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Evaluation of Total Petroleum Hydrocarbons (TPH) and Some Related Heavy Metals in Soil and Groundwater of Ubeji Settlement, Warri Metropolis, Nigeria

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ABSTRACT

Soil and groundwater samples in areas of oil spill in Ubeji settlement, Warri metropolis, Nigeria, were collected in order to determine the oil and grease, total petroleum hydrocarbons (TPH) and some related heavy metals in the samples. Control samples were taken from a low density residential area in Delta State (Ekrejeta in Abraka) which is relatively free from petroleum activities. The parameters were evaluated in order to determine the quality of the soil and groundwater of Ubeji settlement, as a follow up on an earlier research conducted on the surface water and sediment of the settlement's river. This research is so important because the local population uses the soil and water resources for agricultural and domestic purposes. Measurements of oil and grease and TPH in samples were done gravimetrically, while atomic absorption spectrophotometry was used for determination of heavy metals. For oil and grease and TPH, the soil had mean concentrations of 1064.90 ± 7.70 and 579.10 ± 9.30 mg kg^{-1}, respectively, while groundwater had 315.15 ± 11.60 and 28.70 ± 1.30 mg L^{-1}, respectively. Mean heavy metal concentration of the soil and groundwater varied between 0.30 ± 0.01 to 215.49 ± 25.33 mg kg^{-1} and 0.03 ± 0.01 to 3.05 ± 0.07 mg L^{-1}, respectively. These values reveal that the investigated samples had higher levels of oil and grease, TPH and heavy metals than the control samples and regulatory standard limits. This however, is an indication of pollution of soil and groundwater of the settlement by petroleum hydrocarbons.

Keywords: contamination, Ekrejeta, fingerprint characterization, human health risk assessment, pollution, Warri Refinery and Petrochemical Company

INTRODUCTION

Nigeria has been exploring and exploiting crude oil for decades. Available data show that in 2009, total oil production averaged 2.20 million barrels per day, with an estimated 37.2 billion barrels of proven oil reserves as of January 2010 (EIA 2010). This increase in crude oil export has made it possible to replace agriculture as the main source of foreign exchange and thus, has become the pivotal pillar of the economy since its discovery. However, the growth of the petroleum industries has lead to increased oil activities from production (exploration and exploitation), transportation, refining to marketing and have resulted to remarkable increase in environmental degradation by oil spills involving pipeline vandalism, blowouts, leakages from tanker trucks and dumping of waste petroleum products, thereby contaminating soil, fresh water, lakes, creeks, estuaries, and groundwater.

According to the Nigerian National Oil Spill Detection and Response Agency (NOSDRA), approximately 2,400 oil spills have been recorded since 2006. The total amount of oil spilled in Nigeria has been estimated to be around 260,000 barrels per year for the past 50 years (an estimated average of 13,000,000 barrels per 50 years) (EIA 2010), with major spill incidents like the Escravos spill in 1978 of about 300,000 barrels, the Forcados terminal tank failure in 1979 of about 580,000 barrels and the Funiwa five blow outs in 1980 of about 400,000 barrels (Jinadu 1989), amongst others.

The aftermaths of these spills have been documented elsewhere (Adeniyi and Afolabi 2002; Riccardi *et al.* 2008). Crude oil, when refined contains a wide range of components such as hydrocarbons, heavy metals, dye additives, antioxidants, corrosion, inhibitors, etc. (Wang and Fingas 2003; Riccardi *et al.* 2008). The refined products 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 waste generated from such processes may contain spent catalysts which are not recovered in most cases but discharged into soil and receiving water bodies where they accumulate in surface waters, sediments of rivers, and ultimately groundwater

Groundwater contamination, with its subsequent degradation is more threatened, more so when it is realized that dynamic equilibrium maintained by gravity and capillary exists between it and surface water (Commendatore and Esteves 2004). Also, contaminated soil causes subsequent pollution of groundwater through infiltration; hence, groundwater is a receiver of contaminants from both soil and surface water, and from other direct sources like leakages from buried chemical tanks.

According to Riccardi *et al.* (2008) the study of pollutant concentrations in contaminated sites, their comparison with threshold limits settled by law and the source apportionment of pollution are three basic requirements to take effective clean-up measures and to settle legal actions. However, the analysis of total pollutant concentration and the comparison with threshold limits settled by law is judged to be sufficient to assess environmental damage.

