Distribution of Trace Elements in Surface Water and Sediments from Crayford Creek in Warri, Delta State of Nigeria

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ABSTRACT

Surface water and sediments collected from Crayford Creek in Warri were analytically treated and analysed for trace metals. The metals analysed were Fe, Cu, Cr, Mn, Pb, Ni, Cd and Zn. These metals were determined using atomic absorption spectrophotometer of model GBC Senso A. A. Australia. The mean concentrations of aforementioned metals in surface water were lower than those of the sediments and metal value varied significantly in the five sample locations (01 – 05). In surface water, the highest mean concentrations were observed in Fe (5.07 mg/l) and Cu (4.30 mg/l) whereas in sediments, the highest mean concentrations were observed in Fe (5841.75 mg/l) and Zn (334.69mg/l). Thus, mean metal levels in sediments exceeded those of surface water indicating that sediments are a sink for metal pollution load. Computation of contamination/pollution index in sediment matrix revealed that Fe and Zn polluted the sediment significantly whereas Cu, Ni and Cd moderately contaminated the sediments. The mean values of metals in this present study were compared with other values reported by other researchers. The elevated metal values were attributed to anthropogenic wastes, runoff, refinery jetty and petroleum explorations around the study area.

Keywords: Crayford Creek, surface water, sediments, trace elements, contamination/pollution index

INTRODUCTION

The availability of trace elements in rivers relates to specific regional geochemistry and inputs from diverse anthropogenic sources. At the same time different industrial effluents and non-point pollution sources, as well as atmospheric precipitation can increase concentrations of trace elements. In the aquatic environment, trace elements can accumulate to toxic levels and cause severe effects to organisms and on human health (Gupta *et al.*; 2009). Factors such as climate and hydrology (Caruso and Bishop, 2009), water chemistry (Matache *et al.*; 2009) and biological activity (Van Hattum *et al.*; 1996) control trace metal deposition and fixation in the sediments, which may act as both sinks and sources of secondary aquatic pollution (Pekey, 2006 and Coynel *et al.*; 2007). The study of both water and sediment geochemistry is, therefore, necessary for the assessment of contamination status, the understanding and prevention of environmental risk (Neumann *et al.*; 2005). Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota (Camuso *et al.*; 1995). These heavy metals generally exist in low levels in water and attain considerable concentrations in sediments and biota.

Water and sediments measured within the city of Kharkov were contaminated by Ag, Pb, Cd, Cu, Cr and Zn which are mainly attributed to municipal waste water inputs and urban run-off. Also, results of the environmental quality assessment showed that element concentrations in the sediments can be considered as potentially toxic to aquatic organisms in sites downstream

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of the waste water discharges (Vystavna *et al.*; 2012). Trace metals such as Cd, Hg, Cr, Pb and U are known to be powerful nephrotoxins (Doul *et al.*; 1980). Metals have the potential to be toxic to living organisms if present at availability above a threshold level. Most urban and industrial run-off contains a component of trace and heavy metals in the dissolved or particulate form (Defew *et al.*; 2004). Heavy metals from incoming tidal water and freshwater sources are rapidly removed from the water body and are deposited onto the sediments (Guzman and Garcia, 2002). Persistent pollutants, such as heavy metals, can remain in the environment unchanged for years and thus may pose a threat to man and other organisms (Thapa and Weber, 1991). Freshwater resource is becoming depleted day-by-day due to the faster rate of deterioration of the water quality. Direct contamination of surface water with metals in discharges from mining, smelting and industrial manufacturing, is a long-standing phenomenon (Mahananda *et al.*; 2005). The heavy metals in water and sediments exhibit seasonal variations. Human inputs affect the concentrations of metals in summer whereas the precipitation inputs in winter dilute metal concentrations to minimum levels (Shomar *et al.*; 2005). Once heavy metals are discharged into estuarine and coastal waters, they rapidly become associated with particulates and are incorporated in the bottom sediment (Iwegbue *et al.*; 2012).

