

Full Length Research Paper

Distribution of trace metals in surface water and sediments of Imo River Estuary (Nigeria): Health risk assessment, seasonal and physicochemical variability

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The distribution of trace metals (Zn, Cu, Ni, Mn, Fe, Co, V, Pb and Cd) in surface water and sediments from Imo River estuary in relation with the physicochemical variables were studied for both dry and wet seasons. The results obtained revealed that trace metal levels displayed marked spatial and seasonal variations in surface water and sediments, which is attributed to both anthropogenic natural processes in the environment. Trace metal levels were generally higher in the sediments than overlying water column. Seasonal variability in trace metal distribution was mostly observed in sediments than in the water phase of the relatively anoxic estuarine ecosystem. The highest average concentration of trace metal in the sediments was recorded for Fe (1101.18 mg/kg) during the dry season while the lowest was recorded for Cd (0.08 mg/kg) during the wet season. For the surface water, highest average concentration was recorded for Zn (0.04 mg/L) for the dry season and the lowest level was recorded for Cd (0.002 mg/L) for both seasons. The levels of trace metals in the water were within the permissible limits of some regulatory bodies. Pearson correlation analysis revealed that some of the physicochemical variables were associated with patterns of trace metals distribution. Based on trace metal concentrations, the health risk assessment based on the chronic daily intake (CDI) and hazard quotients (HQ) were calculated. Zinc and cadmium contributed most to the total intake through drinking water. As HQ for all trace metals were less than unity, it is suggested that there is little or no significant health risk to the exposed population.

Key words: Trace metals, surface water, sediments, seasons, Imo River estuary, Nigeria.

INTRODUCTION

In Nigeria, a large number of rural and suburban dwellers derive their drinking water from groundwater and surface water resources such as rivers, lakes and reservoirs. Therefore, the quality of drinking water remains a critical

factor in the Nigerian public health (FMWR, 2000). More so, that Nigeria is among 80 countries of the world reported to be facing water deficit (Ahuja, 2012) calls for reliable information for effective management,

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preservation and utilization of available natural waters. As an index of contamination, the presence of trace metals in fresh water ecosystems has been a major concern to many (Iqbal et al., 2013; Muhammad et al., 2011; Tamasi and Cini, 2004). This concern is due to the fact that trace metals constitute one of the most insidious and dangerous contaminants known to man. The accumulation of these metals in the environment may constitute a threat to aquatic biota where they are often accumulated. This leads to an amplification of their levels along the food chain. This poses serious health implications as well as a threat to food security.

Sediments are considered as suitable medium to study the contamination of aquatic environment because they represent the sink of multiple contaminant sources (Sprovieri et al., 2007). Apart from being a final reservoir for these contaminants, sediments act as their secondary sources in relation to changes in environmental physicochemical characteristics and response to human activities such as dredging (Sprovieri et al., 2007; Eggleton and Thomas, 2004). Sediments are important carriers of trace metals in the hydrological cycle and because metals are partitioned within the surrounding waters, they reflect the quality of aquatic system. As a result, pollutant species in sediment cores have been used as "pollutant records" in some studies (Chatterjee et al., 2007). In order to design abatement programmes for contaminated environments, it is often useful to understand the behaviour of the contaminants in relation to certain environmental conditions, both physical and chemical. This has necessitated the study of the influence of certain environmental factors on the distribution of legacy chemical toxicants in aquatic environments.

It is of interest to examine the distribution of trace metals in surface water and sediments of a turbulent estuary such as the Imo River in South Eastern Nigeria. The study area has witnessed massive changes in industry and shifts in population and social culture. A significant ecological change is pronounced in this estuarine environment due to huge discharges of domestic, agricultural, and industrial wastes coupled with increased agricultural activities and emergence of an aluminium smelting company. The estuary has become vulnerable to chemical pollutants. To the best of our knowledge, there has been no research on the distribution of trace metals in the surface water and sediments of the estuary in relationship with physicochemical variables as well as the consideration of risk of human exposures to the metals through drinking water.