This study was carried out in sequel to the spill incidence which occurred on the 3rd July 2007 where petroleum oil from the Warri Refinery and Petrochemical Company leaked into the Ubeji river and its surrounding soil and the confirmatory result of Adewuyi *et al.* (2011), who extracted high levels of total petroleum hydrocarbons and heavy

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metals in the surface water and sediment of the river consequent upon the spill. Thus, the determination of total petroleum hydrocarbons and related heavy metals (Cd, Cr, Cu, Pb, Ni and Zn) in soil and groundwater of the settlement was done as a follow-up to the previous research done on the settlement's river in order to assess the extent of pollution of arable soil and drinking water.

MATERIALS AND METHODS

Site description and sampling

The study area is the soil of residential area in Ubeji, located behind the Warri Refinery and Petrochemical Company. Ubeji is located in the Warri South Local Government area of Delta State, Nigeria. Warri South has a land mass of 11,000 km^2 and lies between latitude $5^0 1^1$ and $6^0 0^1$ North and longitude $5^0 50^1$ and $5^0 4^1$ East. It is bounded in South East by Bomadi and Burutu LGA, East by Okpe LGA and Ethiope East; West by Warri North and South by the Atlantic Ocean which forms the extreme coast. The vegetation of Warri has been described elsewhere (Omo-Irabor *et al*. 2008; Adewuyi *et al.* 2011).

80 surface soil samples (0-15 cm soil depth) and 96 groundwater samples were collected from 4 locations distribution over Ubeji settlement in October, 2008. Detailed sampling procedures are described elsewhere (Zuo *et al.* 2007; Riccardi *et al.* 2008). Control samples were collected from Ekrejeta, beside the Delta State University, Abraka, in likewise manner.

Chemicals and reagents

Analytical grade reagents were used. Silica gel (Kieselgel $60F_{254}$ 70-230 mesh), nitric acid (HNO_3) hydrochloric acid (HCl), perchloric acid ($HClO_4$) and the metal standards solutions were purchased from Sigma-Aldrich, Fluka, Switzerland. Hexane (C_6H_{14}), sodium sulfate (Na_2SO_4), dichloromethane (CH_2Cl_2) and paraffine oil were purchased from Merck, Goa, India and the deionised water was purchased from the International Institute of Tropical Agriculture (IITA), Ibadan, Nigeria.

Preservation of samples

Groundwater samples collected for total petroleum hydrocarbons (TPH) were stirred and filtered using glass filter papers. The filtrates were collected while the residues (suspended particles) were discarded. The samples were fixed with concentrated HCl to pH = 2, while samples for heavy metals determination were fixed in the field with 3 ml HNO_3 per litre of sample. The samples were stored in an ice chest. Soil samples collected from the sites were wrapped with degreased aluminum foil and polythene bags for TPH and heavy metals respectively, and stored in the ice chest before transporting to the laboratory for analysis (Adewuyi *et al.* 2011).

Method for analysis

The analytical test procedures used to assess soil and groundwater contamination by petroleum products are total petroleum hydrocarbons and heavy metals determinations (Adeniyi and Afolabi 2002; Osuji and Adesiyan 2005; Sameck-Cymerman *et al.* 2005; Osuji and Onojake 2006; Adewuyi *et al.* 2011).

Total petroleum hydrocarbons

The conventional TPH analytical methods (Environmental Protection Agency (EPA) method 418.1 and 1664; gravimetric determination) have been used widely to investigate sites that may be contaminated with petroleum hydrocarbon products (EPA 1979c; Murray 1994; EPA 1996a).

Extraction of oil and grease

Extraction of soil and groundwater samples for oil and grease were carried out following standard procedures (EPA 1999; Muniz *et al.* 2004; Mohsenzadeh *et al.* 2010).

For water samples, oil and grease was extracted using EPA method 1664 (EPA 1999). 4 replicates of 400 ml of homogenized water sample, acidified to pH = 2, was extracted three times (sequential extraction) with 20 ml *n*-hexane (for each extraction) using a separating funnel. The extracts were dried over Na_2SO_4 and the solvent evaporated in a rotary evaporator. The extracts were desiccated, weighed and further evaporated. This procedure was repeated until constant weights of oil and grease were obtained.

