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EVALUATION OF TOTAL HYDROCARBON (THC) LEVELS IN OIL POLLUTED COASTAL AREAS OF SOUTH EASTERN NIGERIA

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ABSTRACT

Analysis of water, sediment and biota for total hydrocarbon (THC) levels five months after the Mobil oil spillage in the coastal areas of Cross River State, South Eastern Nigeria, was carried out. THC levels in water, sediment and biota samples were determined by colorimetric method after extraction with distilled n-hexane. Result showed elevated THC mean levels in water (149±81.11 mg/l), sediment (339.2 ± 245.7 mg/kg) and biota (198.9 ± 50.08 mg/kg), indicating a polluted environment. THC levels in water at all sampling locations were above 10mg/l being the maximum recommended limit of FEPA. In sediment and biota, THC values exceeding 100mg/kg and 25mg/kg, respectively, were observed, indicating that sediment and biota were highly impacted. THC levels in water correlated significantly (r = 0.632) with THC levels in the sediment (P = 0.05). Bioconcentration factors (BCFs) in 70% of the water samples were higher than unity. Although there was low BCF in about 70% of sediment samples, BCF in water significantly correlated (r = 0.689) with BCF in sediment (P = 0.05), indicating that the more the THC levels in the water column in relation to sediment, the more the biota were impacted.

KEY WORD: Oil spillage, Total hydrocarbon, Bioconcentration factor, Polluted environment, Coastal Areas.

INTRODUCTION

GESAMP (1982) defined marine pollution as the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of seawater and reduction of amenities. This implies that discharge of substances such as oil which have adverse effects on marine fauna and flora, the intertidal organisms and the fragile ecosystem would constitute marine pollution (Asuquo, 1994).

The impact of oil spillage on the environment is most often assessed from changes in the physical, chemical and biological components of the ecosystem. The impact on the coastline of oil spilled in open sea depends largely on the relative conditions of the shoreline; the more sheltered the shore, the longer oil remains (Clark *et al.*, 1997).

Among the most notable oil spills in the world are the Torry Canyon, off the coast of Cornwall, United Kingdom, in which 95,000 tons of oil were lost in 1967, and the Amoco Cadiz, off the coast of Britany with an estimated discharge of 220,000 tons in 1978. Similar spills and environmental pollution have trailed oil prospecting and production in Nigeria, particularly in the Niger Delta regions (Nwankwo and Ifeadi, 1988). For instance, on January 12, 1998, there was a reported pipe burst in Mobil Unlimited Idoho platform that resulted in the discharge of about 40,000 barrels of oil into the Atlantic

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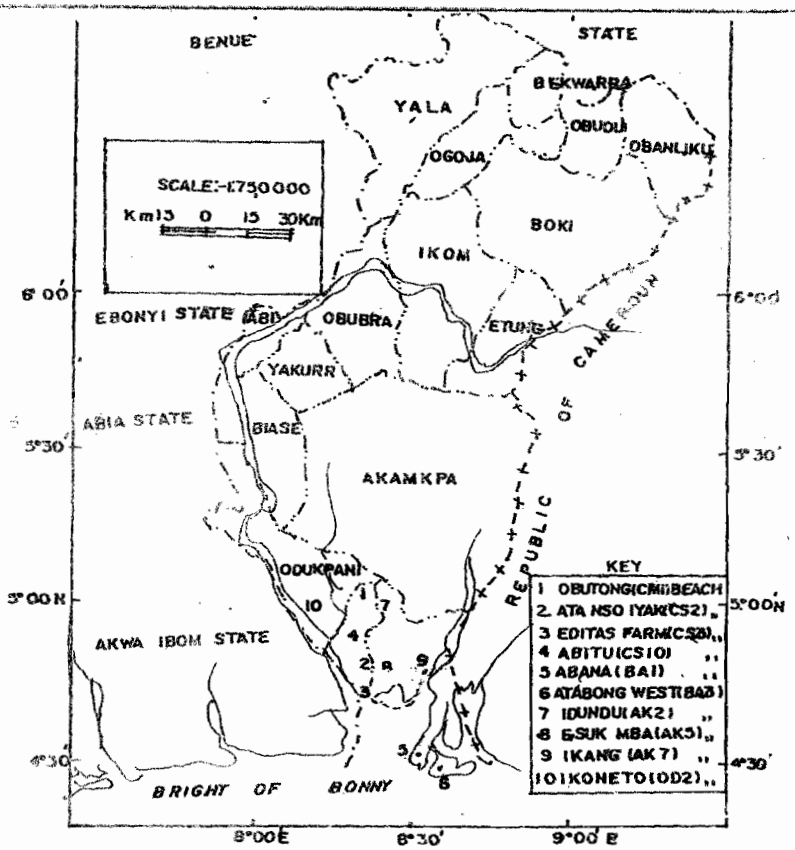