MATERIALS AND METHODS

Study site

The study area is the southern segment of the Imo River estuary in Ikot Abasi, Akwa Ibom State (Southeast Nigeria). The area lies between latitudes 4°30' N and 4°45' N and longitudes 7°19' E and 7°45' E. The Imo River estuary opens into the Atlantic Ocean at the

Bight of Bonny. The estuary has a shallow depth ranging from 5 to 8 m at flood and ebb tides though some spots may be deeper. The area is a multi-use resource for artisanal and commercial fishing and transportation. Other economic activities in and around the estuary include oil exploration and aluminium smelting. The climate of the area is characterised by distinct wet and dry seasons. The area is a mangrove estuarine ecosystem.

Sample collection

Fourteen sampling locations were strategically chosen along the length of the Imo River Estuary (Figure 1). At each sample stations, two subsamples were made into composites for dry and wet seasons, making a total of forty eight samples. The top 20 cm of the bottom sediments were collected using a Van Veen grab sampler and transferred into plastic containers (Loring and Rantala, 1992). Water samples were collected at the depth of 10 cm below the water surface using one litre polyethylene plastic containers. The samples were stored in ice-packed coolers and transported to the laboratory where they were kept in a freezer at -4°C before analyses. During sampling campaigns, some physicochemical parameters (pH, conductivity, salinity and redox potential) were measured *in situ* using a handheld multi-parameter probe (YSI 556, YSI Incorporated, USA).

Sample pretreatment and preparation

Water samples for trace metal analysis were filtered using a pre-weighed acid wash 0.45 µm pore size polycarbonate filters. Filtrates were acidified with concentrated trioxonitrate (HNO₃) (V) acid to a pH below 2 to minimise precipitation and adsorption of metals on the walls of the containers. Sediment samples were air-dried and ground using porcelain mortar and pestle. The texturally equivalent petite fractions (< 75 µm) of the sediments were separated by sieving through a 230 mesh nylon sieve. About 1 g of the powdered forms were digested with 20 dm³ aqua regia (3HCl:1HNO₃) and concentrated to < 2 dm³ volume on a silica beaker. The solutions were filtered into acid-washed 100 dm³ volumetric flask after being rinsed with deionised water. Further, the solutions were made up to 50 dm³ with deionised water prior to trace metal analysis.

Instrumental analysis by AAS

Analysis of filtrates and digests for trace metals were done using atomic absorption spectrophotometer (UNICAM 939). Prior to analysis, 200 ml aliquot of the filtered water samples were extracted by chelation with ammonium pyrrolidine dithiocarbamate reagent (APDC) into 20 ml methyl isobutyl ketone (MIBK) as the extraction solvent as reported by Hatje et al., (2003). Standard solutions of each metal were prepared for calibration. Reagent blanks and the replicate samples were analyzed for quality control. The detection limits of the metals under study were: Cu 0.1 mg/L, Zn 0.01 mg/L, Ni 0.001 mg/L, Mn 0.01 mg/kg, Iron 0.1 mg/kg, Co 0.001 mg/kg, V 0.01 mg/kg, Pb 0.1 mg/kg and Cd 0.1 mg/kg. Other details of the analytical procedures are reported elsewhere (Hatje et al., 20013; Aktar et al., 2010).

Risk assessment procedure

Risk assessment of environmental contaminants is concerned first with identifying the hazards which substances or energy may pose threat to the health of people, animals and plants including the damages they may cause to structures and commodities and,

