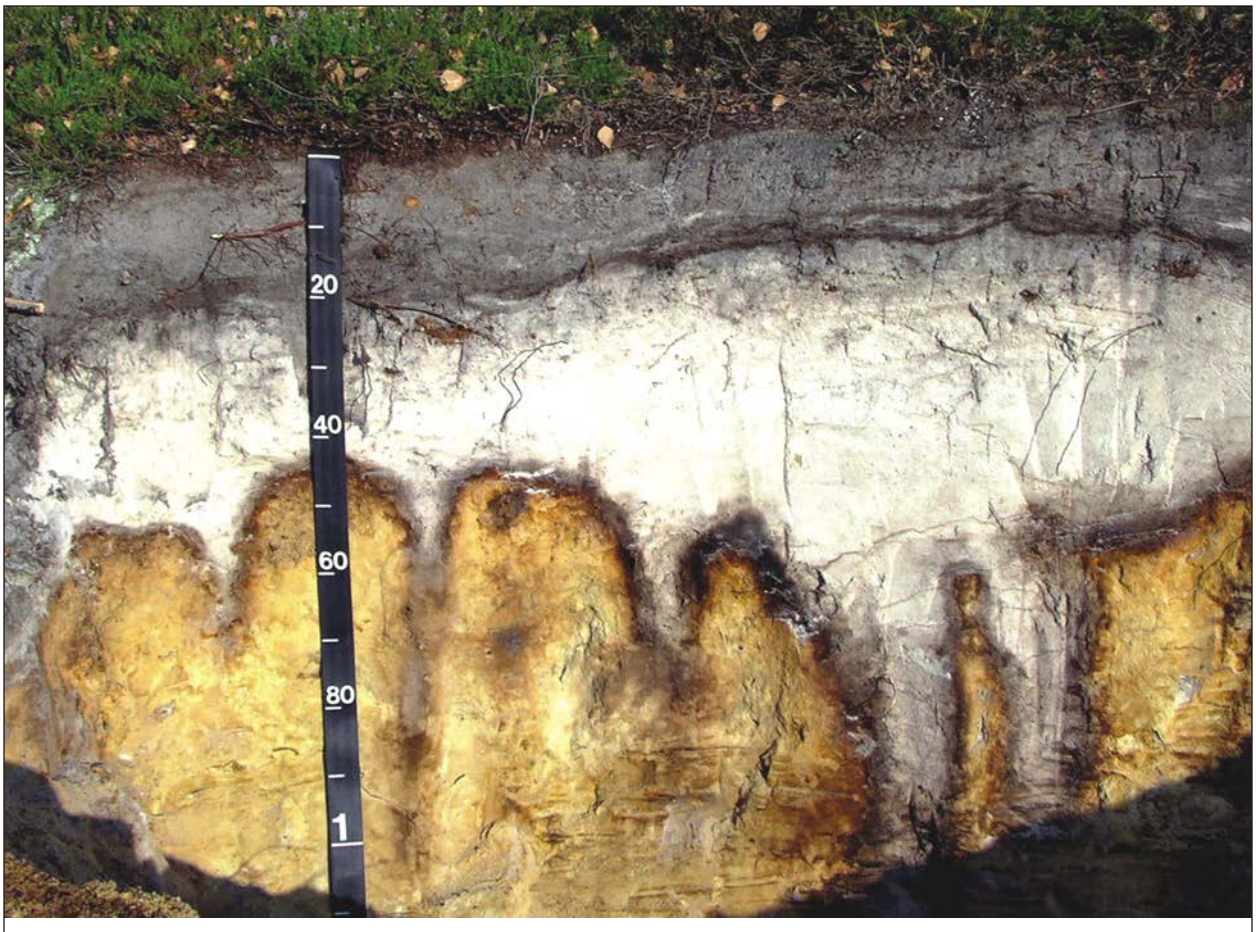

International Journal of Soil Science

ISSN 1816-4978

Academic Journals Inc.

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International Journal of Soil Science 8 (1): 1-16, 2013
ISSN 1816-4978 / DOI: 10.3923/ijss.2013.1.16

Quality Characteristics of Soil Close to the Benin River in the Vicinity of a Lubricating Oil Producing Factory, Koko, Nigeria

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ABSTRACT

Oil pollution is a topical issue in Nigeria and other parts of the world and this is especially so where oil prospecting and processing takes place because of its adverse effect on human and animal health. It became necessary to carry out an environmental audit of the soils of an area suspected of receiving oil pollutants from a lubricating oil factory , this is especially so when oily material are mixed with soil and this is visible. Soil samples were collected from five sampling stations and two control sampling stations (These were collected so as to act as background values with which comparison could be made). These were analyzed for heavy metals by flame absorption spectroscopy after digestion with 2 M HNO_3, Total Organic Extract (TOE) and Total Petroleum Hydrocarbons (TPH) by gravimetric method after extraction with methanol followed by hexane and the physicochemical parameters by standard methods. Important results include average values of pH (5.86±0.32), TOE (56300±19000 mg kg^{-1}), TPH (38700±12000 mg kg^{-1}), Zn (562±510 mg kg^{-1}), Pb (227±160 mg kg^{-1}), Cr (total) (94.5±150 mg kg^{-1}), Cd (2.0±2.9 mg kg^{-1}), total organic carbon (2.83±0.56%) and sand (91.7±1.3%) in the study area. The average concentrations of the pollutant parameters with the exception of Pb were higher in the study area than in the control area. The average concentrations of Cd, Zn, Pb and Cr exceeded guideline values with which they were compared. The average concentrations of TPH in the sampling stations exceeded Environmental Guideline and Standards for the petroleum industry in Nigeria soil/sediment intervention value for mineral oil (5000 mg kg^{-1}). The average pH of the sampling stations fell below guideline range of the Canadian Soil Quality Guidelines (SQGs) with which they were compared. The results confirmed that the soils of the study area are heavily polluted with petroleum hydrocarbons and heavy metals.

