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Determination of Total Petroleum Hydrocarbons and Heavy Metals in Surface Water and Sediment of Ubeji River, Warri, Nigeria

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ABSTRACT

This study discusses the determination of petroleum hydrocarbons and heavy metals in the surface water and sediment of Ubeji River. This was done to assess the level of pollution of the river. In early October 2008, 50 surface water and sediment samples were collected randomly from the study area and likewise from the control site (Awba Dam in University of Ibadan). Gravimetric analysis was used to determine total petroleum hydrocarbon (TPH), while heavy metals were determined by atomic absorption spectrophotometry (AAS). The mean values obtained for surface water and sediment for the studied site are: Surface water: pH = 5.6 ± 0.2, oil and grease = 209.3 ± 15.4 mg/l, TPH = 73.5 ± 4.8 mg/l, cadmium (Cd) = 0.285 ± 0.001 mg/l, chromium (Cr) = 0.845 ± 0.009 mg/l, copper (Cu) = 0.572 ± 0.003 mg/l, lead (Pb) = 1.55 ± 0.01 mg/l, nickel (Ni) = 0.632 ± 0.042 mg/l, zinc (Zn) = 2.33 ± 0.02 mg/l. Sediment: Oil and grease = 3234.3 ± 205.2 mg/kg, TPH = 1602.4 ± 115.3 mg/kg, Cd = 0.050 ± 0.000 mg/kg, Cr = 50.6 ± 1.68 mg/kg, Cu = 45.2 ± 3.1 mg/kg, Pb = 49.5 ± 2.0 mg/kg, Ni = 42.6 ± 16.4 mg/kg and Zn = 185 ± 3 mg/kg. Unpaired *t*-test at 95% confidence limit showed a significant difference between the values obtained for the study area and the control site. The study location was found to have a higher concentration of oil and grease, TPH and heavy metals than the control site. The value obtained for the study location also exceeded the WHO (1991) water quality criteria for drinking, aquatic life support and recreation, while sediment values exceeded the interim sediment quality guidelines (ISQG) (CCME 1996). Hence, the results revealed that the Ubeji River is under pollution threat and underscore the need for early remediation if adverse health defects are to be prevented.

Keywords: bioremediation, health defects, oil, spillage, unpaired *t*-tested

INTRODUCTION

The discovery of the black gold (crude oil) in commercial quantity, at Oloibiri, River State in 1956 marked the beginning of oil pollution in Nigeria (Aremu 1998). In February 1959, Nigeria became an oil exporter when the production reached 600 barrels per day. By July 2007, Nigeria was the 11th largest oil producer in the world (Nigerian Tribune 2007) and the 3rd largest oil exporter to the United States of America (The Guardian 2007).

This increase in crude oil exportation has made crude oil to replace agriculture as the main source of foreign exchange in Nigeria and thus, has become the pivotal pillar of her economy since its discovery. However, this has resulted in a remarkable increase in environmental degradation of soil, fresh water, lakes, creeks, estuaries and the general ecology of the oil-rich Niger Delta area.

The behaviour of the petroleum hydrocarbons upon entering the freshwater system is intimately linked with the chemical type of contaminant, the mode of entry and physical characteristics of the receiving freshwater system (Aremu 1998). The behaviour of a bulk of crude oil spilled into rapidly flowing water will be different from one spilled into still water. Non-volatile components may restrict the evaporation of volatile ones by the formation of a physical barrier; this in turn may favour dissolution as the route of loss and hence encourage greater entry into the water than to the atmosphere. Several processes combine and interrelate to produce weathering. The process are described by the following terms; spreading, drifting, emulsification, mousse formation, dispersion, sedimentation, re-suspension from sediment and tar ball formation. These, as well as other physical and chemical processes are in operation, viz. evaporation, dissolution, sorption, photolysis and auto oxidation (Couillard 1986; Robotham and Gill 1989; Aremu 1998).