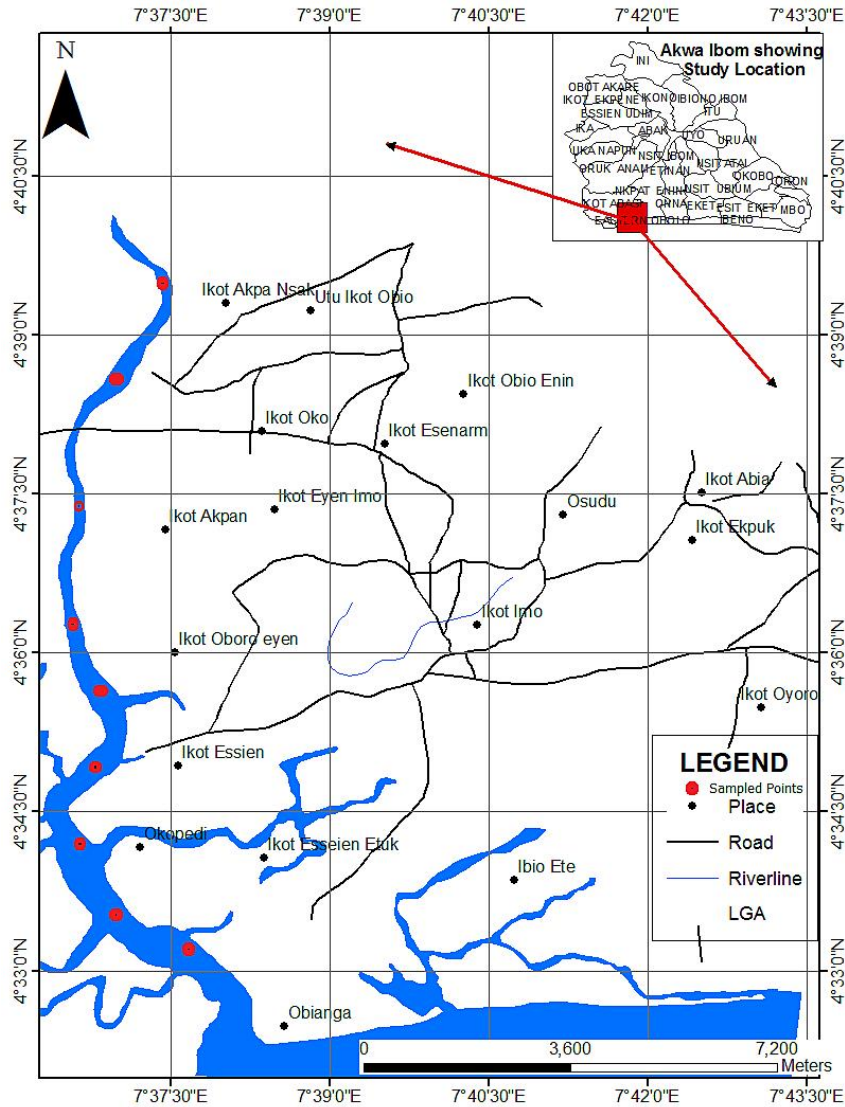


Figure 1. Imo River Estuary showing sample locations.

secondly, with quantifying as well as estimating the probability of these types of harm occurring (Alloway and Ayres, 1993).

Although the study area is an estuary characterised by mixing from both freshwater rivers and streams with inputs from the ocean, some local inhabitants use the source of water for drinking purposes. The major difference between risk assessment and mere comparison of monitoring data with permissible limits is that in risk assessment exposure routes, quantity of toxicant, frequency of exposure and body weight of the exposed individual is considered. It therefore becomes an imperative tool for assessing risk of target groups.

Daily intake of trace metals

This study focuses on the oral ingestion pathway. The chronic daily intake (CDI) through the drinking of water was calculated using a modified equation from Kavcar et al., (2009) as shown below:

$$CDI = \frac{C \times DI}{BW} \tag{1}$$

Where, C, DI and BW represent the concentration of trace metals in water (mg/L), average daily intake rate (2 l/day for an adult) and average body weight (70 kg for an adult) according to USEPA (1989).