Soil samples, prior to extraction, were thawed and freed of vegetation, pebbles and debris. Samples were air dried, crushed and sieved for grain size distribution using a standard set of stainless sieve. Four replicates of 100 g of soil samples were transferred into paper extraction thimbles. Total oil and grease (TOG) was extracted using Soxhlet apparatus for 8 h with a mixture of C_6H_{14} and CH_2Cl_2 (1:1, v/v). A rotary evaporator was used to concentrate the organic extracts, which were then filtered through Whatman filter paper (No. 4) with 1 g sodium sulfate. The solvent was further evaporated in a rotary evaporator to determine the weight of dry extract. Percentage of TOG was calculated and compared based on soil dry weight.

Extraction for TPH (silica gel clean-up)

Silica gel chromatography was used to fractionate the oil and grease extracts. Silica gel, a polar adsorbent, absorbs polar organic substances such as vegetable oil and retains them so that non-polar hydrocarbons are eluted. The constant weights of the fractionated hydrocarbon extracts gave the TPH (Adeniyi and Afolabi 2002).

TPH analysis

The constant weights of the final extracts were determined by gravimetry (EPA 1999; Adeniyi and Afolabi 2002; Adewuyi *et al*. 2011). The results obtained for oil and grease and TPH in soil and groundwater are shown in **Tables 1** and **2**, respectively.

Quality assurance and quality control for TPH

In the evaluation of methods for analysis of hydrocarbons, in environmental samples, the quality of a method is not judged by the percentage of fat extracted alone, but also by a number of factors like reproducibility, ease of application of method, cost and time of the analysis (Akporido 2008). The loss of some of the hydrocarbons of interest cannot be ruled out. To this end, the extent to which the compound of interest is recovered also plays a vital role in conjunction with the factors earlier mentioned. Two replicates of the homogenized soil and groundwater samples were subjected to recovery studies by spiking samples with 2 ml of paraffin oil standard (Akporido 2008). The spiked samples were extracted and analyzed accordingly. **Tables 3** and **4** show the average recoveries of the oil in the soil and groundwater samples, respectively.

Heavy metals digestion methods

For groundwater samples, nitric acid digestion of water samples was done for heavy metals following standard procedure (Momodu and Anyakora 2010; Adewuyi *et al*. 2011). The method has also been described elsewhere (Hseu 2004). To ensure the removal of organic impurities from the samples and thus prevent interference in analysis, the samples were digested with concentrated nitric acid. 5 ml of the concentrated nitric acid was added to 5 ml of the water samples and the mixture evaporated on a hot plate to a final volume of 3 ml. Another 5 ml of concentrated HNO_3 was added to the mixture and refluxed for 30 min, after which the mixture was heated on hot plate while the concentrated HNO_3 was added until the mixture was light coloured. The resulting sample was filtered and the filtrate made up to 50 ml with deionised water before analysis.

Soil samples prior to digestion, were also thawed and freed of vegetation, pebbles and debris. Samples were also air dried, crushed and sieved for grain size distribution using a standard set of stainless sieve. Nitric-perchloric acid digestion has been used as standard methods for the digestion of heavy metals in soil samples. The method has been described elsewhere (Hseu 2004). One gram of samples was placed in a 250-ml digestion tube and 10 ml of

Table 1 Results of oil and grease, TPH and heavy metals content of soil in the two sampling sites viz; Ubeji and Ekrejeta settlements (control) in comparison with the natural range in soil and the toxicity characteristic leachate (TCL) limits.

Sites	Oil and grease (mg kg^{-1})	TPH (mg kg^{-1})	Heavy metals (mg kg^{-1})					
			Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
Ubeji	1064.90 ± 7.70	579.10 ± 9.30	0.30 ± 0.01	28.43 ± 0.45	35.28 ± 7.30	47.02 ± 1.26	27.81 ± 3.28	215.49 ± 25.33
Control	268.20 ± 6.30	7.60 ± 0.80	0.02 ± 0.00	20.04 ± 1.71	5.12 ± 0.01	35.54 ± 0.46	12.46 ± 0.33	138.28 ± 8.67
Natural range	-	-	0.003-0.30	-	5.00-20.0	2.00-20.0	2.00-750	1.00-900
TCL limits	-	-	-	5.00	-	5.00	-	-

Results are represented in Mean and Standard Deviation, $n = 4$.

Table 2 Results of oil and grease, TPH and heavy metals content of groundwater in the two sampling sites viz; Ubeji and Ekrejeta settlements (control) in comparison with DPR (1991), WHO (1971), FEPA (1991) and USEPA (2010) limits/standard for potable and Domestic water.

