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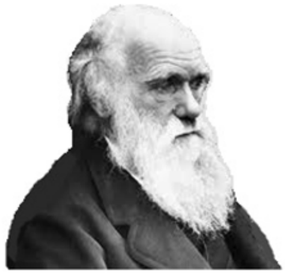

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Distribution of Trace Elements in Surface Water and Sediments from Warri River in Warri, Delta State of Nigeria

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ABSTRACT

The pollution of surface water and sediments by heavy metals has become a difficult thing to deal with due to their toxicity and accumulative behavior. The present study was undertaken to provide information on the concentrations and distribution of selected heavy metals in surface water and sediments from Warri River, and to compute a contamination/pollution index of heavy metals. Surface water and sediment samples were collected using standard methods and then analysed for nine trace metals. These metals were determined using a Flame Atomic Absorption Spectrophotometer – UNICAM 929. According to our results, the mean concentrations of the select metals in the sediments were higher than those of the surface water. The figures, however, varied significantly in the six sample locations (SW1–SW6). In the sediments, the highest mean concentration was of Fe (504.13 mg/kg) in location SW1, whereas in surface water, generally, the highest mean concentration was of Fe (1.23 mg/l). In other words, mean metal levels in the sediments exceeded those of surface water. This indicates that sediments are a sink for metal pollution loads. Computation of contamination/ pollution index in sediment matrix revealed that Cd moderately polluted the sediment, Zn, Fe, Ni slightly, yet significantly contaminated the sediment, while Cu, Cr and Mn very slightly contaminated the sediments. The mean values of metals in this present study were compared with other values reported by other researchers. The higher than normal metal values were attributed to anthropogenic wastes, runoff, refinery jetty and varied petroleum related activities in the area.

***Keywords*:** Contamination, pollution index, Warri River, Trace elements

1. INTRODUCTION

Pollution is one of the most important problems around the World in which thousands of millions of world inhabitants suffer health problems related to industry and atmospheric pollutants. Industrialization and urbanization have led to environmental pollution wideworld (Filazi et al, 2003). According to Chen and Chen 2001, industries have been responsible for discharging effluent containing heavy metals such as zinc, copper, manganese, cadmium, mercury, arsenic, barium, nickel, lead, vanadium chromium, etc. into our environment. Plants absorbs metals from contaminated soils as well as from deposits on different parts of the plants exposed to the air from polluted environment (Zurera et al, 1987). These heavy metals in water generally exist in low levels and attain considerable concentrations in sediments and biota. Plants species and varieties vary in their capacity for heavy metal accumulation. Increase in concentrations of heavy metals in soil increases the crops uptake depending on the specie. Today, heavy metals are well recognized as potentially toxic to plants and other living organisms (Zurera et al, 1987). Inability of heavy metals to be metabolized by the body make them toxic and accumulate in the soft tissue (Nwajei and Iwegbue, 2007).

Heavy Metals like Ag, Pb, Cd, Cu, Cr and Zn are contaminated within the city of Kharkov these are mainly attributed to municipal wastewater inputs and urban run-of and as a a result of this the sediments can be considered as potentially toxic to aquatics as regards to the environmental quality assessment taken (Vystavna *et al.*; 2012). Cd, Hg, Cr and Pb are examples of heavy metals known to be powerful nephrotoxins (Doul *et al.*; 1980). Metals have the potential to be toxic to living organisms if present at above a threshold level. Heavy metals are found in most urban and industrial run-off in the dissolved or particulate form (Defew *et al.*; 2004).

Heavy metals are rapidly deposited onto the sediments from incoming tidal water and freshwater sources (Guzman and Garcia, 2002). There is a decrease in the availability of freshwater reouces due to the faster rate of deterioration of the water with metals in discharges from mining, smelting and industrial manufacturing, is a long-standing phenomenon (Mahananda *et al.*; 2005).

Heavy metals can remain in the environment unchanged for years and thus becomes dangerous to man and other organisms (Thapa and Weber, 1991). The concentrations of Heavy metals in summer and winter are generally affected by human inputs and precipitation respectively. (Shomar *et al.*; 2005). Heavy metals rapidly become associated with particulates and are incorporated in the bottom sediment once they are discharged into estuarine and coastal waters (Iwegbue *et al.*; 2012). Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissue (Nwajei and Iwegbue, 2007). The heavy metals that most commonly cause problems in human are lead, mercury, cadmium, arsenic, nickel and aluminum. These metals tend to accumulate in the brain, kidneys and immune system where they can severely disrupt normal function (Passwater and Cranton, 1993; Gerstner and Huff, 1997, Dibofori-Orji and Edori 2013).

Sediments can also be used to record the history of river pollution because heavy metals are always deposited in them.(Yu *et al.*; 2001; Wepener and Vermeulen; 2005). Therefore, sediment quality data provide essential information for evaluating ambient environmental quality conditions in aquatic ecosystem. Warri River receives industrial and anthropogenic wastes arising from different activities. 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 Warri River; secondly to compute a contamination/pollution index of heavy metals in the surface water and sediments of the river under study.

2. MATERIALS AND METHODS

Description of Study Area

The study was carried out at six tributaries of Warri River in Delta State, Nigeria. The Warri River flows through the adjourning mangrove swamp forest area of the southern part of Nigeria, where the drainage and catchment areas are probably very rich in decaying organic matter and humus. Warri River stretches within latitude 5°2’ - 6°00’ N and longitude 5°24’ - 6°2’ E. Its source is around Utagba Uno and runs in a Southwest direction passing between Oviorie and Ovu-inland and southwards at Odiete through Agbarho to Otokutu and Ugbolokposo (Egborge, 2001). It turns southward to Effurun and forms a 'W' shape between Effurun and Warri. Important land marks in this River stretch are Enerhen, Igbudu, Ovwian and Aladja (steel town), Warri Ports, main Warri market, NNPC Refinery, Globe star. Six locations chosen for this study are as follows:

Table 1. Sample Locations of the study

S/NO.	Water	Sediment	LOCATION	COORDINATES
1	WW1	SW1	Workson Nig Ltd Jetty	N5^{O} 31^{I} 49^{II} E5^{O} 42^{I}43^{II}
2	WW2	SW2	Ogunu	N5^{O} 30^{I} 52^{II} E5^{O} 44^{I}0^{II}
3	WW3	SW3	Ugbuawangue	N5^{O} 32^{I} 43^{II} E5^{O} 42^{I}31^{II}
4	WW4	SW4	Enerhen	N5^{O} 32^{I} 42^{II} E5^{O} 47^{I}48^{II}
5	WW5	SW5	Npa	N5^{O} 30^{I} 52^{II} E5^{O} 43^{I}59^{II}
6	WW6	SW6	Ogbeijaw	N5^{O} 30^{I} 43^{II} E5^{O} 44^{I}43^{II}

Water Sampling and analysis

500 ml of the water sample was collected from each station (01 – 05). Each sample was filtered in acid-washed filter holder and through 0.45 μm pore size membrane filters. The first few millimeters were used to rinse, discarded, and the filtrate was transferred to labeled clean acid-washed sample bottles, acidified with concentrated nitric acid and stored at 40C prior to analysis of total metal contents by Flame Atomic Absorption Spectrophotometer – UNICAM 929.

Sediment Sampling and analysis

One hundred and Forty four (144) sediment samples were collected from the different locations from the Warri River. The sediments 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 40 °C. Thereafter, these sediments were dried in an oven at 500C and sieved through a 20 μm sieve. Samples were ground in an agate mortar. One gram (1.0 g) of the respective homogenized sample was dissolved with 20 ml of concentrated nitric acid, 5ml of concentrated hydrochloric acid and 2ml of concentrated perchloric acid in 100ml Teflon beaker. Then the samples were respectively heated to 1600C on a sand bath to ensure complete extraction for 3 hours. After cooling, the solutions were filtered and diluted using deionised water in 50 ml volumetric flasks, made up to 100ml, and labeled for metal analysis (Shomar *et al.*, 2005) using by Flame Atomic Absorption Spectrophotometer – UNICAM 929.

Quality Control

Glass wares and sample containers were cleaned with Suprapure (Merck). All acids used for Analytically sequential chemical extraction were of analytical grade. In all determination the 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:

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

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

Metal DPR (2002)	Target Value (mg/kg) (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)

Heavy metals were found in surface water and sediments of Warri River after the analysis. From the study there were variations in the level of heavy metal in both water and sediment samples. Mean concentrations of metals in surface water were lower than the concentrations found in sediment matrix (Oguzie 2003 and Nwajei *et al*, 2014) (See Tables 2 and 3). It could be that pollutants are deposited in bottom sediments.

Heavy Metal Contents in Surface water

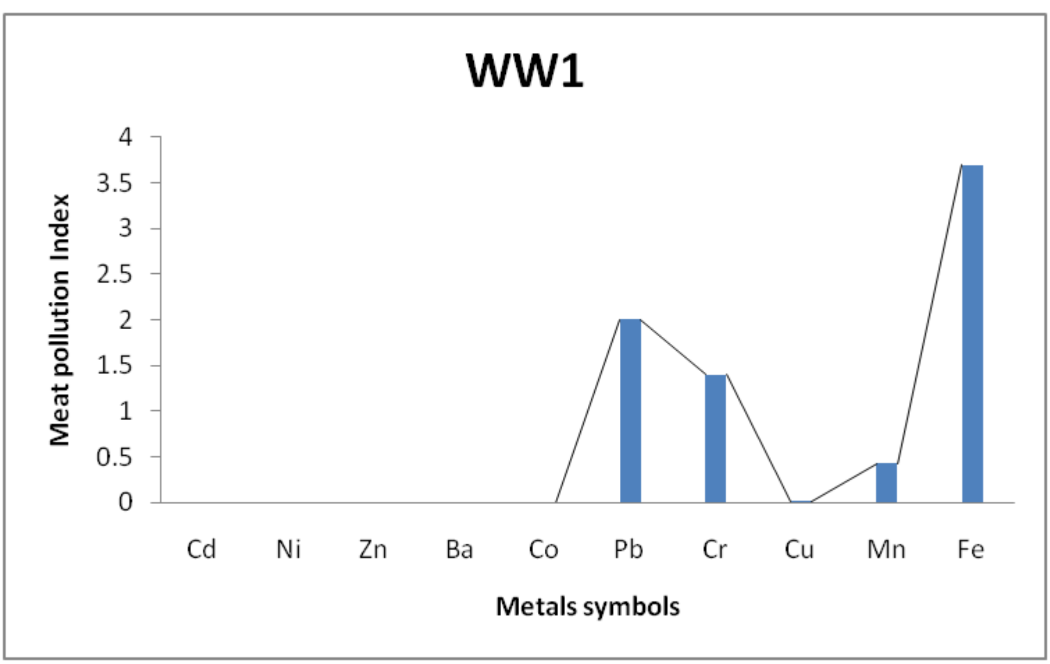
Table 4. Mean ± SD and Range of Metal Concentrations (mg/l) in Surface Water from Warri River

