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Petroleum hydrocarbons and limiting nutrients in *Macura reptantia*, *Procambarus clarkii* and benthic sediment from Qua Iboe Estuary, Nigeria

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Abstract The levels of total petroleum hydrocarbons in two commonly consumed benthopelagic shellfishes, *Macura reptantia* and *Procambarus clarkii*, harvested from benthic sediment of Qua Iboe Estuary were determined using a gas chromatography with flame-ionization detector. Seventy-two (72) samples each of benthic sediment and the shellfishes were collected monthly between June 2003 and February 2004 covering the peak periods of the wet and dry seasons. Concentrations of hydrocarbons were highly variable and ranged between 5.00 and 232.00 μg/g dry weight of benthic sediment, 3.05 and 11.30 μg/g dry weight of *M. reptantia*, 1.62 and 9.00 μg/g dry weight of *P. clarkii*. Pearson's correlation analysis of total hydrocarbon concentrations in subtidal sediments with levels in the fauna species yielded positive significant ($P < 0.05$) correlations in *M. reptantia* ($r = 0.737$) and *P. clarkii* ($r = 0.924$). This is indicative of a long term and chronic accumulation of hydrocarbons in the estuarine ecosystem, reflecting the potential for exposure of the resident biota and the risk to human health.

Keywords Petroleum hydrocarbons · Shellfishes · Sediment · Estuary · Nigeria

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1 Introduction

Qua Iboe Estuary is a mesotidal palustrine ecotone of the parent river, Qua Iboe River (07°30′–08°20′W, 04°30′–05°30′N) located within the Niger Delta region of Nigeria. The estuary is characterized by fine sandy beaches fringed with tidal mudflats and mangrove swamps (Ekwere et al. 1992; Essien and Ubom 2003). It is a valuable recreational and ecological asset that drains a catchment area of about 7092 km^2 with a short course to the sea at the Bight of Bonny.

The socioeconomic development of the Niger Delta region of Nigeria has significantly impacted the Qua Iboe Estuary. This estuary serves as a major recipient of all petroleum and sewage wastes produced by multi-national oil companies located in the area, faeces and domestic refuse generated by the rapidly expanding settlements. It is also subjected to the effects and influences of ichthyocides used by local fishermen for fishing. Estuaries and coastal zones, particularly near industrial and high population density centres, are of special concern, as they could receive unprecedented exposure to chemical contamination due to source proximity. Toxic organics and inorganics, such as hydrocarbons, trace metals in aquatic environment have the potential of offering toxic effects on coastal and marine organisms, and can eventually be hazardous to human health (Klerks et al. 2004; da Silva et al. 2007)

Hydrocarbons especially polycyclic aromatic hydrocarbons (PAHs) arise from both anthropogenic and natural sources, although the former generally predominates (Law and Biscaya 1994). The majority of hydrocarbons in pelagic habitat could either be taken up by biota or sedimented, and deep-water depositional areas are generally regarded as sinks for hydrocarbons. Petroleum hydrocarbons have strong affinity for organic and particulate matter because of their physicochemical properties, and sediments can form primary depositories for them (Law and Klungsφyr 2000).

Several determinations of hydrocarbon load in environmental samples could be utilized for assessing possible impacts of crude oil spills and in routine monitoring programs (Klerks et al. 2004). Elevated concentrations of hydrocarbons have been reported for sediments from lacustrine and palustrine biotopes receiving significant anthropogenic inputs (Law and Andrulewicz 1983), and are not independent on sediment type (Prahl and Carpenter 1983), grain-size distribution, concentration and type of organic matter present, bioturbation and redox status of the sediments (Law and Klungsφyr 2000). The occurrence of enhanced levels of trace metals and hydrocarbons especially in sediments can be a good indication of anthropogenic sources of pollution (Davies et al. 1991; Binning and Baird 2001). Toxic trace metals and hydrocarbons can be bioconcentrated in seafoods, especially in shellfishes, such as mussels, oysters and cockles to levels in excess of public health standards, thus presenting a health hazard to those eating them (Clark et al. 1997; Magliette et al. 1995; Szefer et al. 1997; Eja et al. 2003; Han et al. 1994).

