Spatio-Temporal Distribution of Heavy Metals in Sediments and Surface Water in Stubbs Creek, Nigeria

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Abstract: Sediment and surface water samples collected from the Stubbs Creek, Nigeria, were analyzed for concentrations of cobalt, iron, lead, nickel, vanadium and zinc using inductively coupled plasma spectrometer (Optima 3000-Perkin Elmer). Mean spatial levels of heavy metals in intertidal sediment (Co:1.20±0.55; Fe: 79.98±6.09; Ni: 22.23±8.48; Pb: 11.95±3.85; V: 38.48±10.58 and Zn: 20.45±8.30 mg kg^{-1}) and temporal composition in subtidal sediment (Co:0.35; Fe: 48.42; Ni: 8.73; Pb: 2.25; V: 18.65 and Zn: 6.82 mg kg^{-1}) were relatively higher than concentrations in surface water (Co:0.19; Fe: 10.41; 6.00; Pb: 0.74; V: 1.81 and Zn: 0.12 mg kg^{-1}). Spatial and temporal variability in sediment and water metal concentrations displayed a consistent distribution trend. The coefficients of variation for the heavy metals revealed the relative high variabilities Co, Fe, Pb, V and Zn in the sediments and Fe, Ni, Pb and V in surface water. The Pearson linear correlation analysis showed that the mean concentrations of zinc, lead, cobalt and nickel in surface water revealed a significantly positive correlated values (p = 0.05) to the levels in subtidal sediment. Correlations between pairs of Co and Zn (r = 0.81, 95% CI = 0.00 to 0.98), Fe and Zn (r = 0.85, 95% CI = 0.14 to 0.98), Ni and Co (r = 0.85, 95% CI = 0.13 to 0.98) in intertidal sediments indicated positive significant (p = 0.05) co-accumulation potentials.

Key words: Sediments, heavy metals, Stubbs Creek, Nigeria

Introduction

Human-mediated activities have locally and episodically introduce numerous potentially hazardous metals to the environment since the onset of industrial revolution (Nriagu, 1996; Celik *et al.*, 2005; Yang and Rose, 2005; Udosen *et al.*, 2006). Aquatic ecosystems are very vulnerable to water and sedimentary pollution. Concern over the environmental, aquatic and human health impacts associated with heavy metals distributions and concentrations in aquatic environments has a long history (Sastry and Tyagi, 1982). Notably, aquatic ecosystems are often polluted with anomalously high levels of toxicants (organic and inorganic substances), which find their way into the aquatic systems with wastewaters and effluents generated from industrial enterprises (Yang and Rose, 2005). Heavy metal accumulation in aquatic ecosystem shows that they are accumulated either in aquatic organisms or in sediments (Malagi *et al.*, 1998; Riba *et al.*, 2003; Yilmaz, 2005). In many studies, sediments have been shown to be the final destination of most metal toxicants following several chemical and biological processes (Bordas and Bourg, 2001).

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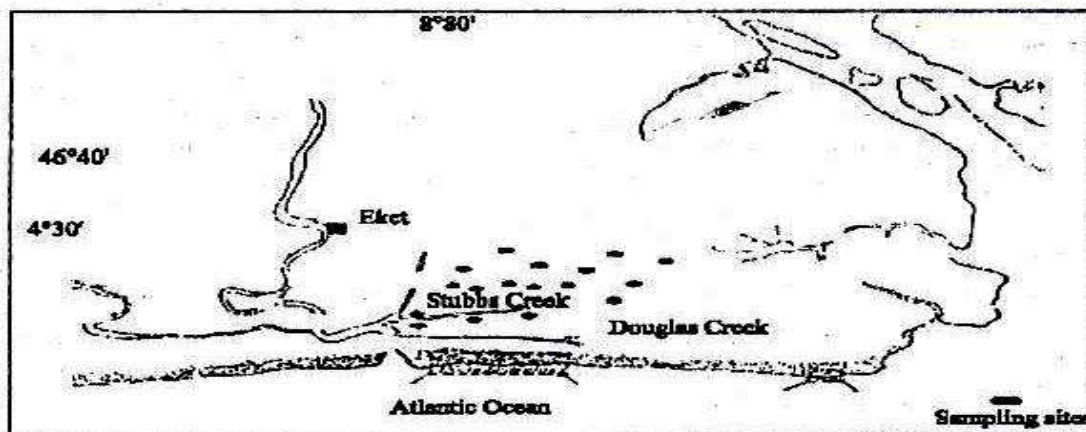
Fig. 1: Map of the Niger Delta region showing sampling area