The toxic effects of crude oil spilled into water bodies include smothering or asphyxiation of the organisms in the water by oil coating, thereby causing death. Oil interferes with photosynthesis and transpiration in plant by penetrating or blocking the pores on the leaves (Jinadu 1989). Also water soluble toxins capable of causing harm to organisms in water bodies could be released. Diving birds could be rendered flightless when oiled; this could result into loss of insulating properties against cold which may eventually lead to death. Oiled seabirds end up ingesting some of the oil in an attempt to clean themselves by preening and this causes enteritis (Boyle 1969; Jinadu 1989).

The toxicological interest of most petroleum hydrocarbon to man are volatile organic compounds (VOCs) and polynuclear aromatic hydrocarbon (PAHs) (Sebastian *et al.* 2001). Study on mice reveals that application of crude oil to skin could cause skin tumours (Clark *et al.* 1988). Crude oil has also been known to cause cancer, fractions of TPH (PAHs and VOCs) cause leukaemia, haematological neoplasms and skin disorders, bladder, scrotum, brain, kidney and lungs cancer (Boffetta *et al.* 1997; Wilkinson *et al.* 1999; Sebastian *et al.* 2001).

The toxicity of metals to man cannot be over emphasized as individuals may become exposed to these metals. The metals also are sorbed through the skin and into the blood streams where they accumulate in tissues and organs

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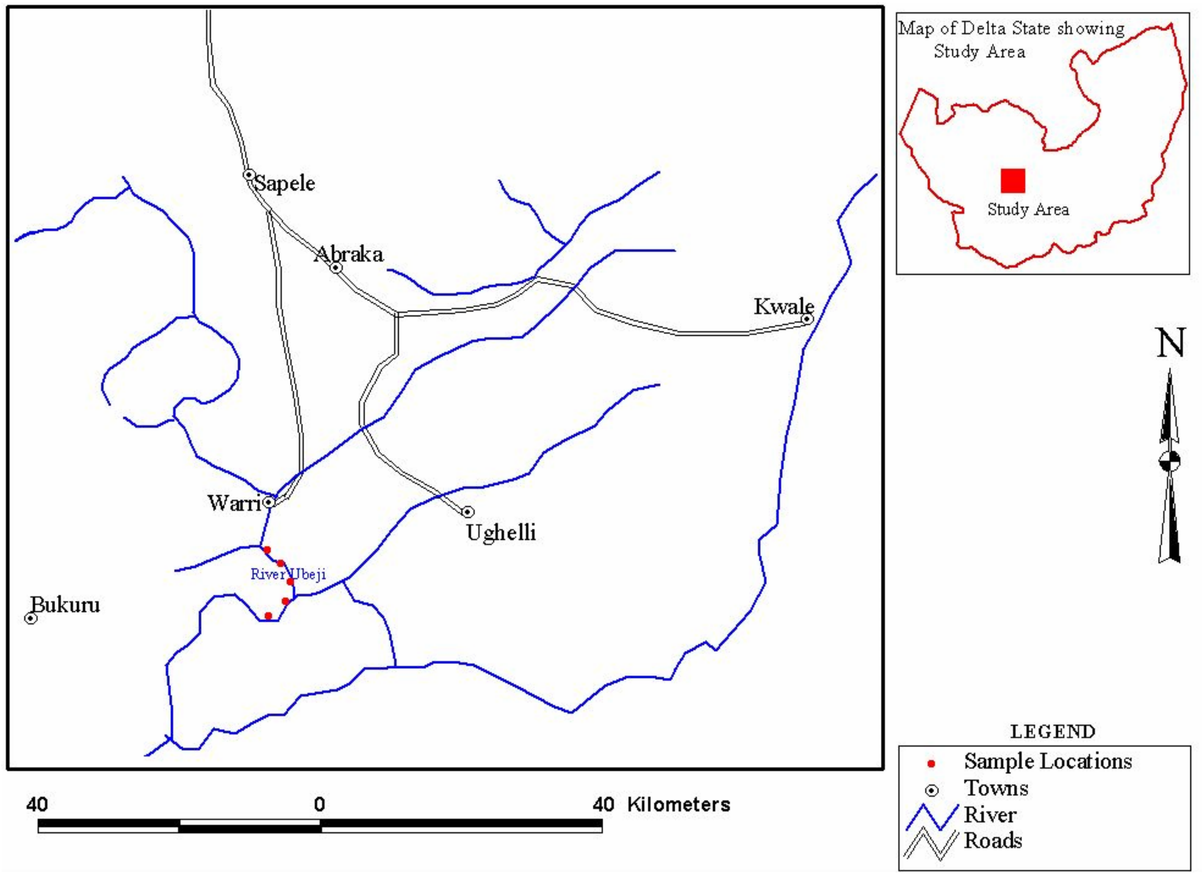