Assessment of hydrocarbon load of aquatic ecosystems using *Procambarus clarkii* or *Macura reptantia* is rare, and considering their consumption in some parts of Nigeria, especially by inhabitants of the coastal communities, investigation using them as organisms (bioindicators) of hydrocarbon pollution is warranted. *P. clarkii* and *M. reptantia* are benthopelagic organisms and they routinely filter large quantities of seawater in their feeding processes and may as a result harbor pathogenic bacteria, viruses and accumulate heavy metals, hydrocarbons and dioxins. They are opportunistic epibenthic faunae that feed entirely on organic matter found in mangrove mud, scavenging whatever food is available. As a result of their feeding habits, hydrocarbons are readily taken up through ingested sediment particles, food and absorption across biological membranes, and can bioaccumulate (Meador et al. 1995). Although, some fin- and shell-fishes have the ability of biotransforming high molecular weight hydrocarbons (HMWHs) via enzymatic activity to more polar, water-soluble metabolites, which can be excreted (Hellou 1996), crustaceans, however, possess reduced capacity for hydrocarbon metabolism (biotransformation). Hence, an accumulated level of hydrocarbons in these aquatic organisms is an accurate reflection of environmental exposure (Meador et al. 1995; Law and Klungsφyr 2000).

Oil-related operations are the most obvious industrial activities in the Niger Delta region of Nigeria. Recent studies by Amadi and Braide (2003) have shown that elevated levels of total hydrocarbon in seafoods from Bonny Estuary were attributed to oil related activities. Incidents of accidental spills or crude oil arising from separation of oil and water at terminals or platforms into the estuary have been reported (Antai 1993; Essien and Antai 2005; Asuquo 1991). Essien and Antai (2005) have reported the negative effect of oil spillage on beach microalgae in Nigeria. The effect was attributed mainly to adverse alterations in the nutritive salts (CO_3^{2-}, Cl^- and SO_4^{2-}) levels of the sandy beach soil of the Qua Iboe Estuary. Many of the epipsammic microalgae especially the cyanobacterial species of *Ahanizomenon flos-aquae, Lyngbya majusculata* and a centric diatom were exposed to contamination levels exceeding normal homeostasis and compensation. They lost their existence in the sandy beach. This indicates that the biodiversity and densities of biota in the estuary may be seriously impacted by oil pollution. In general, there is an increased restiveness in the study area and in the Niger Delta region, and daily clashes between youths of the communities where oil is exploited and government security agencies, multinational companies is a common occurrence owing to pollution of the coastal waters as a result of episodic oil spill occurrences, as well as associated offshore petroleum activities. Notably, the documentation of occurrences, concentrations and seasonal dynamics of petroleum hydrocarbons and other environmental contaminants in sediment, surface water and biota of these sensitive ecosystems are practically scanty or non-existence.

This research is therefore an attempt at providing an independent documentation of the petroleum hydrocarbon load in the mangrove sediment of the area as well as levels in two commonly consumed shellfishes found within the region. Incidentally, there was an oil spill that occurred in the course of this study, thereby proffering us the opportunity of juxtaposing the pre- and post-contamination levels of petroleum hydrocarbons accumulation in *M. reptantia*, *P. clarkii* and benthic sediments from the Qua Iboe Estuary, Nigeria.

2 Materials and methods

2.1 Sampling sites

Three sampling sites in the Qua Iboe Estuary ecosystem were selected. These were designated as IWKP (Iwo-Okpom), MKPN (Mkpanak) and UKPG (Upenekang). The IWKP sampling site is located in the estuarine region of the river and the others, above the tidal head of the freshwater reaches of the estuary (Fig. 1).

