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Characteristic Levels of Total Petroleum Hydrocarbons in Soil, Sediment and Surface Water of an Oil Impacted Area in the Niger Delta

C.M.A. Iwegbue[a]*, G.E. Nwajei[a] and F.O. Arimoro[b]
[a]Department of Chemistry, Delta State University, P.M.B. 1, Abraka, Nigeria
[b]Hydrobiology Unit, Department of Zoology, Delta State University, P.M.B. 1, Abraka, Nigeria

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Abstract. Soil, bottom sediments and surface water were collected at several points in Abalagada-Aboh area in the Niger delta, Nigeria, that had previously received spilled crude oil. The samples were analyzed for total petroleum hydrocarbon contents. Petroleum hydrocarbon concentrations varied significantly among various environmental matrices. The concentrations ranged widely between 2.80-785.6 mg/kg, 2.84-804.74 mg/kg, 0.30-865.64 mg/kg and 0.03-22.99 mg/kg for surface water, sediments, topsoil and subsoil, respectively. The samples showed elevated concentrations of hydrocarbon when compared to the control site.

Keywords: petroleum hydrocarbons, soil, sediment, surface water, oil spill, Niger delta

Introduction

Petroleum hydrocarbon oils have environmental importance due to their toxicity to human systems, plants and animal resources (Onianwa and Essien, 1999). Hydrocarbon species can enter the soil environment from a number of sources. The origin of the contaminants has a significant bearing upon the species present. Unlike other chemicals (notably pesticides), hydrocarbons are generally not applied to soils and the contamination results almost entirely from misadventure. Major sources of hydrocarbons in the environment include leakage from underground storage tank, spillage during refueling and lubrication, drilling, transfer and handling of crude oil (such as at tanker terminals and oil refineries). Shale oil retorting plants provide another source of hydrocarbon (Sadler and Connell, 2003). Microbes are mostly sensitive to changes and may increase several fold in response to addition of extraneous carbon sources such as crude oil, used engine oil and grease (William, 2002).

Alteration in composition of hydrocarbons occurs as they get into soil. Clearly, those hydrocarbons that are the most strongly sorbed onto soil organic matter are the most resistant to loss or alteration by other processes. Conversely, the more volatile/soluble hydrocarbons are the most susceptible to change by volatilization/reaction/leaching/biodegradation. The ultimate result is "weathering" of the hydrocarbon mixture discharged into the soil, with accompanying change in its composition and a preferential transport of certain fractions to other environmental compartment (Sadler and Connell, 2003).

As crude oil infiltrates into the soil, it considerably affects the structure and welting ability of the soil and a complete breakdown of structure and dispersion of oil particulate have been noted. The rate of oil movement through the soil largely depends on the type of oil, organic matter content, moisture content of the soil and depth of the water table. The oil physically displaces soil, air and water. This has been considered a significant factor in promoting anaerobic conditions in soils.

The objective of the present study is to determine the characteristic levels of petroleum hydrocarbons in soil, sediment and surface water of oil-impacted area. The result of this study will provide useful information about the extent of contamination, guidance to remediation technique and complement the array of data now available on different aspects of the environment of the Niger delta.

Study area. Abalagada-Aboh is located in the north of the Niger delta, south central Nigeria and within the Ndokwa east local government area of delta state. The study area lies within the coordinates 454400 - 464000 E and 181750 - 183000 N. The Abalagada area houses one of the largest oilfields in the Niger delta and is characterized by crisscrossing of pipelines and multiple oil wells. Apart from farming and fishing, the major industrial activities in this area include of oil and gas exploration and exploitation. There was an accidental spillage on the 11th of October, 2003, followed by fire outbreak that lasted for 30 days.

Materials and Methods

Soil samples were collected within a quadrant 1.5 km x 1.5 km, around the impacted area. This quadrant was further divided into twelve cells (125 m x 125 m), each cell denoting a sampling point. Composite samples, consisting of at least 5 random ones, were taken in each cell at two depths, 0-15 cm and 15-30 cm.

*Author for correspondence; E-mail: maxipriestley@yahoo.com

The samples were air-dried and sieved through 2 mm mesh. The sediment and the surface water were collected from the adjoining water bodies that had received different degrees of crude oil impact. Total hydrocarbons in the surface water were determined after appropriate extraction with xylene and column clean up at 425 nm using Spectronic 20 spectrophotometer. For comparison, a control sample was collected from a farmland 3 km away from the impacted area with no case history of oil spillage.

pH in water was measured with a glass electrode using 1:2.5 samples/water ratio (McLean, 1982), particle size distribution of the soil by hydrometer method for silt and clay and dry sieving for sand fraction (Rueejiwk, 1995). Total organic carbon was determined by wet dichromate oxidation method of the Walkley and Black (Nelson and Sommer, 1982).

