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Hydrocarbon Distribution in Sediments from the Southeast Coastal Region of Bangladesh

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Abstract: The research deals with the study of the nature of hydrocarbons occurring at the coastal region of Bangladesh to assess the extent of hydrocarbon pollution in the marine environment. Accordingly, five sediment samples were analyzed for extraction of soluble organic matter, fractionation of extract into aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds, molecular composition analysis of aromatic and aliphatic hydrocarbons' fractions and integration of results for the study of the nature and origin of hydrocarbons in the marine environment. Hydrocarbons present in the sediment samples might have originated from three main sources: a) biosynthesis of aquatic organisms and/or diagenesis of alteration of bacteria, zooplankton, phytoplankton and higher plant derived organic matters; b) migration of immature oil seep from deeper sources and c) direct incorporation of fossil hydrocarbons discharged into the sea water by various sea-going vessels. The total hydrocarbons in five sediment samples from the study area ranged from 71.73 to 359.21 ppm. Recommendations are made to take appropriate measure for the protection of the marine environment from further pollution.

Key words: Aliphatic hydrocarbon, aromatic hydrocarbon, polar compounds, bay of Bengal, oil spill.

Introduction

The input of oil from anthropogenic sources into the marine environment has decreased during the past decade. This is largely due to measures required by international conventions on the prevention of marine pollution by oil from shipping. Estimates in 1981 showed that 3.2 million tones of oil per year enter marine environments from oil sources; the estimate for 1990 is 2.35 million tones (GESMAP Reports and Studies No. 50). There is increasing evidence that the input of land-based sources has so far been underestimated; enclosed and semi-enclosed coastal areas receive far higher amounts than have been indicated in global estimates.

Petroleum and petroleum hydrocarbons in the marine environment are remarkably stable except the light fraction of that evaporates. Hydrocarbons dissolved in the water column eventually destroyed by bacterial action, though it should be pointed out that the most toxic compounds are also the most refractory ones.

The so called 'tainting' of fish and shell fish by oil spills has been recognized for many years. But it has recently been realized that oil passes through the intestinal barrier and is incorporated and stabilized in the lipid pool of the organisms (Blumer *et al.*, 1970). It has been widely assumed that fish and shellfish 'tainted' by oil will be again fit for human consumption after 2 weeks to several months.

In Bangladesh, this type of pollution caused by petroleum hydrocarbon is taking place and its far-reaching effects are falling in the environment. Only one study has been conducted so far on the hydrocarbon pollution in the water column of the Bay of Bengal, although such study is very important for better utilization and proper preservation of the fish and fishery products for the greater well being of the country. Hydrocarbon varied from 87.48 to 251 µg/L in the water samples from the Karnafuly estuary, harbour area and coastal water (Mahmood, 1993). Nearly, 1200 ships and 40-50 oil tankers in Chittagong Port and about 600 ships in Mongla Port are handled annually (Majumder and Uddin, 1992). According to the Department of Shipping of Bangladesh about 2500 registered power-driven river crafts and numerous unregistered power-driven boats including oil tankers play in the coastal waters of Bangladesh. Besides, the number of power-driven trawlers and boats engaged in fishing in the Bay of Bengal is about 3000 (Majumder and Uddin, 1992). Ship scrapping operations in Chittagong and Mongla are also responsible for oil pollution. Accidental oil spillage from oil tanker was also reported in the Bay of Bengal within Bangladesh territorial waters in 1989. An oil tanker, M. T. Fillott spilled out about 2247 tones crude oil near Kutubdia Channel. Another oil spillage from the tanker T. T. Energy was reported in Khulna region, which caused an oil slick

over an area about 40 miles along the Sundarbans mangrove forest. This hydrocarbon may bio-accumulate thus causing harmful effect. This realization leads to the present study of distribution of hydrocarbon in sediments in the south coastal region of the Bay of Bengal, Bangladesh. The substrata in the Upper Tertiary sequence of the hills of Chittagong region comprise mainly loose sand stone, silt stone and shale beds, which are predominantly plane bedded (all through cross bedding and ripple marks are present in some areas). These hills constitute a part of the southern extension of the Himalayan Mountain system, and are believed to have taken their present form sometime in the late Pleistocene. The main objective of the present study is to assess the distribution of aliphatic hydrocarbon, aromatic hydrocarbon and polar compounds in sediments in the southeast coastal region of Bangladesh.