Key words: Soil samples, Benin river, physicochemical parameters, heavy metals, total petroleum hydrocarbons

INTRODUCTION

Petroleum hydrocarbons and heavy metals contamination have different sources, prominent among which are the petroleum prospecting and processing industries, petroleum transportation, refined petroleum product (gasoline, diesel etc.) processing industries (e.g., refineries), petroleum product distribution industries (petroleum product depots, filling stations), petrochemicals and lubricating oil producing industries (Forstner and Wittman, 1983; NRC, 1985; GESAMP, 1993). Oil spillages aggravate the input of petroleum hydrocarbons into the environment. The Niger delta Region of Nigeria is an area in which many spillages have occurred (Hinrichson, 1990;

UNEP, 1984, 2011; Okoko and Ibaba, 1999). It has been observed that a total of 6817 oil spills which represents a loss of three million barrels of oil to the environment occurred between 1976 and 2001 and over 70% of this quantity of oil was not recovered (UNDP, 2006). Some of the factors which bring about these spillages in the Niger Delta includes: corrosion of pipeline, production operation and saboteur/theft (Nwilo and Badejo, 2007). Impact of petroleum spillage can be very severe, they include: damage to and loss of biodiversity, depletion of arable land, depletion of available potable water and blockage of water ways. These occurs especially when the concentrations of these pollutants in water, soil, sediments and biota are observed to be high (Burger *et al*., 1991; Proffitt and Devlin, 1998; Luiselli *et al*., 2004, 2006; UNEP, 2011; Okereke *et al*., 2007; Amadi *et al*., 1996; Odokuma and Okpokwasili, 2004; Osuji and Adesiyan, 2005; Pudo and Fubara, 1988; Snowden and Ekweozor, 1987; Ekweozor, 1989; Anyakora *et al*., 2011; Mmon and Deekor, 2010; Onianwa *et al*., 2001; Asia *et al*., 2007; Ebuehi *et al*., 2005; Nduka and Orisakwe, 2009; Williams and Benson, 2010; Olajire *et al*., 2005; Adeniyi and Afolabi, 2002; Osuno, 1981; Akporido and Imah, 2009; Iwegbue *et al*., 2008; Uzoekwe and Oghosanine, 2011; Sojinu *et al*., 2010; UNEP, 2011).

The Benin River has its origin source from a place a distance of 150 km in the North-eastern direction from Koko town. Koko town is in the petroleum prospecting and processing area of Western Niger Delta. Petroleum prospecting does not however take place in the immediate vicinity of the town. There is at present a high volume of fishing and the collection of other animal resources such as lobsters in the Benin River waters. The lands adjoining the Benin River are also used for farming. The arable crops include *Dioscorea* sp. (yam), *Solanum lycopersicum* (tomatoes), *Manihot esculenta* (cassava), *Zea mays* (maize), *Ananas comosus* (pineapple), vegetables such as *Telfairia occidentalis* (fluted pumpkin). *Mangifera indica* (mango), *Elaeis guineensis* (oilpalm), *Cocos nucifera* (coconut) and *Carica papaya* (pawpaw) are some of the tree fruit crops grown in the area. There had not been a major incidence of crude oil spillage in the vicinity of Koko town. There was however the incidence in which hazardous waste from a European country was dumped in a certain location in the town. This attracted the attention of the Federal Government of Nigeria and the International community (Kocasoy, 2003). Many studies reported have focused attention on the effects of activities in the upstream sector (i.e., on crude oil prospecting and processing) on the environment in the Niger delta. Much less attention has been given to the effect of activities of the downstream sector on the environment of the Niger delta. Some studies have been carried out and reported on the effects of effluents from refineries and petroleum products depots and from various petroleum products distribution outfits (Uzoekwe and Oghosanine, 2011; Otokunefor and Obiukwu, 2005; Adeniyi and Afolabi, 2002). Iwegbue *et al*. (2008) attributed the high concentrations of total petroleum hydrocarbon observed in the auto-mechanic waste dumps to be derived from used lubricating oils spilled into the waste dumps by the auto-mechanics. This therefore means that the entry into the environment of lubricating oils in effluents from a lubricating oil producing factory should have a much bigger impact on water, soil, sediment and biota with these pollutants (petroleum hydrocarbons and heavy metals). The hypothesis of this study is to assess the effect of effluents from a lubricating oil producing factory on the physicochemical parameters, the heavy metal contents and the oil contents (total organic extracts and total petroleum hydrocarbons) in soils near and around the factory since from the above, effluents from such a factory should affect these parameters in soils of such an environment. There is currently a dearth in information on the effect of effluents from a lubricating oil producing factory on water, soil, sediment of the environment of such a factory. This study examined the

effect of effluent from a lubricating oil producing factory located in Koko town by the Benin River by determining the concentration of Total Organic Extracts (TOE), Total Petroleum Hydrocarbons (TPH) and selected heavy metals (Cd, Zn, Pb, Cr and Ni) in soil. Soil physicochemical parameters-pH,% organic carbon i.e., TOC (total organic carbon), % organic matter i.e., Total Organic Matter (TOM), soil texture (clay, silt, sand) were also determined.

MATERIALS AND METHODS

Description of study area and design of study: The study area is given in Fig. 1. The lubricating oil producing factory is located in the town (i.e., Koko) and is also by the river. The factory which also produces plastic jerry cans for packaging the product for distribution besides the production of lubricating oil discharges its effluents into the Benin river within the town. Seven sampling stations were established on the river for the purpose of this study two stations upstream to the point of discharge of effluents and these also acted as the control area sampling stations, they are at Ubakporo (UBAK) and Arunologbo (ARUN) (Fig. 1). One sampling station is at the point of entry of effluent into the Benin River (PEE) and the remaining four are downstream to the point of entry of effluents, they are; Ajalugbeti (AJA) sampling station (next to PEE), followed by Uba-Iro (UBA), Uba-Tailor (UB-TA) and Ilogun (ILOG) the furthest sampling station downstream. They are about 1.2 km distance from each other successively.