Total hydrocarbon content of the soil and sediment samples was determined by the method of Intergovernmental Oceanographic Commission (IOC) as described by Onianwa and Essein (1999). 100 g of the soil/sediment sample were refluxed with 100 ml of methanol in a container containing about 3.0 g of KOH for 2.5 h. The refluxed mixture was filtered and the filtrate was extracted with 2.5 ml portion of redistilled hexane. The combined extracts were evaporated to about 1.0 ml, subjected to clean up in a silica column and eluted with *n*-hexane. The eluate was subsequently evaporated to isolate the hydrocarbon oil, which was then weighed. All samples were analysed in triplicate and relative standard deviation (RSD) between triplicate analysis was < 6%. A recovery test of the procedure was carried out by spiking five analyzed soil samples with different amounts of hydrocarbon oil and then repeating the analysis. An average recovery of 93.4 ± 4.7% (Mean ± SD) was obtained.

Results and Discussion

Some physicochemical characteristics of the soils and the sediment examined are given in Table 1. The soils and sediment were moderately acidic with mean pH of 5.22 (4.82-7.24), 5.94 (4.64-7.39) and 5.33 (4.51-6.64) for topsoil, subsoil and sediment, respectively. The pH values were predominantly higher in the surface soils except for few sites that have pH values higher than that of the topsoil. This is in line with the observations of Kabala and Singh (2001). This moderately acidic to near neutral pH is the typical characteristic of anaerobic soils and sediments of the Niger delta (Iwegbue *et al.*, 2006a, 2006b; Isirimah, 1987; Odu *et al.*, 1985). The particle size distribution was predominantly clay fraction in both topsoil and subsoil. The clay content is moderately variable with coefficient of variation of 21.5% and 45.3% for the topsoil and subsoil, respectively. The total organic carbon (TOC) was generally high at all sites. The mean level of TOC was 8.84% (range 0.89-40.37 %) for topsoil and 1.82% (range 0.15-15.11%) for the subsoil. The high value of total organic carbon content of the soil may be due to the contribution of organic carbon of the crude oil. Heavily impacted sites showed high TOC values compared with less impacted sites. The organic matter content of the sediment was 0.73 ± 0.47% (range 0.26-1.76). The mean organic matter recorded in this study was far lower than the levels reported by Horsfall *et al.* (1999) for Okirika river system in Nigeria and by Gupta and Pant (1983) for eutrophic lakes in Naini Tal, UP India.

Total petroleum hydrocarbons. The results of total petroleum hydrocarbon content of surface water and sediments and soils of the impacted area are presented in Table 2 and 3, respectively. Analysis of variance ($p > 0.05$) revealed apparent and significant variation in the concentrations of total petroleum hydrocarbons (TPH) at a given site depth, when one site is compared with other sites.

The surface soils showed higher concentration of total hydrocarbons compared with the subsurface soils, except for site 3. Heavily impacted area showed higher concentration of petroleum hydrocarbons. The content of petroleum hydrocarbon in the soils was generally low in spite of the extent of impact.

Table 1. Some physicochemical properties of impacted soils and sediment

Parameter/	Top soil (0-15 cm)			Sub soil (15-30 cm)			Sediment		
profile	Mean±SD	Range	CV(%)	Mean±SD	Range	CV(%)	Mean±SD	Range	CV(%)
Sand (%)	36.6±16.3	10.1-61.5	44.3	47.0±23.4	20.2-82.1	49.8	-	-	-
Silt (%)	22.1±12.6	3.6-52.4	57.3	16.0±8.6	22-30.6	54.0	-	-	-
Clay (%)	41.1±8.8	26.9-53.4	21.5	37.0±16.7	8.9-61.5	54.3	-	-	-
pH(H_2O)	5.4±0.7	4.8-7.2	13.8	5.96±1.1	4.6-7.9	18.1	5.3±0.9	4.51-6.64	17.0
TOC (%)	8.8±14.5	0.9-40.4	163.5	1.82±3.23	0.2-11.5	177.0	0.7±0.5	0.26-1.7	56.0
EC(µS/cm)	1702.6±3452.6	55.4-9383.0	202.7	328.8±489.4	41.9-1814	149.0	82.9±18.6	49.6-118.0	22.4
CEC(C mol/kg)	19.5±48.0	1.1-170.1	245.0	8.53-7.6	8.9-24.5	89.0	-	-	-

TOC = total organic carbon; EC = electrical conductivity; CEC = cation exchange capacity

