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Infrared and gravimetric estimation of total petroleum hydrocarbons in water and sediment: A case study of ondo coastal water, Nigeria

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ABSTRACT

The presence of pollutants in aquatic environment has become a source of worry to the global community. Levels of one of these major aquatic pollutants, petroleum hydrocarbon, were studied in sediment obtained from five villages in Ilaje community of Ondo State, Nigeria. The samples were analysed using gravimetric and infrared(IR) spectroscopic methods. The results displayed wide variations with concentration decreasing with depth. The concentrations(in μgg^{-1}) in the water as recorded by the gravimetric(IR results in brackets) methods varied between 0.11(12.0) to 2.55(24.0) while in sediment between 61.8(24.0) to 199.3(135.0) respectively. The aliphatic components were found to be generally higher than the aromatic components. The data obtained displayed a low level of microbial degradation and high adsorptive sedimentation. The comparative assessment with the reference site is indicative of anthropogenic inputs of petroleum hydrocarbons due to oil spill, being the only noticeable source into this environment. The results showed that the gravimetric method is more sensitive to TPH in sediment while the IR is of better response to water.

KEYWORDS

Total petroleum hydrocarbons(TPH);
Gravimetry;
Infrared(IR) spectroscopy;
Sediment;
Oil pollution.

INTRODUCTION

Petroleum hydrocarbons are very complex mixtures and the complexity increases with increasing carbon number[22]. For several decades, petroleum products have become very common pollutants in the environment as considerable amount are discharged into the environment through industrial effluents, vandalization, spillage (as applicable in the present study)e.t.c. Hydrocarbons species can enter the aquatic environment from a number of sources. Unlike other chemicals, its contamination result almost entirely from misadventure. Although the majority of hydrocarbon in the aquatic environment of Nigeria and in particular, Ondo coastal water, are anthropogenic in nature, researchers have shown that some natural sources of this chemical exist[15]. There is also a body of evidence to show that certain organism notably higher plants are capable of synthesizing hydrocarbons[5] and these too could find their way into aquatic environment. These later sources are however

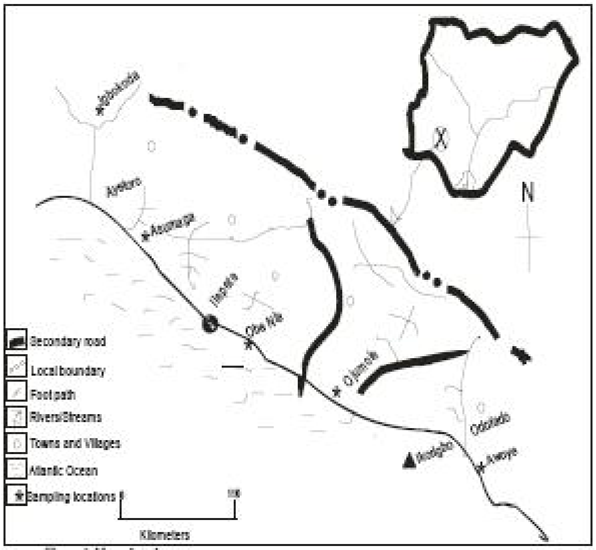

Figure 1: Map of study area

fairly minor and are unlikely to result in significant contamination.

Moreover, the determination of the contribution from petroleum and biogenic sources is possible only on a relative basis[16].Total petroleum hydrocarbon (TPH) in this context refers to the measurable amount of petroleum based hydrocarbon in the matrices (water and sediment) considered. Aromatic as a classe are common environmental contaminant at petroleum release sites with some, especially the monoaromatics having significant water solubility, and mobility within the environment. Some, such as the polycyclic aromatic hydrocarbons. (PAHs) can be persistent contaminants, particularly in sediment and soil matrices[22]. The PAHs has also been identified as a potential carcinogen[19].The analysis of TPH generated through oil spill into water and sediment is a serious challenge to the chemist. The phenomenon of weathering further complicates the problems associated with profiling of hydrocarbons at contaminated sites. Consequently, the process of sampling, storage, extraction, clean-up, separation and identification/quantification deserves careful monitoring.

This paper reports on the determination of TPH in water and sediment samples. The study became necessary because the disenchanted, depressed and abandoned people of Ilaje Community of Ondo state, Nigeria, by simple inspection, observation, and interviews, had constantly and painstakingly for some years lived in an uneasy relationship with economic, agricultural and medical uncertainty due to persistent negligence after oil spill incidence. Moreover, no published investigative data has been reported on the TPH within the area.

