Full Length Research Paper

Distribution and temporal variation of selected heavy metals in sediment of River Osara mainstream drainage in North Central Nigeria

Olatunji Olatunde Stephen[1]* and Osibanjo Oladele[2]

[1]Department of Chemistry, Faculty of Applied Sciences, Cape Peninsula University of Technology, Bellville, Western Cape, South Africa.
[2]Department of Chemistry, Faculty of Science, University of Ibadan, Ibadan, Oyo State, Nigeria.

The concentration levels of selected iron-ore composite heavy metals were investigated in mainstream sediment of River Osara traversing by Itakpe iron-ore deposit and mining area in North Central Nigeria. The sediment samples collected along the drainage course, up-, mid- and downstream for 24 months were digested using standard methods, and levels of Cd, Cr, Ni, Cu and Pb determined using flame atomic absorption spectrophotometer (AAS). The mean concentrations of Pb, 15.63±2.35-18.98±2.04 mg/kg was the highest followed by Ni, 5.20±1.79-15.83±3.04 mg/kg, relative to other metals. The concentrations of Cu and Cr were 3.18±1.14-10.02±2.89 mg/kg and 1.12±0.27-20.93±4.89 mg/kg, respectively, while Cd, 0.24±0.12-0.40±0.26 mg/kg was the least. There was significant (p < 0.05) positive correlation between the concentration of the measured metals with organic carbon level in sediment, with coefficient of correlation γ=0.68, Cd; γ=0.69, Ni; γ=0.54, Cr; γ=0.85, Pb and γ=0.81, Cu implying that metals levels in sediments are partly defined by organic carbon levels. Seasonal fluctuations were observed in sediment concentrations of metals with higher concentration during dry season than in wet season. The concentration of heavy metals in River Osara sediment by Itakpe iron-ore deposit and mining area are low and within natural concentration levels. The result could serve as benchmark required for effective water management and environmental monitoring.

Key words: Heavy metals, concentration, bottom sediment, iron-ore, monitoring, River Osara, Nigeria.

INTRODUCTION

Bottom sediments of aquatic ecosystems are sinks for contaminants, including heavy metals (Yusuf and Osibanjo, 2006). They are able to record and reflect atmospheric signals and nature of the overlying waters (Kakulu and Osibanjo, 1988). Being an integral part of the dynamic hydro-geochemical system involved in the cycling of elements, sediment can accumulate and store, or release heavy metals and other toxic elements to the watershed, depending on conditions defined by the pH, redox potential, organic matter and grain size distribution of the sediment (Davis et al., 1991; Forstner, 2004). As a result, aquatic sediments are used to monitor environmental and natural changes occurring in local, regional or global watersheds and/or changes in aquatic ecosystems forced by anthropogenic factors. This is because of their ability to bear signatures of contaminant inputs and build up from natural and anthropogenic sources including the atmosphere, surface run off, domestic and industrial discharges (Forstner, 1985). The accumulations of elevated levels of heavy metals in sediments of many rivers were reported severally (Amiard et al., 1987; Pardo et al., 1990; Bryan and Langston, 1992; Gupta and Karuppiah, 1996;

*Corresponding author. E-mail: snf_olatunji@ymail.com. Tel: +27822912934.

Figure 1. Watershed and drainage pattern of study area (Source: GSN, 1986).

Weng et al., 2008; Inengite et al., 2010).

The concern for heavy metals arises from their non-degradable and persistence nature, tendency for bioaccumulation and ecological toxicity, detrimental effect on aquatic biota and human health. For instance heavy metals such as copper, cobalt and arsenic were reported to be hepatotoxic, causing a liver condition referred to as liver cirrhosis (Hutton, 1987). Cadmium is known to cause kidney damage, hypertension and sperm deformation. Mercury, lead and arsenic toxicity results in neuro-degeneration and senility with possibility of irreversible brain damage. Alzheimer's, Parkinson's disease and dementia are caused by elevation of aluminium in human. Cancer, abdominal pain, skin lesions, speech impairment and autism, loss of hearing, vision and movement are among the potential toxic effects of heavy metals (Hammer and Hammer, 2004; Bakare-Odunola, 2005).