Methods of collection and preservation of samples: Samples of soil were collected twice every season (i.e., once in each quarter of the year). Samples were collected in dry and rainy seasons for two years. The sampling design consisted of delimiting in every sampling station a sampling area of 70×70 m. This sampling area was then divided into 100 grid plots of 7×7 m area. Thus, thirty three grid plots were randomly selected. From these plots, three replicates of pre-determined quadrates were established and soil samples were taken from each. Samples were manually taken at 0-15 cm (surface) and 15-30 cm (subsurface). Grab samples collected at the surface and subsurface separately from the 33 grid plots were mixed together in well labeled plastic (polyethylene) bags to obtain one surface and subsurface composite samples, respectively. These were then transferred to the laboratory. Samples were analyzed for the following soil quality characteristics: pH, Total Organic Carbon (TOC), Total Organic Matter (TOM), soil particle size analysis (soil texture: clay, silt and sand), Total Organic Extracts (TOE), Total Petroleum Hydrocarbons (TPH) and the heavy metals (Cd, Zn, Pb, Cr and Ni). Samples for TOE and TPH were stored at below O°C for transfer to the laboratory. At the laboratory they were kept in deep freezers at -10°C until time for analysis. Soil samples for other physicochemical parameters and the heavy metals were air-dried in the laboratory.

Analytical procedures: Soil pH was determined by dipping glass electrodes of pH-meter in the supernatant liquid of a mixture of soil and water in a ratio of 2:1 of water to soil in which soil has settled down. The Walkley-Black method (Walkley and Black, 1934) was used in the determination TOC. The value of TOM was obtained from results obtained for TOC by multiplying value of TOC by 1.724 (Walkley and Black, 1934). Particle size analysis was carried out by using the hydrometer method as described in manual by Allens (1989) to obtain percentage for clay, silt and sand. TOE of soil was determined by first extracting the soil with methanol using the reflux method and re-extracting the extract obtained from first extraction with three portions of hexane (30 mL) into

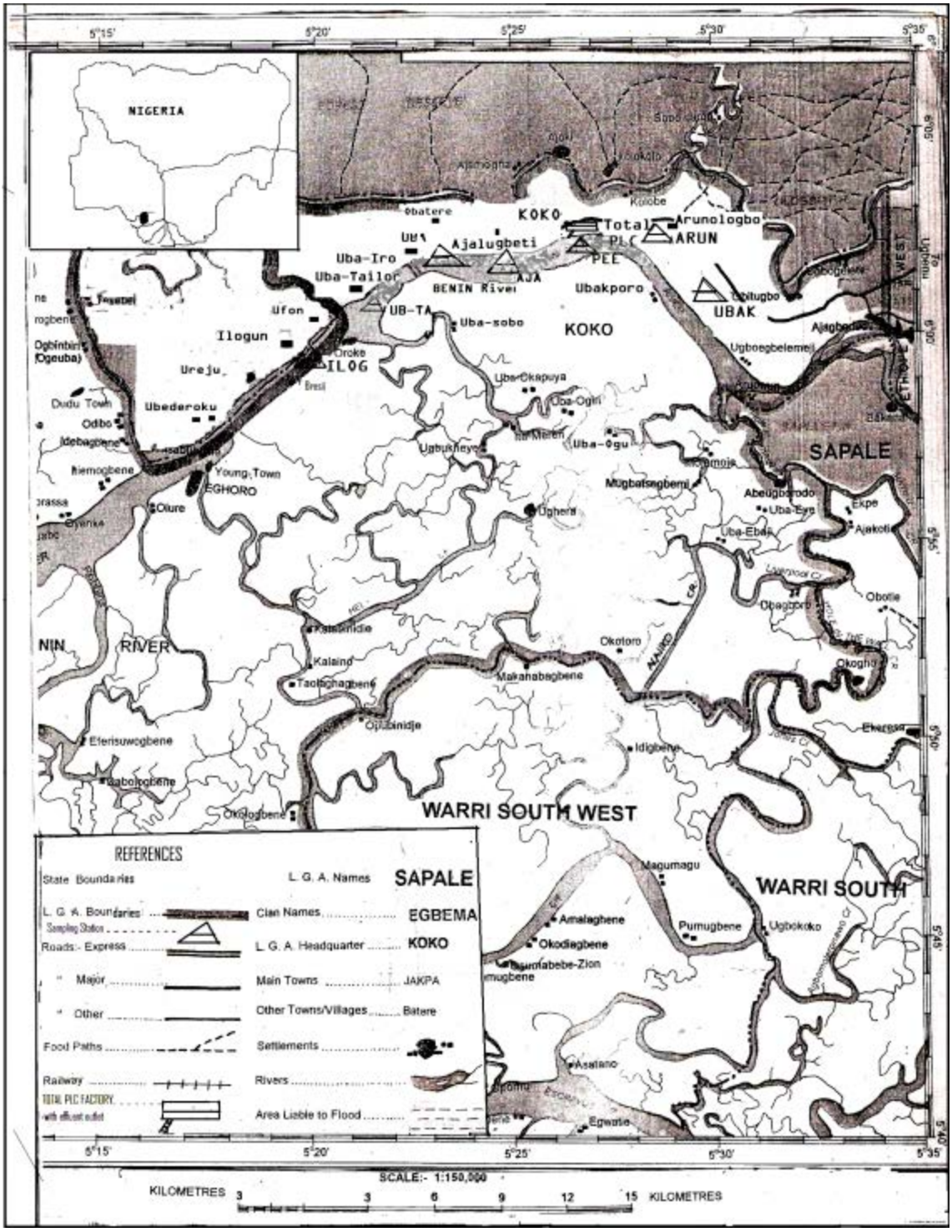

Fig. 1: Map of study area showing section of Benin River and the location of lubrication oil producing factory (Directorate of Land and Survey, Governor's Office, Asaba, Nigeria 200)

a round bottom glass flask passing it though a Whatman filter paper containing 2 g of anhydrous sodium sulphate pre-moistened with hexane. Much of solvent was removed by distillation at reduced pressure. Oil solution in solvent was transferred into weighed, clean dried glass vial where the oil (TOE) was allowed to dry to constant weight (Berthou *et al.*, 1981; Oudot *et al.*, 1981; Adekambi, 1989). The concentration of TOE was obtained from this by calculation as shown below:

$$\text{TOE (mg kg}^{-1}) = \frac{(A-B)\times 10^6}{\text{Dry weight of experimental sample (g)}} \quad (1)$$

