Environmentalist (2008) 28:195–202
DOI 10.1007/s10669-007-9127-3

Metal contamination of surface water, sediment and *Tympanotonus fuscatus* var. *radula* of Iko River and environmental impact due to Utapete gas flare station, Nigeria

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Published online: 2 September 2007

Abstract Inter-seasonal studies on the trace metal load of surface water, sediment and *Tympanotonus fuscatus* var. *radula* of Iko River were conducted between 2003 and 2004. The impact of anthropogenic activities especially industrial effluent, petroleum related wastes, gas flare and episodic oil spills on the ecosystem are remarkable. Trace metals analyzed included cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), vanadium (V) and zinc (Zn). Sediment particle size analysis revealed that they were characteristically psammitic and were predominantly of medium to fine grained sand (>73%), less of silt (<15%) and clay (<10%). These results correlated with low levels of trace elements such as Pb (0.03 ± 0.02 mg kg^{-1}), Cr (0.22 ± 0.12 mg kg^{-1}), Cd (0.05 ± 0.03 mg kg^{-1}), Cu (0.04 ± 0.02 mg kg^{-1}) and Mn (0.23 ± 0.22 mg kg^{-1}) in the sediment samples. This observation is consistent with the scarcity of clayey materials known to be good scavengers for metallic and organic contaminants. Sediments indicated enhanced concentration of Fe, Ni and V, while other metal levels were relatively low. The concentrations of all the metals except Pb in surface water were within the permissible levels, suggesting that the petroleum contaminants had minimal effect on the state of pollution by trace metals in Iko River. Notably, the pollutant concentrations in the sediments were markedly higher than the corresponding concentrations in surface water and *T. fuscatus* tissues, and decreased with distance from point sources of pollution.

Keywords Trace metals · Water pollution · Sediment · Coastal environment · Nigeria

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1 Introduction

In recent years, rivers in Nigeria have been subjected to pollution attributed to industrial and domestic sources of pollutants, owing to unethical practices and poor enforcement of environmental laws and regulations. Most natural aquatic ecosystems are severely threatened by human-mediated contamination because several industrial establishments are concentrated near river basins for obvious reasons (Uthe et al. 1986; Ntekim et al. 1992; Yahya 1994; Tarras-Wahlberg et al. 2000; Oketola et al. 2006). Studies have shown that apart from anthropogenic sources of heavy metals in sediment and biota, concentrations of metals in aquatic ecosystems could arise from atmospheric deposition, drainage basin and land-use histories (Yang and Rose 2005).

Concerns about inputs, effects and fate of inorganic and organic pollutants relative to the health and vitality of aquatic ecosystems have begun to emerge in Niger Delta and have lead to quite a number of researches in areas considered as pollution hotspots especially from petroleum related activities. One of the principal reasons for this is that many toxic and bioaccumulative chemicals such as metals, organochlorine pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and dioxins, which are found in only trace amounts in water, can accumulate to elevated levels in sediments. In addition to providing sinks for many harmful chemicals, sediments can also serve as potential sources of pollutants to the water column when conditions change in the receiving water system (e.g. during periods of anoxia, after severe storms), as well as highlight the integrated picture of the events taking place in the water column (Wakeham and Carpenter 1976; Binning and Baird 2001; Udosen and Benson 2006).

In aquatic ecosystems, heavy metal aquo-perturbation arising from industrial related activities can be determined using polluted river sediments in relation to the surface water (Binning and Baird 2001; Ramirez et al. 2005; Udosen and Benson 2006). In most cases, the concentration of trace metals in intertidal and subtidal sediments has been found to exceed their levels in the water column (Horowitz 1991) therefore prompting studies that are focused on the latter as well as sediment. Also, there has been a considerable interest in evaluating heavy metal load in aquatic organisms (Szefer et al. 1997; Ramos et al. 1999; Rashed 2001).

The southern part of Nigeria is an area of active petroleum exploitation activities, thus exposing the rivers in these areas to risk of contamination from petroleum and associated pollutants. There have been reported incidences of oil spillage and seepage in addition to gas flaring in the area (Asuquo 1991; Antai 1993). These spillages have the potential of introducing heavy metals and mineral hydrocarbons into aquo-terrestrial environments which ultimately settle unto sediment matrices (Medeiros 2005; Udosen and Benson 2006).