The low hydrocarbon content of soil could be attributed to rapid microbial degradation, evaporation of the lighter fractions and the fire outbreak which might have burnt off substantial amount of petroleum hydrocarbons. However, apart from burning, other alteration processes are responsible for the low content of petroleum hydrocarbons; Salanitro *et al.* (1997) found that 70-90% of the C_{11} - C_{22}, 40-60% of the C_{23} - C_{34} and 35-60% of the C_{35} - C_{44} fractions of fresh crude oil were lost after 3-4 months of bioremediation in optimal conditions. Similarly, under favourable conditions, most important components of petrol and diesels (< C_{15}) are lost by weathering processes, including biodegradation, transformation, volatilization, and leaching. Low concentration of hydrocarbons at the studied sites, could be probably due to these processes. Total petroleum hydrocarbon levels recorded in this study were lower than values reported for impacted soils by Onianwa (1995). However, heavily impacted sites have concentration within the range reported by Onianwa and Essien (1999) and Adekambi (1989) for oil producing regions of Nigeria. The toxicity of petroleum hydrocarbons in the soil has been studied with reference to a range of species, including bacteria, algae, earthworms and plants and a range of lethal to sublethal effects, such as on seed germination, root elongation and reproduction. The toxic effects appeared over a large range of test concentrations; the most effective concentrations were >1000 mg/kg. The lowest EC_{50} for seed (typically lettuce) germination studies are in the range of 2000-3000 mg/kg (Saterbak *et al.*, 1999; Chaineau *et al.*, 1997). However, the concentration of total hydrocarbons recorded herein is lower than the range and, therefore, not liable to produce any toxic effect on the crops.

Table 2. Characteristic levels of petroleum hydrocarbons in surface water and sediment

Sites	Surface water (mg/l)	Sediment (mg/kg)
1.	6.33±0.44	7.07±0.42
2.	4.82±0.39	22.29±1.12
3.	3.25±0.20	4.81±0.29
4.	3.81±0.38	4.96±0.19
5.	2.58±0.18	1.15±0.10
6.	14.78±1.33	10.45±0.63
7.	785.6±62.85	804.74±48.28
8.	4.26±0.25	12.99±0.91
9.	2.80±0.20	2.84±0.71
Means±SD	92.03±260.12	98.81±265.56
RSD (%)	283.6	268.8

Table 3. Characteristic levels of total petroleum hydrocarbons in the soils

Sites	Topsoil (0-15 cm) (mg/kg)	Subsoil (15-30 cm) (mg/kg)
1.	0.30±0.02	0.03±0.001
2.	5.37±0.48	4.21±0.01
3.	3.68±0.22	7.91±0.63
4.	67.97±4.75	5.37±0.37
5.	117.88±7.07	2.84±0.17
6.	12.99±1.04	1.99±0.16
7.	30.42±1.52	6.22±0.44
8.	25.51±1.53	1.15±0.08
9.	32.41±1.93	6.22±0.56
10.	12.99±0.77	22.99±0.30
11.	78.97±4.74	5.37±0.32
12.	865.64±51.93	8.76±0.35
Control site	3.50±0.48	0.30±0.02

The sediments showed higher concentrations of petroleum hydrocarbons than those in the overlying surface water at all sites except for sites 5 and 6. As expected, heavily impacted sites showed higher concentrations of petroleum hydrocarbons e.g. Sites 2, 7, and 8. The levels of total petroleum hydrocarbons reported in this study are far below the upper limit levels reported for sediments of some Nigerian rivers (Onianwa and Essien, 1999).

For soils, all sites showed significant higher concentration of total petroleum hydrocarbons as compared to the control sites except for sites 1, 2 and 3. These sites have total petroleum hydrocarbon content similar to levels observed at the control site suggesting that these areas were not severely affected by the oil spillage. The levels of petroleum hydrocarbons found in the subsurface region are similar to the levels found in unpolluted soils. Probably, petroleum hydrocarbon contamination was restricted only to topsoil due to low permeability, resulting from the clay content of these soils. High organic carbon content increases sorption of most hydrocarbon compounds, reducing their availablity to plants etc. in soil. For example, Dorn *et al.* (1998) and Salanitro *et al.* (1997) found that soils with high organic content have toxic endpoint at concentrations at least double, and up to eight times that of soil with low organic content. It has been found that hydrocarbon contamination in fine soils 2-6 times less toxic (higher endpoint concentrations) than contamination in coarse soils for similar reasons (CCME, 2000). Total petroleum hydrocarbon content of the soil showed no significant correlation with any soil physiochemical characteristics suggesting that the source of hydrocarbons in the soil was purely anthropogenic.

Conclusion

The concentration of petroleum hydrocarbons in the study area is comparatively low and most sites have values in the range of 1.0-865.4 mg/kg. Thus, the levels found in soil, sediment and surface water in this study showed some slight elevation when compared with the baseline levels. The result reveals that petroleum hydrocarbon contamination is primarily restricted to the surface region of the soils.

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