Sites	pH*	Oil and grease (mg L^{-1})	TPH (mg L^{-1})	Heavy metals (mg L^{-1})					
				Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
Ubeji	5.80 ± 0.20	315.50 ± 11.60	28.70 ± 1.30	0.05 ± 0.00	0.64 ± 0.00	0.03 ± 0.00	3.05 ± 0.07	0.55 ± 0.00	1.14 ± 0.00
Control	6.70 ± 0.30	4.10 ± 0.50	1.00 ± 0.20	0.03 ± 0.00	0.42 ± 0.00	0.01 ± 0.00	2.15 ± 0.00	0.29 ± 0.00	0.16 ± 0.00
DPR	6.5-8.5	-	-	-	0.03	1.00	0.05	-	1.5
WHO	6.5-8.5	0.10	-	0.01	0.05	1.00-1.50	0.01-0.05	-	5.00-15.0
FEPA	-	-	-	0.01	0.05	1.00	0.05	0.01	5.00
USEPA	6.5-8.5	0.10	-	0.005	0.10	1.30	0.015	0.073	5.00

Results are represented in Mean and Standard Deviation, $n = 4$.
DPR = Department of Petroleum Resources, WHO = World Health Organization, FEPA = Federal Environmental Protection Agency, and USEPA = United States Environmental Protection Agency.
pH* has no units

concentrated HNO_3 was added. The mixture was boiled gently for 30-40 min to oxidize all easily oxidizable matter. After cooling, 5 ml of 70% $HClO_4$ was added and mixture was boiled again, gently until dense white fumes appeared. After cooling, 20 ml of deionised water was added and mixture was boiled further to release any fumes. The solution was cooled and filtered through Whatman No. 42 filter paper and < 0.45 µm Millipore filter paper and transferred quantitatively to a 25 ml volumetric flask by adding deionised water.

Heavy metals analysis

The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the final solutions were determined by atomic absorption spectrophotometer Buck Scientific 210VGP.s. The instrument's setting and operational conditions were done in accordance with the manufacturer's specifications. The instrument was calibrated with analytical grade metal standard stock solutions (1 mg L^{-1}). The results obtained for heavy metals in soil and groundwater are shown in **Tables 1** and **2**, respectively.

Quality assurance and quality control

Metal recoveries was done, two replicates of the homogenized soil and filtered water samples were subjected to recovery studies by spiking samples with metal standards about the same concentrations of the analyte of interest, digested and analyzed. **Tables 3** and **4** show the average recoveries of metals in the soil and water samples, respectively. A blank was run for each digestion procedure to correct the measurements and to check all reagents and procedure for interferences and cross contamination.

RESULTS AND DISCUSSION

The result of pH, oil and grease, TPH, and heavy metals contents in soil and groundwater are shown in **Tables 1** and **2**. The mean pH value (5.8 ± 0.2) for groundwater in the study site, is lower than the control value (6.7 ± 0.30) (**Table 1**), and the 6.5–8.5 standard range recommended by the World Health Organisation and the Department of Petroleum Resources for portable water (WHO 1971; DPR 1991; USEPA 2010). This may be attributed to acid rain which percolates the soil and contaminates the groundwater. Acid rain is formed by combination of water vapor and acidic gases; which are NO_x (NO and NO_2), SO_x (SO_2 and SO_3) and CO_x (CO and CO_2), released into the atmosphere from the refinery as flare gases. This is supported by the pH value recorded in a previous study for surface water samples collected from the settlement's river (Adewuyi *et al.* 2011). Also, previous reports have shown that SO_2 is emitted into the atmosphere of the study area, at the rate of 400,000 tons per year (Ogunkoya and Efi 2003). The SO_2 and other flare gases emitted from the Refinery combine with water vapour in the atmosphere to form acid rain which percolates the soil and ultimately degrade groundwater by decreasing the pH (Olobaniyi and Efe 2007). A similar trend has been observed before (Omo-Irabor *et al.* 2008).

Also, from the tables, it could be seen that the mean concentrations of oil and grease in the soil and groundwater of the study site is 1065 ± 8 mg kg^{-1} and 316 ± 11.5 mg L^{-1} respectively, whereas the control site has mean values of 268 ± 6 mg kg^{-1} and 4.1 ± 0.5 mg L^{-1}, respectively. Oil and grease represent the total petroleum hydrocarbon and non petroleum hydrocarbon components present in the samples, the result of this study support the assertion that Ubeji soil and groundwater may have been contaminated significantly. This can be correlated with the levels of TPH recorded in the location.