Heavy metals represent significant sources of pollution for the aquatic environment as a result of changes in pH, redox potential, diagenesis or physical perturbations within their primary sedimentary sinks. The occurrence of enhanced concentrations of heavy metals especially in sediments may be an indication of human-induced perturbations rather than natural enrichment through geological weathering (Davies *et al.*, 1991; Binning and Baird, 2001; Eja *et al.*, 2003). Heavy metals are non-biodegradable and they persist in the environment and may become concentrated up the food chain (Eja *et al.*, 2003), leading to enhanced levels in liver and muscle tissues of fishes (Benson *et al.*, 2005), aquatic bryophytes (Mouvet *et al.*, 1993; Chmielewska and Medved, 2001) and aquatic biota (Ramos *et al.*, 1999). It therefore means that the biota, water and sediment quality of an aquatic ecosystem could determine the quantitative and qualitative levels of heavy metals in tissues of fauna and flora of the ecosystem. Heavy metal distribution and bioavailability in both sediments and the overlying water column have to be considered to obtain a better understanding of interactions between the organisms and their environment. Besides physicochemical parameters, untreated effluents, accidental oil spills, wastewaters from on- and off-shore facilities could directly or indirectly influence the hydro-biochemical integrity of aquatic ecosystems.

The Stubbs Creek is a freshwater tributary of the Qua Iboe River, which together with Widenham Creek links the estuary with Cross River Estuary. Stubbs Creek, located in Ibeno area of Akwa Ibom State, Nigeria, is of economic importance to petroleum industry cited in the area. The creek is continuously exposed to significant anthropogenic impacts arising from crude oil terminal/tank farm located close to it. Sewage effluents from industrial and domestic sources are discharged untreated into the creek. Therefore, toxicants introduced anthropogenically into it are bound to bioaccumulate in sediments. The majority of studies to date focused on Qua Iboe River and the associated estuary. However, Udosen (2001) and Ntekim *et al.* (1992) reported on heavy metals pollution of the upper reaches of the Qua Iboe Estuary while little or no data are available on the pollution indices of the lower reaches of the estuary and associated creeks, where petroleum exploitation and exploration activities pose direct threats to the ecosystem. Studies on the creeks especially Stubbs Creek have been greatly hampered due to accessibility challenges. The pre-industrial status of heavy metals in the surficial and benthic sediments, and interstitial water of the Stubbs Creek is not well known,

The aim of this study is to look at the spatial and temporal distributions of some heavy metals (Co, Ni, V, Fe, Pb and Zn) in sediments and surface water of Stubbs Creek and compare their concentrations with the sediments and water quality in Qua Iboe river. It also discusses some of the factors which affects the distribution of the metals in the surface water column and sediments. The information will provide a baseline data for future use.

Study Area

The Stubbs Creek is an inter-riverine, palustrine biotope that connects Qua Iboe River with Cross River and is located (latitude 4° 30'- 4° 35' N and longitude 7° 55'- 8° 05' E), within the Niger Delta region of Nigeria (Fig. 1). The Creek is a left bank tributary of Qua Iboe River, which is under the tidal influence of the Atlantic Ocean. Stubbs Creek is used for fishing, transport and discharge of industrial and domestic wastes.

Materials and Methods

Intertidal sediment samples were obtained with a 6.5 cm diameter corer to a depth of 30 cm. Subtidal sediment samples were collected using a modified Van veen Grab sampler (0.1 m²). Sediments collected were stored in clean plastic bottles, labeled and taken to the laboratory for further treatment and analysis. Water samples were collected using clean 1litre glass containers (Radojevic and Bashkin, 1999). Fifty-four surface water and intertidal sediment samples were obtained separately in triplicates from each location for six months (May-October, 2003). Eighteen subtidal sediments were also collected during the period. Monthly sampling of surface water, intertidal and subtidal sediments were carried out.

All sediment samples were oven dried at 80 to 100°C, gently crushed and sieved to collect the < 63 μm grain size. Accurately weighed (1.0 g) samples of sieved sediments were treated with 10 mL of 0.25 M HNO_3, heated to dryness and thereafter 10 mL of 0.25 M HNO ,and 3.0 mL of $HClO_4$ added. The solution was then heated to fume in a fume chamber. Sample solutions were obtained by leaching the residues with 4.0 mL of HCl and thereafter filtered and diluted with distilled water to 100 mL mark (Binning and Baird, 2001). The solutions were analyzed for metals inductively with coupled plasma spectrometer (Optima 3000-Perkin Elmer).