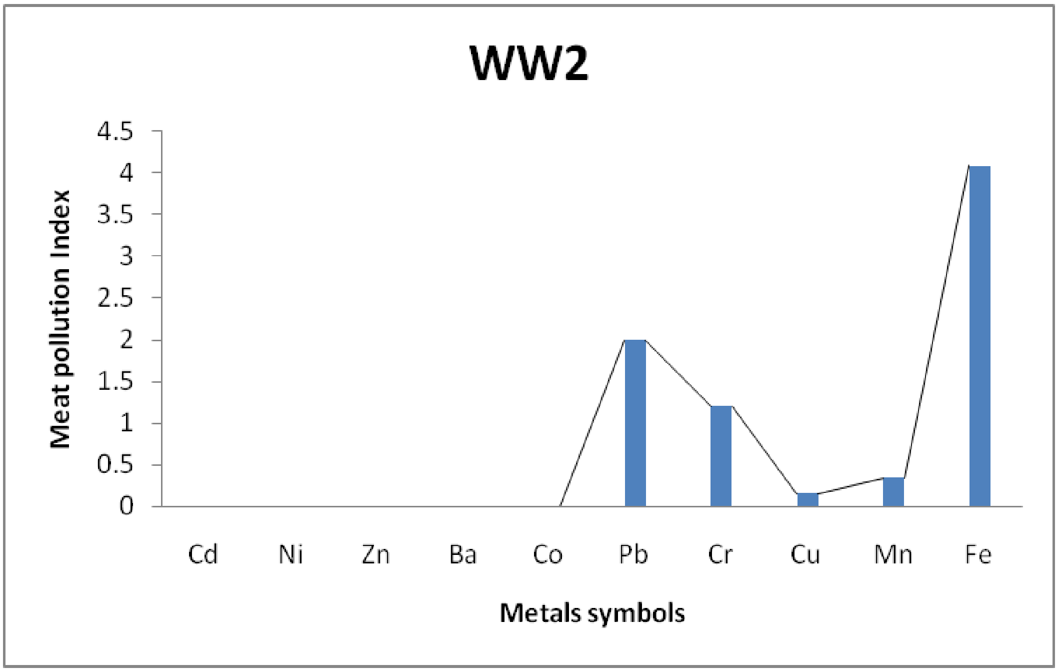
Metal	WW1	WW2	WW3	WW4	WW5	WW6	WHO Limits
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zn	0.11±0.09 (0.04±0.38)	0.15±0.13 (0.10-0.15)	0.13±0.10 (0.04-0.36)	0.21±0.19 (0.08-0.72)	0.12±0.09 (0.03-0.29)	0.43±0.57 (0.03-1.33)	-
Ba	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	-
Co	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07
Pb	0.02±0.01 (0.01-0.01)	0.02±0.01 (0.01-0.06)	0.04±0.03 (0.01-0.08)	0.02±0.02 (0.01-0.08)	0.03±0.02 (0.01-0.09)	0.03±0.03 (0.01-0.08)	0.01
Cr	0.07±0.01 (0.06-0.07)	0.06±0.01 (0.06-0.0)	0.07±0.02 (0.05-0.08)	0.08±0.02 (0.06-0.10)	0.08±0.02 (0.07-0.10)	0.06±0.00 (0.06-0.06)	0.05
Cu	0.04±0.01 (0.03-0.05)	0.03±0.01 (0.02-0.04)	0.02±0.01 (0.02-0.03)	0.03±0.01 (0.03-0.03)	0.04±0.01 (0.04-0.04)	0.03±0.01 0.02-0.04	2.00

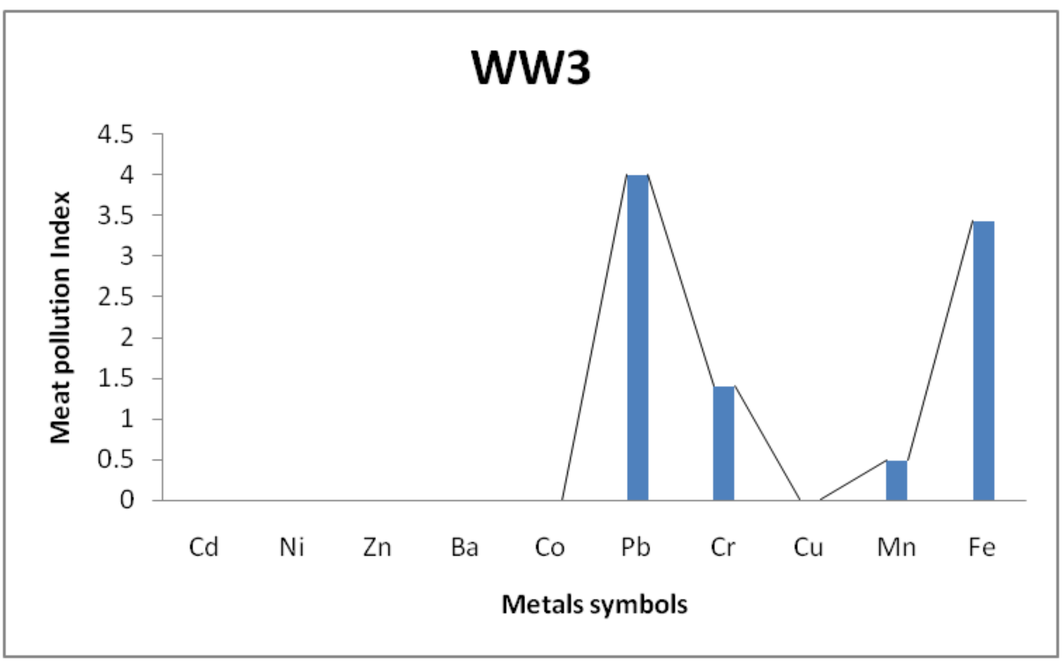
Mn	0.17±0.08 (0.05-0.30)	0.14±0.11 (0.05-0.43)	0.20±0.10 (0.04-0.36)	0.17±0.09 (0.06-0.36)	0.11±0.05 (0.06-0.20)	0.140±0.13 (0.06-0.52)	0.40
Fe	1.11±0.68 (0.20-2.41)	1.23±0.55 (1.23-1.94)	1.03±0.52 (0.34-1.76)	0.87±0.51 (0.12-1.91)	1.09±0.64 (0.21-1.91)	0.96±0.40 (0.41-1.73)	0.30

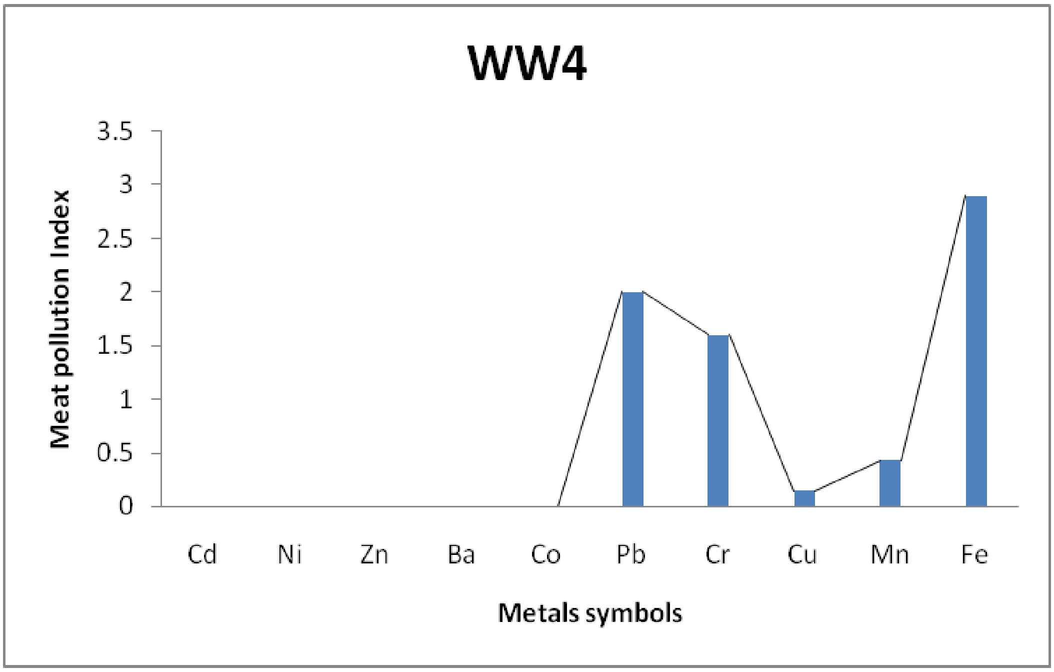
WW1: Water from Warri River sample 1; (1.19-4.04): Range of Metal Concentration