Where:
A = Weight of TOE obtained for sample (g)
B = Weight of TOE obtained for blank (g)

Concentration of TPH was obtained from the extract of TOE by clean-up which involved re-dissolving TOE in hexane in a beaker and adding 4 g of activated silica gel (for column chromatography) and stirring with a magnetic stirrer for 5 min before passing it through the same process used for obtaining TOE from extract. Calculation was also as done for TOE. Soil samples for heavy metals determination were first digested by adding 10 mL of conc. HNO_3 to 1 g of soil and digesting with heating and occasional swirling for 2 h. The digest solution was made up to the mark in a 50 mL volumetric flask. Concentrations of heavy metals were determined from the digest solution by flame atomic absorption spectrophotometer as described in manual by Allens (1989).

Quality assurance programme: Blanks and duplicates were analyzed as part of the quality control measures. The percentage recoveries of TOE, TPH, Cd, Zn, Pb, Cr, Ni, in soil were also determined. The following results of average% recovery of the metals, TOE and TPH for five determinations were obtained: Cd (93.5±1.7%), Zn (103±5.5%), Pb (95.6±2.8%), Cr (94.1±1.5%), Ni (90.5±1.3%), TOE (91.3±2.2%) and TPH (92.4±1.7%). All the percentage recoveries fell between 90 and 110 showing that they are good percentage recoveries.

Statistical procedures/packages employed:

- Comparison of mean of concentrations of each parameter in the four seasons studied: This was carried out using analysis of variance (ANOVA-single factor) with Microsoft excel (2007 version) at 0.05 confidence level
- Comparison of mean of concentrations of each parameter in the five sampling stations in the study area: This was also carried out using analysis of variance (ANOVA-single factor) with Microsoft excel (2007 version) at 0.05 confidence level
- Comparison of mean concentrations of some parameters (TOE, TPH) in study area with control area: t-test (two sample, assuming equal variance) (2-tailed) with Microsoft excel (2007 version) at 0.05 confidence level
- Comparison of mean of a set of values for two areas i.e., study area with control area: student t-test was employed at 0.05 confidence level
- Bivariate correlation of values of parameters (pollutant parameters) in matrix: Pearson (2- tailed) correlation was employed from the Statistical Package for the Social Sciences (SPSS) at 0.01 and 0.05 confidence levels

RESULTS AND DISCUSSION

The results showed that the average concentrations of the two oil parameters for the study area are: TOE (563000±19000 mg kg^{-1}) and TPH (38700±12000 mg kg^{-1}) and these were very high as expected (this expectation is borne out of the fact that oil scum were visible in the soil samples from most of the sampling stations). These high concentrations of the two oil parameters indicated that the soils of this area constantly receive high concentrations of these substances from a point source. The average concentrations of the trace heavy metals in the study area are: Cd (2.0±2.9 mg kg^{-1}), Zn (562±510 mg kg^{-1}), Pb (227±160 mg kg^{-1}), Cr (94.5±150 mg kg^{-1}) and Ni (0.07±0.22 mg kg^{-1}). The concentrations of each of these metals in the soil with the exception of Ni were very large. It is worth noting that most of these heavy metals are trace components of petroleum. The low average concentration obtained for Ni is however unexpected since Ni is one of the two prominent trace elements in petroleum (the other being vanadium) and also if the heavy metal pollutant in these soil samples actually came from waste petroleum products entering the environment. An explanation for this could be that much of Ni was removed during the process of refining of petroleum to give petroleum products. A comparison of levels of each parameter in each of the sampling stations showed that there was no definite pattern of variation of levels of parameters with distance of sampling station from point of entry of effluent into the river to downstream to the last sampling station (Ilogun) (Table 1). This may be due to the addition of pollutants to the river after the point of entry of effluents into the river brought in by tributary streams. Also storm water runoff from soils in oil prospecting areas may have brought into the river these pollutants thus increasing their values in the water and soils adjoining the river downstream from the point of entry of effluents. All these factors will not allow the expected gradual decrease in the value of pollutant parameters downstream from the point of entry of effluent. TOE and TPH have their highest concentrations at Ilogun sampling station TOE (78300±23000 mg kg^{-1}) and TPH (48800±6900 mg kg^{-1}). Both parameters have their lowest concentrations at PEE: TOE (38000±19000 mg kg^{-1}) and TPH (32000±15000 mg kg^{-1}). The differences in concentrations of TOE and TPH in the sampling stations are statistically significant (ANOVA-Single factor). The high concentrations of TOE and TPH at Ilogun may be as a result of an additional source of oil probably from oil spills derived from oil prospective activities near to the area.