MATERIALS AND METHODS

Study area

Ondo State is made up of eighteen(18) Local Government councils and with a total land area of 14,793,189 square kilometers. The State lies between longitudes $4^{0}30^{11}$ and $6^{0}14^{11}$ East of the Greenwich meridian, $5^{0}45^{11}$ and $8^{0}15^{1}$ North of the Equator. This means that the state lies entirely in the tropics and is bounded in the South by the Atlantic Ocean. The research focuses upon the river within the Ilaje communities in Ese Odo Local Government Area of the state. The area remains the major if not only source of marine seafood like fish(of diverse species), crabs and periwinkles to the state and to a greater extent the nation. It is an area where dramatic and impactive oil spillages had and still occurring as a result of oil activities by chevron and shell petroleum companies. Salinity increases in the river at high tide, and decreases at low tide. The climatic condition of the area is humid with a temperature range of 26.2-27.6^{0}C.The area map of the study area is as shown in figure1.

Chemicals and apparatus

As part of the quality assurance protocol, all the chemicals used were of analytical reagent grade. The dichloromethane(DCM), hexane and tetrachloro methane(TCM) were all doubly distilled in all glass apparatus while the alumina, silica gel, sodium chloride and sodium sulphate were soxhlet extracted with n-hexane for 8hours each. All glassware used were thoroughly cleaned with hot detergents and rinsed with distilled water, then methanol and finally dried in the oven at 120^{0}C for about 6 hours.

Sampling and preservation

Five villages were examined in this study(TABLE 1) with one other location at Igbokoda as a reference. The exact positions of the sites were noted using the global positioning system(GPS), to record the actual global coordinates on the earth surface. Divers were used in most of the sampling locations for sediment col-

TABLE 1: Site identifications and coordinates

	Names of communities	pH (sediment)	Latitude (degree)	Longitude (degree)	Altitude (meters)
1	Ayetoro (town)	7.9-8.4	$06^0 06^1$ 12.4^{II}	$004^0 46^1$ 36.0^{II}	12
2	Asumaga	6.0-6.1	$06^0 03^1$ 20.9^{II}	$004^0 39^1$ 58.9^{II}	12
3	Obe Nla	6.9-7.0	$06^0 00^1$ 51.9^{II}	$004^0 52^1$ 40.2^{II}	16
4	Ojumole	6.6-7.4	$05^0 56^1$ 05.4^{II}	$004^0 53^1$ 10.2^{II}	13
5	Awoye	6.8-7.8	$05^0 55^1$ 01.2^{II}	$004^0 58^1$ 49.8^{II}	12
6	Igbokoda 1	6.8-7.2	$06^0 09^1$ 12.3^{II}	$004^0 44^1$ 32.4^{11}	10

TABLE 2: Recovery data of oil in sediment with gravimetric analysis

Amount of oil added mg/L	Amount recovered mg/L	% recovery
2.00	1.65	82.15
3.00	2.54	84.2
4.00	3.61	90.3
10.00	8.95	89.5
25.00	23.16	92.6
Mean±S.D		87.9±4.2

TABLE 3: Precision data of oil in sediment with gravimetric method

Amount of oil added mg/l	Amount recovered mg/l
5.00	4.55
5.00	4.61
5.00	4.67
5.00	4.59
5.00	4.63
Mean ± S.D	4.60± 0.45

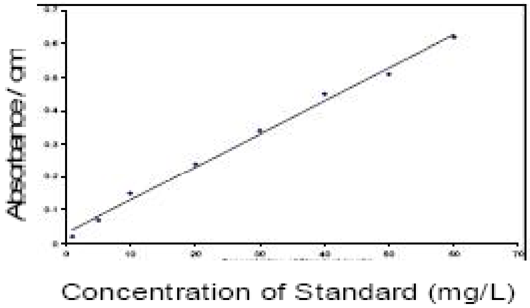

Figure 2: Calibration graph of the synthetic oil used

lections because of the depth of the ocean. Contamination of the field samples were avoided by using clean, appropriate samplers and containers.

In addition, samples of water collected in the Winchester glass bottles were acidified to pH 2 with concentrated hydrochloric acid immediately after collection. To each sample, about 15ml of DCM was added and the sample bottles finally closed with aluminium foil-lined cap. The sediment samples were also collected using APHA standard method[2]. Samples were collected and rapped inside aluminium foil after proper labeling. The samples were subsequently placed inside coolers containing ice-bag and transferred into the laboratory where they were preserved in the freezer prior to analysis.