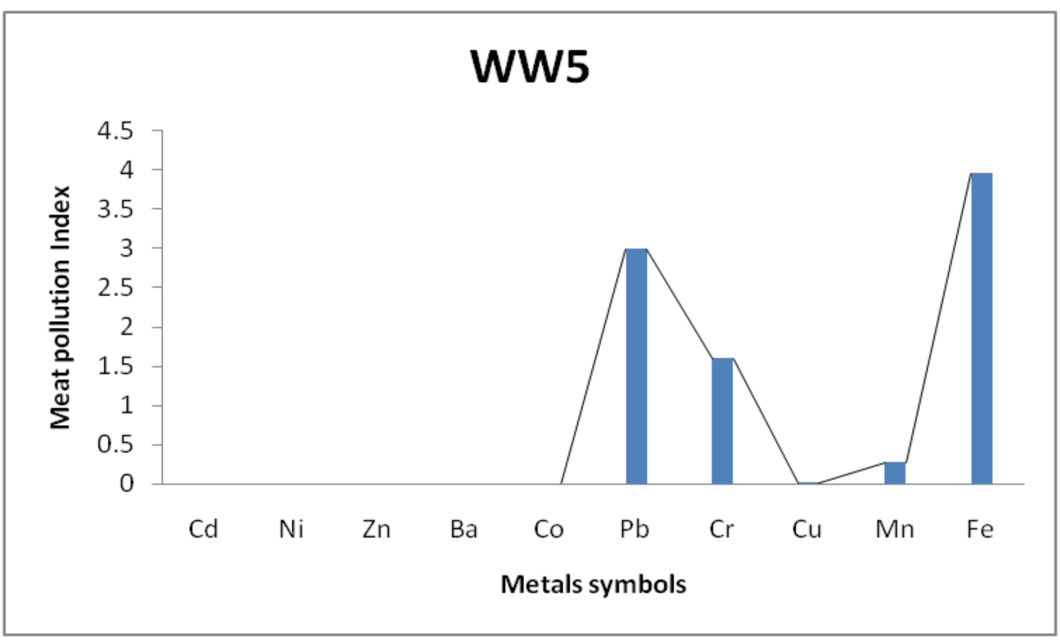
All metals analysed are among toxic chemicals that are of health significance in drinking water. In fact Cd, Ni, Co and Ba were below detection limit, only Pb, Cr, Fe levels were above the required and allowable limits WHO for drinking water whereas Cu, Zn and Mn and Zn levels were within the allowed concentrations for drinking water. Although Fe is not considered as a critical metal but its concentrations exceeded the acceptable standard set by WHO (1995). All pollutants arising from crude oil explorations, anthropogenic wastes and other industrial and domestic sewages find their ways through various channels into Warri River. The mean concentrations of metals in surface waters in this study were slightly lower than those concentrations reported by Iwegbue *et al.*; (2012) from the Orogodo River in both dry and wet seasons, Faanu *et al.* (2011) in water around the vicinity of 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 result of the analysis of Cd, Ni, Co and Ba in surface water of the Warri River was below detection limit. However, metals such as Fe, Cu, Mn, Pb, Cr and Zn showed slight variations in their concentrations from the six locations over the period of study.

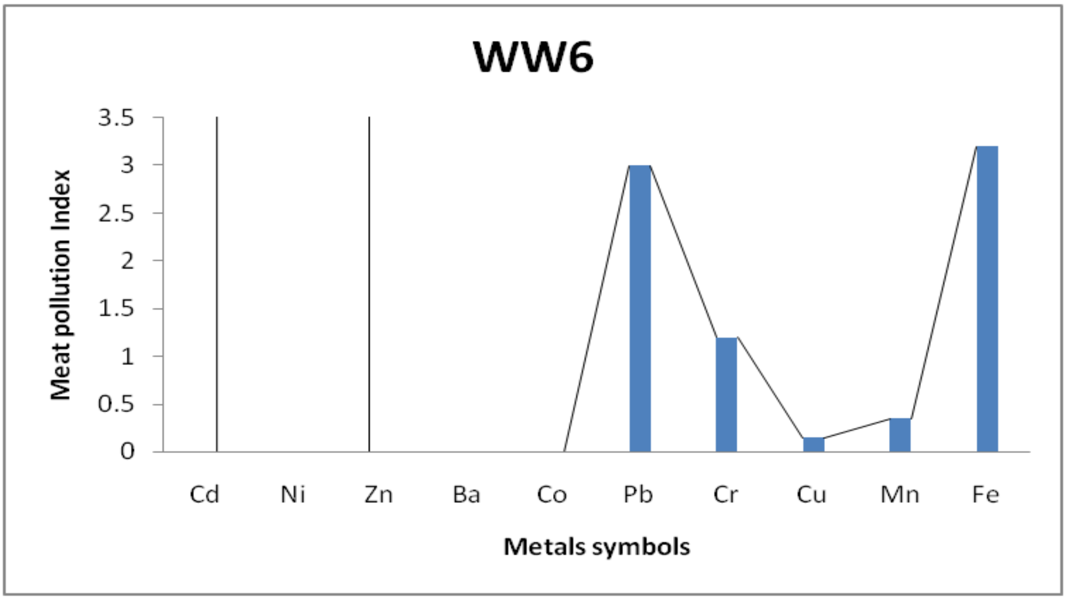



WW2
Meat pollution Index
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Cd
Ni
Zn
Ba
Co
Pb
Cr
Cu
Mn
Fe
Metals symbols


