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Trends in Heavy Metals and Total Hydrocarbon Burdens in Stubbs Creek, a Tributary of Qua Iboe Estuary, Nigeria

¹Essien D. Udosen, ¹Nsikak U. Benson and ²Joseph P. Essien

¹Department of Chemistry,

²Department of Microbiology, University of Uyo, P.M.B. 1017,
Uyo, Akwa Ibom State, Nigeria

Abstract: The levels of some heavy metals: zinc (Zn), nickel (Ni), cobalt (Co), vanadium (V), iron (Fe), lead (Pb) and total hydrocarbon content (THC) in surface water and intertidal sediment collected monthly between May and November 2003 from Stubbs Creek were determined using Unicam 939/959 atomic absorption spectrophotometer and chromatography, respectively. The statistical data obtained showed that the concentrations of iron was higher in water and sediment from downstream (SCD), midstream (SCM) and upstream (SCU) locations. The results indicated that the trends in mean levels of heavy metals in sediment and water samples were Fe>V>Ni>Zn>Pb>Co and Fe>Ni>V>Pb>Co>Zn, respectively. Highest THC levels was recorded in downstream water and samples, with mean concentrations $0.061 \pm 0.07 \text{ mg L}^{-1}$ and $77.05 \pm 27 \text{ mg kg}^{-1}$, respectively. The coefficients of variation for the heavy metals and total hydrocarbon contents were also computed and used in determining their variability and distribution in water and sediment. Correlation analysis of THC in water with respect to sediment showed no significant relation except at SCU location. Pollution implications of these metals together with associated health hazards are discussed.

Key words: Heavy metals, hydrocarbon, sediment, Stubbs Creek, Nigeria

INTRODUCTION

The pollution of rivers, lakes, underground water, bays, oceans and streams with chemical contaminants (heavy metals, organics and inorganic compounds) has become one of the most critical environmental problems of the century. Non-degradable, bio-persistent stock pollutants such as heavy metals and mineral hydrocarbons could get into aquatic environment from a wide range of natural and anthropogenic point/non sources. In aquatic ecosystems, heavy metals are contained in four reservoirs, namely, the suspended sediment, the bottom sediment, the surface water and the pore water (Matagi *et al.*, 1999). Studies have revealed that contaminants in aquatic systems are usually in pore water-surface water-sediment dynamics with the bottom sediment acting as the major depository of heavy metals and mineral hydrocarbons (Adams *et al.*, 1992; Ademoroti, 1996).

In recent years, environmental concerns relative to the health and vitality of aquatic ecosystems have become an emerging issue in Niger Delta region of Nigeria. One of the principal reasons for this is that many toxic and bioaccumulative chemicals [such as metals, dioxins, mineral hydrocarbons, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorophenols]; which are found in only trace amounts in overlying water column, can accumulate to elevated concentrations in epipellic and benthic sediments (Udosen and Benson, 2006; Benson *et al.*, 2007). Effluents and wastewaters discharged by crude oil-processing and petrochemical

industries are usually characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbons, phenols, surface-active substances, sulfides, naphthylenic acids and other chemicals (Suleimanov, 1995). The Niger Delta is host to several on- and off-shore oil platforms and refineries which generate large quantities of effluents daily. These effluents are discharged into the littoral aquatic systems in the area sometimes without proper treatment.

In response to concerns raised regarding water/sediment quality in Niger Delta water bodies, several studies have been reported (Asuquo, 1998; Akpan *et al.*, 2002; Udosen and Benson, 2006). In the brackish Qua Iboe Estuary such studies are scanty. However, Ekwere *et al.* (1992) carried out geochemical studies of sediments in the Qua Iboe Estuary and associated creek, while Ubom and Essien (2003) studied the distribution and significance of epipsammonic micro algae in the coastal shore of the Qua Iboe River Estuary and have just reported the epipellic algal profile of the mixohaline swamps of Qua Iboe Estuary (Essien and Ubom, 2004). Reports on studies on the metal burdens of the upper reaches of the Estuary are available (Udosen, 2001), while little or no report is available on the pollution statuses of the lower reaches of the estuary and associated Creeks, where many of the petroleum exploration and exploitation activities are conducted.