Studies revealed that heavy metals are composite associates of iron ore, occurring in different amounts especially Mn, Cr, Ni, Pb, Cd, Cu, Ti, V, W and Zn (Nriagu, 1989; Thomas, 1992; Kabata et al., 2001). Iron-ore mining operations and mineral beneficiation processes can endanger the integrity of rivers, especially downstream due to particulate depositions from mining, haulage and crushing, acid mine drainage and ore processing wastes. Substantial amount of heavy metals in mine wastes, tailings and low grade ore may also enter into soil and aquatic environments via atmospheric, industrial wastes disposal and improper disposal

of sewage sludge. This could lead to metal enrichment in water and sediment body, and consequently ecosystem damage, which can affect adjoining water systems. Although mining activities at Itakpe iron ore deposit, Nigeria is abysmally low due to non-operational; there is a potential risk of contamination of River Osara due to its proximity to the iron-ore deposit, mining area and the ore beneficiation plants by direct and indirect discharge of mine waste, mine tailings, spent liquor and other effluents. Evaluating the baseline sediment geochemistry of the aquatic environment around the mineral deposit vein is crucial to understanding the existing heavy metals status. Information such as this will serve as basis for monitoring environmental changes that may be induced in River Osara either by natural, mining or other anthropogenic forces.

This study therefore investigates the baseline concentration levels of selected iron ore composite associated heavy metals in sediments of River Osara in order to define benchmark for future monitoring.

MATERIALS AND METHODS

Study area

Study location is within the section of River Osara traversing past the Itakpe ferruginous iron-ore deposit, and down beyond the mineral beneficiation plant and industrial area of Nigeria Iron Ore Mining Company in Kogi State, located within the Lokoja – Okene area delimited by latitudes 7° and 8°N and longitudes 6°and 7°E, in North Central Nigeria (Figure 1).

Table 1. Ranges and mean concentrations (mg/kg) of heavy metals, pH and organic carbon in sediments from River Osara at Itakpe.

Sample identity	pH	Organic Carbon (%)	Cd (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Pb (mg/kg)
ITK/SM/D/03-04							
Concentration range	6.52-7.29	3.90-7.30	0.17-0.51	1.78-3.23	9.41-23.52	3.75-10.23	13.67-18.11
Mean (Standard Deviation)	6.90 (0.28)	5.60 (1.22)	0.40 (0.26)	2.37 (0.55)	14.46 (4.09)	6.61 (2.34)	15.75 (1.49)
ITK/SM/D/04-05							
Concentration range	5.90 -7.07	3.20-5.60	0.17-0.32	15.53-27.91	12.34-22.57	6.00-14.50	14.92-19.08
Mean (Standard Deviation)	6.57 (0.40)	4.52 (0.95)	0.24 (0.12)	20.94 (4.89)	15.83 (3.04)	10.02 (2.89)	16.96 (1.45)
ITK/SM/W/03-04							
Concentration range	6.78-7.25	3.60-6.50	0.16-0.32	0.78-1.54	2.86-8.16	1.58-6.36	15.81-22.17
Mean (Standard Deviation)	6.98 (0.14)	4.96 (1.01)	0.25 (0.05)	1.12 (0.27)	5.20 (1.79)	3.18 (1.14)	18.98 (2.04)
ITK/SM/W/04-05							
Concentration range	6.36-7.23	3.30-5.90	0.18-0.42	9.72-15.37	7.28-20.06	1.73-10.76	12.97-19.64
Mean (Standard Deviation)	6.89 (0.28)	4.18 (0.76)	0.30 (0.08)	12.79 (1.93)	12.91 (4.30)	4.88 (2.64)	15.63 (2.35)

Codes: ITK-Itakpe; SM-sediment sample; D-dry season, W-wet season; 03-04 - year 2003-2004 and 04-05-year 2004-2005.

Sediment sampling

Eighty sediment samples were randomly collected from the mainstream depth of River Osara, at the up-stream, mid-stream and down-stream flow portion around Itakpe iron ore deposit area on N 07° 37′ 420″, E 006° 18′ 284″ during dry and wet seasons, spanning a period of twenty-four months between 2004 and 2005.

Samples digestion and analysis

Sediment samples were sorted, air-dried, pulverized and screened through 2 mm mesh nylon sieve. The 2 mm sieved sediment samples were digested according to the methods described by Andersson (1976), Onianwa (2000), and Smejkalova et al. (2003) with slight modifications. Five grams each of sediment samples was weighed into 250 ml teflon beakers and digested with 50 ml, 2 M nitric acid, in water bath. The digests were filtered into 100 mL volumetric flask and quantified for Cd, Cr, Ni, Cu and Pb using flame atomic absorption spectrometer (FAAS) Unicam 969.