WW3
Meat pollution Index
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Cd
Ni
Zn
Ba
Co
Pb
Cr
Cu
Mn
Fe
Metals symbols


WW4
Meat pollution Index
3.5
3
2.5
2
1.5
1
0.5
0
Cd
Ni
Zn
Ba
Co
Pb
Cr
Cu
Mn
Fe
Metals symbols


WW5
Meat pollution Index
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Cd
Ni
Zn
Ba
Co
Pb
Cr
Cu
Mn
Fe
Metals symbols



Figures WW1-WW6. Bar plots of Pollution Index of Surface Water from Wari river

Heavy Metal Contents in Sediments

Table 5. Mean ± SD and Range of Metal Concentration (mg/kg dry weight) in Sediment from Warri River

Meta	SW1	SW2	SW3	SW4	SW5	SW6
Cd	2.17±0.84 (1.19-4.04)	2.26±1.95 (1.05-8.01)	1.88±0.78 (1.00-3.34)	2.25±2.21 (0.42-8.73)	2.05±1.77 (0.92-5.76)	2.23±2.19 (0.74-8.11)
Ni	6.09±1.57 (3.14-8.96)	5.63±2.51 (1.98-9.36)	5.31±1.32 (3.08-8.35)	5.65±1.96 (3.53-8.97)	4.92±1.86 (2.24-7.56)	5.85±2.04 (2.10-8.26)
Zn	9.08±2.75 (5.66-14.66)	10.50±4.40 (4.76-15.47)	11.60±3.47 (6.62-16.35)	9.26±2.16 (5.62-11.54)	10.26±2.95 (6.27-18.32)	9.55±3.56 (5.80-18.87)
Ba	0.09±0.05 (0.03-0.18)	0.10±0.07 (0.02-0.26)	0.12±0.09 (0.02-0.30)	0.11±0.07 (0.02-0.02)	0.15±0.17 (0.03-0.62)	0.12±0.10 (0.02-0.32)
Co	0.20±0.18 (0.01-0.60)	0.19±0.21 (0.02-0.71)	0.17±0.08 (0.06-0.36)	0.16±0.13 (0.02-0.02)	0.17±0.09 (0.08-0.36)	0.16±0.12 (0.03-6.90)
Fe	504.13±119.00 (347.31-684.18)	446.94±134.65 (232.14-657.34)	457.50±143.51 (209.84-677.2)	419.50±241.08 (101.6-725.81)	460.67±210.72 (212.54-903.12)	489.48±190.79 (204.30-863.3)
Cr	0.59±0.34 (0.04-1.11)	0.72±0.33 (0.01-1.35)	0.64±0.19 (0.35-1.01)	0.62±0.32 (0.25-1.31)	0.75±0.43 (0.18-1.56)	0.48±0.32 (0.08-1.24)
Cu	0.17±0.25 (0.01-0.09)	0.56±0.49 (0.10-1.35)	0.23±0.38 (0.04-1.40)	0.25±0.31 0.03-0.90	0.58±0.50 (0.05-1.32	0.57±0.53 (0.04-1.46)
Mn	3.24±1.32 (0.18-5.30)	4.93±2.59 (2.03-9.39)	2.80±1.67 (0.97-5.92)	4.62±2.97 (1.42-10.43)	3.16±2.81 (0.10-9.12)	4.33±2.32 (0.31-6.90)
Pb	4.51±2.18 (2.20-10.36)	5.37±2.51 (1.98-9.36)	4.72± 2.37 (2.56±9.42	6.34±2.45 (2.67-9.50)	6.44± 2.66 (2.11-10.47)	4.70±1.91 (1.27-8.75)

SW1: Sediment from Warri River sample 1; (1.19-4.04): Range of Metal Concentration

In the sediment, the highest mean concentration of Fe (903.12 mg/kg), Cr (1.56 mg/kg), Ba (0.62 mg/kg) and Pb (10.47 mg/kg) were recorded at the station SW5 while the highest concentration of Cu (1.46 mg/kg) and Zn (18.87 mg/kg) were observed in station SW6, Ni (6.09 mg/kg) and Mn (10.43 mg/kg) and Cd (8.73 mg/kg) were obtained at station SW4 dredging site. The levels of Ni, Mn and Cd in sediments at station SW4 may be connected with the incessant sand dredging and filling operations in the location at the time of sampling (Oguzie, 1996). The physical process of dredging according to Sly (1997) and Oguzie (2003) could help to release pore solutions (rich in heavy metals) in the sediment. Similar reason might be responsible for higher values of Fe, Cr, Ba, and Pb at the location SW5 where occasional dredging is done to allow for shipment of raw materials hand rolled products in and out of the Jetty. Sediment samples taken at locations SW5 and SW1 ranked the 1st and 3rd in value of Pb (10.47 and 10.46 mg/kg). This might suggest the predominance of Pb compounds associated with gasoline and fumes from vehicular traffic, which characterize the locations. Largerweff and Specht (1970) reported the burning of gasoline and fossil fuels as source of Pb in urban aerosols and roadside dust, which get flushed, into the aquatic environment through flood run-off and atmospheric precipitation.

The Highest mean concentrations of Fe were obtained in the six locations (01 – 06) (Table 5) in this study when compared with other metals analysed in sediments of Warri River.

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 contamination. The mean concentrations of Fe in the six locations of the river were lower than 5000 mg/kg which is the target value set by Department of Petroleum Resources (DPR) (2002). The mean concentrations of Fe in the six locations were lower 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.

Copper is present in sediments analysed from the six locations. The mean Cu levels range from 0.01 to 0.90 mg/kg for location SW1; 0.10-1.35 mg/kg for location SW2, 0.04-1.40 mg/kg for SW3, 0.03-0.90 mg/kg for SW4,.0.05-1.32 mg/kg for SW5, 0.04 to1.46 mg/kg. Highest and similar concentrations of Cu were recorded in sediment matrix from locations SW1 to SW6. The computation of contamination/pollution index showed very slight 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 (35.00 mg/kg) set by the Department of Petroleum Resources (DPR, 2002) and those values reported by Shomar *et al.*; (2005) and Vukovic *et al.*; (2011).