Stubbs Creek is a major freshwater tributary of the Qua Iboe Estuary which together with the Widenham Creek links the Qua Iboe Estuary with the Cross River Estuary. The Creek constitutes a major inlet into the land and is often utilized by inhabitants of the oil producing communities of the Niger Delta as the main source of drinking water and transport route. It is a multi use resource with fishery as the most dominant. The Creek also serves as the receiving water body for domestic and industrial wastes especially petrochemical wastes. Therefore, the Stubbs Creek represent a pathway and a potential sink for sediment pollutants originating from human activity and natural run-off. In the tropics, pollution from natural run-off is common during the rainy season months of May, June, July, August, September and October. In this study the rainy season trends of heavy metals and total hydrocarbon distributions in the surface water and bottom sediments of Stubbs Creek are presented.

MATERIALS AND METHODS

Study Area

Stubbs Creek is a small left bank perennial rainforest freshwater tributary of Qua Iboe River that is located in the Coastal riverine ridges of the Niger Delta, Nigeria. The creek is bounded by latitudes 4°3'N and 4°8'N and by longitudes 7°55'E and 8°05'E (Fig. 1). The creek is located in an area characterized by a humid tropical climate. The annual rainfall is 42021 mm with a peak in July-August. Least rainfall occurs between December and February. Although the swamps and creeks experience regular tidal inundations, there are fluctuations in salinity between the rainy and relatively drier months. Tidal amplitude is low, the mean being 2.01 m at spring tides and 1.07 m at neap tides (Ukpong, 1995; Essien and Ubom, 2003). Tidal currents which are strong at the mouth of the estuary but weak along the upper ridges and creeks, play an important role in the distribution of biota and chemical pollutants in the estuary and associated Creeks (Ubom and Essien, 2003).

Sampling Procedure

Water samples were collected from the Stubbs Creek at three locations viz., upstream (SCU), midstream (SCM) and downstream (SCD), at an interval of 500 m apart and were filtered, labeled and stored in plastic bottles fitted with airtight stoppers. Sample meant for TPH measurements were collected using glass bottles (Artiola *et al.*, 2004). Preservation of samples was done by adding 1.5 mL concentrated trioxonitrate (v) acid (HNO₃) to 1 L of sample to give pH < 2. The sediment samples were collected using a 6.5 cm diameter corer to a depth of 10 cm. Samples from each site were extruded from the corer into a tray and homogenized before storing in calico cloth bags. Samples were air-dried