Determination of organic carbon in sediment

The method of Walkley and Black, 1934 was used: 5 g of sediment samples were weighed each into 250 ml teflon beakers. Each sample was rapidly subjected to dichromate oxidation by addition of 50 ml potassium dichromate 0.5 M, $K_2Cr_2O_7$ and 2.5 ml concentrated sulphuric acid in 5% $FeSO_4$. Excess $Cr_2O_7^{2-}$ were titrated with 0.25 M ferrous ammonium sulphate [$Fe(NH_4)_2$ $(SO_4)_2.6H_2O$].

Determination of sediment pH

The pH of the sediment samples were determined according to the method described by McLean, (1982). 1:1 mixtures of sediment samples and distilled water in glass beakers were gently stirred to enhance H^+ release. The resulting mixtures were allowed to stand for 30 min and the sediment pH measured using a pre-calibrated pH meter.

Recovery studies

Analyte recovery was conducted on spiked sediment sample in triplicates; at low, medium and high spike concentrations. The spiked samples were subjected to the same sample treatment and analysis method. The results showed good efficiency in analytes digestion and recoveries. The percentage recoveries and coefficient of variation of the spiked replicate samples were Cd, 90.45-93.81%, C.V 3.87-6.75%; Cr, 79.64-85.92%, C.V 9.16-18.42%; Ni, 89.34-94.68%, C.V 8.58-15.84%; Cu, 85.19-92.55%, C.V 6.34-14.71% and Pb, 82.75-92.10%, C.V 7.29-10.98%, Pb.

RESULTS AND DISCUSSION

Concentrations of heavy metals in sediments

The results showed variations in concentration levels of heavy metals in the analysed sediment (Table 1). Theseasonal concentrations range (mg/kg) of the heavy metals detected in the sediments showed that Pb, 15.63±2.35-18.98±2.04 mg/kg had the highest concentration levels relative to the measured metals. This was followed by Ni, 5.20±1.79-15.83±3.04 mg/kg and then Cu, 3.18±1.14-10.02±2.89 mg/kg. The concentration ranges of other metals in River Osara sediment were Cr, 1.12±0.27-20.94±4.89 mg/kg and Cd, 0.24±0.12-0.40±0.26 mg/kg being the least. The distribution of heavy metals in sediments is in the order Pb > Ni > Cu > Cr > Cd, with the values indicating heterogeneous quantities at different sampling points. This is consistent with the findings of Toma et al. (1981) in fine fractions of continental shelf sediments of Western Nile. The metals retention potential of the sediment may be attributed to the levels of sediment organic carbon (4.18 ±0.76-5.60±1.22%). Heavy metals are usually associated with organic matter and fluidized sediment clay minerals, with

variable crustal composition consisting of soluble and insoluble silica, alumina and iron/manganese oxy-hydroxides (Fe_2O_3/MnO) (Rothwell et al., 2007). Ma and Rao (1997) noted that heavy metals are not evenly distributed in their different speciated matrices. The sediment pH values were near circum-neutral with seasonal means ranged 6.57±0.40-6.98±0.14.

The pH, organic carbon, clay minerals and iron/manganese flux contributes to the total sediment retention capacity in aquatic systems. Material exchange also took place between water column and the sediment system, in which metal partitioning occurs between sediment and water. The mechanisms for mobilization, distribution or accumulation of heavy metals in inland freshwater and marine sediments may include weathering of primary minerals, association and dissolution of metals with iron-manganese oxy-hydroxides and aqueous speciation. The concentrations and variations in distribution of heavy metals in aquatic sediments is a function of metals solubility, the density established when they combine with other contaminants and the effect of organic matter and clay minerals heterogeneity on sorption and desorption of the metals.

Cadmium

The concentration of Cd in sediment ranged 0.17-0.51 mg/kg with mean concentration 0.40±0.26 mg/kg during dry season 2003/2004 and 0.17-0.32 mg/kg with mean 0.24±0.12 mg/kg during dry season 2004/2005. Cadmium concentration during wet season 2003/2004 ranged 0.16-0.32 mg/kg with mean 0.25±0.05, while during wet season 2004/2005 the concentration ranged 0.18-0.42 mg/kg with mean value 0.30±0.08 mg/kg. The relative standard deviation for Cd concentration ranged between 6% during wet season to 26% during dry season. The result showed fairly consistent Cd concentration with low distribution variation through the evaluated column upstream and downstream during the study period. This can be attributed to Cd stabilization, enhanced by less perturbation of the surface sediment. Lovern (2000) reported that stability in Cd concentration may be due to complex assemblage induced by sorption density of sediment reactive site. Seasonal variations in Cd concentrations were low and ranged between ± 0.05 mg/kg, Cd to ± 0.26 mg/kg, Cd, indicating slight homogeneity in sediment concentration levels and distribution.