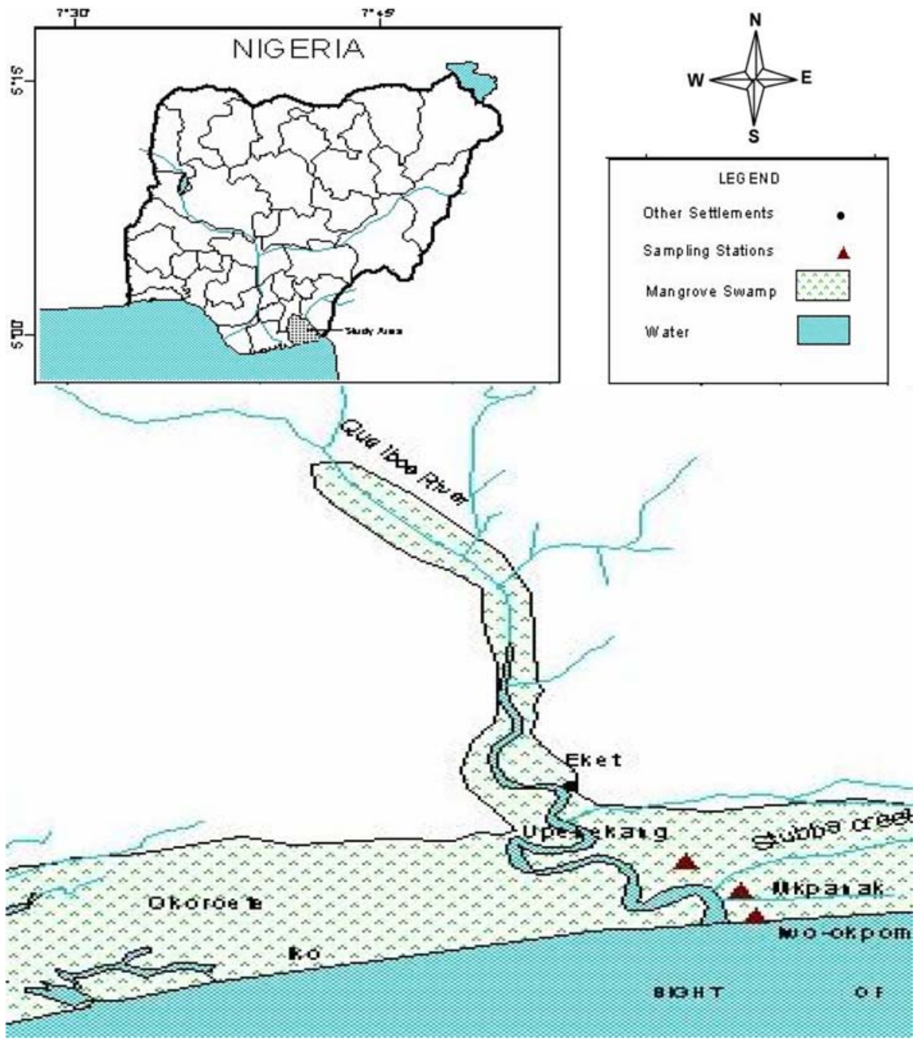

Fig. 1 Qua Iboe Estuary with the sampling locations at Iwo-Okpom, Mkpanak and Upenekang Inset: Map of Nigeria showing the study area

2.2 Sediment sampling and analysis

Sampling was carried out monthly between June 2003 and February 2004. The months of sampling were chosen to reflect the peaks of the rainy and dry seasons. Benthic sediments consisting of 72 samples were collected in the wet (June–September 2003) and dry (November 2003–February 2004) seasons, using a modified van veen (0.1 m^2) grab sampler (Radojevic and Bashkin 1999; Loring and Rantala 1992) at each of the designated sites. Sediments collected were stored in clean, well-labeled glass jars with PFTE-lined lid at about 4°C and transported to the laboratory for analysis.