Sediment determination by gravimetry and infrared methods

The gravimetric method was employed after a careful, satisfactory preliminary recovery and precision experiments were carried out given an average % recovery (TABLE 2) of 87.9±0.8 and average precision (TABLE 3) of 4.60±0.12.The sediment digestion method involves the extraction in a soxhlet extractor with DCM followed by saponification with 0.7M-KOH. The non-saponifiable lipids (containing the petroleum hydrocarbons) were partitioned with three, 25ml aliquot of n-hexane in glass separatory funnels. The volume was reduced on a water bath maintained at 30^0C. The final evaporation of the extract was carried out under nitrogen gas inside the fume cupboard. The total extractable organic matter(TOE) was determined by evaporating a known amount of the extract(0.1ml) and weighing the residue. The extractable organic matter is given as follows:

TOE.(μg/g)=Wt.of residue(μg)×vol.of extract(ml)/Amount evaporated(μl)×quantity of sample extracted (g)

The entire procedure above was repeated for the total petroleum hydrocarbons(TPH) determination using the IR except that TCM was used in place of DCM though with extra cares because of its carcinogenic effect. The wet weight: dry weight ratio was calculated following the standard method of moisture determination of weight lose after drying at 105^0C for 3hours.

To clean up the extract, a Pasteur pipette fitted with a solvent cleaned glass wool plug was first filled with 0.5g deactivated silica gel(5%w/w water). The column was rinsed thrice with 2ml hexane; the sample extract was then placed on top of the column. The petroleum components were totally eluted with 12ml of hexane in all. The extract was evaporated to dryness inside fume cupboard. The weight by difference gives the weight of the total hydrocarbons.

In separating the aliphatic from the aromatic, about 1.15g of deactivated neutral aluminium oxide(5% w/w water) was used. The elution was performed with hexane(for aliphatic) and hexane with DCM(for aromatic) on ratio basis. The different eluates were evapo-

TABLE 4: Total petroleum hydrocarbons in sediment and water by gravimetric methods

Locations	%mois ture	W.wt/ D.wt	TOE µg/g	TPH^b µg/g	TPH^a mg/l	THC µg/g
Ayetoro	23.2	2.14	426.2	116.9	0.18	116.9
Asumaga	17.4	1.82	227.2	135.7	0.27	135.7
Obe Nla	32.9	2.45	236.4	145.7	2.13	145.7
Ojumole	48.6	3.24	398.9	199.3	3.49	199.3
Awoye	43.1	2.63	307.4	183.8	3.26	183.8
Igbokoda	15.7	1.24	182.9	61.8	0.29	61.8

Mean± S.D , 140.5±49.3, 1.6±1.6; w.wt: wet weight; D.wt: dry weight, TOE: total organic extract; a: concentration in water; b: concentration in sediment

TABLE 5: Correlation results of TPH in sediment and water with depth

	TPH_{Sed}	TPH_{Wat}	Depth
Sediment	1	-0.903*	-0.889*
Water	0.902*	1	0.856*
Depth	0.864*	0.953**	1

*Significant at the 0.05 level (2-tiled). N=6 in each case; **Significant at the 0.01 level (2-tailed); Gravimetric and infrared pearson coefficients are shown above and below the diagonal line respectively; TPH_{sed} &TPH_{wat} : Total petroleum hydrocarbons in sediment and water respectively

rated to dryness and the weight of the vial accurately taken.

Extraction of water for IR and gravimetric

About 750ml aliquot of the water sample saturated with about 100g of NaCl was placed into 2L separatory funnel. The samples were extracted by shaking vigorously with three portions of 15ml TCM(for IR) and about 20ml of DCM(for gravimetry). The extracts were pooled together separately and washed thrice with three portions of 15ml of 0.1M Na_2CO_3 in a 100ml separating funnel and the organic layer separated and finally dried with anhydrous sodium sulphate. Infrared measurements were taken at 2930cm^{-1} and the corresponding concentrations obtained by comparing with the IR calibration graph(Figure 2) obtained with the three standard synthetic reference oil(n-Hexadecane, iso-octane and benzene in ratio 15:15:10 respectively). Working standards was prepared from the stock solution by serial dilution of the stock. For gravimetric determination, the procedures for cleaning and separation into aliphatic and aromatic for sediments were carefully followed. A blank sample was obtained by risen an empty bottle with TCM and carried through the procedure stated above in order to detect possible interferences form the glass container and the reagents used.