Table 1: Mean soil quality characteristics for each sampling station

	Control area		Study area				
Parameters	Arunologbo	Ubakporo	Benin river	Ajalugbeti	Uba-Iro	Uba-Tailor	Ilogun
pH	5.70±0.31	6.00±0.18	6.15±0.21	5.40±0.17	6.16±0.08	5.83±0.13	5.82±0.27
TOC (%)	3.54±0.21	2.47±0.90	3.02±0.41	2.94±0.19	3.02±0.23	2.19±0.73	3.00±0.61
TOM (%)	6.10±0.37	4.3±1.5	5.20±0.72	5.06±0.33	5.21±0.39	3.7±1.3	5.18±0.97
Clay (%)	5.22±0.36	3.79±0.25	4.8±1.2	5.87±0.56	4.25±0.44	4.5±1.4	3.93±0.58
Silt (%)	4.24±0.25	4.35±0.92	3.61±0.32	3.84±0.53	3.79±0.76	3.61±0.60	3.54±0.34
Sand (%)	90.3±1.4	92.0±0.7	91.7±1.4	90.5±1.2	92.0±1.1	91.9±1.9	92.3±0.4
TOE (mg kg^{-1})	22700±9900	20000±7500	38000±19000	58900±7900	46500±5200	56900±11000	78300±23000
TPH (mg kg^{-1})	15000±5500	12500±4800	32000±15000	33700±15000	37400±5800	42700±7700	48800±6900
Cd (mg kg^{-1})	ND	ND	1.4±1.4	4.5±4.9	1.0±1.2	2.0±2.6	1.0±1.2
Zn (mg kg^{-1})	380±72	153±140	5.89±230	229±110	1150±790	301±290	550±220
Pb (mg kg^{-1})	550±300	5.0±4.8	165±170	201±160	202±110	155±160	413±380
Cr (mg kg^{-1})	64±48	25±20	290±260	58±26	51±36	31±25	49±29
Ni (mg kg^{-1})	ND	ND	0.14±0.35	0.01±0.01	0.13±0.35	0.03±0.04	0.01±0.01

Values are Mean±SD, ND: Not detected

Table 2: Mean soil quality characteristics for two dry and two rainy seasons

Parameters	First dry season	First rainy season	Second dry season	Second rainy season
pH	5.94±0.37	5.87±0.30	5.87±0.35	5.79±0.29
TOC (%)	2.82±0.44	2.78±0.57	2.79±0.72	2.93±0.57
TOM (%)	4.81±0.88	4.79±0.98	4.8±1.2	5.06±0.99
Clay (%)	4.49±0.86	4.6±1.1	4.6±1.3	4.8±1.1
Silt (%)	3.50±0.15	3.54±0.25	3.94±0.94	3.69±0.26
Sand (%)	92.1±0.7	9.8±1.4	91.5±1.9	91.5±1.3
TOE (mg kg^{-1})	60100±18000	55600±1900	54300±23000	55300±20000
TPH (mg kg^{-1})	43300±11000	40600±12000	35600±13000	35600±12000
Cd (mg kg^{-1})	0.70±2.2	3.2±4.5	0.80±0.79	3.2±1.8
Zn (mg kg^{-1})	539±510	595±550	539±490	581±540
Pb (mg kg^{-1})	219±160	226±170	217±160	245±170
Cr (mg kg^{-1})	90.2±150	94.8±160	94.5±160	98.5±140
Ni (mg kg^{-1})	0.01±0.01	0.01±0.01	0.22±0.41	0.03±0.03

Values are Mean±SD

There was no marked seasonal variation in the values of all the physicochemical parameters and the heavy metals (Table 2). The average concentrations of TOE (60100±18000 mg kg^{-1}) and TPH (43300±11000 mg kg^{-1}) in the first dry season are the highest in the four seasons. These results together with the average concentrations of TOE (55600±19000 mg kg^{-1}) and TPH (40600±12000 mg kg^{-1}) in the first rainy season illustrate the high concentrations of these two parameters (i.e., TOE and TPH). The average concentrations of Zn (581±540, Pb (245±170 mg kg^{-1}) and Cr (98.5±140 mg kg^{-1}) all in the second dry season are the highest in the four seasons studied (Table 2). The average concentrations of most pollutant parameters were higher in the subsurface soil (i.e., 15-30 cm) than at the surface (i.e., 0-15 cm) (Table 3). This is very much unexpected for TOE and TPH. The concentrations of TOE and TPH in the subsurface are 62900±22000 mg kg^{-1} and 38900±14000 mg kg^{-1}, respectively and the average concentrations of TOE and TPH for surface soil are 48600±14000 mg kg^{-1} and 38900±10000 mg kg^{-1}, respectively (Table 3). A look at the values of TOC, silt and clay showed that these were higher in the subsurface soils than in the surface soils. The implication of this is that the subsurface soils have higher retention ability for pollutants than the surface soil. This factor must have been responsible for most of the pollutant parameters being higher in the subsurface soils than in the surface soils. A comparison of the levels of parameters of the study area with those of the control area (Table 4) showed that the concentrations of TOE, TPH and the heavy metals, with the exception of Pb are higher in the study area than in the control area. This can be seen in Table 4, the average concentration of TOE in the study area is 56300±19000 mg kg^{-1} while that of control area is 21400±8600 mg kg^{-1}. The average concentration of TPH in study area is 38700±12000 mg kg^{-1} while that of control area is 13800±5100 mg kg^{-1} and the average concentration of Cr in study area is 94.5±150 mg kg^{-1} while the average concentration in the control area is 44±41 mg kg^{-1}. Also the average concentration of Zn in study area is 562±510 mg kg^{-1} and that of control area is 266±160 mg kg^{-1}. A comparison of mean concentration of TOE and TPH of study area with that of control area using t-test (two sample, assuming equal variance) showed that the differences in concentrations are statistically significant. Direct calculations based on actual averages of the parameters in study area and control area (Table 4) showed that the average concentration of TOE in the study area is 2.63 times that of control area, the average concentration of TPH of study area is 2.80 times that

Table 3: Soil quality characteristics for surface and subsurface of soil

Parameters	Surface (0-15 cm)	Subsurface (15-30 cm)
pH	5.88±0.35	5.87±0.86
TOC (%)	2.59±0.64	3.08±0.34
TOM (%)	4.5±1.2	5.28±0.57
Clay (%)	4.2±1.0	5.1±1.0
Silt (%)	3.42±0.28	3.94±0.58
Sand (%)	92.4±1.1	91.0±1.2
TOE (mg kg^{-1})	48600±14000	62900±22000
TPH (mg kg^{-1})	38900±10000	38900±14000
Cd (mg kg^{-1})	2.4±3.5	1.6±2.1
Zn (mg kg^{-1})	703±610	423±320
Pb (mg kg^{-1})	212±150	242±170
Cr (mg kg^{-1})	67±19	124±210
Ni (mg kg^{-1})	0.11±0.30	0.02±0.02

Values are Mean±SD, TOC: Total organic carbon, TOM: Total organic matter, TOE: Total organic extract, TPH: Total petroleum hydrocarbon