Fig. 1 Map of Delta State showing study area.

like liver and kidney causing adverse effects to man (Benedict *et al*. 1989). The toxicity of heavy metals varies from one heavy metal to another and in the same element may have different toxic effects depending on its chemical form and its speciation (Kakulu 1985; WHO 1991; Aremu 1998).

This study was carried out sequel to the incidence which occurred on the 3rd of July, 2007, where fuel from the Kaduna storage tanks of the Warri Refinery and Petrochemical Company leaked into the Ubeji River and its surrounding soil. The determination of the level of petroleum hydrocarbons and heavy metals; Cd, Cr, Cu, Pb, Ni and Zn of the surface water and sediment was done to assess the extent of pollution of the river.

DESCRIPTION OF STUDY AREA

Ubeji river is located in Warri South Local Government Area of Delta State in the Western Niger Delta of Southern Nigeria (**Fig. 1**). Warri South has a land mass of 11,000 km^2 and lies between latitude 54 and 62° N and longitude 5 and 5.8° E (Egborge *et al*. 1986). The elevation is low ranging from below sea level to about 30 m. Warri South is bounded in the south-East by Bomadi and Burutu L.G.A., East by Okpe L.G.A. and Ethiope East, West by Warri North and South by the Atlantic Ocean, which forms the extreme coast. It also lies within the mangrove swamp.

Fig. 2 View of the Ubeji River in October 2008 (dry season) after the spill.

MATERIALS AND METHODS

Sampling

Sampling was done during the dry season, precisely in October 2008 (**Fig. 2**). A total of 50 water and sediment samples were collected and mixed together to form bulk representative samples. Ubeji river was divided into 5 strata and from each stratum, 10 water and sediment samples were collected randomly to form a composite for each samples. The 5 composites for each samples were then mixed together and homogenised to obtain a bulk composite. Water and sediment samples were collected from Awba Dam, the control site in likewise manner. Plastic and glass cups where used to obtain water samples for petroleum hydrocarbons and heavy metals respectively, while Eckman grab sampler was used for obtaining sediment samples. Water samples were filtered and preserved on site with Hydrochloride (HCl) for petroleum hydrocarbons and Hydrogen nitric (HNO_3) for heavy metals and stored in temperature medium of <4°C.

Determination of petroleum hydrocarbons

Filtered water samples were subjected to liquid-liquid extraction, while sediment samples were air dried, homogenized, sieved and extracted using hot extraction (Sohxlet extractor). A gravimetric method was used to determine oil and grease (IOC 1982; Massoud *et al*. 1995).

Extracts were subjected to silica gel clean-up to remove polar organic substances leaving non polar hydrocarbons in the solvent. Gravimetric method was used to determine the total petroleum hydrocarbons (TPH). The TPH was analysed for PH using gas chromatography (GC). Analyses were performed with a Perkin model 5890 gas chromatograph equipped with a Ni 63 electron capture detector. A low polar HP-5 column of 30 m length, 0.32 mm i.d. and 0.25 µm film thickness was used. Nitrogen was used as the carrier gas at a flow rate of 50 ml/s. Data were processed using an HP 3396 integrator. The operating parameters were as follows: injector temperature set 240 and 310°C for the detector, the oven temperature was programmed at 150°C initially (5 min hold) and increased to 310°C at 5°C/min to give an analysis period of 35 min.

Determination of heavy metals

Filtered water samples were digested with nitric acid. Sediment samples were subjected to nitric acid and perchloric acid digestion. Digests were analysed for Cd, Cr, Cu, Pb, Ni and Zn using Buck Scientific Model 210VGB. The instrument's setting and operational conditions were done in accordance with the manufacturer's specifications and according to Singh and Narwal (1984).