Fig.1: Map Of Cross River State Showing Sampling Locations

coastline of Nigeria, which is the subject for this study.

Hydrocarbons are known to be the major components of crude oil and petroleum products (Britton, 1984), and their presence in the environment above regulatory consent limits indicates pollution. Polyaromatic hydrocarbons (PAHs) such as benzo (a) pyrene, anthracene and anthrenes present in crude oils are carcinogenic (National Research Centre, 1985). Therefore, the ingestion of hydrocarbon-contaminated seafood exposes consumers to increased risk of human cancer and other associated physiological problems, as many marine and estuarine fish and shellfish accumulate PAHs from oil polluted water and sediment while feeding (GESAMP, 1993). Thus, it is important, from human and general biological considerations, to determine the levels of THC in water, sediment and the biota following an oil spill incident.

Therefore this study was undertaken as a post impact assessment of the Mobil Nigeria Unlimited oil spill from the 24" Idoho Qua Iboe Terminal (QIT) pipeline rupture of 12th January, 1998, on the coastal and estuarine areas of Cross River State, South Eastern Nigeria. The study was carried out five months after the spill, i.e., from May, 1998 to June, 1998. The aim of the study was to determine the levels of the THC in water, sediment and biota, and the level of bioaccumulation or bioconcentration of THC by direct uptake from water and sediment into the biota as a consequence of oil pollution.

MATERIALS AND METHODS

The study area description and physical

oceanography of the coastline

Figure 1 shows the map of Cross River State which is located in the southeastern part of Nigeria, occupying the lowland area, east of the Niger. Cross River State is traversed by the Cross River (from where it derives its name) with several creeks and tributaries. While the upper Cross River has a savanna vegetation, the lower part is covered by thick mangrove swamp forest and characterized by heavy rainfall (ca 620mm or more) during the year. The Cross River State offshore region is well established, being the most fertile fishing ground in Nigeria in view of its hydrological characteristics.

Regarding the physical oceanography of its coastline, Cross River State has a low-lying coastline ranging from fine sandy beach at Abana/Atabong (Figure 1) to mud (silty-clay) upstream at Ikang and Ikoneto. There are semi-diurnal tides (tidal height, 3m) from the sea that travel upstream to Itu in the neighouring Akwa Ibom State, a distance of about 80km. Thus there are ample chances for oil spills being washed back and retained inland upstream. Moreover, the Cross River State's coastal region is situated at the convergence where two principal ocean currents, northward rising Benguela current and eastward flowing Guinea current converge. These currents flow through areas where crude oil prospecting such as the Idoho platform is highly intensive. Therefore oil spilled from both regions of the ocean currents is transported by prevailing winds and waves into Cross River estuary, the adjoining mangrove swamps, tidal flats, creeks and tributaries. The low-lying shoreline is easily disposed to the adverse effects of oil spills.

