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Article

Influence of organic matter type on the distribution of tri-aromatic hydrocarbons in Tertiary mudstones in the Sylhet Basin, Bangladesh

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Abstract

The distribution and behavior of tri-aromatic hydrocarbons (especially alkylphenanthrenes) have been investigated in twenty-four mudstones from the Tertiary succession in the Sylhet Basin of Bangladesh. Phenanthrene (P) and methylphenanthrenes (MP) were abundant in most samples, whereas anthracene and methylanthracene (MA) were detected only in some samples. Abundances of the 1,7-dimethylphenanthrene (DMP) isomer are significant relative to other DMP isomers. Overall correlation between the methylphenanthrene index 3 (MPI 3) and T_{max} (426 – 449 °C) is poor in this basin. Abundances of MA, pimanthrene (1,7-DMP) and 1-MP are relatively high in the lower part of the succession. Higher plant organic matter is abundant in the lower part of the succession (middle Eocene to early Miocene), whereas planktonic organic matter is relatively abundant in the middle and upper parts (middle Miocene to Pleistocene). These alkyl-isomers thus originated from terrigenous sources. High phenanthrene/alkylphenanthrene ratios in the mudstones can be related to oxic environmental conditions. Based on detailed aromatic distribution patterns and their isomer ratios, we conclude that the compositions of P, MP and DMP isomers in the Sylhet Basin were probably controlled by organic matter sources, rather than by thermal maturity in the early stage of the oil window.

1. Introduction

The distributions of phenanthrene and alkylphenanthrenes in ancient sediments and crude oils are of special interest in many organic geochemical studies because these distributions change with increasing maturity (Radke et al., 1982a, 1982b; Radke and Welte, 1983; Angelin et al., 1983; Radke, 1987; Garrigues et al., 1988; Sampei et al., 1994; Budzinski et al., 1995; Kaneko and Takeda, 1995). This indicator covers a wide range of organic maturity, from the beginning of the oil window to the condensate stage. Indices for these compounds such as methylphenanthrene ratio (MPR), methylphenanthrene index (MPI), methylphenanthrene distribution fraction (MPDF) and dimethylphenanthrene ratio (DMPR) were developed in the 1980's (Radke et al., 1982a, 1982b; Radke and Welte, 1983; Angelin et al., 1983). Generally, these aromatic indices have linear correlations with vitrinite reflectance (R_o) over a wide range of maturity, in contrast to aliphatic biomarker indices such as steranes and hopanes, which correlate only at maturities below the oil window. The quantitative relationships between the phenanthrene homologue indices and R_o differ between individual sedimentary basins, due to differences in kerogen type in the sediments. However, the influences of the differing types of organic matter on the distribution of phenanthrene homologues are not well known, because

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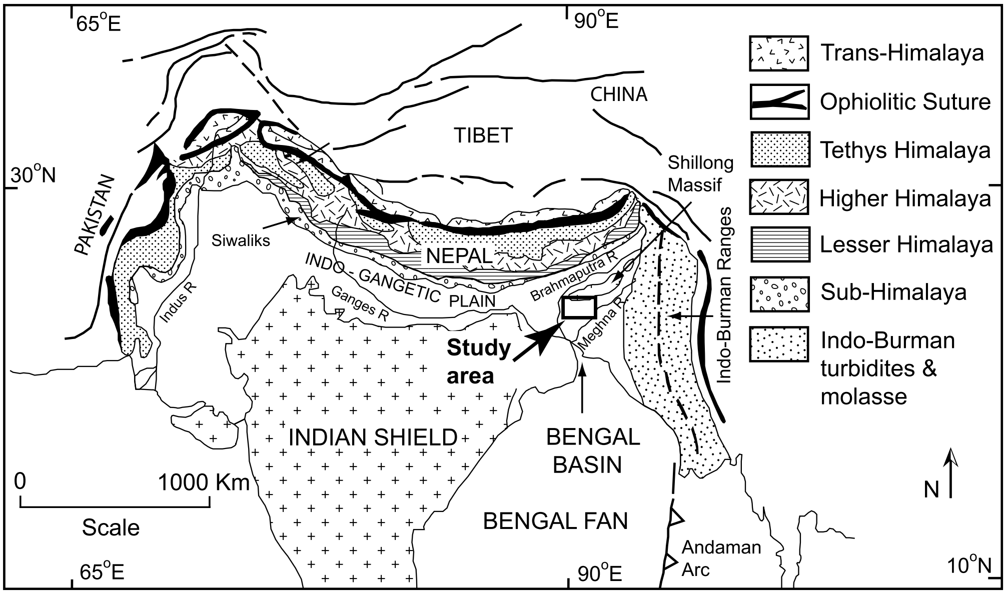

Fig. 1. Map showing major geographic features of the Bengal Basin and adjoining areas and location of the study area (modified from Uddin and Lundberg, 1998).

few basins have the appropriate combination of a narrow maturity range and wide variation of kerogen type. Consequently, research on this issue has been quite limited.