Another obvious environmental unfriendly concern within the southern region of Nigeria is the phenomenon of acid rain. The resulting high levels of acidity in the environment manifest as severe corrosion of iron roof sheets, skin irritation, infertile agricultural soils, destruction of fish life and fisheries production of the waters, deterioration of the quality of surface and ground waters and many other negative effects (Akpan 2003; Edet et al. 2004; Ishisone 2004). Air-borne particulates derived from fossil fuel combustion also contain trace (heavy) metals (Fishbein 1981). These pollutants are potentially deleterious to aquatic plants and animals and can as well devalues the integrity of water bodies. Ecological perturbations and bioaccumulation in aquatic organisms arising from riverine discharges through on- and off-shore crude oil exploitation activities have been reported (Wakeham 1996; Azvedo et al. 2002; Chinda et al. 2004; Essien and Antai 2005).

Information from a variety of sources indicates that sediments and fauna in aquatic ecosystems throughout Niger Delta are contaminated by a wide range of toxic and bioaccumulative substances, including metals, mineral hydrocarbons, etc. (Ekwere et al. 1992; Ebong et al. 2006; Udosen and Benson 2006; Benson et al. 2007a, b). In response to concerns raised regarding the quality of Iko River surface water and sediment, this investigation was initiated to assess the heavy metal (cadmium, chromium, copper, iron, lead, manganese, nickel, vanadium and zinc) load of the ecosystem. Periwinkles (*Tympanotonus fuscatus* var. *radula*) widely consumed and commercially harvested from the area were also investigated for their heavy metal burden.

1.1 The study area

Iko is located within the petroleum belt of the Niger Delta, Nigeria (latitude7° 30′ N and 7° 45′ N, and longitude 7° 30′ E and 7° 40′ E) (Fig. 1). The river has a shallow depth ranging from 1 to 7 m at flood and ebb tide. Iko River takes its rise from Qua Iboe River catchments and drains directly into the Atlantic Ocean at the Bight of Bonny (Ekpe et al. 1995). It has many adjoining tributaries and creeks, and part drains into Imo River Estuary, which, opens into the Atlantic Ocean. The shoreline of Iko River is characterized by soft-dark mud flats, usually exposed during low tide, mangrove swamps, shoals and sand bars. The river has semi-diurnal tides and has a length of more than 20 km and an average width of about 15 m. The climate of the area is characterized by distinct wet and dry seasons. The wet season begins in April and lasts till November, while the dry season covers the period from November to March. Iko area is characterized by a humid tropical climate with rainfall reaching about 3,000 mm per annum. The river is of high economic and ecological importance, as it supports the livelihood of a large number of artisan fishermen. Gas flaring from a horizontally positioned nozzle (Fig. 2) by a petroleum exploration company in the area was a common phenomenon.

2 Materials and methods

2.1 Sampling procedure and sample preparation

The sediment samples were collected from 10 sampling stations (ST1–ST10) using modified Van Veen grab sampler and stored in calico bags, before being transported to the laboratory. All sediment samples were oven dried at 80–100°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_3 and 3.0 ml of $HClO_4$ added. The solution was then heated to fume in a 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 with inductively coupled plasma spectrometer