The mean concentration of TPH in soil and groundwater of the study site (579.10 ± 9.30 mg kg^{-1} and 28.7 ± 1.30 mg L^{-1}, respectively) exceed the values for the control samples (7.60 ± 0.60 mg kg^{-1} and 1.00 ± 0.20 mg L^{-1}, respectively). The levels observed in the study site are comparable with those found by Adewuyi *et al.* (2011) for the surface water and sediment of the site's river and is also comparable with that found elsewhere for polluted sediments and lakes (Osuji and Onojake 2006), where the estimated petroleum levels in the soil of Ebocha-8 oil spillage in Niger Delta were found to be 20600 ± 4970 mg kg^{-1} and 1670 ± 361 mg kg^{-1}, respectively for surface and subsurface depth of the oil polluted soil. The values for groundwater also follow a similar trend with those documented for water samples collected from the local streams of San Carlos in North Eastern Ecuador, where the TPH values were found to be 10 to 288 times high than the EU guideline limit (Sebastian *et al*. 2001).

Besides hydrocarbons, some heavy metals can give information about the origin of contamination, since crude oils and heavy distillates contain a wide range of trace metals. Cu, Ni and Zn for example are present in the oils as metallo-porphyrin complexes as well as non-porphyrin complexes and their concentration increases with increasing hydrocarbon heavy fraction contents. Also petroporphyrins breakdown very slowly in the environment, their presence is useful to point out past spill. In addition, Pb can be useful for the age dating of a spill because Pb alkyls are the most commonly used gasoline additives (Gondal and Mastramarino 2002; Riccardi *et al.* 2008).

Table 3 Percentage recovery for analytes in groundwater.

Analytes	Amount present (mg L^{-1})	Amount added (mg L^{-1})	Mean amount recovered (mg L^{-1})	% Recovery
TPH	28.7	28.3	53.5 ± 4.0	88
Cd	0.05	0.05	0.09 ± 0.01	109
Cr	0.63	0.70	1.18 ± 0.09	79
Cu	0.03	0.05	0.07 ± 0.00	78
Pb	3.05	4.00	6.69 ± 0.77	92
Ni	0.55	0.50	0.92 ± 0.17	74
Zn	1.16	1.50	2.53 ± 0.08	91

Table 4 Percentage recovery for analytes in soil.

Analytes	Amount present (mg kg^{-1})	Amount added (mg kg^{-1})	Mean amount recovered (mg kg^{-1})	% Recovery
TPH	7.20	7.50	13.7 ± 0.80	86
Cd	0.30	0.50	0.71 ± 0.50	82
Cr	28.43	30.00	54.23 ± 1.40	86
Cu	35.20	40.00	68.90 ± 1.60	84
Pb	47.02	50.00	92.02 ± 2.50	102
Ni	27.81	27.00	50.41 ± 1.20	83
Zn	215.49	220.0	421.1 ± 23.0	93

The results of heavy metals show that their levels are in considerable amount in the soil and groundwater of the study site and are higher than the control site values (**Tables 1** and **2**). Mean Cd, Cr, Cu, Pb, Ni and Zn values for control site soil samples (mg kg^{-1}) (**Table 2**) are 0.02 ± 0.00, 20.04 ± 1.71, 5.12 ± 0.01, 35.54 ± 0.46, 12.46 ± 0.33 and 138.28 ± 8.67, respectively, whereas the values for soil sample in the study site are 0.30 ± 0.01 mg kg^{-1}, 28.43 ± 0.45 mg kg^{-1}, 35.28 ± 7.30 mg kg^{-1}, 47.02 ± 1.26 mg kg^{-1}, 27.81 ± 3.28 mg kg^{-1} and 215.49 ± 25.33 mg kg^{-1}, respectively. There are significant difference in the concentrations of metals in the study site and the control's. This is similar to previous observations (Marcus and McBratney 1996; Davis 1997; Metwally *et al.* 1997; Adeniyi and Afolabi 2002; Adewuyi *et al.* 2011) and may be taken as an indication of heavy metals pollution of Ubeji soil. This is not unlikely as heavy metals are found associated with petroleum (Adeniyi and Afolabi 2002; Akporido 2008; Adewuyi *et al.* 2011). This values are high enough to cause public concerns, since most of them (Cd, Cr, Pb, and Ni) are not required even in small amounts by living organisms (Asia *et al*. 2007). The mean concentrations of Cd in the soil of the study site (0.30 ± 0.01 mg kg^{-1}) is at the upper boundary limit of the range of values given for natural occurring Cd levels in soils, while the control site value (0.02 ± 0.00 mg kg^{-1}) is within the safe concentration range for natural soils. Cr levels for the two sites (28.43 ± 0.45 mg kg^{-1} and 20.04 ± 1.71 mg kg^{-1}) are in excess of the toxicity characteristic leachates procedure limits of 5 mg kg^{-1}, while Cu levels in the study site (35.28 ± 7.30 mg kg^{-1}) is relatively higher compare to the normal range of 5 to 20 mg kg^{-1} in natural soils. But the control value for Cu 5.12 ± 0.01 mg kg^{-1} is within the safe range for natural soils. Pb concentrations in the two sites (47.02 ± 1.26 mg kg^{-1} and 35.54 ± 0.46) are higher than the TCL limits of 5 mg kg^{-1} and natural occurring concentration of lead in soil, which ranges from 2 to 20 mg kg^{-1} (Asia 2007). Interestingly, Ni concentration for the two sites (27.81 ± 3.28 mg kg^{-1} and 12.46 ± 0.33 mg kg^{-1}, respectively) are within the normal range of 2 to 750 mg kg^{-1} for natural soils. Zn had values (215.49 ± 25.33 mg kg^{-1} and 138.28 ± 8.67 mg kg^{-1}, respectively) which are also in the concentration range of 1 to 900 mg/kg for natural occurring Zn in soils. These results follow the same trend with that obtained by Asia *et al.* (2007) for soil in the Niger Delta.