Collection of samples

Water and sediment samples were collected in triplicates from ten sampling locations chosen randomly out of the fishing settlements of the coastal and estuarine areas (Figure 1). The sampling locations are shown in figure 1. Water samples which were to be analysed for total hydrocarbons, were collected at 10cm depth at low tide in 500ml brown glass bottles sealed with aluminium foil until extraction within five days of collection. Also, water samples which wee to be analysed for physico-chemical parameters, were collected in one litre polyethylene bottles. Superficial sediment samples were taken by the use of a hand-driven sediment auger. All samples were taken to the laboratory in labeled polyethylene bags stored in ice-cooled boxes at approximately 4°C for analysis within five days. This was to check physical, chemical and biological changes of the samples at the interval between sampling and analysis.

The biota samples consisted of five shrimps (*Desmoscaris trisponosa palaemonetes africanus*) collected from each sediment sampling location and taken in labeled polyethylene bags, stored at 4°C in ice-cooled boxes, and carried to the laboratory for tissue analysis.

Treatment and Analysis of Water and Sediment Samples

Water temperature, pH, electrical conductivity (EC) and salinity were measured *in-situ*. The water temperature was measured with Oxyguard Handy Mk 11 electronic meter with ± 1.0 units accuracy. The pH was measured with a WTW-pH-90 electronic meter with accuracy of ± 09 units. The electrical conductivity and salinity were recorded with WTW-LF-90 conductivity meter (at ± 1.0 µs/cm accuracy).

In the laboratory, extraction of THC in water was carried out with distilled n-hexane (Analar Grade BDH) and quantified by gravimetry ± 0.0001% (Rump and Krist, 1988, Ausquo 1999). The extract was subsequently concentrated by evaporation. THC (mgl^{-1}) contents were measured at 430nm using a DR/3000 HACH spectrophotometer.

Sediment samples were air-dried, ground with wooden roller and sorted through a 2mm mesh sieve. The pH of the sediment was determined in 1:2 soil/water ratio. The electrical conductivity (EC) of sediments was measured in 1:2 soil/water extract with WTW-LF-90 conductivity meter (at ± 1.0µs/cm accuracy). Particle size measurement was carried out by the hydrometer method of Bouyoucos (1951). This

TABLE 1: Mean levels of physico-chemical factors in water of oil-polluted coastal areas of Cross River State

Sampling Station	Temp. (°C)	pH	EC (µs/cm)	Salinity (ppt)
AK2	30.5 ± 0.8	5.5 ± 0.05	1133.1 ± 0.6	6.02 ± 0.01
AK5	31.2 ± 0.1	5.8 ± 0.10	1184.6 ± 0.3	7.20 ± 0.06
AK7	31.8 ± 0.3	8.6 ± 0.05	4625.4 ± 0.5	9.53 ± 0.25
BA1	30.1 ± 0.1	8.8 ± 0.11	7692.1 ± 0.2	18.0 ± 0.26
BA3	34.0 ± 0.1	8.9 ± 0.15	2923.1 ± 0.4	19.0 ± 0.15
CS2	30.8 ± 0.2	6.0 ± 0.25	2620.2 ± 0.1	4.7 ± 0.25
CS3	28.3 ± 0.2	5.1 ± 0.15	1125.0 ± 0.3	6.73 ± 0.16
CS10	34.7 ± 0.3	5.5 ± 0.30	6000.0 ± 0.1	3.9± 0.05
CM1	30.3 ± 0.5	7.2 ± 0.15	1530.1 ± 0.8	1.1 ± 0.01
OD2	30.4 ± 0.1	6.1 ± 0.12	1640.0 ± 0.2	0.93 ± 0.01
Range	28.3 – 34.7	5.1 – 8.9	1125 0 – 7692.1	0.93 – 19.0
Mean	31.2 ±1.9	6.8 ± 1.5	3047.4 ± 2311.6	7.7 ± 6.3

involved weighing about 100g of air-dried soil samples into Bouyoucos cup and adding 50ml of sodium-hexametaphosphate solution followed by stirring for 30minutes. The mixture was left overnight in a 250ml measuring cylinder followed by shaking by inverting the cylinder up and down. After 40 seconds the first reading which gave the percentages of clay and silt was recorded. The second reading was then taken after two hours as percentage sand.