Lead

The concentrations of Pb were slightly variable between sampling points. Sediment of Pb concentration ranged 13.67-18.11 mg/kg with mean levels 15.75±1.49 mg/kg during dry season 2003/2004 (Table 1), while Pb sediments concentration ranged 14.92-19.08 mg/kg with mean Pb level 16.96±1.45 during dry season 2004-2005. The concentration of Pb during wet season 2003/2004 ranged from 15.81-22.17 mg/kg with mean range of 18.98±2.04 and Pb, 12.97-19.64 mg/kg with mean range of 15.63±2.35 mg/kg during 2004/2005. Contrary to the observed seasonal trend with concentration depletion during wet season, Pb enrichment of about 20.5% was observed during wet season 2003/2004 study period. The reason for this cannot be readily explained, because Pb concentration detected in sediment sample during the subsequent study period 2004/2005 followed seasonal distribution trend. However the seasonal mean concentration levels of Pb were not significantly different ($p > 0.05$). Also the concentration levels detected upstream and downstream were not significantly different ($p > 0.05$). This is consistent with the findings of Violante et al. (2010) who reported that Pb level in sediment is controlled by sediment pH and redox state.

Nickel

Nickel concentration was variable and ranged between 9.41-23.52 mg/kg with mean levels 14.46±4.09 mg/kg during dry season 2003/2004 (Table 1). The concentration was fairly consistent though slightly higher during the subsequent dry season 2004/2005 with sediments Ni concentration ranged 12.34-22.57 mg/kg and mean concentration of 15.83±3.04 mg/kg. There was significant depletion ($p < 0.05$) in Ni levels during wet season 2003/2004, perhaps as a result of increase in the volume of water in the river and flow turbulence. Hence the detected wet season concentration of Ni ranged 2.86-8.16 mg/kg with mean 5.20±1.79 during 2003/2004. Nickel level during subsequent wet season 2004/2005 was hardly depleted (< 0.001%) with Ni concentration ranged 7.28-20.06 mg/kg, and mean 12.91±4.30 mg/kg. The least concentration of Ni, 2.86 mg/kg was observed in mainstream drainage sediment upstream with the highest Ni, 23.52 mg/kg measured in the downstream edges beyond the industrial iron ore beneficiation plant.

Copper

The concentration of Cu ranged 3.75-10.23 mg/kg with mean concentration 6.61±2.34 mg/kg in sediment samples during dry season 2003/2004, and 6.00-14.50 mg/kg with mean 10.02±2.89 mg/kg during dry season 2004/2005. Copper concentration observed during wet season 2003/2004 ranged 1.58-6.36 mg/kg with mean 3.18±1.14, while during wet season 2004/2005 the concentration ranged 1.73-10.76 mg/kg with mean value 4.88±2.64 mg/kg. The concentrations of Cu detected in sediment during dry season 2003/2004 were significantly lower than in the subsequent season 2004/2005 with an enrichment of about 35%. This may be as a result of changes in arable land use which were considered as a

major source of Cu in adjoining water column (Kaizer and Osakwe, 2010; Darrell, 2009). Ma and Rao (2007) suggested that the concentration of Cu may be a function of their levels in the parent materials.

Chromium

There was significant Cr enrichment of 8.5-12.5 fold factor during study period 2003/2004 and 2004/2005. This is likely to be as a result of hydro-geochemical processes due to the flow of the river through basement intercalated by sediment, or from land based sources. This is because Cr is known to exist in minor amount in ferruginous quartzite and is reported to be soluble. Chromium concentration ranged from 1.78-3.23 mg/kg with mean concentration of 2.37±0.55 mg/kg during dry season 2003/2004 and 15.53-27.91 mg/kg with mean of 20.94±4.89 mg/kg during dry season 2004/2005. Chromium concentration during wet season 2003/2004 ranged from 0.78-1.54 mg/kg with mean of 1.12±0.27 while during wet season 2004/2005 the concentration ranged from 9.72 - 15.37 mg/kg with mean value of 12.79±1.93 mg/kg.