Zinc is present in the sediment of Warri River. The concentrations range from 5.66 to 14.66 for location SW1; 4.76 to 15.47 mg/kg for location SW2; 6.62 to 16.35 mg/kg for location SW3; 5.62 to 11.54 mg/kg for location SW 4; 6.27 to 18.32 mg/kg for location SW and 5.80 to 18.87mg/kg for location 6. Sample locations SW5 and SW6 have higher concentrations of Zn, when compared with location SW1, SW2, SW3 and SW4. Zn level in the study area could be attributed to the high concentrations of Cd and Fe in that Zn occurs in nature with other metals of which Fe and Cd are the most common which supports the work of Dallars and Day, (1993). The contamination/pollution index calculated revealed 'very slight contamination' of the sediments by Zn. The concentrations of Zn observed in this study were lower than the concentrations reported by Iwegbue *et al.* (2012), Faanu *et al.* (2011) and Shomar *et al.* (2005). The mean concentrations of Zn in this study were higher than threshold effects and probable effect levels of Zn in sediments which are 124 mg/kg and 271 mg/kg respectively (FDEP, 1994).

Manganese concentrations in the sediments of Warri River ranged from 5.60 to 104.13mg/kg from location SW1 to SW6. The highest Mn levels were observed in sediment from location SW6 which was nearer to Market and Shell Petroleum Development Company (SPDC site). However, contamination/pollution index value calc ulated for Mn showed very slight contamination of sediment by Mn. The mean Mn concentrations observed in the six 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 the levels observed in the six sediment locations from the study.

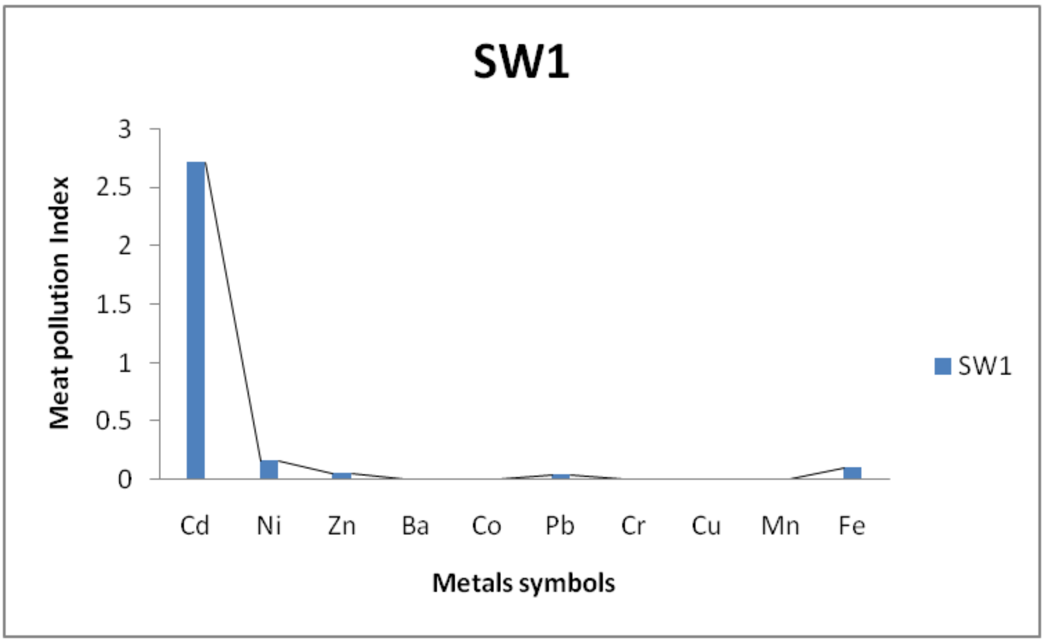
The mean concentrations of Co and Ba in sediments from the six samples locations varied very slightly. This shows that the level of contaminants was the same. These levels of Co and Ba in the sediment observed in all the sample location were less than 0.10 mg/kg which indicates very slight contamination. The presence of Co and Ba are traceable to activities of petroleum exploration and discharge wastes arising from industries through runoff into the creek.

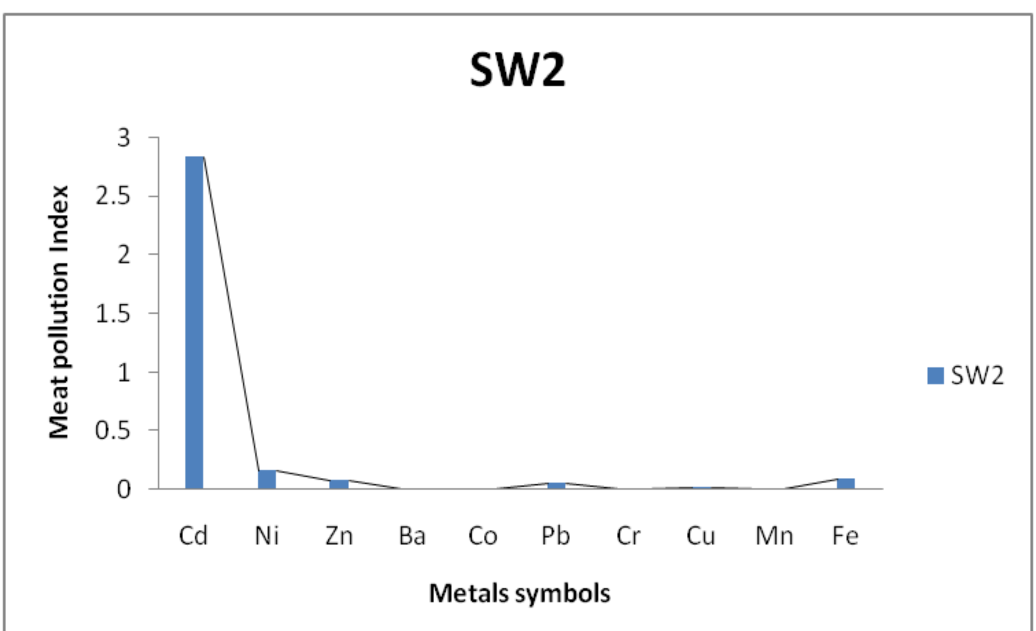
Lead concentrations in the sediments of Warri River ranged from 1.98 to 10.47mg/kg from location SW1 to SW6. The highest Pb levels were observed in sediment from location SW5 which was nearer to Market and Shell Petroleum Development Company (SPDC0 site). However, contamination/pollution index value calculated for Pb showed very slight contamination of sediment by Pb. The mean concentrations of Pb observed in this study were higher than those levels reported by Nwajei *et al*., 2014, Iwegbue *et al.* (2012); Vystavna *et al.*; (2011) and lower than Ogaga *et al.* (2015), Rabee *et al.* (2011).