Hossain et al. (2009) reported that organic matter in mudstones in the Sylhet Basin of Bangladesh was deposited in three different stages, and also that the range of maturity in the succession was relatively narrow (R_{o}, ~0.5 – 0.7%). We here further investigate the phenanthrene homologues in this basin to determine the influence of kerogen type on the methylphenanthrene indices. We report data obtained from GC–MS for phenanthrene (P), anthracene (A), methylphenanthrene (MP), methylanthracene (MA), ethylphenanthrene (EP) and dimethylphenanthrene (DMP) isomers extracts. These are the principal compounds in aromatic fractions from Tertiary mudstones in the Sylhet Basin. The methylphenanthrene isomer ratios, especially MPR, MPDF and DMPR, are commonly used as indicators of thermal maturity in sedimentary rocks (Radke et al., 1982a, 1982b). Structures of phenanthrene and anthracene, and definition of parameters are shown in Appendix A.

2. Geological setting

The Bengal Basin is located between the Precambrian Indian Shield Platform to the west and the Mesozoic-Tertiary Indo-Burman Folded System to the east (Fig. 1). It is bounded to the north by the Precambrian Shillong Massif, and to the south it plunges into the Bay of Bengal. The Sylhet Basin, a sub-basin in this system, is located within the Bengal Foredeep, a tectonically complex province of the Bengal Basin, and lies at the confluence of Ganges and Brahmaputra rivers originating from the Himalayas. The Sylhet Basin is important for its hydrocarbon reserves, and contains numerous subsurface synclinal and anticlinal structures. The synclines were filled with late Neogene to recent sediments. Anticlinal structures include the Atgram, Sylhet, Chattak, Kailas Tila, Beani Bazar, Patharia, Fenchuganj, Rasidpur and Habiganj anticlines (Fig. 2). These anticlines are faulted, but usually contain hydrocarbons.

The Sylhet Basin forms a large elongated trough (Figs. 1 and 2), and contains a very thick pile of sedimentary sequences mainly of Tertiary age. The Tertiary Sylhet succession consists of alternating beds of sandstone, siltstone and mudstone (Khan, 1991; Reimann, 1993;

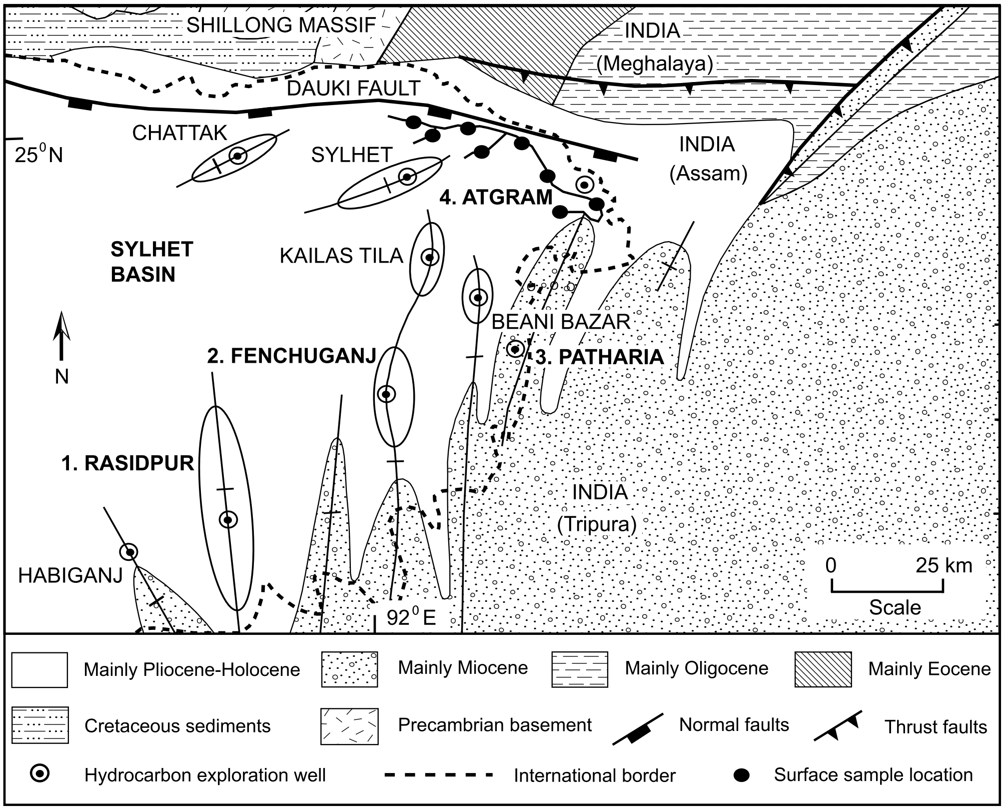

Fig. 2. Geological map of the Sylhet Basin and surrounding areas, showing location of the surface outcrop sampled and major hydrocarbon exploration wells (modified from Hiller and Elahi, 1984). Drill core samples were taken from the Rasidpur, Fenchuganj, Patharia and Atgram wells.

Najman et al., 2008) and is successively divided into the Jaintia, Barail, Surma, Tipam and Dupitila Groups in ascending order. These groups range from Paleocene to Pleistocene in age, as summarized in Table 1.