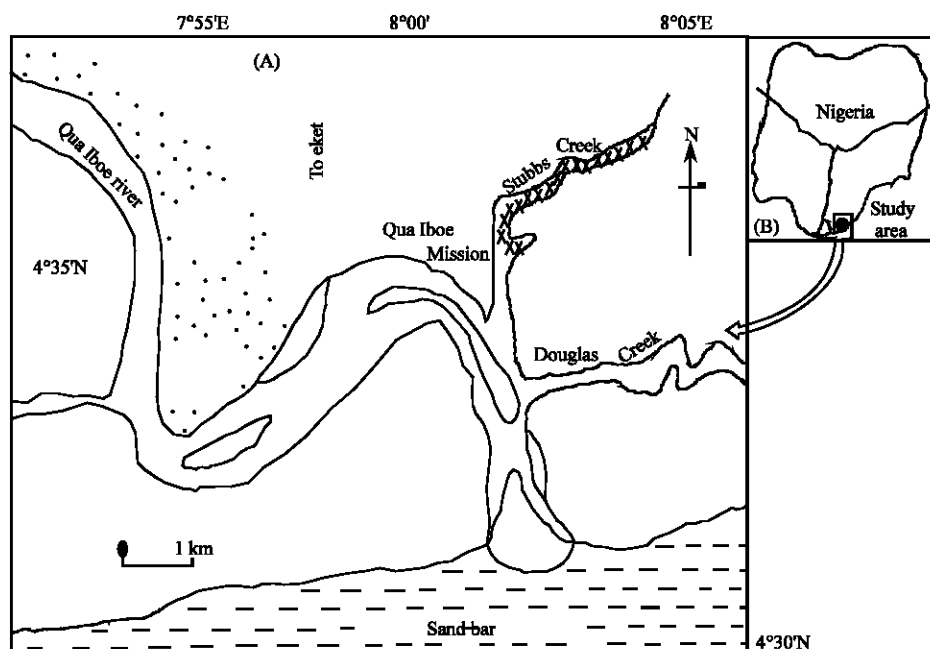


Fig. 1: (A) Qua Iboe River Estuary showing the location of the Stubbs Creek (Study Area) (B) Nigeria showing the location of Qua Iboe Estuary

and latter oven dried at 70-100°C, gently crushed with a rolling pin to disaggregate and later sieved to collect the < 63 μ grain size before storing in fresh bags. Water and sediment samples were obtained monthly in triplicates at each location between May and October, 2003. Therefore, a total of 54 water/sediment samples each were collected from the Stubbs Creek.

Analytical Procedure

Each sample was weighed (1.0 g) into a 100 cm³ beaker and 10 cm³ of HNO₃ acid was added. This was heated to dryness and thereafter, 10 cm³ HNO₃ and 3.0 cm³ of perchloric acid (HClO₄) were added and the solution heated to fume. Sample solutions were obtained by further treating the residues with 4.0 cm³ of hydrochloric acid (HCl) and then filtered and diluted with distilled water to 100 cm³ mark. Sample solutions were thereafter used for metal determinations using Unicam 939/959 Atomic Absorption Spectrophotometer (Radojevic and Bashkin, 1999). Similarly, analysis for total hydrocarbon content (THC) followed a standard procedure (APHA, 1985). 50 cm³ of extracted water and sediment samples were acidified with 0.1 M H₂SO₄ (5.0 cm³) followed by the addition of diethylether (25 cm³) and the mixture was then vigorously shaken. Organic layer separated out was filtered and re-extracted with diethylether (25 cm³) followed by filtration. This procedure was repeated for each sample before evaporation under hood in a dessicator placed inside a fume cupboard. The resulting residue was absorbed in ether and chromatographed through a silica gel column. The filtrate was evaporated to dryness while the residue was weighed to determine the hydrocarbon content using the formula.

$$\text{THC (mg L}^{-1}\text{)} = \frac{\text{Residue (mg)}}{\text{Volume of sample}} \times 1000$$

RESULTS AND DISCUSSION

The mean concentrations, standard deviations and coefficients of variation of the metals zinc (Zn), nickel (Ni), vanadium (V), cobalt (Co), iron (Fe) and lead (Pb) and the total hydrocarbon contents in water and sediment samples from upstream (SCU), midstream (SCM) and downstream (SCD) sites are given in Table 1 and 2. The results of mean concentrations are reported by calculating the 95% confidence interval using student t-test. The linear regression and correlation coefficient (r) between total hydrocarbon content in water and sediment samples from the upstream, midstream and downstream sites are shown in Table 3.