THC in sediment was determined after extraction with redistilled n-hexane before measuring the total hydrocarbon content colorimetrically at 430nm using a DR/3000 HACH spectrophotometer.

Biota Treatment and Analysis

The cuticles of shrimps from each location were removed and 2-3 of the underlying muscle were homogenised in tissue grinder. The homogenase was digested for hydrocarbon extraction by refluxing with 5% KOH in methanol (ICES, 1991).

After refluxing for 2 – 3 hours (until complete digestion occurred), 20% NaCl solution in distilled water was added to the digest, cooled and repeatedly extracted with 50ml of n-hexane. All extracts (yellow in colour) were combined and concentrated on a rotary evaporator under reduced pressure (Fossato and Siviero, 1974). The Optical Density (OD) at 430nm was determined using DR/3000 HACH spectrophotometer. This gave the THC level in the biota.

In establishing the relationship between exposure and the amount of THC accumulated

from water or sediment by the biota, bioconcentration factor (BCF) was calculated relative to water and to sediment, according to McEldowney *et al.*, (1994):

Statistical Analysis

The association between THC levels in water and THC levels in sediment on the one hand. and between water and sediment BCF on the other, was determined, using the statistical method, correlation coefficient analysis (Bailey, 1981, Miller and Miller, 1984).

RESULTS

The results of physico-chemical analysis of water and sediment are presented in Tables 1 and 2. The pH of water ranged from alkaline 5.1 – 8.1 with a mean pH of 6.8 ± 1.5, while that of sediment ranged from 5.1 – 6.3 with a mean of 5.9 ± 0.35 (Table 1).

Electrical conductivity (EC) in water ranged from 1125.0 to 7692.1 µs/cm with a mean of 3047.4 ± 2311.6 µs/cm at a mean temperature of 31.2 ± 1.9°C. The EC values of sediment were less than 1.0 Ds/m in 60% of the sampling locations (Table 2).

The salinity of the water samples was relatively low, ranging from 0.93 to 19.0 parts per thousand (ppt). with a mean of 7.7 ± 6.3 ppt. The highest salinity levels were obtained at Abana beach, BA1 (18.0± 0.26 ppt) and Atabong West, BA3 (19.0± 0.15ppt).

The texture of the sediment samples varied from sand to silty clay with sand fraction greater than 70% in 60% of thee sampling locations

THC levels in water samples ranged from 92.28 to 331.8 mg/l with a mean level of 149 ± 81.11 mg/l, as shown in Table 3. Very high levels above 10mg/l were obtained at some locations. The highest levels being 263.2 and 331.8 mg/l were observed at Abana (BA1) and Atabong West (BA3) Beaches of Bakassi peninsula, respectively. In the sediment samples, THC levels varied from 112.4 to 884 mg/kg with a mean of 339.2 ± 245.7 mg/kg. The highest value of 884 mg/kg was observed at Atabong West (BA3).

TABLE 2: Mean levels of physico-chemical factors in sediment of oil-polluted coastal areas of Cross River State.

Sampling Station	PH	EC (DS/m)	BS (%)	Sand (%)	Silt (%)	Clay (%)	Texture
AK2	6,2 ± 0.01	0.279 ± 0.06	78	66.4	14	19	SL
AK5	5.9 ± 0.10	0.345 ± 0.01	75	74.4	6	13	SL
AK7	6.3 ± 0.02	1.474 ± 0.12	73	86.4	12	5.0	LS
BA1	6.12 ± 0.25	1.157 ± 0.01	52	92.4	6	3.0	SS
BA3	5.8 ± 0.01	1.421 ± 0.05	61	77.6	8.6	11.2	SL
CS2	6.1 ± 0.01	1.418 ± 0.01	79	70.4	4.6	9.0	SL
CS3	5.8 ± 0.10	0.678 ± 0.05	81	66.4	11.	19.0	SL
CS10	6.1 ± 0.20	0.619 ± 0.01	65	61.4	2.	19.0	SL
CM1	5.1 ± 0.11	0.128 ± 0.06	78	70.4	20.	9.0	SL
OD2	5.6 ± 0.01	0.091 ± 0.06	44	20.4	6	19.0	SL
Range	5.1 – 6.3	0.091 – 1.474	44 – 81	20.4–92.4	2-12	12.6 ±6.2	
Mean	5.9 ±0.35	0.76 ±0.56	68.6 ± 12.7	68.6 ±19.4	9.02±5.3	11.6±6.2	