3. Samples and Analytical Methods

Twenty-four representative mudstones from the Sylhet succession were investigated in this study. Locations of the sample sites and drill core positions are illustrated in Fig. 2. The ages of the samples range from late Eocene (Jaintia Group) to Pleistocene (Dupitila Group), with most samples taken from the Miocene part of the sequence (11 samples; Surma Group). Powdered samples approximately 35 g in weight were subjected to extraction using a mixture of 9:1 DCM (dichloromethane) and MeOH in a Soxhlet apparatus for 72 h. Elemental sulfur was removed using Cu granules. The aliphatic and aromatic hydrocarbon fractions were separated directly, using activated thin layer chromatography (Kiselgel 60 PF254, Merck). The aromatic hydrocarbon fractions were analyzed using a Shimadzu QP2010 instrument, equipped with a automatic temperature-programmable injection system and fused silica column (30 m × 0.25 mm i.d.). Helium was used as the carrier gas, and oven temperature was programmed from 50 to 300 °C at a rate of 8 °C/min. The mass spectrometer was operated in electron ionization mode at 70 ev. Full scan spectra were recorded over a range *m/z* 50 to 850 at a scan rate of 0.5 s.

The P, A, MP, MA, EP and DMP isomers were identified by multiple ion chromatograms (*m/z* 178, 192 and 206).

Table 1. Stratigraphy of the Sylhet Basin, Bangladesh (after Khan, 1991; Reimann, 1993; Najman et al., 2008).

Age	Group	Formation	Lithology
Recent	Alluvium	Alluvium	Sand, silt and clay
Late Pleistocene	Dihing	Dihing	Sandstone with interbedded shale
Pliocene–Pleistocene	Dupitila	Dupitila	Pebbly sandstone and sandstone with subordinate siltstone
Late Miocene–Pliocene	Tipam	Girujan Clay	Mottled clay with subordinate sandy clay and sandstone
		Tipam Sandstone	Massive sandstone with subordinate shale
Middle–late Miocene	Surma	Bokabil	Shale with interbedded sandstone and siltstone
		Bhuban	Alternation of sandstone, sandy shale and siltstone
Late Eocene–early Miocene	Barail	Renji	Yellowish brown sandstone, shale and coal lenses
		Jenam	Grey to brownish siltstone, silty shale and sandstone
Late Eocene	Jaintia	Kopili Shale	Shale with subordinate sandstone and thin limestone
Early–middle Eocene		Sylhet Limestone	Grey fossiliferous limestone
Paleocene–early Eocene		Tura Sandstone	Alternation of sandstone and limestone, with shale and coal seams

4. Results

The analytical data (percentages) and isomer ratios for the Sylhet mudstones (10 drill core and 14 surface samples) are listed in Tables 2 and 3 respectively. Representative distributions of P, A, MP, MA, EP and DMP are shown in Fig. 3. Most samples in the succession contain high proportions of P, but those in the Barail and Jaintia Groups are lower than those at the top. 3-MP, 2-MP, 9-MP and 1-MP isomers were detected in all samples, but 9-MP and 1-MP are abundant in the lower part of the succession (Table 2). Distributions of A and MA are irregular, with both often below the detection limit in the middle and upper parts of the sequence. However, both are persistently present (A, 2.10 – 21.44; MA, 0.58 – 15.34) at the base of the sequence in the Jaintia and Barail Groups, and in the lowermost sample in the Surma Group (Table 2).

Among the EP isomers, 9- + 1-EP (average 5.62) has the highest relative abundance, even though it was not detected in eight of the 24 samples analyzed. Significant amounts of the 3-EP (av. 2.96) and 2-EP (av. 3.09) isomers are also present, and both were detected in all samples.

The DMP in the succession is characterized by relatively high abundances of the 1,7-DMP isomer, with significant amounts of 2,7- and 3,6-DMP (Fig. 3), consistent with the presence of pimanthrene. The summed distribution of 1,3- + 2,10 + 3,9- + 3,10-DMP is higher than other summed distributions in most samples (Table 2).

Alkylphenanthrene ratios (MPR, MPDF and DMPR) range from 0.66 to 2.14, 0.25 to 0.62 and 0.18 to 0.78 respectively (Table 3).

5. Discussion

The tri-aromatic hydrocarbons in the Sylhet mudstones are characterized by higher P distribution with significant inputs of MP and DMP isomers. Methylphenanthrenes are generally used as maturity parameters based on the thermodynamic stability of isomers. Generally, substitution of methylphenanthrene isomers compounds with α-positions is lesser thermal stability over related isomers with β-positions (Radke et al., 1982a, 1982b; Radke et al., 1986; Budzinski et al., 1995). In the present study, MPI 3 (Angelin et al., 1983) shows a good correlation with MPR ($r = 0.89$). Therefore, interference by possible coelution of 4-MP and 1-MP with 9-MP may not affect MPI 3 in the Sylhet mudstones. However, MPI 3 and MPR show very weak correlation with a representative maturity indicator, $T_{\max}$ (Fig. 4a and 4b). This suggests that in this basin MPI 3 is not precise as a maturity indicator, according to the influence of other factors.