Materials and Methods

Description of the sampling area: Sampling stations were selected between the Karnafuly river estuary and the Kutubdia Channel of Bangladesh (Fig. 1). The Karnafuly river originates from the higher Arakan-Yoma and cut across the main ranges of the hill tracts and enters Chittagong from the north-east corners of hill tracts at 23°50'N and 92°47'E and falls into the Bay of Bengal at 22°14'N and 91°47'E leaving the Chittagong city on its right bank after traveling a course of 121 miles. The Kutubdia Channel is situated in between 21°48'N and 21°54'N and 91°52'E and 91°55'E.

Table 1: Vessels travel in the sampling region (Chittagong port area) over the last decades.

Year	Number of vessels travel during the year			Total
	Foreign vessel	Bangladesh vessel	Oil tanker	
1985	872	138	83	1093
1986	857	131	72	1060
1987	833	107	81	1021
1988	918	171	109	1198
1989	938	179	97	1214
1990	1051	133	113	1297
1991	775	94	67	936
1992	910	90	76	1076
1993	920	126	101	1147
1994	926	119	99	1144

Five stations were selected, each at 3 miles interval between the Karnafuly River estuary and the Kutubdia Channel. The sediment samples were taken from June 14, 1998 to June 17, 1998. Vessel travels in the sampling region (Chittagong port area) over the last decades are shown in Table 1 and oil and oily substances

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Table 2: Oil and oily substances discharged from the Chittagong area.

Oil and oil emulsion source	Estimated amount of discharge
Chronic spoilage of crude oil during transportation operations in Chittagong port	6000 metric tons / year *
Ballast waters	Not known
Bilge waters	2.4 million gallons/ year
Leakage loss of fuel from mechanized vessels, dry docks, fish harbours, etc.	Not known
Oil emulsion from workshops	Not known
Crude oil residue, process oil and wash water from refinery	5000 metric tons/year
Refuse oil from ship breaking activities near Fauzdarhat	400kg/year

* Assuming 0.5% spillage during crude oil transfer at Chittagong Port.