Surface water samples (SCW) were also collected from the upstream (UPS), midstream (MDS) and downstream (DNS) sections of the creek. The samples were collected with the aid of clean 1 L capacity plastic bottles, filtered, labeled and treated with 1.5 mL of concentrated HNO_3 to give a pH ≤ 2 (Radojevic and Bashkin, 1999). Analysis of water samples for heavy metals was done using coupled plasma spectrometer (Optima 3000-Perkin Elmer).

One gram of each intertidal sediment sample was weighed into a pre-weighed dry crucibles and contents covered with lids. These were placed in a muffle furnace and the temperature gradually increased to 500°C for 4 h. The samples were removed, cooled to room temperature in desiccators and thereafter reweighed. The loss-on-ignition (L.O.I) was equated to organic matter (Radojevic and Bashkin, 1999).

Results and Discussion

The results for heavy metals concentration in the surface water at the upstream, midstream and downstream locations of the creek (Fig. 2) have shown that the temporal water composition ranged from 0.09±0.05 to 0.31±0.09 mg kg^{-1} for Co; 6.42±0.15 to 12.65±1.05 mg kg^{-1} for
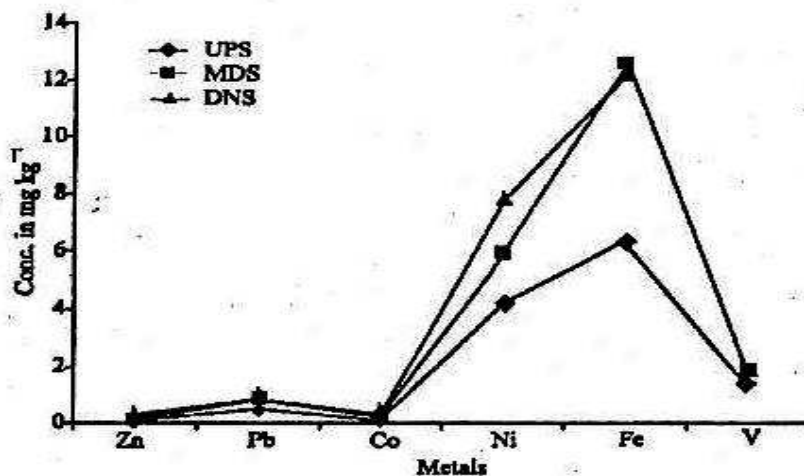
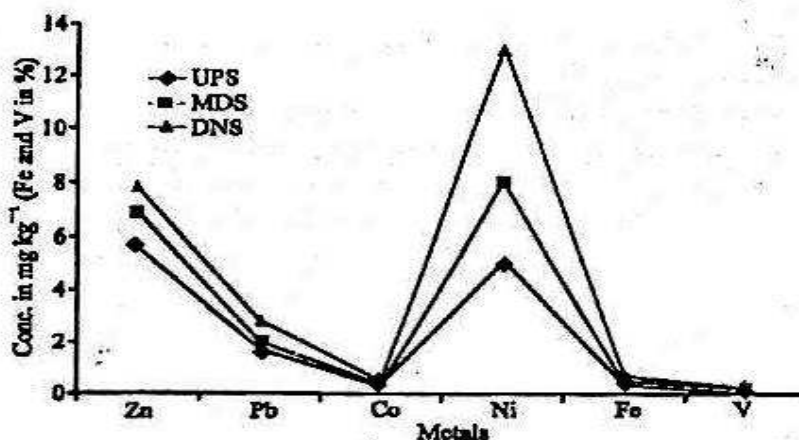Fig. 2: Mean concentrations of heavy metals in surface water from Stubbs creek

Fig. 3: Mean concentrations of heavy metals in subtidal sediments from Stubbs creek

Fe; 4.27±1.38 to 7.78 v 1.14 mg kg^{-1} for Ni; 0.53±0.13 to 0.89±0.06 mg kg^{-1} for Pb; 1.49±0.33 to 1.99±0.05 mg kg^{-1} for V; 0.07±0.02 to 0.20±0.04 mg kg^{-1} for Zn. At the different locations, Fe recorded the highest mean concentrations while Zn indicated the lowest mean levels.