Table 4: Comparison of the results of determination of soil quality characteristics of study area with control area

Parameters	Study area	Control area
pH	5.86±0.32	5.86±0.29
TOC (%)	2.83±0.56	3.00±0.84
TOM (%)	4.9±1.0	5.2±1.4
Clay (%)	4.6±1.1	4.50±0.80
Silt (%)	3.67±0.52	4.30±0.66
Sand (%)	91.7±1.3	91.1±1.3
TOE (mg kg^{-1})	563000±19000	21400±8600
TPH (mg kg^{-1})	38700±12000	13800±5100
Cd (mg kg^{-1})	2.0±2.9	nd
Zn (mg kg^{-1})	562±510	266±160
Pb (mg kg^{-1})	227±160	275±350
Cr (mg kg^{-1})	94.5±150	44±41
Ni (mg kg^{-1})	0.07±0.22	nd

Values are Mean±SD, nd: Not detected, TOC: Total organic carbon, TOM: Total organic matter, TOE: Total organic extract, TPH: Total petroleum hydrocarbon

of control area and the average concentration of Cr in study area is 2.11 times the concentration in control area. Also the average concentration of Zn is 2.11 times that of the control area.

A comparison of the average levels of the parameters of study area with Soil Quality Guidelines (SQGs) (Table 5, 6) revealed that the average pH of soils of AJA (5.40±0.17), UB-TA (5.83±0.13) and ILOG (5.82±0.27) fell below the range of pH for all the land uses (6-8) of the Canadian Soil Quality Guidelines (SQGs) for the protection of the Environment and Human health (Table 5) (CCME, 1999). This means that soils of these sampling stations are too acidic for all the land uses listed. The average concentration of Cd for AJA (4.5±4.9 mg kg^{-1}) and UB-TA (2.0±2.6 mg kg^{-1}) exceeded, respectively the agricultural land use guideline value (1.40 mg kg^{-1}) and so based on this the land in the two sampling stations may not be suitable for agriculture with respect to cadmium. The average concentration of Cr (total) in PEE sampling station (290±260 mg kg^{-1}) exceeded guidelines values for all the land uses in the Canadian SQGs for protection of the

Table 5: Average concentration of heavy metals and pH in each sampling station compared with the Canadian soil quality guideline for the protection of the environment and human health value for each metal (CCME, 1999)

Parameters	Guideline values				Sampling station (Mean±SD)				
(mg kg^{-1})	Agricul-tural	Residential/parkland	Commercial	Indust-rial	Benin river	Ajalugbeti	Uba-Iro	Uba-Tailor	Ilogun
pH	6-8	6-8	6-8	6-8	6.15±0.21	5.40±0.17	6.16±0.09	5.83±0.13	5.82±0.27
Cd	1.4	10	22	22.0	1.4±1.4	4.5±4.9	1.0±1.2	2.0±2.6	1.0±1.2
Total Cr	6.4	6.4	87	87.0	290±260	58±26	51±36	31±25	49±29
Pb	70	140	260	600	165±170	201±160	202±110	155±160	413±38
Ni	50	50	50	50.0	0.14±0.35	0.01±0.01	0.13±0.35	0.03±0.04	0.01±0.01
Zn	200	200	360	360	589±230	229±110	1150±790	301±290	550±220

Table 6: Average concentration of TPH and the heavy metals in the sampling stations compared with values for seven other soil quality guidelines (SQGs)

	Conc. (mg kg^{-1})						
Country/name of sampling station	TPH	Cd	Zn	Pb	Cr (total)	Ni	References
Norway (guideline value)	-	1.00	150	50	100.0	30.0	Reimann *et al.* (1997)
Netherlands (action level)	-	12.0	720	530	380.0	210	Reimann *et al.* (1997)
Netherlands (guidance for further investigation)	-	6.00	380	310	240.0	120	Reimann *et al.* (1997)
Switzerland (guideline values)	-	0.80	200	50	-	-	FOEFL (1987)
Japan (environmental quality Standards for soil pollution)	-	0.01 mg L^{-1} (in sample solution) 1.00 mg kg^{-1} (rice Agric land)	-	0.01 mg L^{-1} (in sample solution)	-	-	EAGJ (1994)
Accompany in guideline for SPDC EIA process (acceptable range)	-	0.70-3.00	10.0-120	5.00-50.0	10.0-100	5.00-50.0	SPDC (2004)
EGASPIN soil/sediment intervention values	5000	12.0	720	530	380.0	210	DPR (2002)
Benin river sampling station	32000±15000	1.4±1.4	589±230	165±170	290.0±260	0.14±0.35	Present study
Ajalugbeti sampling station	33700±15000	4.5±4.9	229±110	201±160	58.0±26	0.01±0.01	Present study
Uba-Iro sampling station	37400±5800	1.0±1.2	1150±790	202±110	51.0±36	0.13±0.35	Present study
Uba-Tailor sampling station	42700±9700	2.0±2.6	301±290	155±160	31.0±25	0.04	Present study
Ilogun sampling station	48800±6900	1.0±1.2	550±220	413±38	49.0±29	0.01	Present study

EAGJ: Environmental agency government of Japan, FOEFL: Federal office of environment, forest and landscape, SPDC: Shell petroleum development company (Nigeria), EGASPIN: Environmental guidelines and standards for the petroleum industry in Nigeria and DPR: Department of petroleum resources (Nigeria), TPH: Total petroleum hydrocarbon