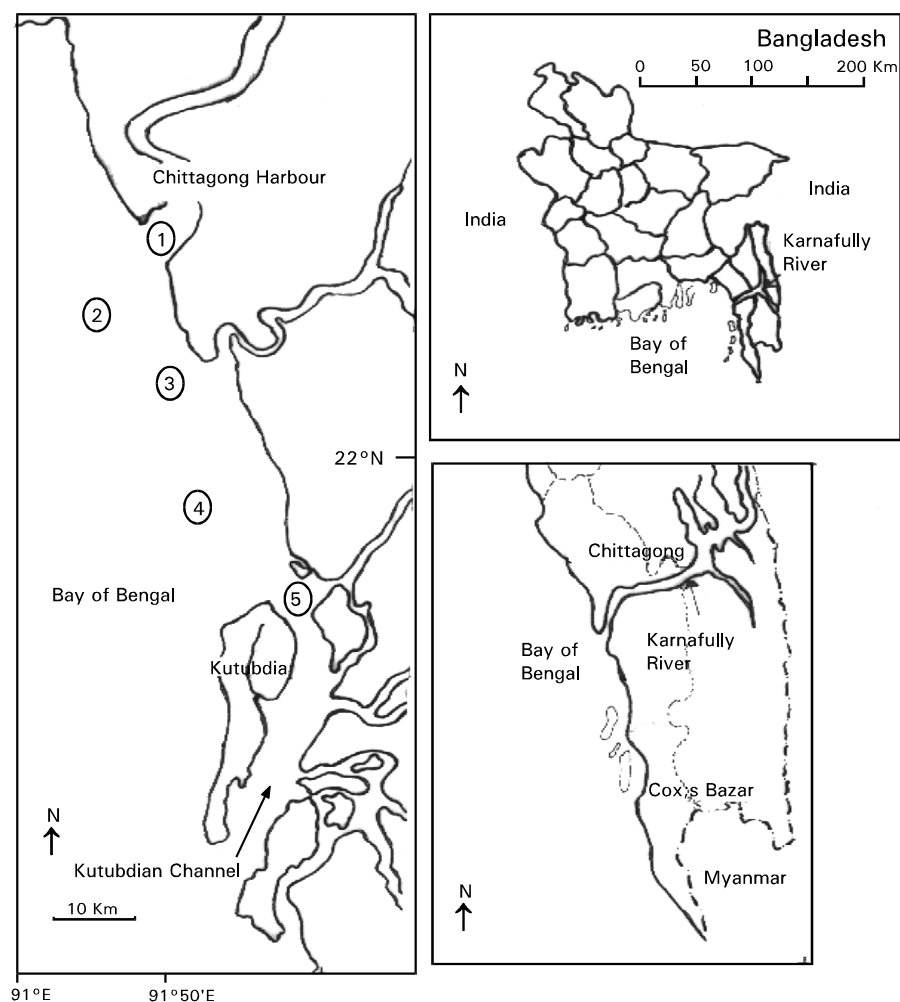


Fig. 1: Approximate geographic location of the sampling area (station wise)

discharged from the Chittagong area are shown in Table 2.

Adsorption chromatography clean-up: A slurry method of layering the supports into the column is used. The column is partially filled with hexane. Eight gm of silica gel are mixed with hexane in a small beaker. With the aid of a glass funnel and stirring rod, the support is poured into the column. Several rinses of hexane will be required to get it all the support into the column. The column is gently tapped to form a homogeneous bed of silica. Finally, 1 gm of Na_2SO_4 is layered on top of the adsorbent bed. The solvent is drained to the top of the bed and further hexane rinses used to ensure the column is cleaned.

One ml of the lipid extract is pipetted into the column and is drained into the adsorbent bed. The column is then carefully eluted

by adding solvents and draining them into the adsorbent bed before adding further aliquot. The saturated hydrocarbons are eluted with a total of 20 ml of hexane. Unsaturated and aromatic hydrocarbons are eluted with 20 ml of 20% MeCl_2 in hexane (v/v) followed by 20 ml of 50% MeCl_2 in hexane (v/v).

Blanks: For the UVF analysis samples are dissolved in hexane. The complete procedural blank value is acceptable for sample correction if its fluorescence reading does not exceed twice the fluorescence reading of the unconcentrated hexane.

Preparation of standards: Standard solutions were prepared from refined or crude oils. Oil standards are prepared in much the same way as the chrysene standards. The density of the oil in gm ml^{-1}

is determined by weighing a measured volume of oil. Then enough oil is transferred to the 100 ml volumetric stock flask to yield a concentration of approximately 0.5 mg oil per ml of hexane. This stock solution is then used to prepare the standard dilutions in the linear calibration range. This is usually in the 0 to 10 gm ml⁻¹ ranges for most oils, but will vary depending on the aromatic content of the oil. Some oils, such as Kuwait crude, are difficult to dissolve and will require much less concentrated primary stock solution than the average values.

When reporting results in terms of oil units, an intercomparison ratio between the fluorescence intensity of the oil and that of chrysene should be calculated according to the formula according to the Reference Methods for Marine Pollution Studies. No. 20. (UNEP/IOC/IAEA., 1992).

$$R = \frac{\text{Fluorescence intensity of chrysene standard}}{\text{Fluorescence intensity of oil standard}} \times \frac{\text{Concentration of oil standard} * \text{g ml}^{-1}}{\text{Concentration of chrysene standard in} * \text{g ml}^{-1}}$$

Spectra: The excitation monochromator is set 23 nm below the emission wavelength and the two monochromators scanned synchronously (Start with excitation at 237 nm and emission at 260 nm). It has set the excitation monochromator slits (or band pass widths) at 10 nm and emission monochromator slits at 3 to 5 depending on instrument sensitivity. Set scan speed at 60 nm min⁻¹ and recorded speed at 3 or 6 cm min⁻¹. Record synchronous spectra between 260 nm and about 525 nm emission. Inspection of these spectra indicated that diesel oil contains mostly substituted naphthalene and no signal due to the higher aromatic. Crude oils show maxima in higher wave length regions. Microbial degradation of the side chains on the aromatic rings will shift emission maxima to shorter wavelengths (as 15 nm).