RESULTS AND DISCUSSION

The analytical results of the mean concentrations of heavy metals and total petroleum hydrocarbons in Ubeji River and Sediment as well as for Awba Dam (Control) are shown in **Table 1**.

pH

The pH for Ubeji River was observed to be acidic and fell below the recommended values of 6-9 (WHO 1991) value for drinking water (6.5-9.5). This result is in line with Aremu (1998) who reported acidic water in the underground water around the Refinery of Warri. He attributed it to the impact of the Refinery's effluents and atmospheric deposition of acid forming substances, such as NOx and SOx from burning of fossil fuels and from internal combustion engines. On combustion most of the sulphur in the petroleum fuel is oxidized to sulphur and at the most 3% of this is further oxidized to SO_3. Although SO_3 is unstable at high temperature below about 325°C, it combines with water vapour in the flue gases to form sulphuric acid, which falls back as persistent mist (Omo-Irabor *et al.* 2008). Also, COx from gas flaring is oxidized to carbonic acid which falls back as acidic rain, thus reducing the pH of the river. Previous reports have indicated that SO_2 is emitted into the atmosphere at a yearly rate of 400,000 tons (Ogunkoya and Efi 2003; Olobaniyi and Efe 2007; Omo-Irabor *et al.* 2008) which has implicated in enhanced rainfall acidity and ecosystem degradation in Warri and so is not limited to the activities of the Warri refinery alone. The pH for the control site was found to be 6.5 ± 0.3 and fell within the WHO (1991) recommended values. This could however, be attributed to the absence of any industrial effluents or atmospheric deposition in the control site. Nevertheless, the pH for both the study and the control sites were within the range for natural freshwaters which is pH 4-9 (MSS 1979).

Oil, grease and total petroleum hydrocarbons

Table 1 shows the mean value for oil and grease for the surface water and sediment in the study location to be 209.3 ± 15.4 mg/l and 3234.3 ± 39.1 mg/kg, respectively, while the control site gave 14.8 ± 3.0 mg/l and 40.5 ± 3.4 mg/kg, respectively. TPH mean concentration for surface water and sediment in the study location were 73.5 ± 4.8 mg/l and 1602.4 ± 8.9 mg/kg, respectively, while that of the control site were 5.1 ± 0.6 mg/l and 29.6 ± 2.9 mg/kg, respectively.

An unpaired *t*-test at 95% confidence limit showed a significant difference between the values obtained for the study location and that for the control site, for both oil and grease and TPH in the surface waters and sediments for the two locations.

Oil and grease includes hydrocarbon, fatty acids, soap, fats, waxes and oil (APHA 1991). The results obtained for oil and grease for the study location (209.3 ± 15.4 mg/l) for surface water is significantly less than that obtained for the sediments (3234.3 ± 39.1 mg/kg). This is so because oil and grease do not mix with water and so, most of them settle at the bottom of the river, thus increasing the concentration in the sediment over time. The high concentration of oil and grease in the surface water and sediments of the study river could be as a result of the spill and also from effluents routinely discharged by the petroleum refinery into the river. Adekanmbi (1989) reported that oil and grease from the petroleum refinery's effluent discharged into rivers could reach 260 mg/l. This value far exceeds the guidelines for interim uniform effluent limit of 10 mg/l) for oil and grease in Nigeria.

Also, the mean result for TPH in the surface water (73.5 ± 4.8 mg/l) and sediments (1602.4 ± 8.9 mg/kg) are higher than that obtained for the control site (5.1 ± 0.6 mg/l) and (29.6 ± 2.9 mg/kg), respectively. Beg *et al* (2003), reported elevated levels of TPH in the sediment from a coastal area in Kuwait recieving effluents from refineries operating in its neighborhood. Average level recorded in the sites was 415 mg/kg, ranging from 6.7 to 2066.9 mg/kg. His results when compared with the sediment quality guidelines (SQGS) (CCME 1999), was observed to be higher, but fell below the probable effect levels (PEL). A similar concentration was also reported by Osuji and Nwoye (2007) for total hydrocarbon content of 3,400-6,800 mg/kg in soil of polluted area of Owaza in the Niger Delta. Also, Osuji and Onojake (2005) estimated petroleum hydrocarbon level in the soil of Ebocha-8-oil spillage in Niger Delta to be 20600 ± 4970 mg/kg and 1670 ± 361 mg/kg for surface and subsurface depth of the oil polluted soil, respectively. They accredited the high level of the petroleum hydrocarbon in the soil to be as a result of the crude oil spill (Osuji and Onojake 2005; Osuji and Nwoye 2007). According to Omo-Irabor *et al*. (2008) a yearly average of 270 oil spills contributing to approximately 100,000 barrels/year of oil have been recorded over the past 20 years (1976-1996) in Warri.