Sediments are considered to be the ultimate sink for many contaminants and play an important role in influencing pollution of rivers and can also be used to record the history of river pollution (Yu *et al.*; 2001; Wepener and Vermeulen; 2005). Therefore, sediment quality data provide essential information for evaluating ambient environmental quality conditions in aquatic ecosystem. The Crayford Creek is one of the coastal creeks in the Niger Delta which receives industrial and anthropogenic wastes arising from the Warri River. Therefore, it became necessary for this study. The objectives of this study are: firstly to provide information on the concentrations and distribution of selected heavy metals in surface water and sediments from Crayford Creek; secondly to compute a contamination/pollution index of heavy metals in the surface water and sediments of the creek under study.

MATERIALS AND METHODS

Description of Study Area

Warri and its environs lie within the Agbada, Akata and Benin formation. Geologically the rock found in this area is sedimentary type which comprises silty clay and sand to top layer. The terrain is flat and about 4m above sea level and located at the shores of Warri River, Enerhen River and Ovwian River. The area also is characterized by hydromorphic soils, which is a mixture of coarse alluvial and colluvial deposits. The soils are poorly drained and accumulated with water because of closeness to the Atlantic Coast. The natural vegetations are of mangrove swamp forests which are rich in wood and non-wood resources. Around the study area, there are refinery jetty, Shell Development Company Residential and Industrial Areas, and Refinery effluent outlet (Fig. 1).

The Sampling and Analysis

The study area (Figure 1) was divided into five stations, each about 500m long numbered from one to five along the Crayford Creek. The samplings were conducted from November 2011 to July, 2012.

Water Samples

500ml of the water sample was collected from each station (01 – 05). Each sample was filtered in acid-washed filter holder and through 0.45µm pore size membrane filters. The first few millimeters were used to rinse, discarded, and the filtrate was transferred to labeled clean

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acid-washed sample bottles, acidified with concentrated nitric acid and stored at 4^0C prior to analysis of total metal contents by Atomic Absorption Spectrophotometry (G B C Scientific Sena A A, Australia).