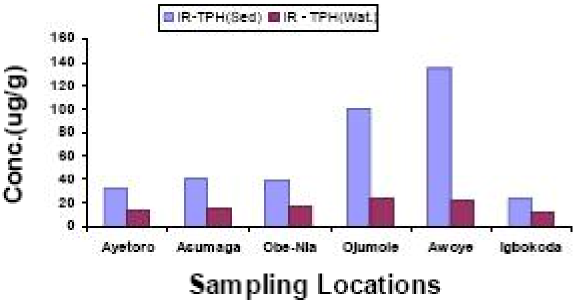

Figure 3 : Distribution of TPH by IR method in water and sediment across study area

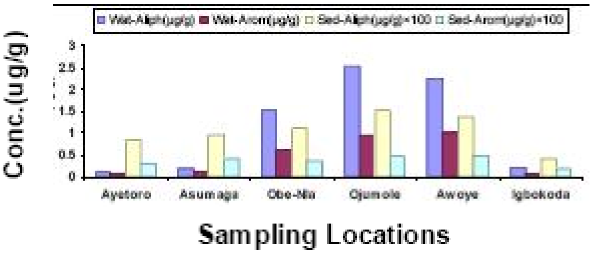

Figure 4: Distribution of aliphatic and aromatic by gravimetric method in water and sediment across study area (Alph-aliphatic, and arom-aromatic)

RESULTS AND DISCUSSION

Results

Levels of petroleum hydrocarbons(TPH) and other parameters in water and sediments by gravimetric method are as presented in TABLE 4.The concentrations (in µgg^{-1}) in the water as recorded by the gravimetric (IR results in brackets) methods varied between 0.11(12.0) to 2.55(24.0) while in sediment between 61.8(24.0) to 199.3(135.0) respectively. The sediment percentage moisture varied from 17.9%(Asumaga village) to 48.6%(Ojumole near Atlantic Ocean). The total organic extract (TOE) gave a range concentration from 227.2µgg-1(Asumaga village) to 426.2ugg-1 (Ayetoro community) on a dry weight basis with a mean value of 292.8µgg-1.

The bar plots in figure 3 and 4 shows the distribution of TPH and total aliphatic and the aromatic hydrocarbons in the water and sediment respectively by the two methods. The variations in the plots are expected considering the relative positions of the villages to the oil wells locations. For sediment, the aliphatic and aromatic hydrocarbons(in µgg^{-1} dry weight) are as follows, with the mean and coefficient of variation(CV) given after the range in parenthesis; 84.6-152.2 (115.4±27.8; CV(24%)) and 32.3-49.2 (40.9±7.1; CV(17%)) respectively while in water, the pattern was 0.11–2.55 (1.44±1.11, CV(77%)) and 0.07–1.01(0.17±0.05, CV (29%) respectively. The impact of depth cannot be underestimated in this report. The concentration of oil increased sharply from 38.5μgg^{-1}sediment at Obe-Nla village to 100.5μgg^{-1}sediment at Ojumole village with a 16-13 meters decrease in sediment depth. This is followed by a gradual increase in the amount of oil to 135.0μgg^{-1} sediment at Awoye village at a depth of 12meters. The results showed that TPH decreases with increasing depth(TABLE 5, r=-0.889).This is because shallow water are often laden with suspended solids providing favourable conditions for sedimentation. Similar pattern has been reported by Burns and Teal[4] and Walker et al.,[23]. The study equally revealed that for both gravimetric and IR methods, TPH in water displayed positive correlation with depth(r=0.856 and 0.953 respectively). However, for the sediment, a strong negative correlation exist in gravimetric TPH with water (r=-0.903) while for the IR, positive correlation (r=0.902) exist with water.

Discussions

Sediment has generally been identified as the main final accumulation site of water-borne constituents derived from both natural and anthropogenic sources. They act as both carrier and possible sources of chemical constituents in waters. Several authors have demonstrated that in an aquatic system the underlying sediments can act as an indicator of processes in the water column[17,18,1].

The data in TABLE 4 indicated appreciable level of total organic extract across the sampling locations including the reference point. The unusually high value obtained at Ayetoro(426.2μgg-1) was not unexpected. This is because the community is a popular and populated settlement. The sediment in this regard serves as reservoirs of wastes carried through run off into the water. The same can be said about Ojumole and Awoye villages, which are equally of appreciable settlements. The relative low level of TOE at the control site relative to the study area is perhaps indicative of some anthropogenic activities and inputs into the aquatic system.