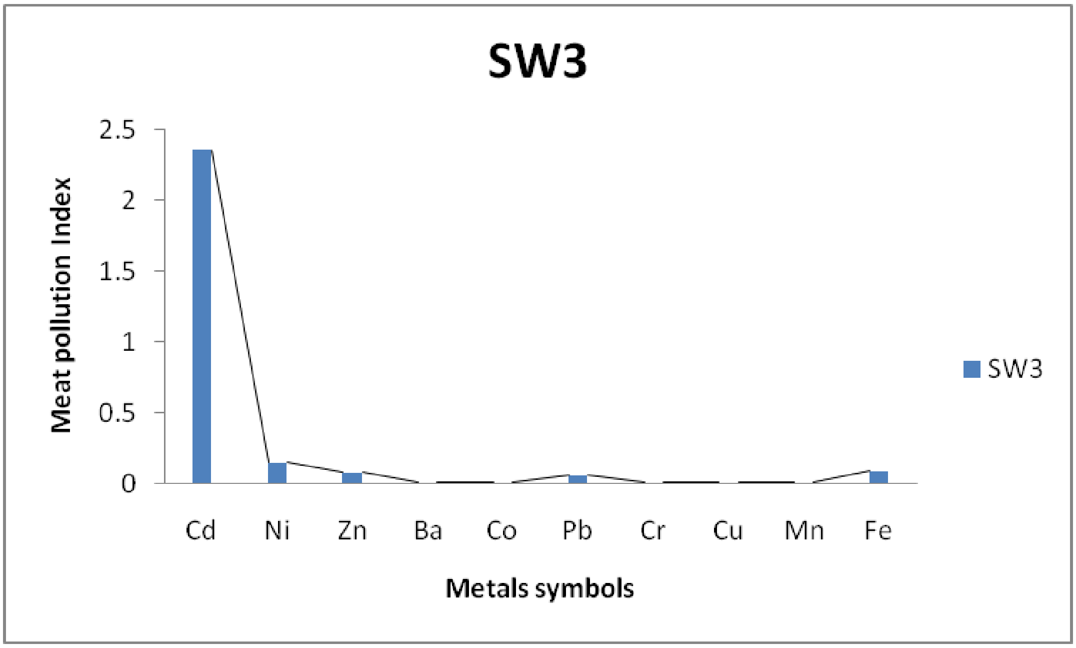
The concentrations of Ni in the sediment varied significantly among the six sample locations with the highest and lowest level from location SW1 (6.09 mg/kg) and SW5 (4.92 mg/kg). The threshold effect level and probable effect level for Ni as set by FDEP (1994) were 15.9 mg/kg and 42.80 mg/kg respectively. A look at the results showed that all the locations have Ni concentrations below the threshold effect level. The calculated contamination/pollution index showed that sediments from Warri River were slightly 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) and Iwegbue *et al.* (2012). The major sources of Ni in sediment from Warri River were attributed to crude oil exploration and the presence of refinery jetty in the vicinity of the study sites.

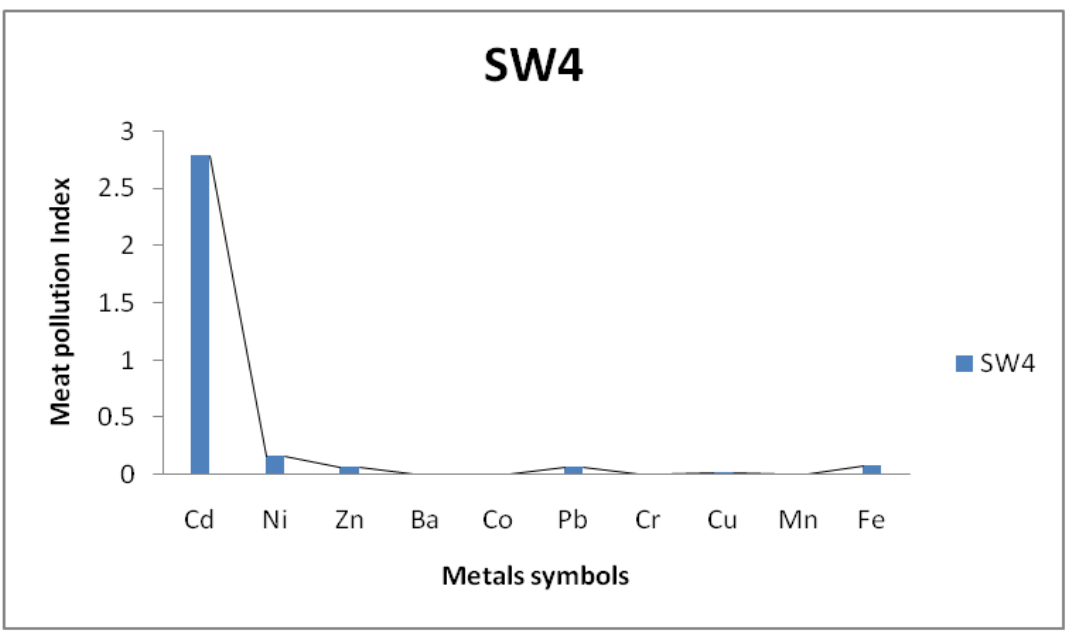
The mean concentrations of Cd in the sediment varied slightly from one sample location to another. The mean levels of Cd are presented as follows: 2.72 mg/kg for location SW 1; 2.26 mg/kg for location SW2; 1.88 mg/kg for location 03; 2.25 mg/kg for location SW4, 2.05 mg/kg for location SW5 and 2.23 mg/kg for location SW6 respectively. The computation of contamination/pollution index showed that the sediments were very moderately polluted 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.