The mean concentrations of metals in subtidal (benthic) sediment at the DNS, MDS and UPS locations were 0.45±0.05, 0.33±0.11 and 0.27±0.09 mg kg^{-1} for Co; 63.22±6.39, 44.67±10.87 and 37.38±3.78 mg kg^{-1} for Fe; 13.03±1.64, 8.02±3.21 and 5.15±1.62 mg kg$^-$ for Ni; 2.94±0.09, 2.07±0.31 and 1.73±0.24 mg kg^{-1} for Pb; 23.12±2.17, 16.60±3.88 and 16.23±1.96 mg kg^{-1} for V; 7.79±0.48, 7.00±0.55 and 5.68±0.03 mg kg^{-1} for Zn, respectively (Fig. 3). The concentrations of the heavy metals were comparatively very high in the downstream subtidal sediments analyzed than those from the midstream and upstream locations. This is an indication of the continuous transport of the metal pollutants down the course of the creek. Pb and Co exhibited very low concentrations compared to Fe and V, which were relatively high. Iron recorded the highest temporal concentration at all locations (Fig. 3). In general, the trend in heavy metal variability and mean concentrations in the subtidal sediments was Ni>Pb>Fe>Co>V>Zn and Fe>V>Ni>Zn>Pb>Co, respectively.

Table 1: Mean concentrations (mg kg⁻¹) in intertidal (epipellic) sediments of Stubbs Creek

Sites	Heavy metals concentrations in (mg kg⁻¹) and LOI%						
	Zn	Pb	Co	Ni	Fe	V	LOI (%)
EPP-1 (5 cm)	12.40±0.62	5.06±0.40	0.85±0.35	16.80±1.50	80.10±4.63	31.80±2.66	3.60
EPP-2 (10 cm)	17.80±0.08	12.10±0.03	1.50±0.70	22.10±1.05	68.50±2.80	51.20±3.00	8.00
EPP-3 (15 cm)	10.60±0.45	13.40±0.11	0.50±0.01	19.00±0.02	55.10±1.05	48.50±0.90	12.50
EPP-4 (20 cm)	22.65±0.36	10.65±0.24	0.80±0.60	11.20±0.02	87.40±6.30	23.60±0.02	10.40
EPP-5 (25 cm)	28.32±0.68	14.50±0.13	1.72±0.32	31.50±3.54	88.30±6.90	34.00±1.60	11.70
EPP-6 (30 cm)	30.90±1.15	16.00±0.56	1.80±0.09	32.80±2.17	100.45±10.0	41.80±1.00	14.50
TEL	124	30.2	-	15.90	-	-	-
PEL	271	112	-	42.8	-	-	-

TEL-Threshold Effect Level.   PEL-Probable Effect Level (Source: FDEP, 1994)

The spatial elemental compositions of intertidal (epipellic) sediment (EPP-1 to EPP-6) analyzed indicated a variation in the concentrations of metals with depth (Table 1). Generally, the concentrations increased with depth and were mostly higher in samples with higher organic content. The enhanced levels of heavy metals in the sediment were expected and were indicative of discharges of large amount of heavy metals and organic matters into the ecosystem. However, the spatial concentrations when compared with the threshold effect levels (TEL) and probable effects levels (PEL) (FDEP, 1994) showed that Ni levels exceeded the sediment quality threshold limit, thus indicating crude oil related sources. Spatial-temporal heavy metal distributions in the surface water, intertidal and subtidal sediments shows varying mean levels of concentration possibly influenced by industrial effluents and domestic wastes discharged into it.

Iron concentration was generally very high in all samples analyzed. Although, iron is one of the essential elements in human nutrition, however, when present at elevated concentration in aquatic ecosystems, serious pollution and health problems could result. According to WHO and US-EPA guideline value and maximum contamination level, concentration value of 0.30 mg L⁻¹ Fe in water is acceptable (Radojevic and Bashkin, 1999). Above 0.3 mg L⁻¹, a condition known as haemo-chromatosis could result. From the results of the analyses, the concentrations of iron in water samples exceeded the regulating limit by a factor of 35%, indicating severe pollution of the Stubbs Creek by Fe. The high level of Fe in the water may be attributed to the discharge of Fe-laden wastes and effluents replete with iron scales from corroded iron pipes, containers and scraps into the water body. Iron concentration as high as 1.28 mg L⁻¹ in petroleum effluent in the region investigated has been reported (Ugochukwu, 2004).