In water samples, zinc, cobalt and lead exhibited very low mean concentrations particularly in SCU sample when compared to iron and nickel, which were relatively high. In the SCU, SCM and SCD samples, Fe had the highest mean concentrations followed by nickel (Table 1). The overall trend in mean levels of the heavy metals was Fe>Ni>V>Pb>Co>Zn at the three sites. However, Fe recorded the highest mean concentration ($12.65 \pm 1.05 \text{ mg L}^{-1}$) in the midstream water samples while Zn indicated the lowest mean level ($0.07 \pm 0.02 \text{ mg L}^{-1}$) in the upstream samples. Although Zn levels in water were generally low, variations between sites were high, being 14.29, 19.52 and 10.07% in SCU, SCM and SCD samples, respectively. Results obtained from water analysis for total hydrocarbon content indicated that mean level was highest in downstream site, SCD, ($0.61 \pm 0.07 \text{ mg L}^{-1}$) followed by $0.46 \pm 0.09 \text{ mg L}^{-1}$ in SCM and $0.29 \pm 0.11 \text{ mg L}^{-1}$ in SCU samples (Table 3).

The result of analysis of sediment samples from the three sites showed that the mean levels of iron were interestingly very high at all sites giving $37.38 \pm 3.78 \text{ mg kg}^{-1}$ at SCU $44.67 \pm 10.87 \text{ mg kg}^{-1}$ at SCM and $63.22 \pm 6.39 \text{ mg kg}^{-1}$ SCD, thus giving the a trend SCD>SCM>SCU (Table 2). On the whole, the trend in mean metal concentrations at SCU was Fe>V>Zn>Ni>Pb>Co while SCM and SCD

Table 1: Mean concentrations (mg L^{-1}) standard deviation and coefficient of variation of metals in water samples from Stubbs Creek

Metal	Monthly mean concentrations			Overall mean		
	SCU ₁	SCU ₂	SCU ₃	$\mu \pm t$	SD	CV (%)
SCU site						
Zinc	0.06	0.08	0.07	0.07 ± 0.02	0.01	14.29
Nickel	3.50	5.00	4.30	4.27 ± 1.37	0.75	17.59
Vanadium	1.35	1.44	1.70	1.49 ± 0.33	0.18	12.14
Cobalt	0.06	0.13	0.09	0.09 ± 0.05	0.03	37.64
Iron	6.35	6.40	6.52	6.42 ± 0.15	0.08	1.36
Lead	0.60	0.45	0.55	0.53 ± 0.13	0.07	14.32
SCM site						
	SCM ₁	SCM ₂	SCM ₃			
Zinc	0.01	0.09	0.13	0.10 ± 0.04	0.02	19.52
Nickel	5.70	6.12	6.05	5.96 ± 0.40	0.22	3.78
Vanadium	1.90	2.01	1.95	1.95 ± 0.11	0.07	3.58
Cobalt	0.15	0.20	0.18	0.18 ± 0.13	0.07	38.89
Iron	12.86	12.00	13.10	12.65 ± 1.05	0.57	4.57
Lead	0.74	0.89	0.80	0.81 ± 0.13	0.07	9.32
SCD site						
	SCD ₁	SCD ₂	SCD ₃			
Zinc	0.20	0.23	0.19	0.20 ± 0.04	0.02	10.07
Nickel	7.90	8.33	7.10	7.78 ± 1.14	0.62	8.03
Vanadium	1.96	2.00	2.03	1.99 ± 0.05	0.03	1.75
Cobalt	0.26	0.31	0.35	0.31 ± 0.09	0.05	14.70
Iron	10.00	13.80	12.70	12.16 ± 3.58	1.96	16.07
Lead	0.92	0.90	0.86	0.89 ± 0.06	0.03	3.42

Table 2: Mean concentrations standard deviation and coefficient of variation of metals in sediment samples from Stubbs Creek (mg kg^{-1})