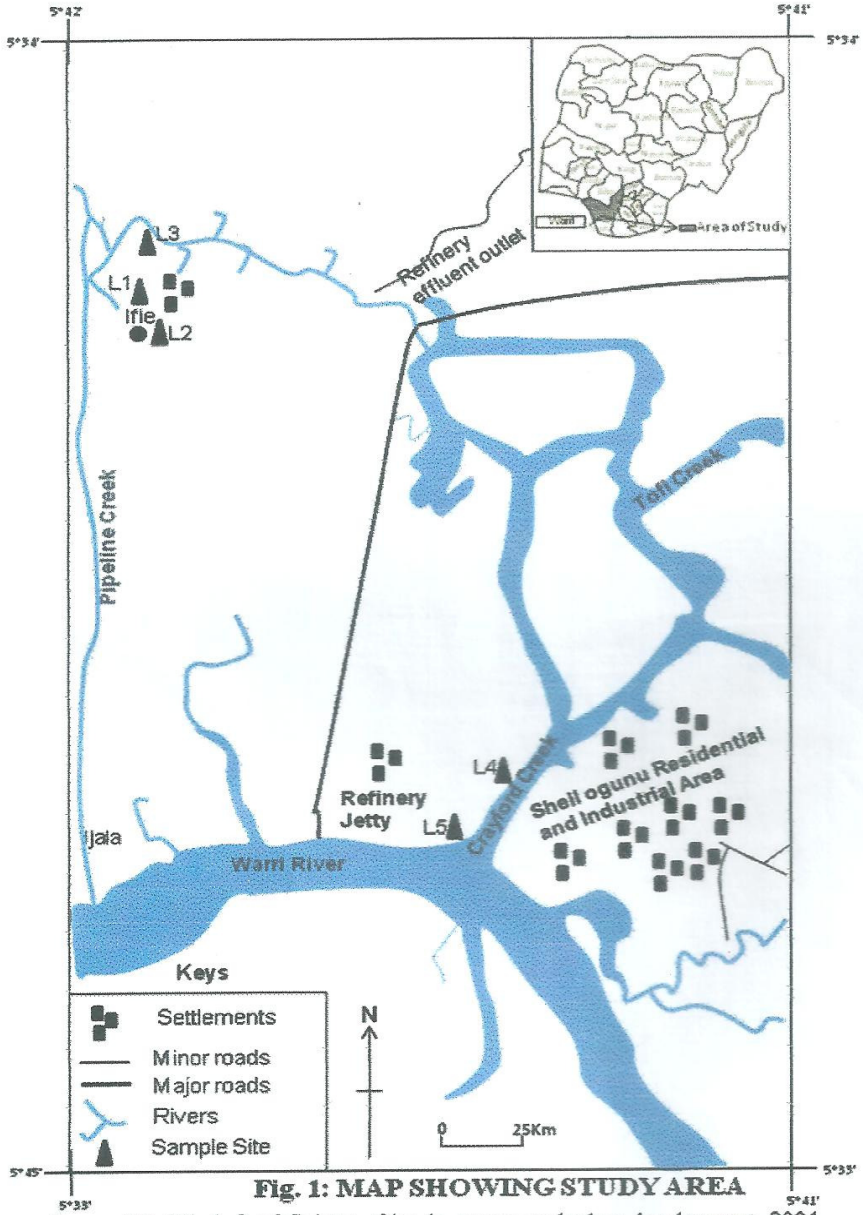

Fig. 1: MAP SHOWING STUDY AREA

Source: Modified after Ministry of lands, survey and urban development, 2004

Sediment Samples

Forty sediment samples were collected from the same locations from the Crayford Creek. They were collected using a stainless steel dredge; and put in polyethylene bags well labeled and sealed. These were transported to the laboratory for storage at 4^0C. Thereafter, the sediments were dried in an oven at 50^0C and sieved through a 20-µm sieve. Samples were ground in an agate mortar. One gram (1.0g) of the respective homogenized sample was dissolved with 20ml of concentrated nitric acid, 5ml of concentrated hydrochloric acid and 2ml of concentrated perchloric acid in 100ml Teflon beaker. Then the samples were

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respectively heated to 160^0C on a sand bath to ensure complete extraction for 3 hours. After cooling, the solutions were filtered and diluted using deionised water in 50ml volumetric flasks, made up to 100ml, and labeled for metal analysis (Shomar *et al.*; 2005) using Atomic Absorption Spectrophotometry (G B C Scientific Sensa A A, Australia).

Quality Control

Glass wares and sample containers were cleaned with Suprapure (Merck). All acids used for sequential chemical extraction were of analytical grade. In all determination analytical blanks were prepared in the same similar ways like the samples. The percentage recovery with respect to certified values were 98% for Cd, 90% for Fe, 94% for Mn, 93% for Cu, 99% for Ni, 96% for Cr and 93% for Zn respectively.

Data Treatment

The contamination/pollution (C/P) index was derived by employing the index as defined by Lacutusu (2002) thus:

$$C/P = \frac{\text{Concentration of Metal in sample}}{\text{Target Value}}$$

The target (reference) value of metals was obtained using the standard table formulated by the Department of Petroleum Resources of Nigeria (DPR, 2002) for maximum allowed concentration of heavy metals in soil.

Table 1.Significance of Intervals of Contamination/Pollution Index

C/P	*Significance*
< 0.10	Very slight contamination
0.10 – 0.25	Slight contamination
0.26 – 0.50	Moderate contamination
0.76 – 1.00	Very severe contamination
1.1 – 2.00	Slight pollution
2.1 – 4.00	Moderate pollution
4.1 – 8.00	Severe pollution
8.1 – 16.00	Very severe pollution
>16.0	Excessive pollution

Table 2. Department of Petroleum Resources (DPR) Target Value

Metal	*DPR (2002) Target Value (mg/kg)*	*Metal*	*DPR (2002) Target Value (mg/kg)*
Cd	0.80	Zn	140.00
Cr	100.00	Co	20.00
Cu	36.00	Hg	0.30
Pb	85.00	Mn	473*
Ni	35.00	Fe	5000*

* Derived from global average (Alloway, 2005)

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RESULTS AND DISCUSSION

The trace metals analysed in surface water and sediments of Crayford Creek in Warri were detected. However, there were variations in the levels of trace metals in both water and sediment samples. A close look at the results for the period of this study showed that mean concentrations of metals in surface water were lower than the concentrations found in sediment matrix (See Tables 3 and 4). This is an indication that pollution loads sink in bottom sediments.