Hazard quotient indices

The degree of harm is estimated in terms of the hazard quotient (HQ) as expressed in the equation from Shah et al., (2012):

$$HQ = \frac{CDI}{RfD} \tag{2}$$

Where, the oral toxicity reference dose (RfD) values are 5.0E-04,

Table 1. Average trace metal levels in surface water and sediment in wet and dry season (mg/L).

| Variables | Season | Zn | Cu | Ni | Mn | Fe | Co | V | Pb | Cd |
|---------------|------------|------------|-----------|-------------|-------------|--------------|-------------|------------------|-------------|-------------|
| Sediments | Wet season | 75.00±0.04 | 7.75±0.05 | 8.22±0.05 | 243.76±0.04 | 1099.58±0.27 | 3.52±0.04 | 12.50±0.04 | 4.82±0.05 | 0.08±0.04 |
| | Dry season | 83.42±0.04 | 7.95±0.04 | 8.50±0.04 | 246.23±0.04 | 1101.18±0.04 | 3.90±0.04 | 12.99±0.04 | 5.08±0.04 | 0.09±0.04 |
| Surface water | Wet season | 0.04±0.04 | 0.02±0.04 | 0.01±0.03 | 0.01±0.04 | NA | 0.004±0.037 | 0.008±0.135 | 0.004±0.037 | 0.002±0.037 |
| | Dry season | 0.03±0.04 | 0.01±0.04 | 0.003±0.032 | 0.01±0.04 | NA | 0.004±0.037 | 0.008±0.135 | 0.004±0.037 | 0.002±0.037 |
| *WHO | | 3.0 | 2.0 | 0.02 | 0.1 | | 0.04 | 0.3 ^a | 0.01 | 0.003 |

NA = not analysed, *WHO permissible values for drinking water, ^aUSEPA (1995).

3.7E-02, 1.4E-01, 2.0E-02, 3.6E-02, 3.0E-01, 3.0E-04, 7.0E-03, mg/kg-day for Cd, Cu, Mn, Ni, Pb, Zn, Co, and V respectively (USEPA, 2005; Iqbal et al., 2013; Muhammad et al., 2010; USEPA, 1995). The exposed population is assumed to be safe when HQ<1 (Khan et al., 2008; Muhammad et al., 2010).

Statistical analysis

Basic statistics were performed using Microsoft Excel while multivariate correlation matrix were performed using Statistical Package for Social Sciences (SPSS) version 15.

RESULTS AND DISCUSSION

Distribution and seasonal variation in trace metal levels

The levels of trace metals in sediment and surface water samples of Imo River estuary for both wet and dry seasons are presented in Table 1. Generally, the levels of trace metals were higher in sediment samples. This may be as a result of simple settlement from the water column or as a result of preferential partitioning of the trace metals to the sediments. Also, adsorption and complexation with organic matter in the sediment as well as precipitation may have been responsible

for this observation (Eggleton and Thomas, 2004). As observed in Table 1, the trace metal levels in sediments appear to be generally higher during the dry season than in the wet season. The dry seasons are usually characterised by marked reduction in the water volume in rivers. This may have influenced the relatively higher concentration of the trace metals during the dry season.

The highest concentration was recorded for Fe; 1099.58 and 1101.18 mg/kg for wet and dry seasons respectively. The least concentration was recorded for Cd; 0.08 and 0.09 mg/kg for wet and dry seasons respectively. The trace metal levels in surface water samples were quite lower than the levels recorded for the sediments. The highest level in surface water was recorded for Zn (wet 0.04 mg/L; dry 0.03 mg/L). The levels of the trace metals in water were all within permissible limits (WHO, 2008).

There was no significant variation in the trace metals levels in the surface water for both seasons. This observation may be due to the fact that the water column is continually and rapidly affected by several environmental changes and flows. As a result, accumulation of trace metals at a point over a period of time is practically impossible, leading to essentially low levels of trace metals. Another factor that may have

influenced the presence of trace metals in the water column was the pH, which was essentially at a neutral point (Table 2). This result indicates that in spite of the higher levels of trace metals in sediment cores, their dissolution into the water column would have been restricted by the almost neutral pH.

