 0.05; 0.01; 0.01$ ). Significant metal/metal correlation coefficient was also found for Ni/Pb ( $p < 0.05$ ) in this season.

**Table 5b** Correlation matrices: Trace metals versus physicochemical parameters in the wet season

|                                | Hg | Pb      | Ni       | V      | Cd     |
|--------------------------------|----|---------|----------|--------|--------|
| pH                             | -  | -0.087  | -0.072   | 0.450  | 0.336  |
| Temperature                    | -  | 0.090   | 0.187    | 0.352  | -0.035 |
| TDS                            | -  | 0.250   | -0.070   | 0.319  | 0.396* |
| Salinity                       | -  | 0.313   | -0.139   | 0.347  | 0.307  |
| Conductivity                   | -  | 0.200   | -0.083   | 0.285  | 0.323  |
| TH                             | -  | 0.123   | -0.279   | 0.305  | 0.158  |
| TA                             | -  | -0.073  | -0.258   | -0.119 | 0.201  |
| BOD <sub>5</sub>               | -  | 0.168   | 0.031    | -0.592 | -0.143 |
| COD                            | -  | -0.065  | 0.140    | -0.619 | -0.301 |
| DO                             | -  | 0.126   | -0.004   | -0.275 | -0.098 |
| TSS                            | -  | -0.090  | -0.176   | -0.411 | -0.222 |
| Turbidity                      | -  | -0.111  | -0.150   | -0.435 | -0.174 |
| SiO <sub>3</sub> <sup>2-</sup> | -  | 0.141   | -0.175   | 0.513  | 0.257  |
| NO <sub>3</sub> <sup>-</sup>   | -  | 0.240   | 0.159    | -0.049 | 0.052  |
| SO <sub>4</sub> <sup>2-</sup>  | -  | 0.080   | -0.120   | 0.459  | 0.095  |
| PO <sub>4</sub> <sup>3-</sup>  | -  | -0.137  | -0.121   | -0.231 | -0.110 |
| Ca <sup>2+</sup>               | -  | 0.253   | -0.295   | 0.411  | 0.121  |
| Mg <sup>2+</sup>               | -  | 0.503** | -0.469** | 0.306  | -0.301 |
| Na <sup>+</sup>                | -  | 0.500** | -0.521** | 0.528  | -0.425 |
| K <sup>+</sup>                 | -  | 0.411*  | -0.486*  | 0.412  | -0.187 |

\* p<0.05      \*\* p<0.01      ● TA- total alkalinity      ● TH- total hardness

In the wet season, the significant correlations were Pb/Mg<sup>2+</sup>; Pb/Na<sup>+</sup>; Pb/K<sup>+</sup>; Ni/Mg<sup>2+</sup>; Ni/Na<sup>+</sup>; Cd/Na<sup>+</sup> and Cd/TDS (p<0.05; 0.05; 0.01; 0.01; 0.01; 0.01; 0.01; 0.01). However, a combination of both seasons revealed many pairs.

#### IV. Discussion

Sampling in dry and wet season was to investigate seasonal variabilities of trace metal levels and assess the contribution of runoff water toward trace metal enrichment. It is also to investigate seasonal changes in levels of some water chemical parameters and how these changes affect the levels of trace metals in water.

The use of APDC/MIBK chelation/extraction system was to (i) minimize the interference of major cations that scatter flame, and (ii) to concentrate the metals and increase sensitivity. For any technique to be of value, it is essential that standards closely resemble the samples with respect to the concentration range of analyte(s) and the matrix of the sample. Thus, standard solutions were made to undergo the same procedure as the samples. Such technique tends to minimize matrix differences between samples and standards and the errors in determination that could arise from such effect. It also compensates for lapses in the efficiency of the analytical procedure.

Wastes entering aquatic systems go into the ecosystem. The response of an aquatic system to waste input is a function of the characteristics of the ecosystem, the nature, quality and quantity of wastes (EPA, 1976). The capacity of any particular aquatic system to transform wastes without damage to the ecosystem (self-purification) is a function of the complexity of such environmental factors as the water flow velocity, volume of water, bottom contour, rate of water exchange, currents, depth, light penetration and temperature, as well as re-aeration capacity and chemical and biological interaction within the system (EPA, 1976).

Most flowing systems have greater re-aeration capacity than standing waters, and flowing system are “open systems” with continual renewal of water; whereas standing systems such as lagoons are “closed systems”, and act as “traps” for pollutants. Thus, the system studied which could be considered ‘open’, has high capacity for self-purification due to oxygen diffusion at the surface, together with dilution, which enables the water to assimilate polluting discharges. Consequently, the levels of the metals were low in spite of heavy loadings from human and sundry sources. The generally low levels are also attributable to the brackish condition of the system which may increase the volatilities of many elements, and analyte loss may occur during the pyrolysis step (Haarvad, 2003).

The absence of significant seasonal differences (p>0.05) in the concentrations of some of the trace metals except Pb and Cd, and higher values in the wet season except Ni (Table 2), may be explained as resulting from high flushing and dilution rates during the rains, in addition to the associated velocity of the system or “solution effect” consequent upon a process whereby ions bound in previous semi-dry land by decaying macrophytes get dissolved as water levels increased with inundation of fringing swamps and riparian zones (Welcome, 1986; King and Nkanta, 1991). Owing to the seasonal influence which brought about elevated levels of Pb and Cd in the wet season, the US EPA (US EPA, 2000) limits for marine/brackish and freshwater are slightly exceeded as presented in table 6.

**Table 6** US EPA maximum allowable levels in water compared with mean levels of the brackish water system

| Metal | Bonny River and Creeks around Okrika (ppb) | USEPA maxima (ppb) |            |
|-------|--|--------------------|------------|
|       |  | Marine             | Freshwater |
| Hg    | ND   | <1.0               | <1.0       |
| Pb    | 21.69                                      | 1.0 – 7.0          | <1.0-7.0   |
| Ni    | 38.84                                      | <100               | <100       |
| V     | 0.14                                       | -                  | -          |
| Cd    | 4.45                                       | <0.5 – 5.0         | <0.2-2.8   |

ND: Not Determined

On the other hand, in the dry season, the inflow of water is at minimal level, and under such condition, sedimentation would become more efficient since water is only disturbed by tidal currents. The significant correlations between  $PO_4^{3-}$  and Pb, V and Cd in this season (Table 5a) suggest that these metals are present in their phosphates probably as particulates. In the wet season (Table 5b), the correlations between major metal cations and the trace metals, Pb and Ni are however, not easily explicable, but that of Cd and TDS is an indication that most of the cadmium is in solution. The negatively significant correlations between the trace metals and physicochemical parameters in both seasons may suggest inhibitive tendencies of these water parameters towards mobilization of these metals to the water column (Marcus et. al., 2013).

## V. Conclusion

In the studied brackish water system, the interplay of chemical and physical parameters has resulted in seasonal variations in the levels of both trace metals and physicochemical parameters. The correlations between trace metals and physicochemical parameters have also been observed to reveal seasonal diagenetic changes. Apart from direct discharge of industrial and domestic wastes, the immense volume of storm water runoff and river waters entering the water, and perhaps hydrodynamics and the characteristic features of the area that are inexplicable, may have played significant roles in transporting metals originating from wastes discharge on land and in small streams, especially during the rains. This phenomenon resulted in elevated levels of lead and cadmium in the water column in wet season.

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