When the oil in samples has been matched as closely as possible to the available standards, then this standard can be used for constructing the calibration curve. First determine the optimum wavelengths for the quantitative measurement. This is achieved by fixing the emission wavelength and obtaining an excitation spectrum. The wave length of optimum excitation was then chosen and fixed and an emission spectrum was obtained. The most sensitive wave lengths would then be those empirically determined from the excitation and emission spectra. For average crude oils these optima are at 310 nm excitation and 360 nm emission and diesel oil optima are at 280 nm/327 nm.

Extraction: Three samples of fish and mussel were mixed to make a common sample for each station and then 5 samples for fish and 5 samples for mussel were extracted by following the method of 35500 or NSTP procedures described by Krahn (1986). In this method, the fish and mussel were mixed with Na₂SO₄ and spooned into 250 ml Teflon jars. Dichloromethane and methanol were added in a ratio of 5:1. Sonicated for about three minutes at settings appropriate to yield efficient extraction. Alternatively, the extracts were shaken for several hours on a mechanical shaker. After extraction, decanted the solvent into a clean flask. The extraction was repeated for two more times, combining all extracts into the flask. The extracts were filtered and derived through the glass wool and Na₂SO₄. The extract volume was reduced. Bitumen's were de-asphalted using a modification method.

Column chromatography: Liquid chromatographic method uses a column containing silica gel supporting a 2-3 cm layer of alumina. Both absorbents were pre-extracted in soxhlet apparatus using extraction solvent for 24 hours and dried at 120°C for several hours. The silica was stored in a clean beaker in the oven at 150°C until use. Clean dry Chromatographic column (I.D. = 0.75 cm. Effective length= 35 cm was slurry packed with alumina at the top and silica gel at the bottom (1:5). Silica was slurry packed

using light petroleum. The alumina was gravity packed during packing, the column was vibrated in order to remove air which could ruin the separation. When packed, the column was washed with about two column volumes of light petroleum before use.

The pre-weight pyrolyzates were transferred from a 3.5 ml vial to the column. Twenty five ml petroleum ether (40 – 60°C) was then added above this. A 250 ml round bottom flask was placed below the column and the top of the column was opened. The petroleum ether (40-60°C) was run through the column and the elute was collected in a clean 250 ml round flask. As the last of the petroleum ether (40-60°C) was running through the column, it was topped up with the next solvent DCM/MeOH (95:5). Twenty five ml of the solvent mixture was allowed to run. At last the process was repeated with Twenty five ml of MeOH. The column was eluted successively with solvent of increasing polarity: petroleum ether (40-60°C), DCM/MeOH (95:5) and MeOH. The basic principle is that the more polar the organic compound the more strongly it is absorbed to column packing. Petroleum ether, a polar solvent, elute only the nonpolar saturated hydrocarbons which are weakly absorbed. DCM/MeOH (95:5) elute the aromatic and some sulphur compounds MeOH removes most of the polar (NSO) compounds.

Each of the fractions separated were collected in pre-weighed 3.5 ml vial and evaporated to dryness to determine their absolute quantity.

Saturated hydrocarbon analysis: Hewlett Packard 5890A Gas Chromatography equipped with FID, split less and on column injector, 19405A sampler/event control module and 3392A Integrator was used. Air and hydrogen for FID were provided from CHROMPACK 50050 Air Generator and PACKARD Y525 Hydrogen Generator respectively. A cylinder containing 99.996% pure Helium was used as the source for carrier gas. Separation was done on a 25 m long HP-1 fused silica capillary column, which was coated inside with cross-linked methyl silicon gum.

A blank run was made under the same operating conditions and kept stored in the memory of the instrument. Then, it was automatically subtracted from the actual sample run to obtain a corrected base line. The arrival time of various compounds and amount of each component is measured by a flame ionization detector (FID) coupled to a microprocessor based data handling equipment which plots a graph of the run called "Gas Chromatograph" integrates the detector signal for each component and produces a report (Table 3).