Sediment pH and organic carbon

The prevailing sediments pH observed during the study ranged from 5.90-7.29 (6.84±0.28), while organic carbon levels ranged 3.20-7.30% with mean value of 4.82±0.99%. According to Lee (1975), the concentration levels of heavy metals found in sediments are dependent on the prevailing pH condition of the hypolimnion water column. There was significant ($p < 0.05$) positive correlation between the concentration of the measured metals with organic carbon level in sediment. The coefficient of correlation were Cd, $\gamma = 0.68$; Ni, $\gamma = 0.69$; Cr, $\gamma = 0.54$; Pb, $\gamma = 0.85$ and Cu, $\gamma = 0.81$. The correlation values are consistent with the observation of Weber et al., (1992) who concluded that the extent of sorption of contaminants such as metals to organic carbon content of sorbents sediments is consistent with the behaviour for partitioning processes. Kile et al. (1999) suggested the existence of an empirical correlation between elemental compositions and natural organic matter, and the extent to which they are sorbed to organic compounds. The concentration of metals detected in River Osara sediments may be attributed to the sorption capacity of sediment and this is defined by the organic carbon content. Sediments also consist of mineral matter flux such as Fe/Mn, onto which metals are sorbed.

Heavy metals distribution in sediment

The variation in the measured heavy metals concentrations ranged from ±0.12 to ±12.68 mg/kg, which indicates that the measured metals are not uniformly distributed. There were variation in concentrations of the heavy metals between sampling points along the river channel, with higher concentration values found in sediments collected from non- tidal area and from entrapped portion of the river bed and other discrete blebs. This showed that heavy metals do not occur as continuous monolayer in the surface sediment. According to Taylor et al. (2002), the distribution of contaminants in river systems cannot be expected to be linear nor simple, as their spatial distribution is controlled by physical processes including stream hydraulics, sediment storage and erosion behaviour. The concentrations of Pb were the highest in the sediment samples which ranged from 12.97-22.17 mg/kg followed by Ni, 2.86-23.52 mg/kg concentrations. The concentrations of Cu and Cr were ranged, 1.58-14.50 and 0.78-27.91 mg/kg, respectively, and Cd, 0.16-0.51 mg/kg being the least. However, Cr had the widest distribution variation followed by Ni, Cu, Pb and Cd in that order.

Seasonal effect on heavy metal concentrations

The seasonal variation of heavy metals concentrations in sediment samples from River Osara at Itakpe are presented in Figure 2.

The concentrations of heavy metals in bottom sediment of River Osara at Itakpe were observed to be lower during wet season than during dry season. This may probably be due to volume increase, increase in flow velocity and flow turbulence which enhances re-dissolution, re-suspension and erosion of metals from the surface of bottom sediments in the water body flow dynamics. Sediment surface are less perturbed under steady flow conditions during dry season, hence metals are sequestered on sediments by organic matter and clay mineral fraction (oxy-hydroxides of Fe/Mn).

Sediments enrichment may also occur during dry season when heavy metals precipitating out of water columns are deposited on bottom sediments. This process enhances the concentration and stabilization of heavy metals. Sediments levels of Ni, Cu and Cr were seasonally changeable, while Pb and Cd levels were fairly stable.