In the laboratory, sediment samples were oven-dried in petri-dishes at 80°C for 2 days, ground into powder and sieved using a 2 mm mesh sieve to remove coarse substances (Radojevic and Bashkin 1999). Precisely, 50.0 g of each sediment samples was weighed and spiked with an internal standard (C_{32}-alkane) (FEPA 2001). These samples were serially extracted with 100 ml methyl isobutyl ketone (MIBK) (BDH Grade), and the extracts allowed to settle. Each extract was centrifuged for 5 min and decanted. The volumes of the supernatant were reduced to about 10 ml over a rotary evaporator maintained at 22°C. For the determination of total hydrocarbon content, a GC Detector was employed and the total peaks obtained were converted to weight using hydrocarbons standard calibration (FEPA 2001). Duplicates and method blanks were treated identically using the same reagents to test for the precision, accuracy and reagent purity used in the analytical procedures, respectively.

Samples meant for grain-size distribution were dry-sieved to separate the <63 μm sediment fraction using a standard sieve set and electric shaker (Abu-Hilal and Khordagui 1994).

2.3 Biota sampling and analysis

The two species of benthopelagic organisms *M. reptantia and P. clarkii* were randomly collected from the study sites (IWKP, MKPN and UKPG) by local fishermen. The shellfishes were also sampled monthly. The biospecimens collected were immediately stored in ice-packed coolers and taken to the laboratory for pretreatment and analysis. In the laboratory, samples were oven-dried at 110°C and later homogenized using a well-cleaned stainless blender (Bilos et al. 1998; Eja et al. 2003). The homogenized biospecimens were acidified with 5.0 ml 0.1 M H_2SO_4 and extracted using 25.0 ml diethyl ether. The total hydrocarbon content of each sample was determined as stated above.

2.4 Total organic carbon analysis

The organic matter (OM) expressed as percentage total organic carbon (TOC) was estimated using the acid dichromate and back titration method as described by Guadette et al. (1974).

2.5 Statistical analysis

The correlation analysis of data obtained was performed between THC levels in *M. reptantia*, *P. clarkii* and benthic sediment using Analyse-It + General 1.71 Statistical software, with level of significance maintained at 95% for each test.

3 Results and discussion

The physicochemical properties of the shellfishes habitat are presented in Table 1. The results indicate that pH levels of the benthic sediment were slightly alkalinic during the wet (7.27–7.93) and dry (7.15–7.47) seasons. Sediment samples collected during the wet and dry seasons exhibited variable percentages of silt, clay and sand. The values show that the benthic sediment was predominantly sandy (60.20–81.21%) with mean sand composition value of 65.45% during the wet season. The mean silt and clay compositions during the wet season were 9.08 and 24.50%, respectively. Similarly, samples collected during the dry season (November 2003–February 2004) exhibited variable percentages of particle size distribution. The sediment samples were characteristically more coarse than fine, implying that they were predominantly sandy with mean

Table 1 Physicochemical characteristics of the estuarine benthic sediments during the wet and dry seasons