Results and Discussion

Physico-chemical characteristics: Physico-chemical characteristics of the 5 sediment samples are shown in Table 4. Total Organic Carbon (TOC) varied from 0.96 to 1.02 wt% and may be defined as organically fair. All of these sediments were slight to moderately carbonaceous as indicated by their 10.11 to 10.62 % carbonate content. Total amount of silt and clay were greater than 66 %, which indicates that might have acted as the good host for rock preservation of organic matter. pH values ranged from 8.93 to 9.15 and electrical conductivity (EC) values ranged from 4.8 x 10⁻³ to 5.6 x 10⁻³ µmhos/cm.

Grain sizes and textural classes: The changes in the sediment textures in the area from the Karnafully estuary to Kutubdia Channel area (Table 4) were possibly due to corresponding changes in morphology (erosion and accretion), oceanographic conditions (changes in wave and wind characters), presence of shell material and also the effect of small seasonal stream.

Extraction and fractionation: The total amount of extract (Table 5) in the 5 samples ranged from 997 to 1633ppm of the sediment. These are consistent with their TOC contents from 0.96 to 1.02% and indicate their moderate concentration in organic matter. The amount of total hydrocarbons (aliphatic and aromatic) in these samples varies from only 3.33 % to as high as 29.16 % of the total extract; remaining 70.84 to 96.67 % are NSO compounds. These data clearly indicate that the organic matter at the sea

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Table 3: Hydro-meteorological parameters of the sampling area during February, 1999 (South Coastal Region of the Bay of Bengal, Bangladesh).

Station no.	Mean discharge (m/s)	Sample Code	Annual mean of MWL (m/PWD)	MTL (m)		Mean evaporation (mm)
				High	Low	
1	Karnafully 1.25	KRE	10.972	2.820	-0.100	120
2	Matamuhury 7.67	MRE	11.041	1.998	-0.901	120
3	Sangu 18.00	SRE	10.912	1.100	-1.300	ND
4	Halda 8.64	HRE	12.200	2.693	-2.262	ND
5	Bak Khali 1.86	BRE	10.980	2.089	-1.082	701

(MWL= Mean Water Level, MTL= Mean Tide Level, ND= Not Detected) (KRE = Karnafully River Estuary, MRE = Matamuhury River Estuary, SRE = Sangu River Estuary, HRE = Halda River Estuary, BRE = Bak Khali River Estuary, Bangladesh.)

Table 4: Physico-chemical characteristics of the collected sediment samples

Sample Code	Lithology			TOC (wt. %)	Carbonate (wt. %)	EC (μ hos/cm)	pH
	Sand % (2.0-0.02mm)	Silt % (0.02 - 0.002mm)	Clay % ($<$ 0.002mm)				
KRE	2	45	53	1.01	10.56	5.5×10^{-3}	9.10
MRE	28	39	33	0.98	10.31	5.1×10^{-3}	9.02
SRE	6	42	52	1.02	10.62	5.6×10^{-3}	9.15
HRE	5	48	47	1.01	10.29	5.0×10^{-3}	9.00
BRE	34	59	7	0.96	10.11	4.8×10^{-3}	8.93

(TOC= Total Organic Carbon, EC= Electric Conductivity)

Table 5: Distribution of Hydrocarbon in the South-east Coast of Bangladesh.

Sample Code	Sample weight (g)	Amount of extract (ppm)	Group Composition of Extract ppm(wt/wt) of Sediment			
			Aliphatic	Aromatic	NSO Compounds	
					Resin	Asphaltene
KRE	96.19	1633.23	135.92	53.02	68.61	2013.72
MRE	43.71	1395.79	134.88	260.83	73.22	1047.90
SRE	65.54	997.19	136.03	135.79	64.08	591.96
HRE	52.65	1187.17	134.37	77.88	117.77	852.87
BRE	66.62	1157.37	132.84	100.57	58.54	773.08

(KRE = Karnafully River Estuary, MRE = Matamuhury River Estuary, SRE = Sangu River Estuary, HRE = Halda River Estuary, BRE = Bak Khali River Estuary, Bangladesh.) (NSO = Non Stable Organic)

bottom sediments of the south coastal region of Bangladesh is immature and may correspond to the early diagenesis stage of organic evolution (Hunt, 1979; Waples *et al.*, 1974). Among the NSO compounds, amount of asphaltene (63.92 to 93.48 %) were much higher than the resins (3.19 to 10.33 %) and offer a positive evidence for their early generation. This was not unexpected from such recent sediments.