Physicochemical variability in relation with trace metal levels and distribution

The results of the physicochemical variables are presented in Table 2. Physicochemical parameters recorded for the study location did not show any significant variation between seasons. Conductivity and pH values were within the permissible limits of WHO (2008). The low conductivity values of the water samples are remarkably reflected in the low levels of soluble trace metals in the water column (Table 2). The high percentage of salinity observed in the water body is indicative of possible mixing of freshwater tributaries and saline Atlantic Ocean. This further suggests high inputs of metals into the water body.

Also, since salinity is mostly related to chloride content (IEPA, 2001), the result indicates possible risk for agricultural and domestic use of the water.

Table 2. Average physicochemical variables of surface water in wet and dry season.

| Season | pH | Conductivity (m scm^{-1}) | Salinity (%) | Redox potential (mV) |
|------------|-----------------|-------------------------------------|------------------|----------------------|
| Wet season | 7.16 \pm 0.03 | 41.63 \pm 0.04 | 26.23 \pm 0.04 | -9.57 \pm 0.04 |
| Dry season | 7.20 \pm 0.03 | 43.21 \pm 0.04 | 28.03 \pm 0.04 | -13.93 \pm 0.04 |
| WHO (2008) | 6.0-9.0 | 4000 | | |

Table 3. Correlation matrix for trace metal levels in sediment during dry season.

| Metal | Zn | Cu | Ni | Mn | Fe | Co | V | Pb | Cd |
|-------|---------|---------|---------|---------|--------|--------|--------|--------|----|
| Zn | 1 | | | | | | | | |
| Cu | 0.707** | 1 | | | | | | | |
| Ni | 0.725** | 0.789** | 1 | | | | | | |
| Mn | 0.706** | 0.492 | 0.628* | 1 | | | | | |
| Fe | 0.393 | 0.648* | 0.595* | 0.000 | 1 | | | | |
| Co | -0.333 | -0.260 | -0.056 | -0.341 | 0.173 | 1 | | | |
| V | 0.641* | 0.646* | 0.841** | 0.722** | 0.287 | 0.023 | 1 | | |
| Pb | -0.064 | -0.018 | 0.061 | -0.376 | 0.174 | 0.479 | 0.065 | 1 | |
| Cd | -0.220 | 0.068 | -0.224 | -0.065 | -0.007 | -0.390 | -0.123 | -0.138 | 1 |

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

On the other hand, the high salinity of the river may help in limiting the bioavailability of trace metals in the estuarine ecosystem thereby protecting estuarine organisms (Lores and Pennock, 1998).

The redox potential characterizes the oxidation-reduction state of natural waters. Redox reactions in aquatic systems are central in element cycling, sorption processes, trace metals mobility and toxicity (Grundl et al., 2011). In this study, the negative redox potential values indicate that the estuarine ecosystem was reducing in nature during the period of investigation. This represents anoxic conditions with low oxygen content. The implication of this is that mobility of trace metals would be limited. This is in good agreement with the observed high but somewhat immobile trace metal levels in the sediment cores (Table 1). As observed by De Jonge et al. (2012), increasing oxygen concentrations due to general water quality improvements can enhance trace metal mobility through oxidation which may release sediment-bound metals to the overlying surface water.

In order to understand the observed distribution of trace metals in relation to their possible sources or inter-relationship, experimental data were subjected to Pearson correlation analysis. In both dry and wet seasons, significant and positive correlations were found for majority of the metals in the sediments, except for Co, Pb and Cd (Tables 3 and 4). Alloway and Ayres (1993) had suggested that positive correlation may result from their co-precipitation in marine and aquatic environments. Vanadium showed significant positive correlation with most of the metals investigated. This result indicates similarity in source of contamination in the study area.

Unlike the similarities and correlation between trace

metals in both wet and dry seasons observed for sediments, significant difference could be observed in the case of surface water (Tables 5 and 6). Negative correlation was observed for redox potential. Strong and positive correlation was observed between Zn, pH, conductivity and salinity in the wet season while V and Cu correlated positively with pH, conductivity and salinity in the dry season.