Table 3: Mean levels of THC in biota, water and sediment from oil polluted coastal areas of Cross River State

Sampling Station	THC Level in Biota (mg/kg)	THC Level in Sediment (mg/kg)	THC Level in Water (mg/l)	BCF	
				Biota/ water	Biota/ Sed.
AK2	289.0 ± 0.12	112.4 ± 0.31	103.16 ± 0.25	2.8	2.6
AK5	126.3 ± 0.25	130.4 ± 0.14	111.88 ± 0.11	1.1	0.9
AK7	247.5 ± 0.15	377.2 ± 0.25	92.28 ± 0.12	2.7	0.6
BA1	195.7 ± 0.25	428.0 ± 0.41	263.2 ± 0.25	0.7	0.4
BA3	204.7 ± 0.25	884.0 ± 0.61	331.8 ± 0.17	0.6	0.2
CS2	161.75 ± 0.60	149.6 ± 0.45	100.84 ± 0.25	1.6	1.1
CS3	172.6 ± 0.71	260.0 ± 0.15	146.8 ± 0.13	1.2	0.7
CS10	41.5 ± 0.10	139.6 ± 0.14	111.48 ± 0.13	1.3	1.0
CM1	230.0 ± 0.31	584.0 ± 0.25	115.2 ± 0.43	2.0	0.4
OD2	220.0 ± 0.08	326.8 ± 0.10	114.7 ± 0.10	1.9	0.7
Range	126.3 – 289	112.4 – 884.0	92.28 – 331.8	0.6 – 2.8	0.4 – 2.6
Mean	198.9 ± 50.08	339.2 ± 245.7	149 ± 81.11	1.59 ± 0.8	0.86 ± 0.7

BCF = Bioconcentration factor, Sed. = Sediment.

$$\text{BCF in water} = \frac{C_{organ}}{C_w} \quad \text{and BCF in sediment} = \frac{C_{organ} \times K_a}{C_{sed} \times r}$$

Where BCF = bioconcentration or bioaccumulation factor, C_{organ} = THC level in biota, C_w = THC level in water, C_{sed} = THC level in sediment, K_a = the soil sorption or partition coefficient which is equal to the ratio of the THC concentration in soil (sediment) to that in water, and r = 2 for organics; and is the empirically determined ratio of suspended matter: sediment concentration (McEldowney *et al.*, 1994)

THC levels in the biota ranged from 126.3 – 289 mg/kg with a mean of 198.9 ± 50.08 mg/kg. Bioconcentration factors (BCF) for biota relative to water and sediment gave mean values of 1.59 ± 0.8 and 0.86 ± 0.7, respectively.

A correlation coefficient r for THC levels between water and sediment was 0.632 at P = 0.05, while the correlation coefficient r for BCF between biota in water and biota in sediment was 0.689 at p =0.05 (Table 3). In each case there was significant correlation.

DISCUSSION

There is paucity of baseline data on the physico-chemical properties of the Cross River State coastal areas where there is intensive oil prospecting in Nigeria. However, between April and July, 1998, Moni Pulo Nigeria Limited in partnership with Brass Exploration Nigeria Unlimited, published a draft report of an Environment Impact Assessment (EIA) study in respect of a proposed oil field development project (Moni Pulo Ltd., 1999), at sites/areas lying between latitudes 664041E to 668226E and 63865N and 72675N in the shallow waters of the Calabar River estuary, 30km offshore Nigeria.