Parameters	Jun.	Jul.	Aug.	Sep.	Mean	R.S.D
Wet season						
pH	7.75	7.27	7.93	7.71	7.67	3.66
Total organic carbon (%)	4.75	5.30	5.10	4.29	4.86	9.11
Carbonate (%)	71.15	55.66	53.61	51.61	58.00	15.39
Sulphate(SO_4^{2-}) mg kg^{-1}	23.06	19.06	17.76	18.39	19.57	12.20
Nitrate (NO_3^-) mg kg^{-1}	35.55	34.89	28.88	34.52	33.46	9.21
Chloride ($C1^-$) mg kg^{-1}	7.95	3.85	3.59	3.78	4.79	43.98
Ammonium (NH_4^+) mg kg^{-1}	43.55	14.14	10.28	13.85	20.46	75.76
Particle size distribution (%)						
Sand	81.21	60.23	60.14	60.20	65.45	16.06
Silt	5.54	10.18	10.38	10.21	9.08	25.99
Clay	13.02	26.23	29.24	29.49	24.50	31.81
Dry season	Nov.	Dec.	Jan.	Feb.	Mean	R.S.D
pH	7.23	7.15	7.47	7.19	7.26	1.98
Total organic carbon (%)	5.39	5.45	5.55	6.36	5.69	7.97
Carbonate (%)	49.19	54.56	55.85	56.08	53.92	5.98
Sulphate (SO_4^{2-}) mg kg^{-1}	17.13	18.71	19.09	19.70	18.66	5.88
Nitrate (NO_3^-) mg kg^{-1}	11.85	8.04	8.04	7.57	8.88	22.49
Chloride ($C1^-$) mg kg^{-1}	4.45	5.57	5.57	5.55	5.54	1.04
Ammonium (NH_4^+) mg kg^{-1}	9.29	10.29	10.88	9.98	10.26	7.55
Particle size distribution (%)						
Sand	69.95	69.42	69.42	67.88	69.17	1.29
Silt	9.53	9.67	9.67	9.72	9.65	0.85
Clay	20.52	20.91	20.91	22.07	21.10	3.18

sand composition value of 69.17%. The mean size distribution of clay and silt were 21.10 and 9.65%, respectively. These results were expected given the relatively fast tidal current that tends to winnow the finer grained sediments.

Organic matter in sediments constitutes the organic fraction derived from living organisms, decomposed and partly decomposed aquatic flora and fauna residues (Radojevic and Bashkin 1999). The TOC in the benthic sediments exhibited variable percentages dry weight organic matter content. Mean monthly TOC ranged from 4.29% dry weight to 5.30% dry weight during the wet season while a 5.39% dry weight and 6.39% dry weight range were obtained during the dry season months. The variability in TOC may be ascribed to the constant physical and chemical changes inherent in the organic fraction of the benthic sediment, as a result of decomposition and mineralization processes (Radojevic and Bashkin 1999).

Investigation of the nutritive salts (CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^- and NH_4^+) levels of the benthic sediments revealed interesting variable values of the respective salts. During the wet season, mean monthly determinations of each nutritive salt found were 20.46 mg NH_3–N kg^{-1}, 4.79 mg Cl^- kg^{-1}, 58.00 mg $C0_3^{2-}$ kg^{-1}, 19.57 mg SO_4^{2-} kg^{-1}, and 33.46 mg NO_3–N kg^{-1}. Similarly, the mean monthly values for the dry season were 10.26 mg NH_3-N kg^{-1}, 5.54 mg Cl^- kg^{-1}, 53.92 mg CO_3^{2-} kg^{-1}, 18.66 mg SO_4^{2-} kg^{-1} and 8.88 mg NO_3–N kg^{-1}. However, it is clear from the results that all the nutritive salts except chloride content in the benthic sediment samples were predominantly higher in the wet season than the dry season values. These high concentrations might have been attributed to the presence of raw sewage, contamination from waste dumps input of fertilizer run offs, domestic waste discharge and industrial effluents particularly those from petroleum facilities located in the study area. Variation in physicochemical characteristic of an ecosystem is known to affect growth of biota and their pollutants accumulation potential (Law and Klungsφyr 2000).