Environment and Human Health (Table 5). Also the average concentrations of total chromium in AJA (58±26 mg kg^{-1}), UBA (51±36 mg kg^{-1}), UB-TA (31±25 mg kg^{-1}) and ILOG (49±29 mg kg^{-1}) sampling stations exceeded, respectively the guideline values for agricultural (6.40 mg kg^{-1}) and residential/park (6.40 mg kg^{-1}) land uses, respectively. The average concentration of Pb in all the sampling stations i.e., PEE (165±170 mg kg^{-1}), AJA (201±160 mg kg^{-1}), UBA (202±110 mg kg^{-1}), UB-TA (155±160 mg kg^{-1}) and ILOG (413±380 mg kg^{-1}) exceeded, respectively the agricultural (70.0 mg kg^{-1}) and the residential/parkland (140 mg kg^{-1}) land uses of the Canadian SQGs for the protection of the environment and human health. Average concentration of Pb in ILOG sampling station (413±380 mg kg^{-1}) exceeded the agricultural (70.0 mg kg^{-1}), residential/parkland (140 mg kg^{-1}) and commercial (260 mg kg^{-1}) land uses, respectively. The average concentration of Zn in PEE (589±230 mg kg^{-1}), UBA (1150±790 mg kg^{-1}) and ILOG (550±220 mg kg^{-1}) sampling stations exceeded, respectively the guideline values for all the land uses. Also the average concentrations of Zn in AJA (229±110 mg kg^{-1}) and UB-TA (301±290 mg kg^{-1}) exceeded, respectively the agricultural (200 mg kg^{-1}) and the residential/parkland (200 mg kg^{-1}) land uses. The discussion above shows that none of the sampling station is suitable for any of the land uses (i.e., they are polluted with respect to all of the land uses) (Table 5).

A comparison of the average concentrations of the five heavy metals (Cd, Zn, Pb, Cr, Ni) and TPH of each of the sampling stations with seven other Soil Quality Guidelines (SQGs) (Table 6) revealed that the average concentrations of the heavy metals in most of the sampling stations are higher than most of the guideline values for the individual metals. It is also observed that the average concentrations of TPH in all the sampling stations far exceeded, respectively the Environmental Guidelines and standards for the Petroleum Industry in Nigeria (EGASPIN) intervention value for mineral oil (petroleum) (5000 mg kg^{-1}) (DPR, 2002). The intervention values of EGASPIN (DPR, 2002) indicate the quality for which the functionality of soil for human, animal and plant life are, or threatened with being seriously impaired. Concentrations in excess of the intervention values correspond to serious contamination (DPR, 2002). The soils in the study area are thus seriously contaminated with mineral oil (petroleum). Usually, such levels of petroleum hydrocarbons in the sampling area sites causes depletion of oxygen in the soil pores because the oil films in the surface and subsurface of the soil reduces or inhibits the diffusion of oxygen into the soil pores. Oxygen is therefore less available to soil dwelling organisms. This situation creates conditions in which anaerobic microorganisms multiply at the expense of the more environmentally beneficial aerobic microorganisms. The replacement of the more beneficial microbes (or non hydrocarbon utilizing microbes) by the more resistant hydrocarbon utilizing microbes creates an imbalance in the proportion of different species. These resistant hydrocarbon utilizing microbes are actually natives of the soil but usually have population explosion in the presence of hydrocarbon pollution of an area as a result of their being able to release energy and form new cells from their ability to oxidize hydrocarbons using oxygen. Their population therefore increases at the expense of the non hydrocarbon utilizing microbes which are unable to form new cells and release energy from the oxidation of hydrocarbons. Heterotrophic microbes are also able to degrade the hydrocarbon and release energy for themselves and also build new cells. The growth in population of hydrocarbon utilizing (i.e., including the heterotrophic microbes) at the expense of the non-hydrocarbon utilizing microbes brings about loss and damage to biodiversity in such an area (Atlas, 1981; Okereke *et al*., 2007).

Pearson's (2-tailed) correlation of the measured parameters of soil (Table 7) showed the following (with correlation coefficient in parenthesis): TOC and TOM (0.985), pH and TOE (0.639),

Table 7: Pearson (2-tailed) correlation matrix for soil parameters

	TOC	TOM	Clay	Silt	Sand	TOE	TPH	Cd	Zn	Pb	Cr	Ni
TOC												
TOM	0.985**											
Clay	0.007	0.017										
Silt	0.236	0.230	-0.269									
Sand	-0.290	0.302	-0.203	-0.711**								
TOE	0.371*	0.337*	-0.052	0.077	-0.006							
TPH	0.160	0.160	-0.113	-0.094	0.242	0.639**						
Cd	0.106	0.113	0.377*	0.125	0.333*	-0.062	0.085					
Zn	0.181	0.169	-0.172	-0.227	0.359*	-0.091	-0.022	-0.144				
Pb	0.046	0.037	-0.166	-0.136	0.206	0.497**	0.127	-0.247	0.171			
Cr	0.115	0.120	-0.048	-0.039	0.041	-0.097	0.109	0.011	0.119	-0.024		
Ni	-0.039	-0.030	0.069	-0.156	0.130	-0.315	-0.178	-0.094	0.121	-0.221	-0.077	

*,**Correlation is significant at 0.05 and 0.01 level (2-tailed), respectively, TOC: Total organic carbon, TOM: Total organic matter, TOE: Total organic extract, TPH: Total petroleum hydrocarbon

Pb and TOE (0.497) are very strongly correlated and their correlation coefficients are significant at the 0.01 level. Also the following pairs are strongly correlated and their correlation coefficients are significant at the 0.05 level: TOE and TOC, TOE and TOM, Cd and clay, Zn and sand. The members of these pairs are either dependent on each other or one is an integral part of the other e.g., TOC and TOM, TPH and TOE, Cd and clay, TOE and TPH and Zn and sand. A pair which does not fall into this category is Pb and TOE (0.497). The members of this pair must have been strongly correlated because they arise from the same source. This source may be the lubricating oil factory through its effluents.