Fig. 1 Map of Ikot Abasi, showing Utapete flow station and sampling stations

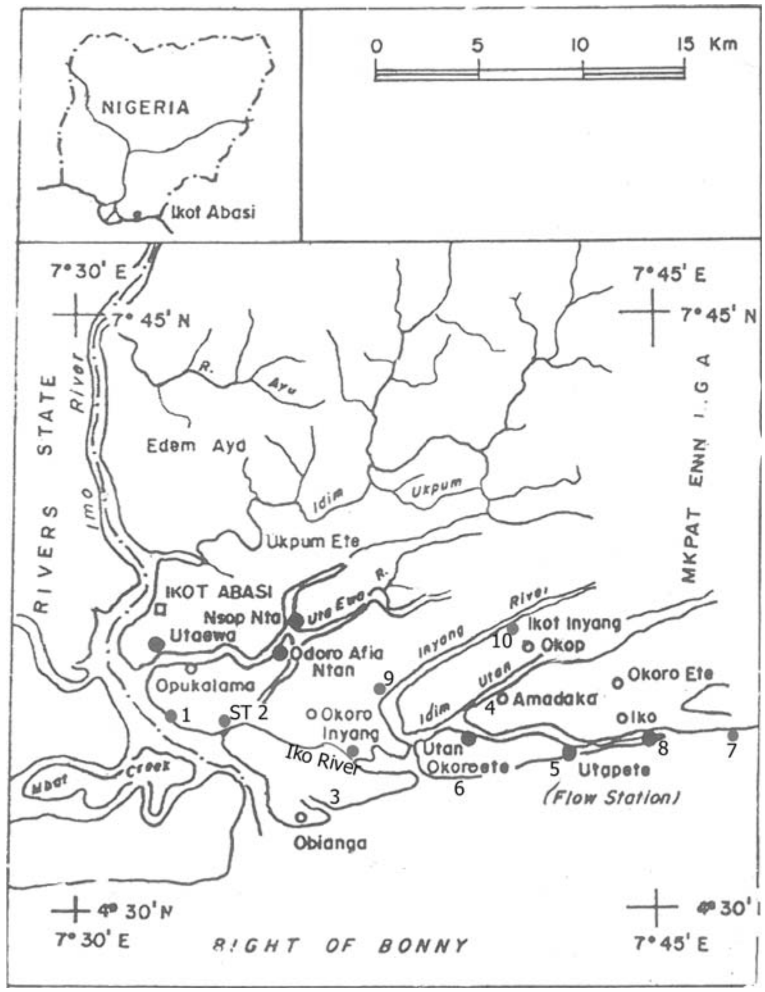

Fig. 2 A picture of the Utapete Flow Station showing an impacted farmland around the gas flaring nozzle (arrowed)

(Optima 3000 Perkin Elmer). Grain size determination of the sediments was performed using standard sieving and sedimentation technique (Folk 1974). Sediment samples were digested with concentrated HCl and HNO_3 (3:1) according to the method by Al-Abdali et al. (1996).

Water samples were taken from 10 sampling stations. The samples were collected with the aid of clean 1 l capacity plastic bottles, filtered, labelled and treated with 1.5 ml of concentrated HNO_3 to give a pH $\leq$2 (Radojevic and Bashkin 1999). Analysis of water samples for heavy metals was done using inductively coupled plasma spectrometer (Optima 3000 Perkin Elmer).

The periwinkles (*T. fuscatus*) were collected by hand picking from the mangrove swamps and sediment close to the 10 sampling stations. The biospecimens were boiled in water for about 5 min and the flesh tissues were separated from the shells, oven dried at 60°C and allowed to cool at room temperature (Ndifon et al. 1997). The dried tissues were ground to powder using an electric blender and thereafter about 5.0 g of each ground sample was digested in a 250-ml Kjeldahl flask with a mixture of (2:1) concentrated nitric acid and perchloric acid (Analar grade). The resultant solution was evaporated to near dryness at 90–100°C and the residue is dissolved in 10 ml 20% nitric acid and filtered. The filtrates were transferred to a 100-ml volumetric flask and made up to mark with deionized water (Radojevic and Bashkin 1999).

All samples were collected to cover the dry (November 2003–February 2004) and wet season months (June 2004–September 2004).

2.2 Chemical analyses

The concentrations of the heavy elements were determined with inductively coupled plasma spectrometer, ICP-AES, (Optima 3000 Perkin Elmer). The following instrumental conditions were used:

Nebuliser flow	0.8 l/min
Argon flow	15 l/min
Auxiliary flow	0.5 l/min
Radio frequency power	1,300 watts

Duplicates and method blanks were employed to test for precision, accuracy and reagent purity used in the analytical procedures.

2.3 Preparation of standard

In order to reduce the detrimental effects of overlapping spectral interferences on element quantitation during metal analyses, an interelement correction standard was prepared by using standardized solution of metals ions prepared from their salts. A mixture of commercially available 100 ppm stock solutions (Analar Grade) of Cd^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Cr^{3+}, V^{4+}, Zn^{2+} and Cu^{2+} were prepared as interelement working standard solutions to verify that the overlapping lines do not cause the detection of elements at concentrations above methods detection limits (MDLs) (Popek 2003).

2.4 Statistical analysis

Correlation analysis and comparative descriptives of data were performed using Analyse-It + General 1.71 Statistical Software®, with level of significance maintained at 95% for each test.

3 Results

The textural characteristics of Iko River sediments are shown in Fig. 3a, b. The particle size distribution of the sediments indicated relatively high percentages of sand ranging between 59.20 and 91.50% during the dry season, and 50.70–93.00% during the wet season. Clay and silt composition of the sediments were however low during both seasons with textural percentage contents ranging between 5.40 and 17.30% clay, 3.10 and 35.40% silt during the dry season. Wet season distributions witnessed a relatively low range (3.90–21.60% clay and an appreciable percentage range of 2.30–42.50 for silt.