Metals

The results (**Table 1**) also show the mean concentrations of the heavy metals in the surface water and sediment of Ubeji River (study area) to be: Cd = 0.285 ± 0.001 mg/l, Cr = 0.845 ± 0.009 mg/l, Cu = 0.572 ± 0.003 mg/l, Pb = 1.55 ± 0.01 mg/l, Ni = 0.632 ± 0.042 mg/l, Zn = 2.33 ± 0.02 mg/l and Cd = 0.050 ± 0.000 mg/kg, Cr = 50.6 ± 1.68 mg/kg, Cu = 45.2 ± 3.1 mg/kg, Pb= 49.5 ± 2.0 mg/kg, Ni = 42.6 ± 16.4 mg/kg and Zn = 185 ± 3 mg/kg while that of Awba Dam (control site) were Cd = 0.005 ± 0.000 mg/l, Cr = 0.360 ± 0.001 mg/l, Cu = 0.005 ± 0.000 mg/l, Pb = 0.944 ± 0.003 mg/l, Ni = 0.341 ± 0.004 mg/l, Zn = 0.455 ± 0.001 mg/l and Cd = 0.100 ± 0.001 mg/kg, Cr = 7.75 ± 0.02 mg/kg, Cu =1.80 ± 0.06 mg/kg, Pb =19.5 ± 6.7 mg/kg, Ni = 3.26 ± 0.06 mg/kg and Zn = 36.5 ± 0.4 mg/kg.

The result further reveals that Cd has the lowest concentration in the study locations for surface water (0.285 ± 0.091 mg/l) and sediment (0.050 ± 0.001 mg/kg), while Zn has the highest concentration for surface water (2.33 ± 0.08 mg/l) and sediments (0.100 ± 0.032 mg/kg). The order of increasing magnitude of the metals for both the surface water and sediment are: Cd < Cu < Ni < Cr < Pb < Zn and Cd < Ni < Cu < Pb < Cr < Zn, respectively. The student's *t*-test was used to ascertain if there are significant difference in the mean values obtained for the study site and the control site. The different means and standard deviations for the study site were compared with that of the control site (unpaired *t*-test). In the unpaired *t*-test, if $t_{cal} \leq t_{tab}$, there was no

Table 1 Heavy metal concentrations in the surface water and sediments of Ubeji River and Awba Dam.

Sites	pH	Oil and grease *(mg/kg)	TPH	Heavy metals (mg/l)					
				Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
Ubeji River	5.6 ± 0.2								
Surface Water		209.3 ± 15.4	73.5 ± 4.8	0.29 ± 0.00	0.85 ± 0.01	0.57 ± 0.00	1.55 ± 0.01	0.63 ± 0.04	2.33 ± 0.02
Sediments		323 4 ± 39.1	1602.4 ± 8.9	0.05 ± 0.00	50.60± 1.68	45.2± 3.07	49.5± 2.03	42.6± 16.41	185.26± 3.33
Awba Dam	6.5 ± 0.3								
Surface water		14.8 ± 3.0	5.1 ± 0.6	0.01 ± 0.00	0.3 ± 0.00	0.01 ± 0.00	0.94 ± 0.00	0.34 ± 0.00	0.46 ± 0.00
Sediments		40.5 ± 3.4	29.6 ± 2.9	0.10 ± 0.00	7.75 ± 0.02	1.80 ± 0.06	19.54 ± 6.72	3.26 ± 0.06	36.52 ± 0.37
WHO[a] (1991)		10	0.2	0.003	0.05	2	0.01	0.02	3
ISQG[b] (1996)		-	-	0.6	37.3	35.7	35.0	-	12.3
PEL		-	-	3.5	90	197	91.3	-	315

Data are expressed as means ± SD of three experiments
[a] World Health Organization
[b] Interim Sediment Quality Guidelines
[c] Probable Effect Level

Table 2 Heavy metal concentrations in the surface waters and sediments of Ubeji River and Awba Dam.