A comparison of the results of determination of the two oil parameters (TPH and TOE) and the heavy metals obtained in the present study with those for similar studies carried out elsewhere is given in Table 8. It can be seen that results obtained for most parameters in the present study are comparable in most cases with results for corresponding parameters in the other studies. In some cases they are higher and in others they are lower. The average concentration of TPH in study area (38700±12000 mg kg^{-1}) or range (9800-61500 mg kg^{-1}) was found to be comparable with those obtained for Agbada oil field (an oil spill site) (124-38600 mg kg^{-1}) and Niger River at Owaza (also an oil spill site) (6800±900 mg kg^{-1}). It was also found to be higher than those obtained for Lagos Auto-mechanic workshop (363±190 mg kg^{-1}) by Adeniyi and Afolabi (2002) and for surface soil of auto-mechanic waste dump (486-4438.7) by Iwegbue *et al.* (2008). The concentration of TPH obtained at this later site (i.e., auto-mechanic waste dump site) was inferred by the authors to have come mainly from lubricating oils in the waste dump by auto-mechanics. It is therefore not surprising that the concentration of TPH obtained in the present study by far exceeded that obtained by these authors for this waste dumpsite since the volume of lubricating oil getting to the soil in the present study area from the Lubricating oil factory is expected to exceed the volume of lube oil that can get to the soil at an auto-mobile mechanic dumpsite. The average concentration of Pb in study area (227±160 mg kg^{-1}) or range (0.00-165 mg kg^{-1}) was observed to be comparable with those obtained for Effurun Auto-mechanic village (a place delimited from a town where auto-mobile repair workshops are located) (68.5±9.9 mg kg^{-1}) (Akporido and Imah, 2009), Niger Delta area (3.40-994 mg kg^{-1}) by Asia *et al.* (2007), Lagos Auto-mechanic workshop (10.7±4.8 mg kg^{-1}) by Adeniyi and Afolabi (2002), Warri river in steel production area

Table 8: Comparison of soil heavy metal, pH and total petroleum hydrocarbon levels around benin river (present study area) with those from studies elsewhere

Country	River/location	Major activities in the area	pH	Conc. (mg kg^{-1}) TPH	Cd	Zn	Pb	Cr (Total)	Ni	References
Nigeria (Niger Delta)	Agbada oil field		124-38600	-	-	-	-	-		Osuji *et al.* (2005)
Nigeria	Auto-mechanic village in Effurun	Repair of Auto-mobiles	6.40±0.58	-	35±10	-	68.5±9.9	-	121±51	Akporido and Imah (2009)
Nigeria	Urashi river (obiobi/obrikom)	Oil spillage area			<0.20	-	0.32-0.80	-	0.53-18.0	Osuji and Onojake (2004)
Nigeria	Niger delta area	Oil prospective area	-	-	0.04-0.95	11.1-27.4	3.40-99.4	1.30-165	1.60-13.6	Asia *et al.* (2007)
Nigeria	Lagos	Auto-mechanic workshop	-	363±190	0.05±0.05		10.7±4.8	1.79±1.1	2.94±3.4	Adeniyi and Afolabi (2002)
Nigeria	Niger river (Owaza)	Oil spillage area	4.9-5.1	6800±900	-	-	-	-	-	Osuji and Nwoye (2007)
Nigeria	Warri river	Steel production area	5.50±0.58	-	8.9±4.8	106±35	126±42	-	52±52	Akporido (2009)
Spain	Guadalquiver river (Marshes)	Park area (Marshes)			230-340	570-4,200,000	3150-126000			Ramos *et al.* (1994)
Australia	Macquarie	Seaport area				47.0	20.0	1020	149	Lottermoser (1997)
Nigeria	Auto- mechanic waste dumpsites	Waste dumps	-	486.7-4438.7 (surface)	-	-	-	-	-	Iwegbue *et al.* (2008)
Nigeria	Benin river	Industrial area								
		Mean	5.86±0.32	38700±12000	2.0±2.9	562±510	227±160	94.5±150	0.07±0.22	Present study
		Range	5.13-6.44	9800-61500	0.00-15.0	23.0-1950	0.00-465	0.00-550	0.00-100	

TPH: Total petroleum hydrocarbon

(126±42 mg kg^{-1}) (Akporido, 2009) and Macquarie seaport area (20.0 mg kg^{-1}) (Lottermoser, 1997). It was found to be higher than that obtained for Urashi river at Obiobi/Obrikom (0.32-0.80 mg kg^{-1}) (Osuji and Onojake, 2004). It was however observed to be much lower than that obtained for Guadalquiver River park area (3150-126000 mg kg^{-1}) (Ramos *et al*., 1994). The average values or range for pH, Cd and Zn were similar to the results obtained in these other studies.

CONCLUSION

The levels of most parameters did not vary with the seasons; concentrations were higher in some of the sampling stations. There was no definite pattern of variation of levels of parameters with distance of sampling stations from point of entry of effluent downstream to the last sampling station (Ilogun) in the study area. The concentrations of TOE, TPH, Zn and Cr were higher in the study area than in the control area. The high acidity observed in the soil will have the effect of increasing the mobility of the heavy metals whose concentrations have been observed to be high (by increasing their solubility in the water in the pore of the soils). This makes the metals ions readily available for uptake by plants roots with the consequence of the entry of the metals ions into the food chain involving human and higher animals. This will inevitably have adverse effect on the health of humans and animals. Also the high concentrations of TOE and TPH will lead to high concentration of Polynuclear Aromatic Hydrocarbons (PAHs) entering the food chain (since concentration of total PAHs can be estimated from the concentration of TOE or oil and grease (NRC, 2003). This will also affect adversely the health of humans and animals.

As has already been observed, the source of these pollutants should be the effluents from the lubricating oil producing factory. The effluents enters the river and during heavy rains and storms, the river usually overflows it banks thus depositing these pollutants in the soils of lands adjoining the river. Stormwater runoffs carries these further inland. The accumulation of these through this mode of deposition with time must have resulted in the high levels of pollutants observed. This pollutant build-up can be curtailed by ensuring that the lubricating oil producing factory properly treats its effluents before disposal of the effluents into the river. Effluent limitation guidelines for the disposal of effluents from the petroleum industry into surface water have been put in place by environmental authorities in Nigeria. One of such is EGASPIN by Department of Petroleum Resources in Nigeria (DPR, 2002). It is however observed that there may be lapses in the monitoring of the industries by this agency of government for compliance with the guidelines. The government should ensure that strict monitoring of industries for compliance is carried out.

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