Observed variability in trace metal distribution in relationship with the physicochemical parameters may be due to the possible differences in the pattern of human activities in the two seasons. Also, characteristics in water chemistry in estuaries are said to be more complicated than in rivers and lakes since they are influenced by the inflow of freshwater from rivers and streams, by tides of the oceans, large salinity, stratification, while the back-and-forth movement of the water during the tides enhance dispersion and mixing (Hemond and Fechner-Levy, 2010). These factors may have greatly affected the divergent patterns in trace metals distribution and relationship with physicochemical parameters in the two seasons studied.

Risk assessment

Chronic daily intake (CDI) and hazard quotient (HQ) indices

The estimated CDI indices for ingestion of drinking water are presented in Table 7; showing values predicted for an exposed adult. The result reveals that Zn contributed most to the CDI of trace metals through drinking water

Table 4. Correlation matrix for trace metal levels in sediment during wet season.

| Metal | Zn | Cu | Ni | Mn | Fe | Co | V | Pb | Cd |
|-------|---------|---------|---------|---------|--------|--------|--------|--------|----|
| Zn | 1 | | | | | | | | |
| Cu | 0.683** | 1 | | | | | | | |
| Ni | 0.702** | 0.758** | 1 | | | | | | |
| Mn | 0.699** | 0.454 | 0.549* | 1 | | | | | |
| Fe | 0.361 | 0.678** | 0.599* | 0.031 | 1 | | | | |
| Co | -0.287 | -0.167 | -0.074 | -0.192 | 0.226 | 1 | | | |
| V | 0.654* | 0.619* | 0.803** | 0.688** | 0.278 | 0.037 | 1 | | |
| Pb | -0.043 | -0.014 | 0.012 | -0.355 | 0.179 | 0.389 | 0.042 | 1 | |
| Cd | -0.247 | 0.061 | -0.218 | -0.041 | -0.024 | -0.432 | -0.137 | -0.166 | 1 |

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

Table 5. Correlation matrix between trace metal levels and physicochemical parameters in surface water during dry season.

| Metal | Zn | Cu | Ni | Mn | Co | V | Pb | Cd | pH | Conductivity | Salinity | R.P |
|--------------|--------|---------|--------|---------|--------|--------|--------|--------|----------|--------------|----------|-----|
| Zn | 1 | | | | | | | | | | | |
| Cu | 0.403 | 1 | | | | | | | | | | |
| Ni | 0.564* | 0.471 | 1 | | | | | | | | | |
| Mn | -0.051 | 0.059 | -0.258 | 1 | | | | | | | | |
| Co | 0.502 | 0.629* | 0.418 | 0.166 | 1 | | | | | | | |
| V | 0.041 | 0.456 | -0.047 | 0.848** | 0.296 | 1 | | | | | | |
| Pb | 0.149 | 0.427 | 0.126 | -0.130 | 0.221 | 0.164 | 1 | | | | | |
| Cd | 0.079 | 0.358 | -0.190 | 0.173 | 0.094 | 0.476 | 0.412 | 1 | | | | |
| pH | 0.315 | 0.685** | 0.552* | 0.087 | 0.351 | 0.534* | 0.317 | 0.476 | 1 | | | |
| Conductivity | 0.445 | 0.746** | 0.399 | 0.235 | 0.383 | 0.620* | 0.528 | 0.345 | 0.781** | 1 | | |
| Salinity | 0.514 | 0.742** | 0.407 | 0.207 | 0.505 | 0.578* | 0.573* | 0.325 | 0.773** | 0.973** | 1 | |
| R.P | -0.201 | -0.618* | -0.530 | 0.193 | -0.245 | -0.264 | -0.214 | -0.477 | -0.920** | -0.588* | -0.564* | 1 |

*Correlation is significant at the 0.05 level (2-tailed), **Correlation is significant at the 0.01 level (2-tailed), RP= Redox potential.