Sites	Heavy metals (mg/l)					
	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
Ubeji surface water (mg/l)	0.29 ± 0.00	0.85 ± 0.01	0.57 ± 0.00	1.55 ± 0.01	0.63 ± 0.04	2.33 ± 0.02
Awba Dam surface water (mg/l)	0.01 ± 0.00	0.36 ± 0.00	0.01 ± 0.00	0.94 ± 0.00	0.34 ± 0.00	0.46 ± 0.00
T_{cal}.	20.586	9.751	22.113	12.510	2.737	26.388
T_{tab}	2.447	2.447	2.447	2.447	2.447	2.447
Ubeji Sediment (mg/kg)	0.05 ± 0.00	50.60 ± 1.68	45.24 ± 3.07	49.52 ± 2.03	42.61 ± 16.41	185.26 ± 3.33
Awba Dam Sediment (mg/kg)	0.10 ± 0.00	7.75 ± 0.02	1.80 ± 0.06	19.54 ± 6.72	3.26 ± 0.06	36.52 ± 0.37
T_{cal}.	-3.852	65.813	49.111	20.280	19.388	154.403
T_{tab}	2.447	2.447	2.447	2.447	2.447	2.447

Data were analyzed by the student's' *t*-test for unpaired data at 95% confidence limit (N = 2 df)

significant difference between the means for heavy metals for the study site and the control site. However, if $t_{cal} \geq t_{tab}$, then there is a significant difference. This is to ascertain if any significant difference exist between the study site and the control site. The unpaired *t*-test at 95% confidence limit (**Table 2**) shows that there exist a significant difference between the results obtained from the study locations and that obtained from the control site. The values show higher concentration of metals in the surface water for both the study and control locations than the WHO (1991) standards, except for Zn (2.33 ± 0.08 mg/l). The results for sediment also show high concentration than the Canadian Council of Ministers of the Environment (CCME) Interim Sediment quality guidelines ISQG (1996) except for Cd (0.05 ± 0.08 mg/kg), which showed a lower value. The results for the two locations were however lower than the Probable Effect Level (PEL). These results are in line with the results of Akporido (2008), Aremu (1998), Kakulu (1985) and Olaifa (2003), who showed that heavy metals like Cd, Cr, Cu, Ni, Pb and Zn which are from petroleum source have higher concentration in surface water and sediment in the Niger Delta areas than in other part of the country, as a result of the impact of the petroleum industries in the area.

The Ubeji River, like the Egbokodo, Ugunu, Umah, Omagino, Ugbuwangwe or Escravos Rivers, which flow through creeks and are not connected directly to the city like the Udu river, therefore it does not receive effluents from other industries than the petroleum industries. So, gradual input of petroleum products into natural water brings about an increase in the metals concentration in the river and sediment with sharp rises in severe cases of spillages. Crude oil contains about 0.3% of its components as trace metals (Korte 1977). So impacts of petroleum operations such as oil drilling, refining, bunkering, transportation and storage serve as major source of trace metals input to the river and since no recent incidence of vandalized pipelines or drilling was done close to the river before now, the increased level of these metals would be from the effluents discharged into the river from the routine refinery's operations and from the crude oil spill.