$T_{\max}$ and vitrinite reflectances (R_o) have limited ranges

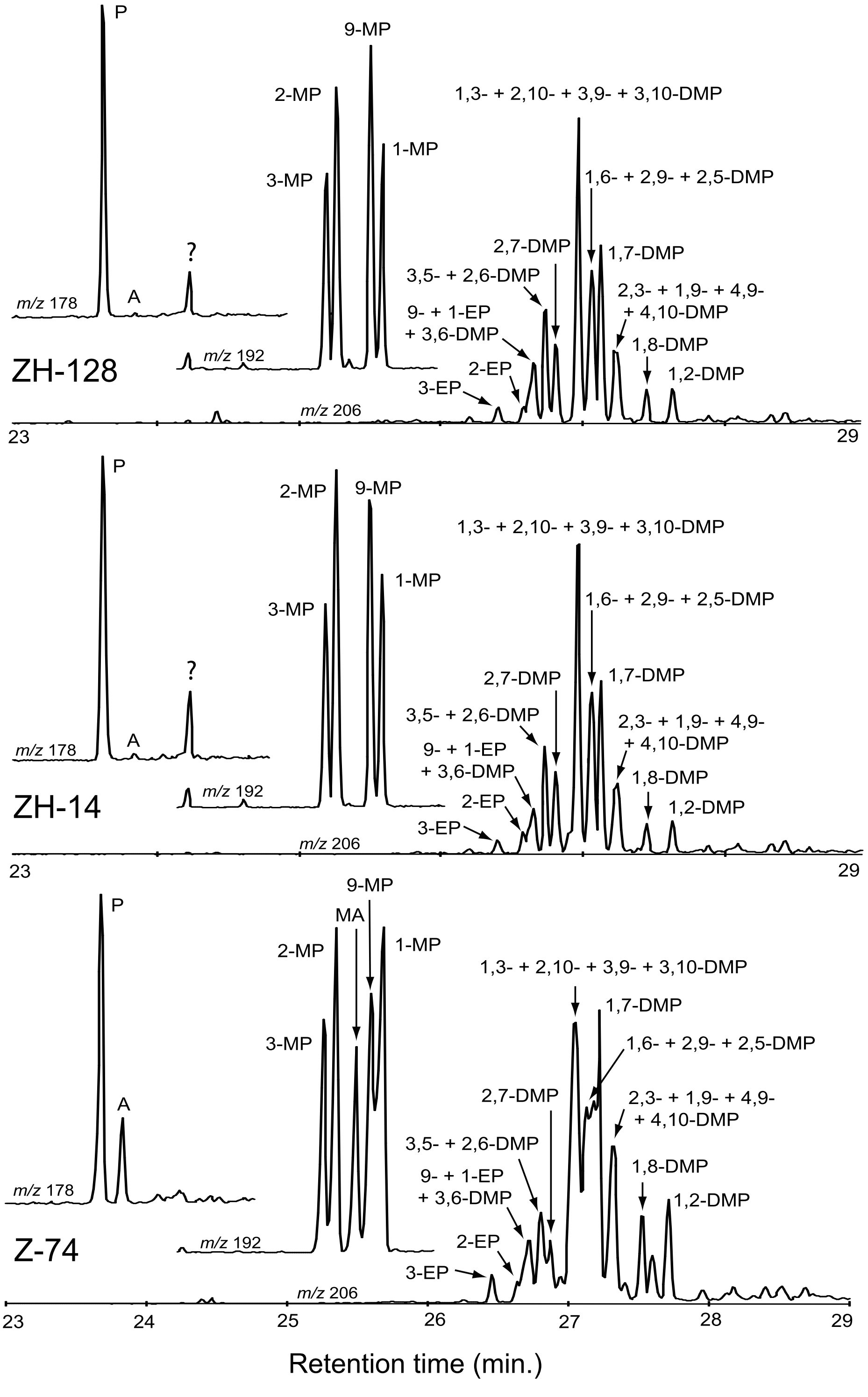

Fig. 3. Partial *m/z* 178, 192 and 206 mass chromatograms for aromatic hydrocarbons of the Sylhet mudstones, showing the distribution of phenanthrene (P), anthracene (A), methylphenanthrenes (MP), methylanthracene (MA), ethylphenanthrenes (EP) and dimethylphenanthrenes (DMP).

Table 2. Concentrations of investigated aromatic hydrocarbons (as the percentage of separate identified *m/z* mass chromatograms) in the Tertiary mudstones, Sylhet Basin, Bangladesh.