Table 3. Mean ± SD and Range of Metal Concentrations (mg/l) in Surface Water from Crayford Creek

Metal in mg/l	*01*	*02*	*03*	*04*	*05*	*WHO Limits*
Fe	5.07 ± 1.29 (3.18 – 6.25)	4.83 ± 1.62 (2.49 – 6.24)	4.83 ± 1.79 (2.10 – 6.30)	4.80 ± 1.79 (1.66 – 6.37)	4.44 ± 1.57 (1.95 – 6.27)	0.30
Cr	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.05
Cu	2.80 ± 0.05 (2.00 – 3.60)	2.50 ± 0.01 (1.80 – 3.20)	1.48 ± 0.02 (0.98 – 2.20)	1.85 ± 0.10 (1.05 – 2.90)	4.30 ± 1.00 (3.00 – 6.50)	2.00
Mn	0.30 ± 0.02 (0.04 – 0.49)	0.32 ± 0.03 (0.05 – 0.45)	0.40 ± 0.03 (0.10 – 0.60)	0.30 ± 0.02 (0.04 – 0.52)	0.35 ± 0.08 (0.20 – 0.78)	0.40
Pb	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01
Ni	0.03 ± 0.02 (0.01 – 0.07)	0.04 ± 0.02 (0.01 – 0.06)	0.03 ± 0.01 (0.01 – 0.05)	0.03 ± 0.02 (0.01 – 0.07)	0.04 ± 0.02 (0.01 – 0.06)	0.07
Cd	0.02 ± 0.01 (0.01 – 0.03)	0.03 ± 0.01 (0.02 – 0.04)	0.04 ± 0.01 (0.01 – 0.05)	0.03 ± 0.02 (0.01 – 0.07)	0.04 ± 0.02 (0.01 – 0.06)	0.003
Zn	0.06 ± 0.04 (0.01 – 0.10)	0.05 ± 0.03 (0.01 – 0.09)	0.06 ± 0.03 (0.01 – 0.10)	0.05 ± 0.04 (0.01 – 0.10)	0.05 ± 0.03 (0.01 – 0.09)	-

Table 4. Mean SD and Range of Metal Concentration (mg/kg dry weight) in Sediment from Crayford Creek

Metal in mg/kg dry wt	*`Sample Site*				
	01	*02*	*03*	*04*	*05*
Fe	5307.25±2442.33 (580.50–7265.00)	5841.75±326.10 (5487.50–6278.00)	5343.42±1414.01 (3075.00-6835.00)	5285.50±1650.02 (2790.00-7125.00)	5710.08±1632.72 (2780.00-7250.00)
Cr	5.80 ± 0.85 (2.02 – 7.95)	6.33 ± 1.65 (3.05 – 9.20)	7.40 ± 2.05 (3.35 – 11.85)	8.08 ± 3.00 (4.50 – 12.60)	8.33 ± 2.00 (6.30 – 12.00)
Cu	12.65 ± 3.25 (6.50 – 14.10)	9.40 ± 2.80 (6.80 – 13.60)	6.65 ± 3.95 (4.70 – 10.00)	9.93 ± 3.80 (5.60 – 13.65)	12.30 ± 4.00 (7.80 – 16.20)
Mn	49.26 ± 14.48 (31.68 – 73.40)	39.98 ± 21.60 (11.95 – 65.13)	40.18 ± 16.56 (17.20 – 64.25)	40.44 ± 29.39 (5.60 – 13.65)	57.27 ± 27.47 (34.63 – 104.13)
Pb	3.06 ± 0.55 (2.01 – 5.85)	3.68 ± 1.20 (1.90 – 6.00)	3.05 ± 0.80 (1.60 – 4.50)	3.00 ± 0.60 (1.40 – 5.20)	3.65 ± 1.00 (2.00 – 5.20)
Ni	11.03 ± 1.87 (7.65 – 14.23)	13.52 ± 2.50 (8.78 – 15.28)	10.93 ± 2.69 (7.66 – 15.13)	9.80 ± 3.26 (5.38 – 13.78)	17.19 ± 4.54 (10.73 – 22.05)
Cd	0.62 ± 0.26 (0.30 – 1.03)	0.58 ± 0.20 (0.33 – 0.85)	0.68 ± 0.26 (0.40 – 1.80)	0.61 ± 0.17 (0.40 – 0.83)	0.68 ± 0.20 (0.48 – 1.00)
Zn	275.62 ± 15.17 (255.90–290.60)	334.69 ± 59.38 (284.60 – 435.25)	314.63 ± 74.79 (245.85 – 438.38)	273.63 ± 19.95 (250.50 – 300.30)	322.81 ± 55.03 (269.88 – 406.40)