Hydrocarbon distribution patterns and their significance: Aliphatic hydrocarbons containing 11 to 20 carbon atoms constitute the first mode and the most abundant group. Their distribution is uniform showing a steady decrease from nC_{11} and onwards. Hydrocarbons containing 21 to 26 carbon atoms constitute a second mode. In this group no even to odd predominance is observed. The rest of the hydrocarbons containing 27 to 35 carbon atoms constitute the third mode. Odd carbon numbered alkanes were very predominant compared with even carbon numbered alkanes among the individual members of this group. These variations in the hydrocarbon distribution patterns among the three distinct modes were typical and indicate their generation from a mixed source of at least three different origins. Contributions from bacteria, zooplankton, phytoplankton higher plants and/or fossil hydrocarbons from deeper sources may have produced these characteristic fingerprints. Volkman *et al.* (1992) proposed that > 100 ppm of total hydrocarbons is one of the six indicators for recognizing petroleum contaminants in sediments and this value may be as high as few parts per thousand (i.e., > 100 ppm). The total hydrocarbon concentration in the 5 sediment samples from the south coastal region of Bangladesh varies from station 1, with only 71.73ppm total hydrocarbon, indicating that this sediment is totally unpolluted, to stations 3, 4 and 5 having 169.06 to 270.05ppm hydrocarbons. According to their molecular distribution patterns, it is believed that these sediments were also unpolluted except from some migrated fossil hydrocarbons of deeper sources. Sediments from station 2 contain 359.21 ppm of

hydrocarbons. It seems higher for an unpolluted sample.

Thus aliphatic and aromatic hydrocarbon distribution patterns in the six different sediment samples from the coastal region of the Bay of Bengal, Bangladesh may indicate their origin from mixed sources: a) biogenic production from and/or diagenetic alteration of bacteria, zooplankton, phytoplankton and other higher plant organic, b) migration of immature to marginally mature fossil hydrocarbons (seep) from deeper sources, and, c) incorporation of minor amounts of hydrocarbon pollutants from the discharges of sea-going vessels, tankers, etc.

Statistical analysis: From the statistical analysis it is observed that the relation between aliphatic/aromatic hydrocarbon values in the sediment extracts and the physico-chemical parameters of the sediment samples were highly correlated, where the correlation values ranged from 0.815 to 0.998 and the significant values ranged from 0.05 to 0.10. The findings of the present investigation are in well agreement with the concluding comment of Leahy and Colwell (1990). The positive correlation between hydrocarbon extracts and the physico-chemical properties of the sediment might be due to diffusion character of the sediment (Joint Group of Experts on the Scientific Aspects of Marine Pollution, 1993).

A study commissioned by Maersk Olie og Gas A/S (COWIconsult, 1986) showed that place exposed to sediment containing a number of oil-based mud were tainted. Thomas *et al.* (1984) also stated that mostly clay rich mud adsorb hydrocarbons quickly. The present findings agree with the comment of the above authors, where hydrocarbon extract values were positively correlated (0.853 – 0.862) with the clay content of the sediment and negatively correlated with the sand and silt contents of the sediment.

In conclusion aquatic sediments from the south coastal region of the Bay of Bengal, Bangladesh belongs to three main lithological classes: silty clay, clay loam and silty loam. These sediments may be defined as organically fair. Their TOC and total extract content

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ranged from 0.96 to 1.02% and 981 to 1633ppm per dry wt. of the sediments. The extracts are composed of 3.33 to 29.16% hydrocarbons and 70.84 to 96.67% polar compounds. These values are indicative of their generation from various organic matters, deposited therein, at immature stage of organic evolution. Extent of hydrocarbon pollution may, still, is limited and within the adaptable range of organisms living therein. It may be speculated that if the rate of this contamination persists for an indefinite time, this limit may be exceeded in the near future. Recommendations are made to take appropriate measures for protection of the marine environment from further pollution.

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