Sample No	Group	Formation	Phenanthrene and anthracene (m/z=178)		Methylphenanthrene and methylanthracene (m/z=192)					Ethylphenanthrene and dimethylphenanthrene (m/z=206)											
			P	A	3-MP	2-MP	MA	9-MP	1-MP	3-EP	2-EP	3,6-DMP	9+1-EP	3,5+2,6-DMP	2,7-DMP	1,3+2, 10+3, 9+3, 10-DMP	1,6+2, 9+2, 5-DMP	1,7-DMP	2,3+1, 9+4, 9+4, 10-DMP	1,8-DMP	1,2-DMP
Z-02-surface	Dupitila	Dupitila	100.00	b.d.l.	20.42	26.85	b.d.l.	31.99	20.74	3.22	3.14	2.82	6.48	10.87	7.03	27.17	14.72	11.12	8.05	2.11	3.27
Z-03-surface	Dupitila	Dupitila	100.00	b.d.l.	24.99	33.56	b.d.l.	23.28	18.17	2.21	2.76	8.38	b.d.l.	14.88	8.76	26.06	11.81	12.33	8.18	2.01	2.62
Z-14-surface	Tipam	Girujan	79.04	20.96	23.86	29.19	b.d.l.	27.05	19.90	2.13	2.15	2.85	6.17	10.87	7.53	29.35	13.28	13.08	6.75	3.77	2.07
Z-15-surface	Tipam	Girujan	100.00	b.d.l.	22.60	33.00	b.d.l.	25.89	18.51	3.07	1.02	4.15	6.61	12.40	8.20	26.48	11.55	14.61	6.62	2.57	2.72
Z-20-surface	Tipam	Tipam	95.06	4.94	24.13	24.78	0.44	25.58	25.07	3.85	2.64	3.20	6.31	8.43	5.23	29.10	13.60	10.94	8.18	5.21	3.31
Z-28-surface	Tipam	Tipam	91.74	8.26	21.98	23.11	1.73	36.40	16.78	2.88	3.06	2.55	6.22	9.07	5.22	34.34	13.93	9.89	7.86	2.74	2.24
ZH-122-well1-1085.4m	Surma	Bokabil	100.00	b.d.l.	19.52	29.57	b.d.l.	30.23	20.68	1.67	1.77	2.84	4.78	10.63	7.63	30.31	14.68	15.21	5.69	2.19	2.60
ZH-126-well1-1249.7m	Surma	Bokabil	100.00	b.d.l.	18.08	32.55	b.d.l.	29.35	20.02	1.34	1.50	2.27	4.60	11.06	7.98	31.33	13.50	15.57	5.78	2.30	2.77
ZH-128-well1-1827.9m	Surma	Bokabil	98.12	1.88	18.89	31.18	b.d.l.	28.51	21.42	1.38	2.12	4.15	b.d.l.	10.33	8.04	29.79	14.88	16.74	6.70	2.81	3.06
ZH-55-well2-2198.0m	Surma	Bokabil	100.00	b.d.l.	26.11	35.79	b.d.l.	21.37	16.73	2.09	0.91	9.50	b.d.l.	19.44	11.20	27.48	11.80	9.30	6.48	1.14	0.66
Z-31-surface	Surma	Bokabil	92.79	7.21	26.08	25.45	b.d.l.	34.97	13.50	3.85	3.26	2.71	6.61	11.00	6.16	31.41	13.25	8.47	8.57	2.67	2.04
Z-35-surface	Surma	Bokabil	93.94	6.06	24.09	23.35	b.d.l.	36.02	16.54	2.87	2.96	2.65	6.21	9.12	5.67	32.78	13.15	10.57	8.44	2.85	2.73
ZH-59-well2-2459.0m	Surma	Bhuban	100.00	b.d.l.	17.44	21.10	b.d.l.	42.33	19.13	2.04	2.74	2.56	5.83	9.53	6.87	31.15	13.80	11.99	7.91	2.53	3.05
ZH-88-well2-3770.0m	Surma	Bhuban	98.21	1.79	15.03	19.18	0.27	43.09	22.43	2.35	2.95	2.44	5.03	7.52	5.27	28.46	13.66	15.08	8.51	4.82	3.91
ZH-14-well3-961.1m	Surma	Bhuban	100.00	b.d.l.	19.15	27.37	b.d.l.	31.65	21.83	1.33	1.44	5.20	b.d.l.	10.73	7.53	29.52	13.82	17.34	6.78	3.08	3.23
ZH-32-well3-2829.0m	Surma	Bhuban	100.00	b.d.l.	18.81	30.16	b.d.l.	24.82	26.21	2.22	8.48	7.88	0.46	4.64	2.54	26.99	7.87	2.41	15.34	17.84	3.33
Z-43-surface	Surma	Bhuban	92.99	7.01	11.40	13.42	0.65	58.91	15.62	3.23	6.62	2.15	4.70	4.30	8.79	30.88	12.77	10.27	9.89	4.80	1.60
Z-55-surface	Barail	Renji	88.94	11.06	14.08	22.13	4.26	32.10	27.43	5.71	4.99	9.70	b.d.l.	5.39	2.66	25.56	9.95	13.10	14.11	4.25	4.58
Z-57-surface	Barail	Renji	92.24	7.76	13.02	19.17	2.57	36.39	28.85	5.27	5.18	9.07	b.d.l.	4.71	2.45	26.55	10.26	11.90	14.85	5.49	4.27
ZH-11-well4-4733.0m	Barail	Jenam	96.63	3.37	15.83	23.08	1.90	35.58	23.61	3.18	2.71	3.51	5.66	7.24	4.17	24.92	10.92	18.56	10.08	4.32	4.73
ZH-12-well4-4735.0m	Barail	Jenam	97.90	2.10	18.09	27.56	0.58	27.29	26.48	2.92	1.99	6.20	b.d.l.	10.04	7.54	24.25	9.28	19.71	10.46	4.23	3.38
Z-70-surface	Jaintia	Kopili	93.49	6.51	12.53	23.09	1.87	36.60	25.91	4.20	3.30	6.19	7.13	5.40	3.04	25.66	11.46	9.76	13.36	4.50	6.00
Z-72-surface	Jaintia	Kopili	95.72	4.28	10.59	19.00	0.99	44.14	25.28	5.54	4.88	6.69	7.17	4.15	2.52	25.82	11.49	11.42	12.05	4.62	3.65
Z-74-surface	Jaintia	Kopili	78.56	21.44	17.50	24.30	15.34	18.43	24.43	2.43	1.63	3.90	b.d.l.	6.21	4.10	22.74	7.90	23.15	12.31	7.00	8.63