Metal	Monthly mean concentrations			Overall mean		
	SCU ₁	SCU ₂	SCU ₃	$\mu \pm t$	SD	CV (%)
SCU site						
Zinc	5.20	5.75	6.10	5.68±0.83	0.45	7.98
Nickel	4.32	6.10	5.00	5.15±1.62	0.88	17.18
Vanadium	15.00	17.00	16.70	16.23±1.96	1.07	6.64
Cobalt	0.23	0.26	0.33	0.27±0.09	0.05	18.77
Iron	35.40	27.22	39.52	37.38±3.78	2.06	5.52
Lead	1.86	1.72	1.62	1.73±0.24	0.13	7.54
SCM site						
	SCM ₁	SCM ₂	SCM ₃			
Zinc	7.35	6.77	6.90	7.00±0.55	0.30	4.34
Nickel	7.35	6.70	10.00	8.02±3.21	1.75	21.80
Vanadium	14.85	18.95	16.00	16.60±3.88	2.11	12.74
Cobalt	0.25	0.36	0.37	0.33±0.11	0.06	20.38
Iron	40.00	51.32	42.68	44.67±10.87	5.92	13.24
Lead	1.90	2.25	2.08	2.07±0.31	0.17	8.43
SCD site						
	SCD ₁	SCD ₂	SCD ₃			
Zinc	7.88	7.50	8.00	7.79±0.48	0.26	3.35
Nickel	12.00	13.50	13.60	13.03±1.64	0.89	6.88
Vanadium	23.00	24.35	22.00	23.12±2.17	1.18	5.10
Cobalt	0.48	0.42	0.45	0.45±0.05	0.03	6.67
Iron	59.28	64.55	65.84	63.22±6.39	3.48	5.47
Lead	2.92	2.90	3.00	2.94±0.09	0.05	1.79

Table 3: Mean concentrations (mg L^{-1}) standard deviation and coefficient of variation of THC in water samples from Stubbs Creek

Monthly mean concentrations			Overall mean		
SCU ₁	SCU ₂	SCU ₃	$\mu \pm t$	SD	CV (%)
SCU site					
0.22	0.35	0.30	0.29±0.11	0.06	22.61
SCM site					
	SCM ₁	SCM ₂	SCM ₃		
0.41	0.50	0.48	0.46±0.09	0.05	10.02
SCD site					
	SCD ₁	SCD ₂	SCD ₃		
0.58	0.60	0.65	0.61±0.07	0.04	5.91

had a different trend viz: $\text{Fe} > \text{V} > \text{Ni} > \text{Zn} > \text{Pb} > \text{Co}$. Data obtained indicated that Co had the lowest mean concentration at three sites with least mean level of $0.27 \pm 0.09 \text{ mg L}^{-1}$ in SCU samples. However, result showed that the highest mean total hydrocarbon content of $77.05 \pm 27.92 \text{ mg kg}^{-1}$ was recorded for SCD sediments samples whereas SCU had the least level ($35.23 \pm 22.67 \text{ mg kg}^{-1}$) (Table 4). The trend in THC mean levels was $\text{SCD} > \text{SCM} > \text{SCU}$. However, SCU recorded the highest coefficient of variation (22.61%) compared with SCD with the least C.V. of 5.91%. The trend in THC mean level in sediments (Table 4) was the same as that observed in water analysis; $\text{SCD} > \text{SCM} > \text{SCU}$. However, the coefficient of variation was quite high in SCU sediment samples (35.03%) while SCM recorded the least variation of 15.02% (Table 4).

The mean concentration of THC in water and sediment samples indicated that the lowest level was recorded at the SCU site ($0.29 \pm 0.11 \text{ mg L}^{-1}$) while the SCD sediment had highest mean level of

Table 4: Mean concentrations standard deviation and coefficient of variation of THC in sediment samples from Stubbs Creek (mg kg^{-1})

Monthly mean concentrations			Overall mean		
SCU ₁	SCU ₂	SCU ₃	$\mu \pm t$	SD	CV (%)
SCU site					
21.00	41.70	43.00	35.23±22.67	12.34	35.03
SCM site					
SCM ₁	SCM ₂	SCM ₃			
33.00	34.00	43.00	36.67±10.10	5.50	15.02
SCD site					
SCD ₁	SCD ₂	SCD ₃			
60.33	80.78	90.05	77.05±27.92	15.20	19.73

Table 5: Correlation Between Total Hydrocarbon Content (THC) in water and sediment