Table 6. Correlation matrix between trace metal levels and physicochemical parameters in surface water during wet season.

| Metal | Zn | Cu | Ni | Mn | Co | V | Pb | Cd | pH | Conductivity | Salinity | R.P |
|--------------|---------|---------|----------|---------|--------|--------|--------|--------|----------|--------------|----------|-----|
| Zn | 1 | | | | | | | | | | | |
| Cu | 0.015 | 1 | | | | | | | | | | |
| Ni | 0.162 | 0.544* | 1 | | | | | | | | | |
| Mn | 0.142 | 0.029 | 0.306 | 1 | | | | | | | | |
| Co | 0.380 | 0.187 | 0.273 | 0.124 | 1 | | | | | | | |
| V | 0.355 | 0.224 | 0.617* | 0.782** | 0.333 | 1 | | | | | | |
| Pb | 0.288 | 0.050 | 0.148 | -0.068 | 0.483 | 0.252 | 1 | | | | | |
| Cd | 0.192 | -0.053 | 0.060 | 0.133 | 0.129 | 0.415 | 0.500 | 1 | | | | |
| pH | 0.641* | 0.230 | 0.594* | -0.016 | 0.486 | 0.449 | 0.426 | 0.278 | 1 | | | |
| Conductivity | 0.713** | 0.495 | 0.606* | 0.185 | 0.378 | 0.607* | 0.513 | 0.348 | 0.775** | 1 | | |
| Salinity | 0.750** | 0.315 | 0.526 | 0.234 | 0.294 | 0.652* | 0.518 | 0.460 | 0.805** | 0.951** | 1 | |
| R.P | -0.193 | -0.566* | -0.676** | 0.241 | -0.207 | -0.302 | -0.278 | -0.422 | -0.678** | -0.646* | -0.577* | 1 |

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

from the Imo River for wet season while Cd contributed most for dry season calculations. Zinc and cadmium

usually occur together (Baird and Cann, 2008). This may be responsible to the high CDI values of the two metals in

Table 7. Summary chronic daily intake (CDI) and hazard quotient (HQ) indices for drinking water from Imo River Estuary.

| Metal | Zn | Cu | Ni | Mn | Co | V | Pb | Cd |
|-------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| Wet season | | | | | | | | |
| CDI | 1.19E-03 | 4.84E-04 | 1.35E-04 | 3.69E-04 | 1.12E-04 | 2.39E-04 | 1.22E-04 | 6.94E-05 |
| HQ | 3.97E-03 | 1.34E-02 | 6.75E-03 | 2.64E-03 | 3.74E-01 | 2.44E-02 | 3.40E-03 | 1.39E-01 |
| Dry season | | | | | | | | |
| CDI | 7.46E-04 | 4.18E-04 | 6.74E-05 | 2.24E-04 | 7.95E-05 | 1.78E-04 | 8.16E-05 | 4.11E-03 |
| HQ | 2.49E-03 | 1.13E-02 | 3.37E-03 | 6.59E-04 | 2.67E-01 | 2.19E-02 | 2.55E-03 | 8.15E-02 |

addition to anthropogenic inputs. There is call for concern over the high intake of cadmium in the study area since the metals belong to the most dangerous class of metal toxicants. The HQ indices are also summarised in Table 7. The highest HQ value was recorded for Cd while the least was recorded for Mn. The HQ indices for all trace metals, which were less than unity, suggest ignorable or no significant risk to the local population drinking water from the studied area.

Conclusion

The study revealed that the Imo River estuary is impacted with very low contamination of trace metals largely influenced by both natural and anthropogenic inputs. The study also revealed that the water body is an anoxic estuarine ecosystem influenced by dynamics both freshwater characteristics and oceanic inputs. The high levels of trace metals recorded in sediment are of major concern since there is possibility of dissolution into the water column and possible uptake and bioaccumulation by aquatic organisms over time. The physicochemical variables also exerted certain influence on each other as well as the trace metal distribution and levels. Trace metal levels in the drinking water were below permissible limits set by WHO and USEPA. Risk assessment based on consumption of water by adults revealed no significant health risk.

Conflict of Interests

The authors have not declared any conflict of interest.

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