In this study, pH and electrical conductivity of water ranged from 5.1 – 8.9 and 1125.0 –

7692.2 µs/cm, respectively. The levels of some physico-chemical parameters obtained by Moni Pulo Ltd., were comparable to those obtained in this study which, of course, started one month later. For instance, the pH and electrical conductivity from Moni Pulo Ltd. (1999) ranged from 7.88 – 8.35 and 17000 – 25000 µs/cm, respectively.

In this study, THC level in water was, on the average, very high (Table 3). In all the sampling locations, THC levels were above 10mg/l, which is the maximum recommended limit (FEPA, 1991). Although Moni Pulo Ltd. did not specifically report on Total Hydrocarbon (THC) levels, oil and grease exceeding 0.001 mg/l reported for the West and Central Atlantic (Portman *et al.*, 1989) was reported. In an earlier study of the physico-chemical characteristics of Calabar River estuary in 1994, Asuquo (1999) reported a mean THC level as high as 27.3 ± 3.9 mg/l implying anthropogenic additions. In this study, the sampling locations showed mean THC level of 149 ± 81.11 mg/l suggesting very high oil pollution. In sediment, high values exceeding 100mg/l were observed in some locations (Table 3), indicating that sediment was highly contaminated by petroleum (Chemical Society of Britain, 1975). A positive correlation between THC levels in water and sediment suggests that sedimentation is an important mechanism of removing the pollutant from the water.

Similarly, THC levels in the biota (Table 3) were abnormally high, sometimes higher in some sampling locations, than the 25mg/kg recommended maximum limit for organisms (GESAMP, 1993). The BCF above unity in water in most locations reflect the high concentration of THC in the biota except in Bakassi locations (BA1 and BA3). On the other hand, BCF in sediment was <1 in 70% of the locations, some of which still had high concentration of THC in biota. This way suggest that the high concentration of THC in biota in the latter is from the water rather than the sediment.

It is difficult to explain the low BCF obtained in some sample locations with high THC in water or sediment, except that certain physical, chemical and biological factors are known to affect the properties of sea oil slick following spillage, and hence their chances of accumulating is the biota (National Reseach Centre, 1985, Clark *et al.*, 1997). For example, the oil may be subjected to processes like oxidation, emulsification, dissolution, microbial degradation, etc., and these may alter the characteristics of the spilled oil (CONCAWE, 1981, Clark *et al.*, 1997). Since some of these factors may differ from one sampling location to another, THC levels in water, sediment and biota, and thus BCF, may also differ from location to location, and may even be very low in water where there is high sedimentation of the spilled oil, resulting in high THC level in the sediment

The nature of sediments, the particul[illegible] load of the water body, water velocity, temperature, salinity, depth, pH, etc., are known to affect the marine environment and accumulation of pollutants in the biota (Kaile, 1971, McEldowney *et al.*, 1974). McEldowney *et al.* (1994) have reported that even within single-species populations, individuals are not necessarily subject to the same level of exposure with age, size, physiological status and past history of exposure, coupled with the fact that dissolved, particulate, organic and inorganic complexes of a pollutant differ in their bioavailability. Bioavailability may be reduced or increased from the textural characteristics of the sediment (Onwurah, 2000). For instance, coarse sand and gravel retain oil at very low concentration due to "weak bonds" in the soil, which are easily washed away, while on the contrary, organic, loam or peat-based soils retain high concentration of oil, and this is more when clay is present (Onwurah, 2000). In this study, sediment samples with sandy loam and high percentage of clay, followed by sediments with loamy soil, yielded higher bioconcentration factor (BCF) than sandy soils (Tables 2 and 3). This may explain, why sampling locations BA1 and BA3 at the Bakassi Peninsula, yielded apparently low BCF.

CONCLUSION

The impact of Mobil UNLIMITED oil spill of 12 January, 1998 was enormous and significantly affected the flora and fauna of the Cross River Coastline. This could have been exacerbated by the unfavourable oceanography of the Cross River Coastline.

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