

Seasonal variation of aliphatic hydrocarbons in sediments of Hooghly estuary, north-east coast of India

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Distributions of hydrocarbons in the estuarine and coastal sediments are influenced by the relative contribution of autochthonous and allochthonous organic matter to the sediments (Parker 1969). Most of the micro-organisms (autochthonous origin) and higher plants (terrigenous origin) contain greater concentration of odd carbon number n-alkanes than even carbon number in the range C₁₄ - C₂₂ and C₂₂ - C₃₅ respectively (Eglinton *et al.* 1962; Han & Calvin 1969; Simoneit 1977). However, recently strong predominance of even to odd carbon number n-alkanes in the C₁₆ to C₂₄ range (Grimalt & Albaiges 1987; Nishimura & Baker 1986) and low predominance in C₂₄ to C₃₈ range (Dembicki *et al.* 1976) have been reported to be from micro-organisms (yeast, fungi and bacteria). Previous study in this estuarine system reveals that micro-organisms in the sedimentary environment during postmonsoon (February) are presumed to be responsible for the predominance of even carbon number n-alkanes (Ghosh *et al.* 1990). Present communication deals with the seasonal impact of the distribution of n-alkanes in the sediments of Hooghly estuary.

Sediment samples were collected monthly during November 1984 to October 1985 from three stations in plastic container. To understand the seasonal variations in chemical components, the calendar year is divided into three seasons. The premonsoon (March to June) is the dry season with occasionally high temperatures. The monsoon (south-west) season (July to October) receives heavy rainfall and the postmonsoon (November to

February) comprised partly of winter season, has lower temperature and lesser precipitation. Sediment samples collected during four months of a season were mixed together and the composite sample has been represented as seasonal sample.

Air dried sediments were refluxed for two hours with methanolic KOH (Farrington & Quinn 1971), filtered and transferred quantitatively using methanol. The separated organic layer was evaporated and dried over anhydrous Na₂SO₄ and passed through Cu powder to remove elemental sulphur (Blumer 1957). The organic layer was saponified and the nonsaponifiable organic component was extracted with peroxide free diethyl ether. Hydrocarbons were separated from nonsaponifiable fraction by TLC (Ghosh & Beal 1979) using plates coated with silica gel G (E. Merck). Solvent system of TLC consisted of light petroleum ether (60° - 80° C), diethyl ether and acetic acid (50:50:1). The hydrocarbon fractions were scraped using chloroform and the purity was checked by repeating TLC before subjecting to gas chromatography.

The gas chromatographic instrument (Pye Unicam, model 104) was equipped with dual glass column and dual flame ionisation detector (FID). The columns used was 3% OV-17 (1.8 m x 3 mm internal diameter). Initial temperature of the oven was 220°C for 4 minutes and programmed at a rate of 6°C per minute. Detector and injection temperatures were 320° and 260°C respectively. Nitrogen (60 ml minute⁻¹) was carrier gas. Identification of hydrocarbons was done by comparing retention

Table 1. Distribution of some lipids fractions in the sediments.

Components	Premonsoon			Monsoon			Postmonsoon		
	Station 1	Station 2	Station 3	Station 1	Station 2	Station 3	Station 1	Station 2	Station 3
Non sap (ppm)	250	450	240	250	510	330	310	680	310
Hydrocarbons (ppm)	220	230	140	100	310	170	110	120	170
HC/Org. C X 100	19.23	5.63	7.73	6.09	5.95	6.94	7.69	2.27	8.01
Org. C (mg g ⁻¹)	1.14	4.08	1.81	1.64	5.21	2.45	1.43	5.29	2.12
CPI of (C ₁₆ - C ₂₂)	0.16	0.10	0.20	0.93	0.38	0.78	0.20	0.26	0.30
CPI of (C ₂₂ - C ₃₆)	0.54	0.45	0.44	0.99	0.99	0.90	0.53	0.76	0.74

times of the peaks of the samples with those of standards. Quantification was done by measuring area under each peak in the chromatogram by triangulation method. The percentage of a particular component was determined by:

$$\% \text{ Component} = \frac{100 \times \text{peak area of the component}}{\text{Total area under all peaks}}$$

Carbon preference index (CPI) values were calculated using following formula (Cooper & Bray 1963).