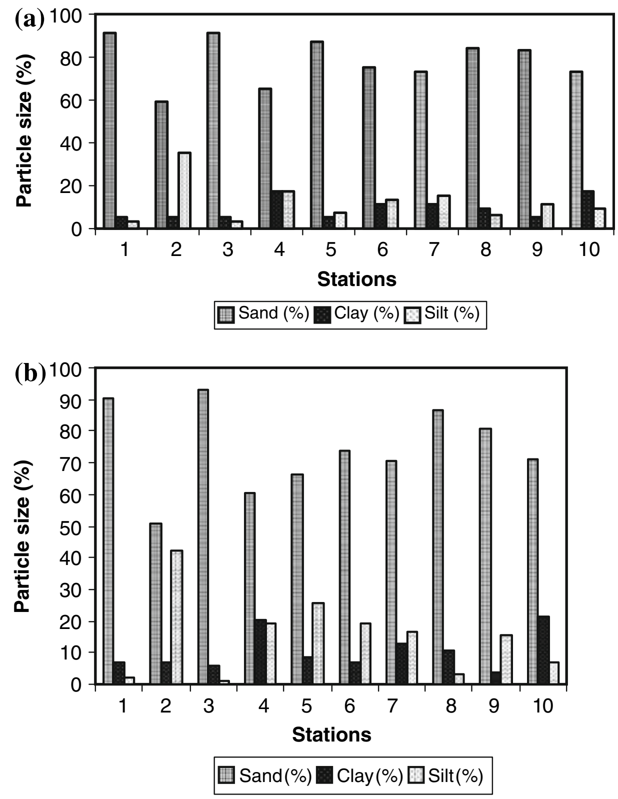

Fig. 3 (**a**) Particle size distribution of sediments during the dry season. (**b**) Particle size distribution of sediments during the wet season

The mean temporal variations of heavy metals in surface water from Iko River during the dry and wet seasons are presented in Table 1. The mean concentrations recorded for the heavy metals were iron, 3.29 mg/l; lead, 0.004 mg/l; copper, 0.13 mg/l; cadmium, 0.04 mg/l; zinc, 0.35 mg/l; manganese, 0.11 mg/l; chromium, 0.006 mg/l; nickel, 0.42 mg/l; vanadium, 0.23 mg/l during the dry season. However, the mean concentrations recorded during the wet season for the heavy metals were iron, 3.60 mg/l; lead, 0.006 mg/l; copper, 0.13 mg/l; cadmium, 0.02 mg/l; zinc, 0.51 mg/l; manganese, 0.03 mg/l; chromium, 0.018 mg/l; nickel, 0.25 mg/l; vanadium, 0.14 mg/l.

The temporal distributions of heavy metals in benthic sediments from Iko River during the dry and wet seasons were variable. Mean concentrations of heavy metals

Table 1 Seasonal heavy metal concentrations (mg/l) and summary descriptives in surface water samples from different stations of Iko River

Heavy metal	Wet season					Dry season				
	Min.	Max.	Mean	S.D.	R.S.D%	Min.	Max.	Mean	S.D.	R.S.D%
Fe	0.66	9.34	3.60	3.04	84.47	0.51	8.51	3.29	2.91	88.52
Pb	0.001	0.02	0.01	0.01	100.00	0.001	0.008	0.004	0.002	51.92
Cu	0.02	0.39	0.13	0.13	104.25	0.02	0.33	0.13	0.12	92.34
Cd	0.006	0.09	0.02	0.02	111.28	0.005	0.07	0.04	0.02	61.98
Zn	0.09	1.06	0.51	0.34	67.89	0.08	0.95	0.35	0.27	76.35
Mn	0.002	0.05	0.03	0.02	91.56	0.01	0.27	0.11	0.12	106.73
Cr	0.005	0.04	0.018	0.01	58.83	0.002	0.03	0.01	0.01	67.86
Ni	0.03	0.91	0.25	0.32	132.09	0.08	0.81	0.42	0.27	62.75
V	0.01	0.57	0.14	0.19	142.05	0.05	0.56	0.23	0.17	74.66

recorded were iron, 42.21 mg/kg; lead, 0.03 mg/kg; copper, 0.04 mg/kg; cadmium, 0.05 mg/kg; zinc, 1.10 mg/kg; manganese, 0.41 mg/kg; chromium, 0.25 mg/kg; nickel, 2.87 mg/kg; vanadium, 1.65 mg/kg, during the dry season. However, mean concentrations of 28.91, 0.03, 0.12, 0.05, 1.47, 0.23, 0.22, 1.62 and 1.15 mg/kg were recorded for Fe, Pb, Cu, Cd, Zn, Mn, Cr, Ni and V respectively, during the wet season (Table 2).