Site	A	B	RE*	r**
SCU ^{w/s}	-14.07	170.00	y = -14.07+170x	0.90††
SCM ^{w/s}	15.57	45.52	y = 15.57+45.52x	0.39†
SCD ^{w/s}	-153.88	378.58	y = -153.88+378.58x	0.89†

RE* = Regression equation, r** = Correlation coefficient, † = Not Significant, †† = Significant

77.05±27.92 mg kg^{-1} . The coefficients of variation obtained indicated that SCD water samples had the lowest (CV = 5.91%), while the highest variation coefficient was calculated for SCU sediment samples (CV = 35.03%). Comparisons of these data highlight a relatively high hydrocarbon distribution load in the upstream than downstream section of the Creek. This may be attributed to closeness of the downstream of the Creek to the estuary, which is under a continuous influence of the tidal currents. A correlation of THC levels in water with respect to sediment revealed an unexpected result. Calculated coefficients showed that there was no significant relationship between THC concentrations in water with respect to sediment (Table 5).

The level of Fe in water and sediment samples from all sites was the highest when compared to the other metals. In water samples, Fe concentration was relatively high ($12.65 \pm 1.05 \text{ mg L}^{-1}$) in the SCM samples while the least level of $6.42 \pm 0.15 \text{ mg L}^{-1}$ was recorded for the SCU samples. Moreover, SCU, SCM and SCD water samples had coefficients of variation of 1.36, 4.57 and 16.07%, respectively. In sediment samples, the Fe concentration was relatively very high with the highest level recorded for SCD samples ($63.22 \pm 6.39 \text{ mg kg}^{-1}$) followed by SCM $44.67 \pm 10.87 \text{ mg kg}^{-1}$ and SCU $37.38 \pm 3.78 \text{ mg kg}^{-1}$, respectively. This may be due to the slow movement of water in the Creek and the possible high absorption ability of the metal by the sediment. The coefficients of variation in sediment when compared with those calculated for water samples showed that Fe was unstable in SCD water samples with coefficient of variation of 16.07% and relatively stable in SCU water sample (CV = 1.36%). The high level of Fe in the water and sediment samples may be attributed to the discharge of Fe-laden wastes and effluent replete with corroded iron pipes, containers and scraps into the water body. The high levels of Fe in the water and sediment samples suggest possible contamination by iron.

The concentration of Zinc in water and sediment samples was generally low in all the locations investigated. The highest concentration of $7.79 \pm 0.48 \text{ mg kg}^{-1}$ in sediment samples was obtained in SCD while water samples from SCU contained the least concentration of $0.07 \pm 0.02 \text{ mg L}^{-1}$. Although zinc is not a human carcinogen, ingestion of large doses ($390 \text{ mg Zn}^{-1} \text{ kg day}^{-1}$ for 3-13 days or about 27 g Zn day^{-1}) of Zn can cause death (ATSDR, 1994). Vomiting, diarrhea, abdominal cramping and in some cases, intestinal hemorrhage can occur from long-term exposure to high doses of zinc (ATSDR, 1994). Similarly, the Pb concentrations in sediment samples were higher than in water samples. The highest concentration of $2.94 \pm 0.09 \text{ mg kg}^{-1}$ was obtained from SCD sediment samples while the least concentration ($0.53 \pm 0.13 \text{ mg L}^{-1}$) was obtained from SCU water samples. The coefficient of variation in water samples when compared with that of sediment samples showed that

Pb was very stable in SCD sediment samples with coefficient of variation of 1.79% whereas it was relatively unstable in SCU water samples ($CV = 14.32\%$). The presence and detection of Pb in the Stubbs Creek may be attributed to Pb-laden effluent discharges and past uses of lead in industrial processes and consumer products (e.g., batteries, gasoline additives, rolled and extruded products, cable sheathing, paint, alloys, pigments etc.). The presence of Pb is risky to life since fishes and aquatic fauna are particularly very vulnerable 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). Moreover, the mean concentrations in water samples exceeded the WHO quality standard of 0.01 mg L^{-1} for drinking water. Thus, the seemingly high level of Pb in the samples suggests pollution of the Stubbs Creek by Pb.