Lead in aquatic environment is risky to life since aquatic organisms used as food are particularly very sensitive to Pb and often retain about a percent of ingested lead which could be taken up by man through food chain (Young and Blevins, 1981). Lead can cause damage to the nervous system and the kidneys and it is a suspected carcinogen (Radojevic and Bashkin, 1999). Children exposed to high lead levels are particularly at risk. The level of Pb in the analyzed water samples showed that the limiting values of WHO and US-EPA, 0.01 and 0.015 mg L⁻¹, respectively were exceeded, indicating contamination of the Creek. The presence of Pb in the Creek may be attributed to anthropogenic discharge of Pb-laden wastes from industrial processes and past uses of various products (e.g. pipes, batteries, paints, petrol, solder and alloy). The levels of Ni and V were spatially and temporally high in all samples. The concentration of nickel in water was higher coming second after Fe. A comparison of Ni concentration in surface water with WHO guideline value of 0.02 mg L⁻¹ and US-EPA maximum contamination level of 0.1 mg L⁻¹ for water showed that the concentration of Ni in the Stubbs Creek is very high and indicate possible pollution.

The relatively high concentration of vanadium and Ni trapped in the sediments and detected in the surface waters may be due to crude petroleum spillages common in the area. Ni may have also come from industrial effluent from the oil company located in the area (Ugochukwu, 2004). Nickel and vanadium frequently occur in crude oil. Some heavy crude oils have up to 45% vanadium pentoxide content in their ash, high enough that it is a commercial source of vanadium (Szatmari *et al.*, 2005). The levels of vanadium indicated in water samples are not high enough to cause any serious pollution threat. However, Ni limiting levels were exceeded and the Stubbs Creek could be said to be contaminated by Ni. Short-term over exposure to Ni is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage and skin irritation.

Cobalt is an essential element which could be introduced anthropogenically into aquatic ecosystems as runoff through application in agriculture as microfertilizers. Notably, Co had the highest coefficient of variation of 57.20% in water. This means that Co was relatively variable in the surface water samples than other heavy metals. The toxicity potentials of Co are quite low compared to many other heavy metals. However, exposure to very high doses can cause severe health effects.

Zinc is equally an essential element in the human diet. Zn deficiency in the diet may be more detrimental to human health than too much of it in the diet (ATSDR, 1994). In aquatic ecosystems, Zn is highly toxic to some aquatic organisms. Although Zn is not a human carcinogen, ingestion of large doses can cause death (ATSDR, 1994). Excessive intake of Zn may lead to vomiting, dehydration, abdominal pain, nausea, lethargy and dizziness (ATSDR, 1994). The level of Zn in the water did not exceed the WHO guideline value of 3.0 mg L^{-1} and US EPA maximum contamination level of 5.0 mg L^{-1}.

Heavy metal pollution caused by industrialization can be investigated in polluted sediments (Binning and Baird, 2001; Ho *et al.*, 2003), lake sediments (Yang *et al.*, 2002; Yang and Rose, 2005) in relation to the surface water. The anomalous levels of heavy metals observed in this study points to anthropogenic inputs and could have a wide environmental implications bordering on bioaccumulation in aquatic flora and fauna. There is a notable difference in concentration of the metals in the sediments and the overlying water column. Thus, the detection of elevated metal concentrations in the creek sediments is a pointer to man induced metal perturbation (Binning and Baird, 2001), integrated into the sediment matrices over time (Hanson *et al.*, 1993). The results of the study confirms earlier reports that analysis of heavy metals in sediments permits their detection which might be absent or in low levels in overlying pelagic column (Davies *et al.*, 1991; Morse *et al.*, 1993).

Correlation among Heavy Metals in Surface Water and Sediments

The correlations among heavy metals in surface water indicated that coefficients between Co, Ni and Zn; Co, Ni, Fe and Pb; Ni Fe and Co; Fe, V and Ni; Fe and V, indicated positively significant (p = 0.05) correlations. Moreover, the correlation coefficients between Co and Ni was very significant (r = 0.91, p = 0.05), indicating the co-accumulation relation of both metals in surface waters.