Table 5. Computation of Contamination/Pollution Index (C/P):Sediment

Metal	*Sample Site*				
	01	*02*	*03*	*04*	*05*
Fe	1.06	1.17	1.07	1.06	1.14
Cr	0.06	0.07	0.07	0.08	0.08
Cu	0.35	0.26	0.19	0.28	0.34
Mn	0.11	0.09	0.09	0.09	0.12
Pb	0.04	0.04	0.04	0.04	0.04
Ni	0.32	0.39	0.31	0.28	0.49
Cd	0.78	0.73	0.85	0.76	0.85
Multiple population	4.69	5.14	4.86	4.55	5.37

Table 6. Computation of Contamination/Pollution Index (C/P):Surface Water

Metal	*Sample Site*				
	01	*02*	*03*	*04*	*05*
Fe	16.9	16.1	16.1	16.0	14.8
Cr	0.20	0.20	0.20	0.20	0.20
Cu	1.40	1.25	0.74	0.93	2.15
Mn	0.75	0.80	1.00	0.75	0.88
Pb	1.00	1.00	1.00	1.00	1.00
Ni	0.43	0.57	0.43	0.43	0.57
Cd	6.66	10.0	13.33	10.0	6.66
Zn	-	-	-	-	-

Heavy Metal Contents in Surface Water

In this study metals such as Cd, Cr, Cu, Pb, Ni and Mn are among toxic chemicals that are of health significance in drinking water. In fact only Cu and Cd levels were above the required and allowable limits whereas Cr, Pb, Ni, Mn and Zn levels were within the allowed concentrations for drinking water. Although Fe is not considered as a critical metal but its concentrations exceeded the acceptable standard set by WHO (1995). The Crayford Creek acts as a sink for all pollution loads arising from Warri River. All pollutants arising from crude oil explorations, anthropogenic wastes and other industrial and domestic sewages find their ways through various channels into Crayford Creek.

The mean concentrations of metals in surface waters in this study were higher than those concentrations reported by Iwegbue *et al.*; (2012) from the Orogodo River in both dry and wet seasons. The mean concentrations of Fe, Cu, Zn, Cd, Cr, Ni, and Pb in surface water in this study exceeded the levels reported by Faanu *et al.* (2011) in water around the vicinity of

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gold mining areas from Ghana and those reported by Ekeanyanwu *et al.* (2010) in surface water of Okumeshi River in Delta State of Nigeria. Mean concentration of metals such as Cd, Mn, Cr, Ni, Pb and Zn reported by Okafor and Nwajei (2007) and Shomar *et al.* (2005) were higher than the concentrations recorded in this study. The analysis of Cr and Pb in surface water of the Crayford Creek showed similar concentrations. The two metals displayed the same trend in the five locations (01 – 05), hence no concentration range was recorded. However, metals such as Fe, Cu, Mn, Ni, Cd and Zn showed slight variations in their concentrations from the five locations over the period of study. This is an indication that seasonal variation of metals in surface water of Crayford Creek did not affect Cr and Pb, but slightly affected other metals analysed under the study.