The concentration of nickel and vanadium in the water and sediment samples were relatively high. The results revealed a high concentration of Ni in the SCD water samples ($7.78 \pm 1.14 \text{ mg L}^{-1}$). On the other hand, the highest concentration of Ni ($13.03 \pm 1.64 \text{ mg kg}^{-1}$) was recorded in the downstream sediment samples. In both the water and sediment samples Ni had the highest coefficient of variation of 21.80% in the SCM sediment samples while the least variation coefficient (3.78%) was recorded for the SCM water samples. These results showed that Ni was very unstable in the SCM sediments and more stable in midstream water samples. The high concentration of Ni which is an important ingredient in many industrial processes (because of its physical properties) in the Stubbs Creek is due to industrial and municipal wastewater and sludge, discharged into it. Moreover, Ni is a constituent of crude oil and could have probably been introduced into the ecosystem during drilling or oil spillage. Small amounts of Ni are needed by the human body to produce red blood cells, however, in excessive amounts it can become mildly toxic. 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 (ATSDR, 1994).

The results also revealed a very high concentration ($23.12 \pm 2.17 \text{ mg kg}^{-1}$) of V in SCD sediment samples compared to 16.60 ± 3.88 and $16.23 \pm 1.96 \text{ mg kg}^{-1}$ in SCM and SCU samples, respectively. From the results of water analysis, the concentration of V in the SCM and SCD samples was almost equal (1.95 ± 0.11 and $1.99 \pm 0.05 \text{ mg L}^{-1}$, respectively). A comparison of the coefficients of variation in water and sediment samples revealed that V was relatively unstable in SCM sediment and SCU water samples having respective coefficients of variation of 12.74 and 12.14%. However, V was more stable in SCD water sample ($CV = 1.75\%$). The relatively high concentration of V trapped in the sediments may be due to crude petroleum oil spillages which is common in the area. The levels of vanadium indicated in water samples are high enough to cause serious threat. Cobalt is an essential element introduced anthropogenically into the aquatic environment via runoff through application in agriculture as microfertilizer. The results of the present study have revealed a low concentration of Co in water and sediment samples of the Stubbs Creek. In the water samples, the lowest concentration of $0.09 \pm 0.05 \text{ mg L}^{-1}$ was recorded for the SCU samples while the highest concentration of $0.45 \pm 0.05 \text{ mg kg}^{-1}$ was observed in SCD sediment samples. The coefficient of variation of 38.89% recorded for SCM water samples was very high compared to 6.67% recorded for SCD sediment samples. This implies that Co was more stable in the latter than in the former. The toxicity of Co is quite low compared to many other heavy metals. However, exposure to very high levels can cause health effects.

CONCLUSIONS

In aquatic environments, surface water and sediments are generally reservoirs for heavy metals and other chemical toxicants. In coastal regions such as the area where Stubbs Creek is located, chemical pollutants is expected at levels several times higher than their natural background values. The data obtained in this study affirms the foregoing assertions. The concentrations of the metals and total hydrocarbon content are higher in the sediments than the overlying water. This could guardedly be

interpreted as indicating that for most part, metals and hydrocarbons discharged into the aquatic ecosystem have been accumulating in the sediment. However, the observed concentrations vary considerably depending on the sampling location with downstream samples having the highest and upstream the least. Metal and hydrocarbon levels in the system expressed as total concentrations provided an estimate of the amount of potentially available contaminants that are carried in the surface water or are loosely associated with the sediments. Statistical analyses have indicated that water and sediment quality guidelines expressed in this way were exceeded for some heavy metals considered, indicating probable human-mediated contributions to the creek. These levels are significantly high and may be of serious danger to aquatic lives and inhabitants of the area in the nearest future.

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