The mean levels of heavy metals in *Tympanotonus fuscatus* (periwinkle) were 3.85 mg/kg for Fe; <0.001 mg/kg for Pb; 0.41 mg/kg for Cu; 0.06 mg/kg for Cd; 9.98 mg/kg for Zn; 0.49 mg/kg for Mn; 0.04 mg/kg for Cr; 0.03 mg/kg for Ni; 0.02 mg/kg for V, during the dry season. However, 3.88, 0.001, 0.34, 0.06, 9.42, 0.49, 0.14, 0.04 and 0.01 mg/kg, were recorded for Fe, Pb, Cu, Cd, Zn, Mn, Cr, Ni and V respectively, during the wet season.

4 Discussion

The textural characteristic at all stations investigated indicated that Iko River sediment is predominantly psammitic. The predominance of sand in Iko River sediments is in agreement with the observation by Ekwere et al. (1992). Relatively high textural percentages of sand were found at stations (ST1–ST4, 9 and 10) along the bank of the river but there were gradual remarkable decrease in a seaward direction (ST5–ST8). Tidal changes and offshore drift currents could be a possible influencing factor regarding the distribution patterns of the sediment fractions (Ntekim et al. 1992). The observation is likely due to low silt contents at stations situated along the bank of the river which is exposed to strong tidal influences especially during the wet season. The particle size distribution correlated with low levels of Pb, Cr, Cd, Cu and Mn in the sediment of the river. However, Fe, Ni and V had significantly ($P = 0.05$) higher concentrations. This observation is consistent with the scarcity of clayey materials known to be good scavengers for metallic and organic contaminants (Matagi et al. 1998).

The concentrations of most heavy metals detected in surface water samples from Iko River were generally low during both seasons. Zinc, manganese, copper and chromium which are considered as essential macro-elements

Table 2 Seasonal heavy metal concentrations (mg kg^{-1}) and summary descriptives in sediment samples from different stations of Iko River

Heavy metal	Wet season					Dry season				
	Min.	Max.	Mean	S.D.	R.S.D%	Min.	Max.	Mean	S.D.	R.S.D%
Fe	10.57	42.46	28.91	12.05	41.69	13.60	60.91	42.21	15.81	37.45
Pb	0.01	0.07	0.03	0.02	60.38	0.01	0.05	0.03	0.02	56.66
Cu	0.01	0.51	0.12	0.16	128.09	0.02	0.08	0.04	0.02	45.27
Cd	0.01	0.16	0.05	0.04	88.27	0.01	0.06	0.05	0.03	64.14
Zn	0.29	5.11	1.47	1.36	92.34	0.35	2.06	1.10	0.63	57.38
Mn	0.05	0.72	0.23	0.22	96.31	0.12	0.85	0.41	0.22	53.41
Cr	0.11	0.51	0.22	0.12	54.89	0.04	0.65	0.25	0.21	82.95
Ni	0.52	3.92	1.62	0.89	55.44	1.42	6.11	2.87	1.54	53.68
V	0.32	2.23	1.15	0.46	40.20	0.92	4.18	1.65	0.98	59.75