P, phenanthrene; A, anthracene; MP, methylphenanthrenes; MA, methylanthracene; EP, ethylphenanthrenes; DMP, dimethylphenanthrenes; b.d.l., below detection limit.

Table 3. Aromatic hydrocarbon ratios for the Tertiary mudstones, Sylhet Basin, Bangladesh. Abbreviations as in Table 2.

Sample No	Group	Formation	A/P	MA/A	MA/MP	MP/P	DMP/P	DMP/MP	MPI 3*	MPR	MPDF	DMPR	2-MP/3-MP	9-MP/3-MP	9-MP/2-MP	9-MP/1-MP	$T_{\mathbf{max}}$* (℃)	Pr/Ph*
Z-02-surface	Dupitila	Dupitila	0.00	0.00	0.00	17.04	33.96	1.99	0.90	1.29	0.47	0.43	1.31	1.57	1.19	1.54	426	1.04
Z-03-surface	Dupitila	Dupitila	0.00	0.00	0.00	7.84	10.87	1.39	1.41	1.85	0.59	0.62	1.34	0.93	0.69	1.28	0	1.07
Z-14-surface	Tipam	Girujan	0.27	0.00	0.00	6.11	10.06	1.64	1.13	1.47	0.53	0.43	1.22	1.13	0.93	1.36	0	0.88
Z-15-surface	Tipam	Girujan	0.00	0.00	0.00	2.38	4.90	2.06	1.25	1.78	0.56	0.54	1.46	1.15	0.78	1.40	0	1.35
Z-20-surface	Tipam	Tipam	0.05	0.61	0.00	7.23	3.94	0.54	0.97	0.99	0.49	0.32	1.03	1.06	1.03	1.02	440	1.43
Z-28-surface	Tipam	Tipam	0.09	0.76	0.02	3.87	4.71	1.22	0.85	1.38	0.46	0.30	1.05	1.66	1.58	2.17	442	0.82
ZH-122-well1-1085.4m	Surma	Bokabil	0.00	0.00	0.00	1.90	1.43	0.75	0.96	1.43	0.49	0.41	1.51	1.55	1.02	1.46	449	0.86
ZH-126-well1-1249.7m	Surma	Bokabil	0.00	0.00	0.00	4.86	5.50	1.13	1.03	1.63	0.51	0.42	1.80	1.62	0.90	1.47	448	0.75
ZH-128-well1-1827.9m	Surma	Bokabil	0.02	0.00	0.00	5.89	8.45	1.44	1.00	1.46	0.50	0.41	1.65	1.51	0.91	1.33	447	0.80
ZH-55-well2-2198.0m	Surma	Bokabil	0.00	0.00	0.00	2.33	1.96	0.84	1.62	2.14	0.62	0.78	1.37	0.82	0.60	1.28	442	0.90
Z-31-surface	Surma	Bokabil	0.08	0.00	0.00	5.04	5.83	1.16	1.06	1.89	0.52	0.38	0.98	1.34	1.37	2.59	438	1.15
Z-35-surface	Surma	Bokabil	0.06	0.00	0.00	3.59	3.76	1.05	0.90	1.41	0.47	0.32	0.97	1.49	1.54	2.18	439	1.21
ZH-59-well2-2459.0m	Surma	Bhuban	0.00	0.00	0.00	7.89	10.98	1.39	0.63	1.10	0.39	0.36	1.21	2.43	2.01	2.21	442	0.86
ZH-88-well2-3770.0m	Surma	Bhuban	0.02	0.55	0.00	3.68	2.47	0.67	0.52	0.85	0.34	0.30	1.28	2.87	2.25	1.92	445	1.38
ZH-14-well3-961.1m	Surma	Bhuban	0.00	0.00	0.00	3.83	3.68	0.96	0.87	1.25	0.47	0.42	1.43	1.65	1.16	1.45	436	1.08
ZH-32-well3-2829.0m	Surma	Bhuban	0.00	0.00	0.00	3.94	4.26	1.08	0.96	1.15	0.49	0.21	1.60	1.32	0.82	0.95	435	0.49
Z-43-surface	Surma	Bhuban	0.08	0.33	0.01	3.86	3.07	0.80	0.33	0.86	0.25	0.30	1.18	5.17	4.39	3.77	438	1.00
Z-55-surface	Barail	Renji	0.12	0.65	0.04	1.83	1.02	0.56	0.61	0.81	0.38	0.23	1.57	2.28	1.45	1.17	431	1.80
Z-57-surface	Barail	Renji	0.08	0.56	0.03	1.78	0.89	0.50	0.49	0.66	0.33	0.19	1.47	2.80	1.90	1.26	429	2.04
ZH-11-well4-4733.0m	Barail	Jenam	0.03	1.20	0.02	2.17	1.37	0.63	0.66	0.98	0.40	0.32	1.46	2.25	1.54	1.51	436	2.79
ZH-12-well4-4735.0m	Barail	Jenam	0.02	0.60	0.01	2.23	1.56	0.70	0.85	1.04	0.46	0.52	1.52	1.51	0.99	1.03	438	2.18
Z-70-surface	Jaintia	Kopili	0.07	0.88	0.02	3.21	1.76	0.55	0.57	0.89	0.36	0.23	1.84	2.92	1.59	1.41	433	3.15
Z-72-surface	Jaintia	Kopili	0.04	0.51	0.01	2.26	1.03	0.45	0.43	0.75	0.30	0.18	1.79	4.17	2.32	1.75	441	3.01
Z-74-surface	Jaintia	Kopili	0.27	1.87	0.18	2.82	2.38	0.84	0.98	1.00	0.49	0.34	1.39	1.05	0.76	0.75	445	2.46