The levels of heavy metals: Cd, Cr, Cu, Pb, Ni, and Zn in the groundwater of the study site are 0.05 ± 0.00 mg L^{-1}, 0.64 ± 0.00 mg L^{-1}, 0.03 ± 0.00 mg L^{-1}, 3.05 ± 0.07 mg L^{-1}, 0.55 ± 0.00 mg L^{-1} and 1.14 ± 0.00 mg L^{-1}, respectively whereas the control values are significantly lower; 0.03 ± 0.00 mg L^{-1}, 0.42 ± 0.00 mg L^{-1}, 0.01 ± 0.00 mg L^{-1}, 2.15 ± 0.00 mg L^{-1} 0.29 ± 0.00 mg L^{-1} and 0.16±0.00 mg L^{-1}, respectively (**Table 1**). From the results, it was observed that all the values except Cu and Zn for the two sites are higher than the Department of Petroleum Resources (DPR), Federal Environmental Protection Agency (FEPA), World Health Organization (WHO) and the United State Environmental Protection Agency (USEPA) limits. The reasons for this variation may not be farfetched, Cu and Zn are essential metals to plants in a number of enzymes processes e.g. alcohol dehydrogenenase, carbonic anhydrase and alkaline phosphatase (Aremu 1998). This could account for the decreased concentrations in the groundwater, as plants absorbs and utilise these metals for several biochemical processes. The levels observed for the other metals (Cd, Cr, Ni and Pb) suggest that the groundwater may pose significant health risk to the consumers. Heavy metals pollution of soil, water and sediment contaminated by crude oil exudates have been reported previously (Pavageau *et al.* 2004; Osuji and Adesiyan 2005; Akporido 2008; Adewuyi 2011). The health risks associated with the ingestion of heavy metals contaminated soil and groundwater are documented elsewhere (Aremu 1998; Asia *et al.* 2007; Adewuyi *et al.* 2011).

CONCLUSION

The high levels of petroleum hydrocarbons and heavy metals extracted from the Ubeji soil and groundwater has provided evidence of severe crude oil contamination of the settlement's soil and groundwater. The levels are high enough to cause public concerns, since residents may ingest, inhale or be directly exposed to these chemicals by skin contact. Exposure to these contaminants may cause carcinogenic and/or non carcinogenic health defects (IARC 2001; Sebastian *et al.* 2001; USEPA 2010; Adewuyi *et al.* 2011) to the residents and livestock. Also, plants can bioaccumulate these metals and magnify them along the food chain leading to man. Even though the pollution appears to have arisen from the Warri Petroleum Refinery and Petrochemical Co., the pollution source is yet to be established. So, there is the need for source characterization and apportionment in order to confirm this assertion and ascertain the percentage of anthropogenic contribution, sources, nature and degree of toxicity. Also, it is highly recommended that human health and ecological risk assessment be carried out as a follow up of this research. These will provide the necessary information needed for an effective cleanup of the settlement.

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