Intertidal and subtidal sediments in riverine, lacustrine and palustrine biotopes are a long-term repository of the residues of petroleum, released to the environment (Law and Klungsφyr 2000). Toxicants of pathogenic origin tend to adhere to fine-grained particulates and are deposited in sediments. The data in Table 2 show that the average monthly concentration of petroleum hydrocarbons in the sediments ranged from 14.33 ± 2.10 µg/g dry weight in June 2003 during the wet season to 208.41 ± 20.92 µg/g dry weight recorded in February 2004, during the dry season. These results show that the levels of THC in the benthic sediment samples were predominantly high in the dry season months especially between December 2003 (88.68 ± 7.15 µg/g dry weight) and February 2004 (208.41 ± 20.92 µg/g dry weight) (Fig. 2). The relatively enhanced levels of THC during these months were suggestive of proxy indication of crude oil pollution, which occurred in November 22, 2003. Previous incidences of hydrocarbon contamination in the Qua Iboe Estuary have been reported by Antia (1993), Asuquo (1991) and Itah and Essien (2005).

Table 2 Monthly mean concentration of total hydrocarbon content (µg/g dry wt.) in *M. reptantia*, *P. clarkii* and benthic sediment from Qua Iboe Estuary Mangrove Swamp

Months	Benthic sediment	*M. Reptantia*	*P. clarkii*
Jun-03	14.33 ± 2.10	4.02 ± 0.99	1.81 ± 0.19
Jun-03	15.66 ± 6.53	4.12 ± 0.89	2.00 ± 0.26
Aug-03	17.16 ± 0.29	3.39 ± 0.22	2.59 ± 0.15
Sept-03	15.26 ± 6.55	4.37 ± 0.06	2.57 ± 0.13
Nov-03	37.05 ± 14.49	4.85 ± 1.35	3.05 ± 0.05
De-03	88.68 ± 7.15	9.77 ± 1.79	6.52 ± 0.81
Jan-04	196.15 ± 15.09	9.48 ± 0.79	7.43 ± 0.96
Feb-04	208.41 + 20.92	7.14 + 0.34	7.98 + 0.94

(Mean ± SD) µg/g dry wt

The monthly mean levels of THC in *M. reptantia* ranged between 3.39 ± 0.22 µg/g dry weight and 9.77 ± 1.79 µg/g dry weight, while *P. clarkii* recorded THC mean levels between 7.98 ± 0.94 µg/g dry weight and 1.81 ± 0.19 µg/g dry weight (Table 2). The THC levels recorded in the biospecimens for the wet season were remarkably low, compared to dry season values, which were relatively high. This may have been attributed to the oil spill that occurred during the dry season, which might have been ingested through sediment and consumption of smaller benthopelagic organisms. Higher concentrations of hydrocarbon content in the biospecimens were found in *M. reptantia* than in *P. clarkii*. This suggests that *M. reptantia* possesses reduced capacity for hydrocarbon metabolism than *P. clarkii* (Meador et al. 1995), thus it has a higher THC accumulating potential than *P. clarkii*. (Table 3).

Statistical analysis of the results revealed that the levels of THC in benthic sediments of the Qua Iboe Estuary correlated very significantly with THC levels in *M. reptantia* ($r = 0.74$, $p < 0.05$) (Fig. 3a) and *P. clarkii* ($r = 0.92$, $p < 0.05$) (Fig. 3b). It is therefore suggestive that the observed levels of THC in the biospecimens investigated are governed by the THC levels of the benthic sediments. Thus, the presence of hydrocarbon contaminants in sediment is a record of short-and long-term, chronic accumulation of such contaminants, and can thus reflect the potential for exposure of the resident biota. This implies that the concentration of petroleum hydrocarbons in benthic sediments of the estuary bears a direct influence on the biota. Therefore, increase in anthropogenic inputs of petroleum hydrocarbons into the estuary may invariably cause enhanced levels of THC in the sediment leading to elevated levels of THC in resident biota of the ecosystem.