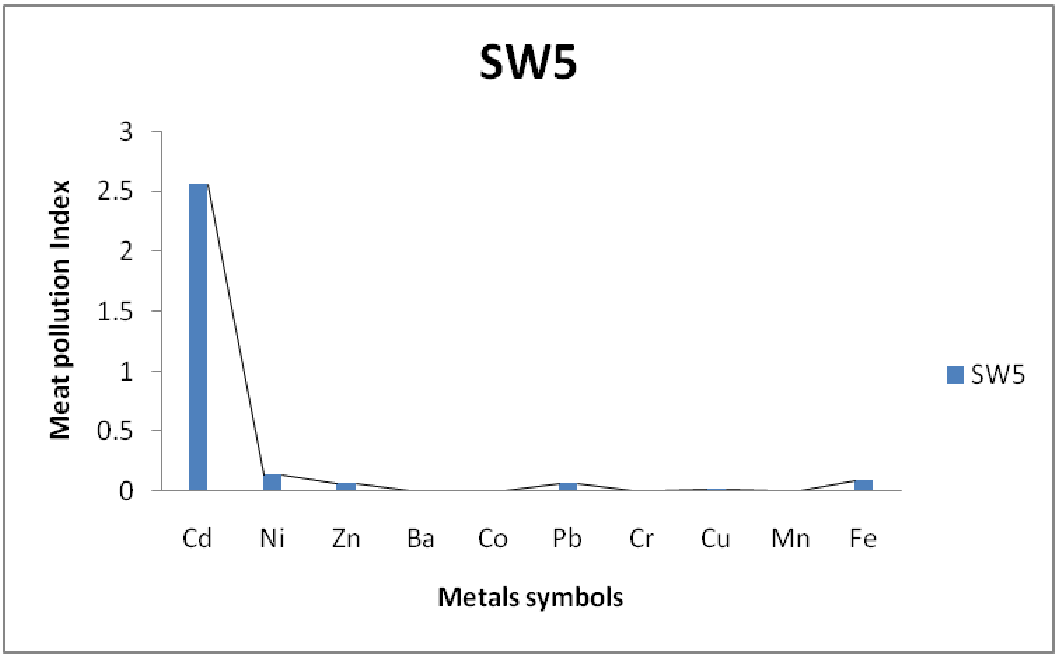
The concentrations of Cr observed in all six sample locations ranges from 0.04-1.11 mg/kg for SW1, 0.01-1.47 mg/kg for SW2,0.35-1.01 for SW3, 0.25-1.31 mg/kg for SW4, 0.18-1.56 mg/kg for SW5 and 0.08-1.24 mg/kg for SW6 respectively. The concentrations varied slightly from one sample location to another.

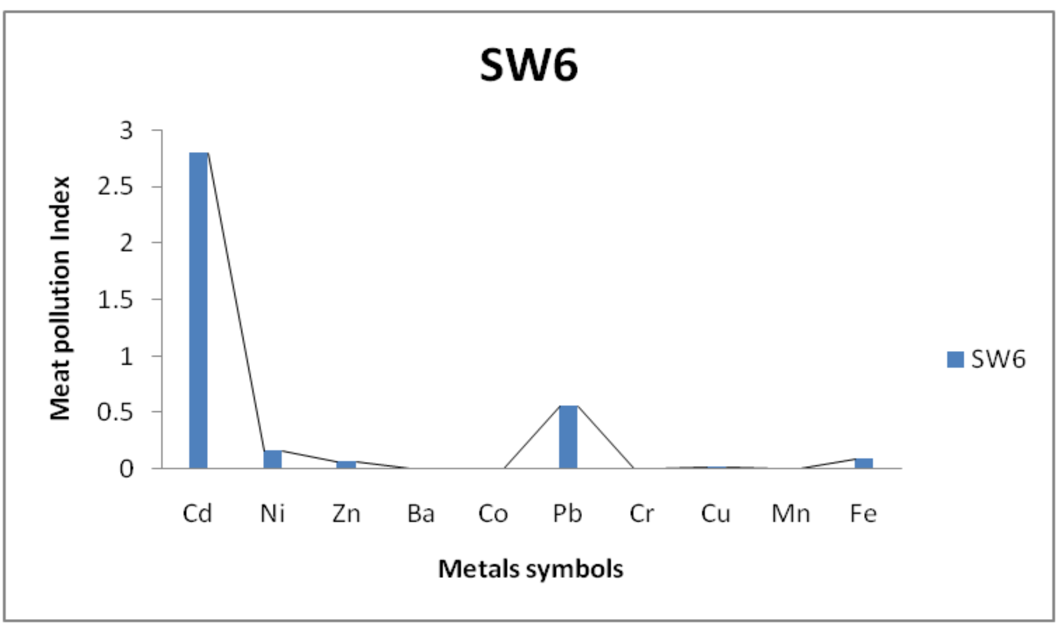





SW3
Meat pollution Index
2.5
2
1.5
1
0.5
0
Cd
Ni
Zn
Ba
Co
Pb
Cr
Cu
Mn
Fe
Metals symbols
SW3


SW4
Meat pollution Index
3
2.5
2
1.5
1
0.5
0
Cd
Ni
Zn
Ba
Co
Pb
Cr
Cu
Mn
Fe
Metals symbols
SW4





Figures. SW1-SW6: Bar plots of Pollution Index of Sediments from Wari river

The calculation of contamination/pollution index showed that the sediments where very slightly contaminated with Cr. The sources of Cr in the study are lower than the levels reported by Nwajei *et al*; 2014 and Shomar *et al*., (2005).

3. CONCLUSION

Matrix samples collected from Warri River were analytically treated and analysed for metals such as Co, Ba 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. In the water samples Cd, Ni, Co and Ba were beyond detection limit. 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. In sediments highest mean concentrations were observed in Fe and Zn. This was not the case for surface water where highest mean concentrations were recorded in Fe. 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 moderately polluted by Cd. Whereas metals such as Cu, Cr, Co, Ni, Ba and Mn, while Zn and Pb very slightly contaminated the sediments significantly. The contamination/pollution of water and sediments of Warri River by heavy metals is caused by runoff, refinery, activities in jetty and S.P. D. C activities around the study area.

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