Heavy Metal Contents in Sediments

Highest mean concentrations of Fe were obtained in the five locations (01 – 05) (Table 4) in this study when compared with other metals analysed in sediments of Crayford Creek. This study however, has revealed that Fe is the most abundant when compared with other metals in the Niger Delta region of Nigeria. A computation of contamination/pollution index has shown that Fe (Table 5) is categorized under slight pollution, since contamination/pollution index is greater than unity. The mean concentrations of Fe in the five locations of the Creek were higher than 5000mg/kg which is the target value set by Department of Petroleum Resources (DPR) (2002). The mean concentrations of Fe in the five locations were higher than those concentrations reported by Iwegbue *et al.*, (2012); Ekeanyanwu *et al.*, (2010); Iwegbue *et al.*, (2007) and Iwegbue *et al.*; (2006). The major sources of Fe in the sediment are discharges of municipal wastes, scrap dumps and runoff from automobile workshops in Warri metropolis and its environs.

Chromium is present in the Crayford Creek sediment. The concentrations range from 2.02 to 7.95mg/kg for location 01; 3.05 to 9.20mg/kg for location 02; 3.35 to 11.85mg/kg for location 03; 4.50 to 12.60mg/kg for location 04 and 6.30 to 12.00mg/kg for location 05. Sample locations 04 and 05 have higher concentrations of Cr, when compared with location 01, 02 and 03. These high concentrations of Cr are attributable to activities of Refinery Jetty and Shell Development Company located very close to sample points 04 and 05. (Fig.1). The contamination/pollution index calculated revealed 'very slight contamination' of the sediments by Cr. The concentrations of Cr observed in this study were higher than the concentrations reported by Iwegbue *et al.* (2012).

On the other hand, concentrations were lower than those levels obtained by Faanu *et al.*; (2011) and Shomar *et al.* (2005). The mean concentrations of Cr in this study were below the threshold effects and probable effect levels of Cr in sediments which are 53.30mg/kg and 160mg/kg respectively (FDEP, 1994).

Copper concentrations were detected in sediments analysed from the five locations. The mean Cu levels range from 6.50 to 14.10mg/kg for location 01; 6.80 to 13.60mg/kg for location 05. Highest and similar concentrations of Cu were recorded in sediment matrix from locations 01 and 05. Also similar levels were observed from locations 02 and 04 while the least levels were recorded in location 03. The computation of contamination/pollution index showed moderate contamination of sediment by Cu in all the locations. The presence of Cu concentration was traceable to anthropogenic wastes and industrial activities around the study area. The mean Cu concentrations in this study were below the target value (35.00mg/kg) set by the Department of Petroleum Resources (DPR, 2002) and those values reported by Shomar *et al.*; (2005) and Vukovic *et al.*; (2011).

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Manganese mean concentrations in the sediments of Crayford Creek ranged from 31.68 to 73.40mg/kg for location 01; 11.95 to 65.13mg/kg for location 02; 17.20 to 64.25mg/kg for location 03; 13.18 to 97.90mg/kg for location 04 and 34.63 to 104.13mg/kg for location 05 respectively. Highest Mn levels were observed in sediment from location 05 which was nearer to Shell Petroleum Development Company (SPDC0 site). However, contamination/pollution index value calculated for Mn showed slight contamination of sediment by Mn. The mean Mn concentrations observed in the five locations exceeded those values reported by Iwegbue *et al.* (2012); Nwajei, (2002) and Ekeanyanwu *et al.*; (2010). On the other hand, the concentrations of Mn reported by Shomar *et al.* (2005) in sediments of the Wetland of Wadi Gaza exceeded these levels observed in the five sediment locations from Crayford Creek in Warri.