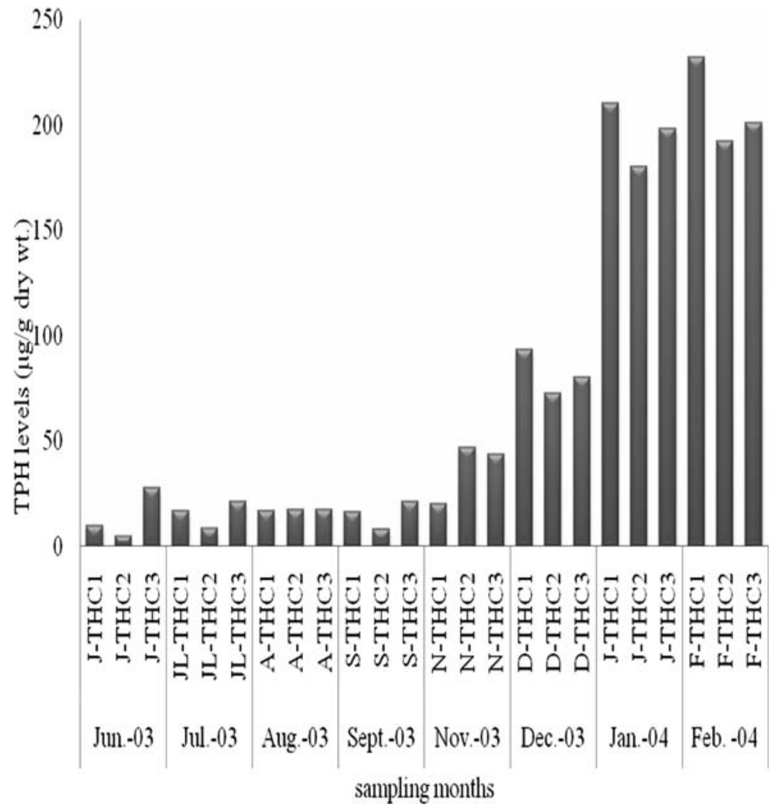

Fig. 2 Monthly variation in total hydrocarbon content (µg/g dry wt.) in benthic sediment samples from Qua Iboe Estuary

Table 3 A comparison of reported THC (µg/g dry wt.) in sediment of the Qua Iboe Estuary and other aquatic ecosystems of the world

Location	THC (µg/g dry wt.)	Source
Qua Iboe Estaury (Nigeria)	18.01–210.23	Present study
Scotian shelf (Canada)	1.0–94.0	Keizer et al. (1978)
Patos Lagoon Estuary (Brazil)	39–11,780	Zanardi et al. (1999)
Falmouth Bay (UK)	48.0	Law (1981)
Victoria Harbour (China)	1,200–1,400	Yang et al. (1991)
Liverpool Bay (UK)	29.0	Law (1981)
Narragansett Bay	50.0–120.0	Farrington and Quinn (1973)
Nearshore UAE (USA)	<0.4–161	Abu-Hilal and Khordagui (1994)
Coast of Oman	0.8–19.0	Burns (1982)
Kuwait	502–154	Literathy et al. (1992)
Guanabara Bay (Brazil)	77–7,751	da Silva et al. (2007)
Baffin Bay (Canada)	1.25–33.75	Levy (1979)
Sao Sebastiao (Brazil)	20–200	Medeiros and Bicego (2004)
Tampa Bay, Florida (USA)	200–4,300	Sherblom et al. (1995)
Todos os Santos Bay (Brazil)	8–4,163	Venturini and Tommasi (2004)

Moreover, the THC levels in benthic sediments also correlated significantly ($r = 0.47$, $p < 0.05$) (Fig. 3c) with total organic carbon of the sediments in the estuary system. This positive relation indicates that petroleum hydrocarbons have strong affinity for organic matter and the later could act as primary sinks for the hydrocarbons (Law and Klungsφyr 2000).