*: cited from Hossain et al. (2009)

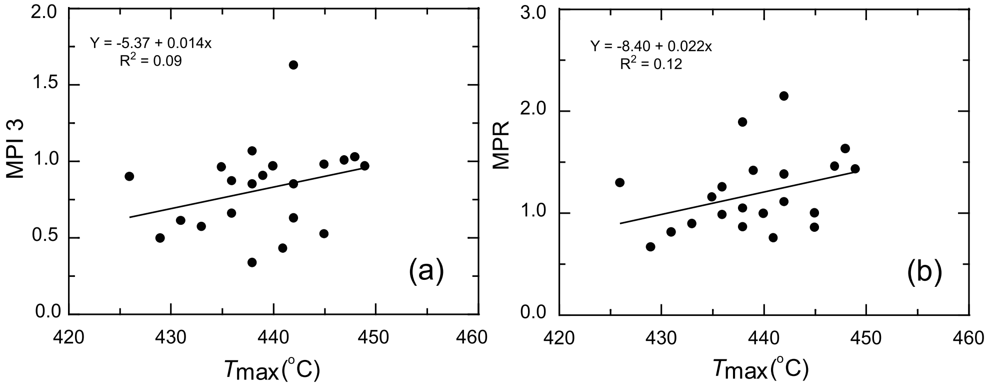

Fig. 4. (a) Relationship between T_{max} (°C) and methylphenanthrene index 3 (MPI 3); (b) Relationship between T_{max} (°C) and MPR. MPI 3 and T_{max} values from Hossain et al. (2009).

of 426 – 449 °C (n = 21; Table 3), and 0.51 – 0.66 % (n = 4; Hossain et al., 2009), respectively. There is a good correlation between T_{max} and R_o ($R_o = 0.00807\ T_{max} - 2.929$, $r = 0.88$, $n = 4$). T_{max} does not show a systematic increasing trend downward in the sedimentary column (Fig. 5), because the samples in this study were taken from four different wells and surface outcrops. T_{max} values (Table 3) indicate that the maturity of these mudstones is confined to a narrow range in the early stage of the oil window. The stratigraphic profile of MPI 3 shows no similar variation with T_{max} (Fig. 5). Although the maturity is restricted to a narrow range, compositions of some phenanthrene homologues show significant variations.

Relative abundances of MA, pimanthrene and 1-MP are high in the lower part of the Sylhet succession (Table 2 and Figs. 5 and 6). These trends are likely to be due to the origin of the organic matter. Anthracene and alkylanthracenes are commonly abundant in coals (Hughes and Dzou, 1995; Yunker et al., 2002) and in carbonaceous sediments rich in Type-III kerogens (Radke et al., 1982b; Garrigues et al., 1988). Anthracenes are less stable than phenanthrene during diagenesis (Stout and Emsbo-Mattingly, 2008), and are absent from petroleum (Yunker et al., 2002). In sedimentary rocks, alkylanthracenes are less abundant than alkylphenanthrenes (Garrigues et al., 1988). Alkylphenanthrenes are partially derived from terpenoids and steroids in biological source materials (Mair, 1964; Streibl and Herout, 1969). Alkylphenanthrene compounds, especially pimanthrene (1,7-DMP), may therefore originate from aromatization of tricyclic diterpenoids and from abietic acid of terrestrial higher plants; the latter is common in pine resin and Type-III kerogen (Wakeham et al., 1980; Radke et al., 1982b; Simoneit et al., 1986; Budzinski et al., 1995). Garrigues et al. (1985) suggested that concentrations of phenanthrene in deltaic sediments could be commonly derived from higher plant terpenoids of the α-amyrin or β-amyrin types. 1,7-DMP becomes enriched due to potential loss of retene (Simoneit et al., 1986; Armstroff et al., 2006). Similarly 1-MP is originally abundant in mudstones which contain terrestrial organic matter (Garrigues et al., 1990; Heppenheimer et al., 1992; Budzinski et al., 1995). Among the MP distributions, 9- and 1-MP isomers are often enriched in immature sediments (Radke et al., 1982a), with predominance of the 9-MP isomer, whereas 2-MP and 3-MP are predominant in Type-II or Type-I organic matter (Radke et al., 1986). The trends shown by MA, pimanthrene and 1-MP in our present study (Figs. 5 and 6) are all consistent with the terrestrial biomarker distribution of abundant oleanane, C_{29} sterane and pristane in the lower part of the Sylhet succession (Hossain et al., 2009). The differences in alkylphenanthrene ratios are responses to source effects, particularly in the lower maturity stage (Radke et al., 1986).