The mean concentrations of Pb in sediments from the five sample locations varied very slightly. This is an indication that the level of contaminants was the same. The computation of contamination/pollution index values was the same (0.04mg/kg) for the five sample locations. These levels of Pb observed in all the sample location did not show contamination of sediment by Pb, since the levels were less than 0.10mg/kg which indicates very slight contamination. The presence of Pb is traceable to activities of petroleum exploration and discharge wastes arising from industries through runoff into the creek. The mean concentrations of Pb observed in this study were lower than those levels reported by Iwegbue *et al.* (2012); Vystavna *et al.*; (2011). The trend of heavy metal accumulation in sediments was attributed mainly to anthropogenic influences and natural processes (Vukovic *et al.*; 2011).

The concentrations of Ni in the sediment varied significantly among the five sample locations with the highest level from location 05 (17.19mg/kg). The mean concentrations of Ni ranged from 7.65 to 14.23mg/kg for location 01; 8.78 to 15.28mg/kg for location 02; 7.66 to 15.13mg/kg for location 03; 5.38 to 13.78mg/kg for location 04 and 10.73 to 22.05mg/kg for location 05 respectively. The threshold effect level and probable effect level for Ni as set by FDEP (1994) were 15.9mg/kg and 42.80 mg/kg respectively. A look at the results showed that only location 05 has Ni concentrations above the threshold effect level. The calculation of contamination/pollution index showed that sediments from Crayford Creek were moderately contaminated by Ni. The mean concentrations of Ni in sediment in this study exceeded those levels reported by Nwajei (2002); Iwegbue *et al.*; (2007); Iwegbue *et al.*; (2006); Iwegbue *et al.*; (2012). The major sources of Ni in sediment from Crayford creek were attributed to crude oil exploration and the presence of refinery jetty in the vicinity of the study sites.

The mean concentrations of Cd in the sediment varied slightly from one sample location to another. The mean levels of Cd in are presented as follows: 0.62 mg/kg for location 01; 0.58 mg/kg for location 02; 0.68 mg/kg for location 03; 0.61 mg/kg for location 04 and 0.68 mg/kg for location 05 respectively. The computation of contamination/pollution index showed that the sediments were very severely contaminated by Cd. The sources of Cd in the study area were attributed waste batteries dumped, automobile scraps, pigments containing Cd in refinery jetty and refinery effluents which enters the water channels and sink in the bottom more noticeable if not the high concentrations of Zn observed in this study. This implies that excess Zn prevents many toxic effects of Cd and Zn deficiency enhances Cd toxicity. The levels of Cd reported in this study were lower than the levels reported by Iwegbue *et al.*; (2007); and Vukovic *et al.*; (2011) whereas the levels of Cd reported by Iwegbue *et al.*; (2012); Iwegbue *et al.*; (2006) and Okafor and Nwajei (2006) were lower than the levels reported in this present study.

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High concentrations of Zn were observed in all five sample locations. The concentrations varied greatly from one sample location to another. The calculation of contamination/pollution index showed that Zn is attributable to refining activities, wood combustion and anthropogenic wastes in Warri and its environs. The threshold effects level and probable effects level of Zn in sediments are 124 mg/kg and 271 mg/kg respectively (FDEP, 1994). These values are lower than the levels recorded in this present study (Table 4).

CONCLUSION

Water and sediments samples collected from Crayford creeks which takes its course from, Warri River were analytically treated and analysed for metals such as Fe, Cr, Cu, Mn, Pb, Ni, Cd and Zn. The mean concentrations of the aforementioned metals were all detected in both surface water and bottom sediment sample and varied significantly over time. The mean concentrations of metals reported in this present study were carefully compared with other similar researches and set standards. The results revealed that metal values in sediments exceeded those levels reported in surface water. Highest mean concentrations were observed in Fe and Zn in sediments. This was not the case for surface water where highest mean concentrations were recorded in Fe and Cu. The results further showed that sediments are the sink of all pollution loads. The computation of the contamination/pollution index showed that the sediments were polluted by Fe and Zn. Whereas metals such as Cu, Ni and Cd contaminated the sediments significantly. The contamination/pollution of water and sediments of Crayford Creek by heavy metals were attributed to runoff, refinery jetty and S. P. D. C activities around the study area.

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