were detected at relatively low concentrations at all stations during the dry and wet seasons. In aquatic ecosystems, these elements could be highly toxic to organisms if they are present at elevated concentrations. However, the levels observed in Iko River surface water did not exceed the permissible limits except Pb (Zn, 3.0 mg/l; Mn, 0.1–0.5 mg/l; Cu, 1–2 mg/l; Cr, 0.05 mg/l) in water as given by WHO (1974) and Zn, 5.0 mg/l; Mn, 0.05 mg/l; Cu, 1.0 mg/l; Cr, 0.05 mg/l) (FEPA 1991). Lead was generally low at all stations during both seasons except at ST7 which recorded a 100% elevated concentration over the permissible value of 0.1 mg/l (WHO 1974). The enhanced Pb level could be attributed to industrial wastewater, wastewater sludge and automobile exhaust deposition. Iron levels were exceedingly high at all stations investigated. Though considered as an essential element in human nutrition, if it is however found in water at enhanced concentrations, serious pollution and health problems may be anticipated. According to WHO and FEPA permissible limit, a concentration of 0.3 mg/l Fe in water is acceptable. In this study, Fe was detected at very high level at all stations, exceeding allowable guideline value by a mean factor of 11.0 and 20.0 during the wet and dry seasons respectively. The high iron levels could be attributed to corroded oil pipelines and submerged well-heads which are constantly attacked by haline waters from the Atlantic Ocean. Atmospheric deposition as particulate fallouts from gas flaring is a potential source of enhanced Fe level in the surface water. The discharge if iron-laden wastes and effluents replete with iron compounds could also be a contributory factor. Fe concentration as high as 1.28 mg/l in petroleum effluent in the region have been reported (Ugochukwu 2004). Also, Fe level recorded in surface water of the river may be assumed as been low considering an average concentration of 10.41 mg/l reported in Stubbs Creek located within the same eco-region (Udosen and Benson 2006). Nickel, an element considered as a component of crude petroleum (Szatmari et al. 2005), was detected at all stations during both seasons at relatively high concentrations, though exceeding permissible limits (0.02 mg/l) (WHO 1974; FEPA 1991), by a factor of 15 and 20 during the wet and dry seasons respectively.

In sediment, all heavy metals investigated except iron, nickel and vanadium, recorded low concentrations (Table 2). This observation is consistent with the scarcity of clayey materials known to be good scavengers for metallic and organic contaminants (Matagi et al. 1998). Once heavy metals are released anthropogenically into lenthic or lotic water systems, they undergo a number of dynamic transformations (Johnston 1993). Sediments have been reported as repositories for heavy metals (Tsai et al. 2003; Udosen and Benson 2006). The heavy metal contents entrapped are always in constant flux with the biota and

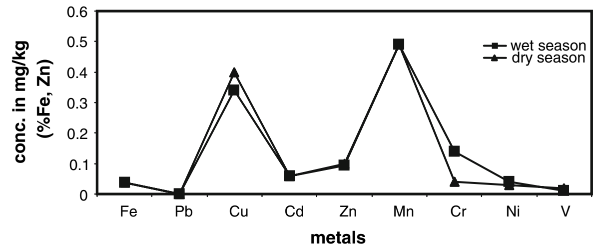

Fig. 4 Mean heavy metal concentrations in *T. fuscatus* var. *radula* during the wet and dry seasons

overlying pelagic column. Apparently, Iko River sediments are not likely to be important sinks for heavy metals from atmospheric fallout, gas flaring and oil exploitation activities in the area. The absence of a sediment sink implies that the pollutants will remain mostly in pelagic column or suspended solids. However, increase in period of heavy metal integration will obviously increase their bioavailability to the biota (Eja et al. 2003).

Heavy metal levels in the periwinkles (*T. fuscatus* var. *radula*) were generally high and variable except for Pb which occurred below detection limit (Fig. 4). Based on mean values except for lead, these concentrations cannot be considered as representing natural levels. As observed by Uthe et al. (1986), periwinkles and other shellfish evidently have the ability to bioconcentrate heavy metals in their edible tissues, though without apparent ill-effect. The ranges of iron, zinc, copper and manganese levels, were however lower than values reported by Ndifon et al. (1997). However, the values obtained in this study are higher than those reported by Mba (1980), Egwelle (1982), Davies et al. (2006).

5 Conclusion

The need to put in place a monitoring strategy to evaluate the impact of oil exploitation activities on the quality of water, sediment and biota of Iko River cannot be overemphasized. From this study, levels of heavy metals detected in pelagic column, biota and sediment may likely come from human-mediated sources. However as noted, sediments are not likely to be important sinks for heavy metals from oil exploitation activities, gas flaring and atmospheric deposition. The moderate existence of sediment as depository for heavy metals implies that the metal toxicants remain mostly in pelagic column or suspended solids. This unique chemistry suggests that the ecology of the river is very fragile and pollutants preferentially remain in the water column. Moreover, with time coupled with increase water-sediment flux, the integration of these metals into sediment will obviously increase their bioavailability to the biota.

The variation in levels of heavy metals in the sediment, biota and the overlying water column of the river shows that the concentrations are controlled by nearness to either functional or abandoned facilities, as well as seasonal changes. The continuous increase in heavy metal levels in the coastal river constitutes a cause for concern as these metals are capable of bioaccumulating in tissues of various biotas, and may also affect the population and distribution of benthopelagic dwellers, as well as resulting in synergistic or antagonistic effects on the infaunal communities.

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