The correlation coefficients among heavy metals in the intertidal sediments mostly ranged between 0.16 and 0.85, except the relation between Zn, Fe and V, which were -0.25 and -0.55, respectively. Correlations between pairs of Co and Zn (r = 0.81, 95% CI = 0.00 to 0.98), Fe and Zn (r= 0.85, 95% CI = 0.14 to 0.98), Ni and Co (r = 0.85, 95% CI = 0.13 to 0.98) indicated positive significant (p = 0.05) co-accumulation potentials. These results indicated that these heavy metals were bound to the creek sediments within the same period and could be said to have a common

Table 2: Correlation Matrix for subtidal sediment samples giving values of coefficients, r, for pairs of heavy metals

	Fe	Pb	Co	Ni	Zn	V
Fe	1	-0.180	0.627	0.429	0.854*	-0.559
Pb		1	0.544	0.696	0.628	0.411
Co			1	0.851*	0.811*	0.165
Ni				1	0.668	0.357
Zn					1	-0.255
V						1

*Significant correlations (p = 0.05)

Table 3: Relationship among heavy metals in intertidal sediments of Stubbs Creek, Nigeria

	Linear relation	r	R^2 (%)
Zn(x) vs Pb(y)	y = 0.291x + 6.004	0.63	39.69
Zn(x) vs Co(y)	y = 0.053x + 0.104	0.81	65.61
Zn(x) vs Ni(y)	y = 0.682x + 8.299	0.67	44.89
Zn(x) vs Fe(y)	y = 1.654x + 46.165	0.85	72.25
V(x) vs Zn(y)	y = -0.200x + 28.146	-0.25	6.25
Pb(x) vs Co(y)	y = 0.077x + 0.274	0.54	29.16
Pb(x) vs Ni(y)	y = 1.529x + 3.950	0.70	49.00
Pb(x) vs Fe(y)	y = 0.753x + 70.978	0.18	3.24
Pb(x) vs V(y)	y = 01.129x + 24.979	0.41	16.81
Co(x) vs Ni(y)	y = 13.195x + 6.465	0.85	72.25
Fe(x) vs Co(y)	y = 0.021x - 0.509	0.63	39.69
Co(x) vs V(y)	y = 3.185x + 34.677	0.16	2.56
Ni(x) vs Fe(y)	y = 0.815x + 61.851	0.43	18.49
Ni(x) vs V(y)	y = 0.445x + 28.585	0.36	12.96
Fe(x) vs V(y)	y = -0.368x + 67.890	-0.55	30.25

anthropogenic pollution origin (Ho *et al.*, 2003). In the subtidal (benthic) sediments, the coefficients of relationship between Ni, Zn and Co, revealed positive significant correlations (Table 2). Also, the relation between Fe and Zn was positively significant (p = 0.05), indicating the importance of Fe in the accumulation of Zn element in sediments.

The correlation between each metal concentration in surface water samples with respect to subtidal sediments at the UPS, MDS and DNS locations for Co, Fe, Ni, Pb, V and Zn were 0.99, 0.67, 0.99, 0.85, 0.59 and 0.90, respectively. From these positively significant (p = 0.05) relations were indicated for Ni, Zn, Co and Pb implying that these metals integrated in sediments following discharges into the ecosystem. Iron and vanadium showed no significant relation but was positively related (Table 3). This however does not mean that the elemental concentration of Fe and V may not have come from the effluent discharges. Their weak relations could be attributed to physical disturbance or diagenesis and/or changes in pH or redox potential, thus causing them to be released into the overlying pelagic column. However, this creates possibilities for further studies on the distribution and speciation of these metals in the creek sediments so as to generate more information on the degree of pollution as well as the actual ecological impact of the discharges on metal availability.

Conclusions

In general, average metal concentration values of Fe, Ni and Pb in the water and sediment samples were higher, indicating probable contribution of some amount of these metals by anthropogenic sources to the Stubbs Creek and the Qua Iboe River System. Iron was found at exceptionally high levels at DNS locations in both the sediments and surface waters. However, Zn, Co and V were found at levels that did not exceed standard guideline values. Long-term accumulation could however, result in

bioaccumulation and increased bioconcentration of these heavy metals in the benthos of the ecosystem. The data obtained in this study affirms the assertion that water, sediments and biota are reservoirs for heavy metals. The depth of sediment can be used to elucidate the record of heavy metal pollution of water in the estuarine system. As noted, the concentration of heavy metals increased with increasing sediment depth, indicating age-long accumulation from anthropogenic sources. Siginificant positive linear correlation coefficients among heavy metals in intertidal and subtidal sediments were established, indicating a common source of heavy metal pollution.

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