4 Conclusion

Pollution challenges posed by episodic crude oil spillages into the littoral aquatic ecosystems of the Niger Delta region of Nigeria appear to be on the increase. Major oil spill incidents in the region represent a significant source of hydrocarbons and other ecological polluters. The

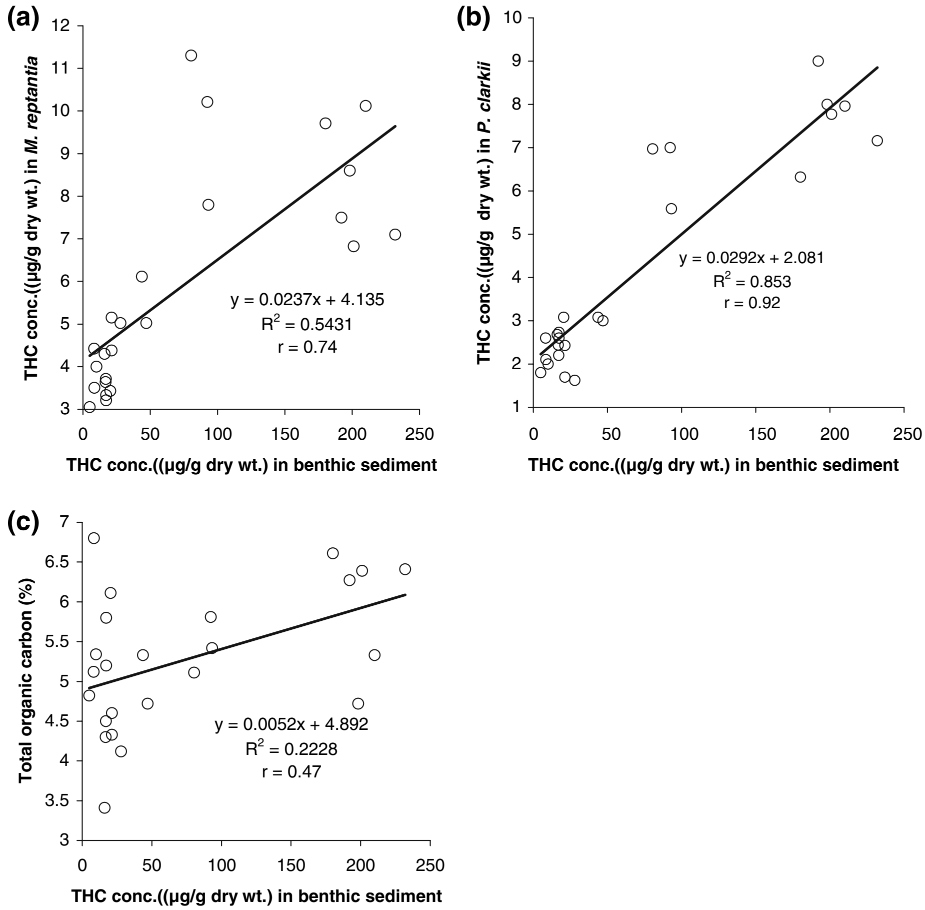

Fig. 3 (a–c) Relations between total hydrocarbon content in benthic sediment and *M. reptantia*, *P. clarkii*, and total organic carbon

present study presents a baseline distribution assessment of total hydrocarbons in *P. clarkii*, *M. reptantia* and benthic sediment of the Qua Iboe Estuary, Nigeria. From the study, benthic sediments have been shown to be the primary depositories of the residues of petroleum released into aquatic ecosystems. Petroleum hydrocarbons have shown strong affinity for sediment—resident organic matter and tend to adhere to fine-grained particulates. Thus the sediment form a major sinks for organic matter. The presence and detection of petroleum hydrocarbons in benthic sediments in the Qua Iboe Estuary is an indication of short- and long-term, chronic accumulation of hydrocarbons, thus reflecting the potential for exposure of the resident biota, and the risk to human health. However, owing to the bioaccumulative potential of *P. clarkii* and *M. reptantia* with respect to hydrocarbon load of the ecosystem and subsequent ''biotransfer'' to human consumers, as well as impacting the composition and diversity of infaunal communities, periodical monitoring and assessment of sediment quality and tissues of these organisms in the coastal waters of the Niger Delta is advocated.

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