Sediment quality

The concentrations of heavy metals detected in this study is consistent with the findings of Obasohan et al. (2006) in sediment from Ogba River in Benin, Nigeria with Cr, 0.99 mg/kg; Ni, 0.71 mg/kg; Cu, 2.68 mg/kg, and lower concentrations of Pb, 1.80 mg/kg and higher Cd level of 1.03 mg/kg. Kakulu and Osibanjo (1988) reported higher concentration levels of Cu, 23.9 mg/kg; Pb, 32.1 mg/kg
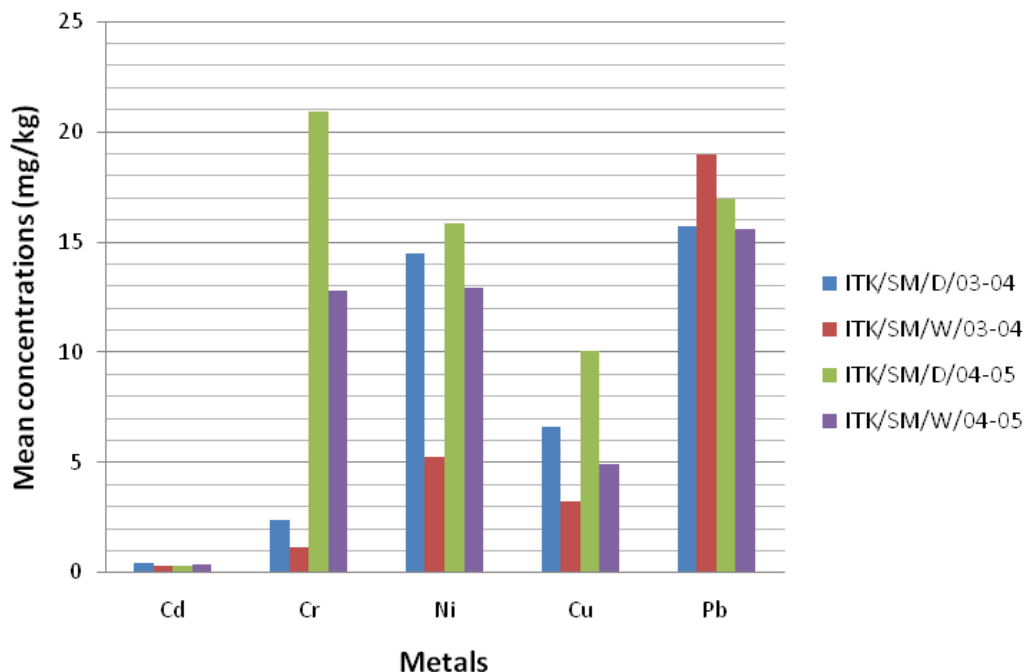
Figure 2. Seasonal variation in concentration levels (mg/kg) of heavy metals in River Osara sediment samples. Code: ITK-Itakpe, SM-sediment, D-dry season, W-wet season, 03-04 - year 2003-2004, 04-05 - year 2004-2005.

and Cd, 0.79 mg/kg in sediment samples from the Niger Delta, Nigeria than levels found in this study, owing to discharge of refinery effluent into the Niger Delta waters. Yusuf and Osibanjo (2006) also reported comparable sediment concentrations of Zn, 35.5 mg/kg; Cu, 11.4 mg/kg; Pb, 11.0 mg/kg and Cd, 0.60 mg/kg with higher level of Mn, 123.4 mg/kg in Ologe Lagoon, South-west Nigeria.

This study's result compares the concentrations of heavy metals found in sediments from rivers studied elsewhere. Biney (1991) reported Cd, <0.20 mg/kg and Pb, 29.30 mg/kg in sediments from Kpong Dam, Ghana, while Cu, 30.30 mg/kg was higher. Watling and Emmerson (1981) reported Cu, 10.5 mg/kg and Pb, 17.8 mg/kg in sediments from Swartkops River South Africa, with higher concentration of Cd, 1.00 mg/kg and Cr, 177.0 mg/kg. The findings of Gabr et al. (2008), in sediments from Suez Canal Egypt with Ni, 14.5±1.5 mg/kg; Cu, 8.8±1.1 mg/kg; and Pb, 13.5±1.5 mg/kg are consistent with these results. Cadmium (1.25±0.2 mg/kg) in sediment of Suez Canal was high compared with 0.16-0.51 mg/kg levels found in River Osara sediment.

Despite the heavy metals seasonal compositional variation in River Osara sediments, the measured concentration values of Pb, Ni, Cu and Cr were low to moderate and below threshold concentrations (Pb, 19.00 mg/kg, Cu, 33.00 mg/kg and Cd, 0.11 mg/kg) recommended by the Joint Group of Experts on the Scientific Aspects of Marine Environment Pollution (GESAMP) for unpolluted sediments, except for Cd (GESAMP 1982).

The detected levels may be attributed to geological variations and crustal structural complexities, the impact of human activities and use of the river bodies as well as input from land based sources.

Conclusion

The concentration of heavy metals in sediment River Osara around Itakpe iron-ore deposit and mining area are variable and within natural levels, except for Cd. This suggests the likelihood of source apportionment of Cd in the river. The distribution of heavy metals in sediments is in the order Pb > Ni > Cu > Cr > Cd with the values indicating heterogeneous quantities at different sampling points. Sediment concentrations of the measured heavy metals were seasonally influenced with higher concentrations during dry season, owing to probably less perturbation of sediment state, gradual and consistent sediment enrichment, due to steady flow of water.

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