The possible thought of the pathways and fate of this contaminant in the environment is of great concern to the scientific community, governmental agencies and non-governmental bodies[6,7,11]. In general, two main factors interact to govern the fate of hydrocarbons in sediment; the penetration of oil which is decided by the permeability of the sediment, often known as primary oil Retention[12]. Other factors such as temperature, moisture and organic material present equally play considerable roles in determining the fate of oil in sediments. The data in this report could have been due to the commutative effect over the years due to population.

The generally high levels in the THC from the study areas compared to the reference location are no doubt indicative of anthropogenic inputs. The major and persistent source of oil into these villages comes through oil spill due to oil activities within these locations. Oil spill usually comes through the Atlantic Ocean into these communities. The distribution of TPH in both matrix along the river course which showed a pattern of decreasing concentration up stream Ayetoro village appear to follow the hydrological dynamics as well as the proximity to the vicinity of discharge. The prevailing conditions of the Atlantic Ocean such as wave, turbulence and wind speed enhances the spreading and dispersion of oil into the various villages. The results of this is reflective in the levels of THP obtained in both sediments and water by both methods at Ojumole and Awoye; villages very close and downstream Atlantic Ocean.

Hydrocarbons, in the form of oil spill which are carried up stream during flood tides take several days to get flushed out of the river system. It is therefore possible that with the high residence time, these hydrocarbons will undergo processes such as spreading, evaporation, dispertion, emulsification, dissolution, oxidation, sedimentation and biodegradation that will facilitate their deposition on the sediment of the up stream limits. The spilled oil can produce a shading effect on the phytoplankton below and inhibit growth. The high concentration in the water may result into the presence of non-volatile, potentially environmentally persistent, water soluble aromatic fractions, with attendant, more severe effect on aquatic biota through adsorption[14]. With the recent commencement of oil exploration in some parts of these villages, unless proper steps are taken, hydrocarbon pollution may be inevitable in the nearest future.

Levels of aromatic hydrocarbons were found to be much lower than the aliphatic counterparts in this report. This is quite in agreement with reported data on petroleum hydrocarbons in sediments within Nigeria [7,22].Additionally, it is not unexpected. This is because for an average crude oil, the paraffinic portion has been reported to be usually grater than the aromatic portion[23].

It must however been emphasized that increased level of THC in sediment as reported in this study by IR technique may also be attributed to the method. The infrared method generally detects many hydrocarbons which may include fatty acids. These fatty acids are noted to be a very large component of non-petroleum hydrocarbons. Increased level especially at locations where oil installations were not located such as Ayetoro, Asumaga, Obe-Nla and Igbokoda(he reference location) also implicated human settlements as one of the main sources of hydrocarbon pollution of the aquatic environment. Possible sources of hydrocarbons into these locations include disposal of crank case oil and lubricants, accidental and intentional discharge of fuel oils and sewage[9,18].

Generally in sediment samples the average levels of TPH are higher than those obtained from the water by both methods. This is in agreement with literature that sediment are ‘sinks’ where chemicals tend to concentrate[10,8] and that sediment could represents a long deposition time of pollutants because organic compounds that have hydrophobic character can accumulate in the sediment and depending on the decomposition rate their concentration may be high. Polycyclic aromatic hydrocarbons(PAHs), because of their hydrophobic character show strong adsorption affinity to solid particles in aqueous matrices[13].

CONCLUSION

The levels of petroleum hydrocarbons in sediment and water from the five villages examined varied widely. This suggests that the matrices from the respective villages are contaminated at varying degrees. The results equally suggest anthropogenic input of oil into the environment, a conclusion justified by comparative assessment with the control site. The source of the oil was identified to be due to oil spillage, since oil operation remains the only noticeable industrial activity within the area. It further reiterates the fact that though oil companies may claimed to have cleaned up the ocean when oil spills, some levels, especially the heavier components might have sank into the bottom sediments

The level of TPH recorded in water in this report is of environmental concern. This is because the level present in water has a direct impact not only on the aquatic biota but also on other recreational activities such as swimming, fishing, boating and irrigation. The toxicological effect of oil in water cannot be overemphasized.

Though, there were no clear indication of oil on the water at the time of sampling, the levels recorded in this report probably resulted from dilution from sediment bed. The data also indicated that the petroleum hydrocarbons entering the area via oil spill are partially degraded, with the residual material accumulating in the sediment layers. It is therefore important to know what type of hydrocarbons are entering the water and are being deposited in the sediment, if the impact the petroleum hydrocarbons will have on the indigenous biological communities exposed to these locations is to be assessed. Moreover, subsequent studies should focus on the effects of the hydrocarbons on the micro organisms through the use of more sophisticated equipment such as gas chromatography mass spectrometry (GC-MS).

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