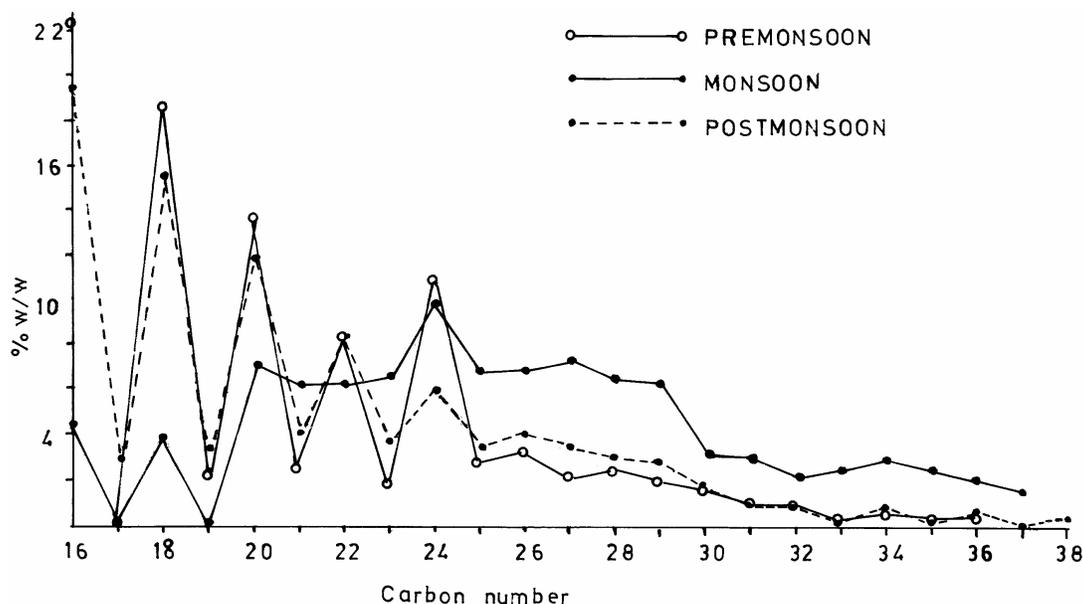
$$\text{CPI of (C}_{22} - \text{C}_{37}) = 1/2 [^{35}\text{C}_{23}/^{36}\text{C}_{24} + ^{35}\text{C}_{23}/^{34}\text{C}_{22}]$$

$$\text{CPI of (C}_{16} - \text{C}_{22}) = 1/2 [^{21}\text{C}_{17}/^{22}\text{C}_{18} + ^{21}\text{C}_{17}/^{20}\text{C}_{16}]$$

The non-saponifiable fraction of lipid varied from 250 to 680 ppm of dry weight of the sediments, corresponding to 9.78 to 21.92% of organic carbon, with comparatively higher values at station 2 during all seasons (Table 1). The percentage

of aliphatic hydrocarbons in the non-saponifiable portion of organic matter were from 17.64 to 88.0%. Total n-alkane content ranged between 100 and 310 ppm of dry weight with maximum at station 2 and minimum at station 1 during monsoon season. The percentage of n-alkanes to organic carbon varied in the range from 2.27 to 19.23.

Seasonal variations of aliphatic hydrocarbons are given in Fig. 1. It is observed that the chain lengths of different constituents of n-alkanes ranged from C₁₈ to C₃₈ carbon number. In premonsoon and post monsoon seasons, the distribution patterns of n-alkanes were similar with C₁₆ (16.6-22.8% w/w) component as major constituents in all the sediments. The C₁₈ (14.0-20.05% w/w) and C₂₀ (10.5-13.9% w/w) n-alkanes were the second abundant hydrocarbons and the concentrations of the

**Fig. 1.** Seasonal distribution of n-alkanes at station 2.

other hydrocarbons are gradually decreased with increase in carbon number.