Trace metals occur in crude oil partly as organometallic compounds from which the geoporphyrins of Ni, Cu and Zn have been identified (Gondal *et al*. 2002). Metalloporphins of Co, Cr, Cd and Zn have been identified in oil shales (Les Ebdon *et al*. 1994). The high concentration of Zn and Pb in the refinery's effluents could be due to the loss of some lead compounds added to improve the antiknock properties of gasoline and the Zn additives added in the production of lubricants at the refinery. However, metals and organometallic species are also incorporated during refining and as catalysts in petrochemical processes, examples of such processes include; production of synthesis gas from methane and carbon monoxide using Ni catalyst. Ni is also used as catalyst in the production of acetylene from calcium carbide and in propylene dimerization and adiponitrile. Zn and Cr are used as catalyst in the production of styrene from ethybenzene. Cu and Cr are used in the production of acetyldehydes, while Cu and Zn are used in the production of acrolein. Cu is also used in cyclohexane production (Mendiguchia 2007). The refinery products seem to show higher toxicity compared to crude oil, since metal speciation is altered and new metals are added to the matrix during the refining processes (Pavageau *et al*. 2004). The wastes generated from such processes may contain spent catalyst which are not recovered in most cases but discharged into receiving water bodies where they accumulate in surface water and sediments of rivers, thereby bioaccumulating along food chains in the ecosystem. Contamination of water and sediments by crude oil and its derivatives is conventionally evaluated by quantification of toxic hydrocarbons, but more recently, Ni, Cd, Cr, Cu, Pb and Zn have been included in the analysis of contaminated water and sediment by crude oil exudates and results show that they can be an important source of contamination for these elements (Osuji and Adesiyan 2005; Sameck-Cymerman *et al*. 2005). Also, the level of these metals could be increased by the volume of boat traffic in the area. Boats and ships use lubricating oil, such contains Zn additives. Cu is known to be one of the active ingredients in antifouling composition, while Pb compounds form the basis of anticorrosive and primer (Kakulu 1985).

The concentration of all the metals studied showed relatively higher levels in the sediments than in the river, except for Cd whose concentration in the sediments (0.050 ± 0.008

mg/kg) were relatively close to that in the surface water (0.285 ± 0.09 mg/l), hence supporting the findings of Ritter *et al.* (2002), who stated that Cd may be release from sediments or dissolved in the surface water or underground water by a decreased pH (pH>7), but remained bound to sediment at pH>7. Cd is found majorly associated with crude oil. Even though the *t*-test analysis shows a significant level of pollution in the studied river, the value of Zn in the surface water of the study location (2.33 ± 0.08 mg/l) was seen to be lower than the WHO 1991 standards (3 mg/l) while a higher value was obtained in the sediments (185 ± 8 mg/kg). This could be attributed to the fact that Zn is an essential metal, as such was absorbed rapidly by suspended plants and microorganisms found in the river for metabolic activities, producing Zn containing enzymes like alcohol dehydrogenase, carbonic anhydrase and alkaline phosphatase (Parisic and Vallee 1969).

The high petroleum hydrocarbon and heavy metals extracted from the Ubeji, surface water and sediment have provided evidence of severe crude oil contamination of the river. Therefore, there is urgent need for a more efficient remediation measure as the *in-situ* burning done previously after the spill was insufficient to restore the integrity of the river. It is recommended that bioremediation be done in the area in other to restore the state of the river. Also, epidemiological studies should be carried out to ascertain the health impact of the spill on the indigenes of the area.

CONCLUSION

The high level of petroleum hydrocarbons and heavy metals extracted from the Ubeji surface water and sediment has provided evidence of severe crude oil contamination of the river. Such condition generally implies massive environment degradation and ecological imbalance resulting to severe health defects among indigenes residing in the area. The deplorable state of the environment may expose indigenes to severe health defects like leukemia, brain damage, mental deficiency, retarded growth especially amongst children, basophilic stippling, anaemia, lungs and kidney cancer, liver necrosis, nephritis and even death. It has also be argued in this work that the major source of crude oil pollution into the river is from the refinery's activities either through effluents discharged or through leakages from storage tanks, since other activities which may introduce crude oil are not directly connected to the area. Therefore, there is urgent need for a more efficient remediation measure as the *in-situ* burning done previously after the spill was insufficient to restore the integrity of the river. However, it is recommended that fingerprint characterization of the petroleum hydrocarbons be done to identify the source of the pollution and also to provide a specific and cost effective remediation measure in order to restore the intergrity of the river. Also, epidemiological studies should be carried out to ascertain the health impact of the spill on the indigenes of the area.

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