An interesting observation is in the monsoon season where specific majority of n-alkane components is almost lost and the concentration of lower molecular weight even carbon hydrocarbons in the range C₁₆ - C₂₀ decrease while the odd carbon number components (C₁₇ - C₃₇) increase to a larger extent in all sediments. Therefore, it seems that during this season, the rate of autochthonous contribution of even carbon number n-alkanes by the presumed microbial population (Ghosh *et al.* 1990) in the sediments is considerably reduced. The intense water circulation at the time of high fresh water discharge and the churning of the bottom sedimentary phase, perhaps resists the microbial activity at the sediment-water interface. Moreover, this peculiar type of n-alkane distribution extends the possibility of their sources other than autochthonous. This assumption can be quantified with the help of carbon preference index (CPI) values and odd to even carbon ratio of the n-alkanes.

High CPI values in sediments have been suggested as due to n-alkanes inputs from non-petroleum sources (Clark & Blumer 1967) especially land derived biogenic hydrocarbons dominated by C₂₇, C₂₉ and C₃₁ components (Eglinton *et al.* 1962). The CPI values of C₁₆ - C₂₂ n-alkanes were lower in premonsoon and postmonsoon seasons (Table 1). However, in monsoon, they were relatively higher. Similar trend in CPI in the range of higher alkanes (C₂₂ - C₃₆) was also ob-

served, but they were usually always higher (0.90-0.99) in monsoon. Thus the increase in CPI values and the distribution patterns of n-alkanes during this seasons are supposed to the addition of odd carbon number homologues to the sediments from the sources which seem to be absent in other seasons. Besides, the odd to even n-alkanes ratios gradually increase in values with the increase in carbon number, reach maximum to C₂₉/C₂₈ and then again tend to decrease (Table 2). During monsoon, this definite order is not maintained. They were generally high and tend to reach to almost unity at C₂₇ and C₂₉ n-alkanes. The n-alkane distribution in sediments in which there are maxima at C₂₉ or less frequently around C₂₉ to C₃₁, has been suggested as typical of higher plant waxes (Simoneit 1977; Ajayi & Poxton 1987). Therefore, it would not be unreasonable to contend that the higher molecular weight odd carbon number n-alkanes (C₂₄ - C₃₈) originating from higher plants has an obvious impact in the sediments. But during premonsoon and postmonsoon seasons, the microbial activity producing relatively higher concentration of even carbon number n-alkanes, may supersede odd carbon n-alkanes. The large amount of terrigenous organic matter associated with fresh water runoff during monsoon months from multiple sources in existing and adjacent eco-systems may be responsible for the occurrence of such type of n-alkanes distribution in the sedimentary environments of this estuarine systems.

Table 2. Seasonal variation in the ratios of odd carbon number to even carbon number hydrocarbon in the sediments at station 1-3.

Components	Premonsoon			Monsoon			Postmonsoon		
	Station 1	Station 2	Station 3	Station 1	Station 2	Station 3	Station 1	Station 2	Station 3
C ₁₇ /C ₁₆	0.16	-	0.14	-	-	0.78	0.14	0.16	0.25
C ₁₉ /C ₁₈	0.22	0.12	0.17	0.88	-	0.84	0.17	0.22	0.22
C ₂₁ /C ₂₀	0.27	0.18	0.22	0.89	0.86	0.83	0.23	0.36	0.38
C ₂₃ /C ₂₂	0.33	0.23	0.23	0.88	1.06	0.89	0.33	0.46	0.51
C ₂₅ /C ₂₄	0.44	0.26	0.25	0.80	0.67	0.84	0.45	0.59	0.56
C ₂₇ /C ₂₆	0.54	0.68	0.58	0.98	1.07	0.86	0.51	0.89	0.77
C ₂₉ /C ₂₈	0.64	0.80	0.71	1.00	0.99	0.81	0.68	0.94	0.97
C ₃₁ /C ₃₀	-	0.61	0.59	0.76	0.97	0.54	0.50	0.53	0.61
C ₃₃ /C ₃₂	-	0.36	0.30	0.87	1.18	0.59	0.46	0.40	0.27
C ₃₅ /C ₃₄	-	0.38	0.25	0.69	0.90	0.63	0.20	0.13	0.25
C ₃₇ /C ₃₆	-	-	0.50	0.40	0.77	0.69	-	0.14	0.11

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