Hossain et al. (2009) reported that terrestrial organic matter was abundant in the lower part of the Sylhet

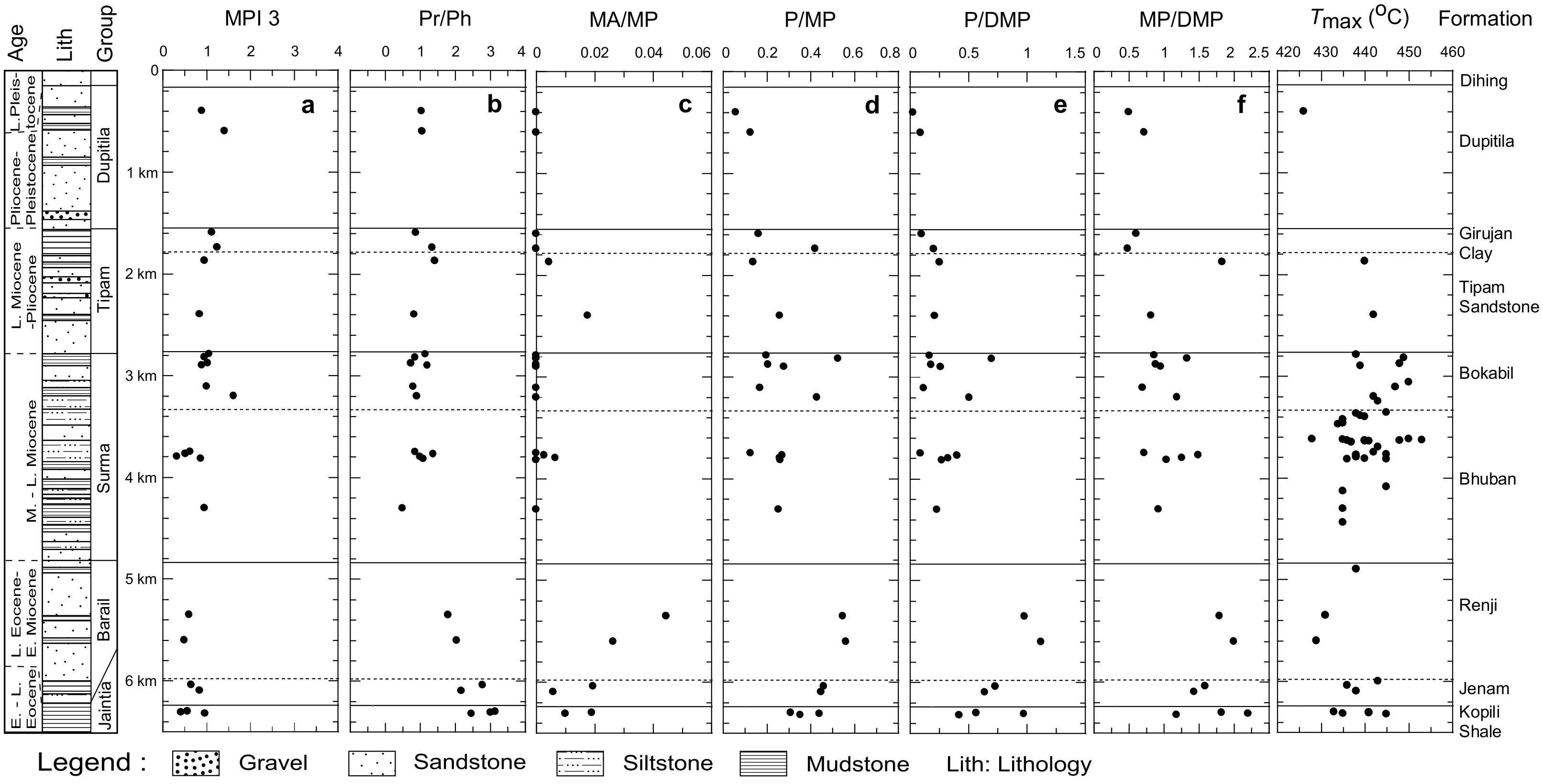

Fig. 5. Vertical distribution of MPI 3, Pr/Ph (pristane/phytane), MA/MP, P/MP, P/DMP, MP/DMP and values in the Sylhet mudstones. MPI 3, Pr/Ph and T_{max} values from Hossain et al. (2009). Abbreviations as in Fig. 3 and 4. Thickness of the stratigraphic column in the Sylhet Basin is a combination of correlated drill core, surface samples and published lithostratigraphic thickness data (Uddin and Lundberg, 1999). The revised stratigraphic thickness data are adopted in this figure.

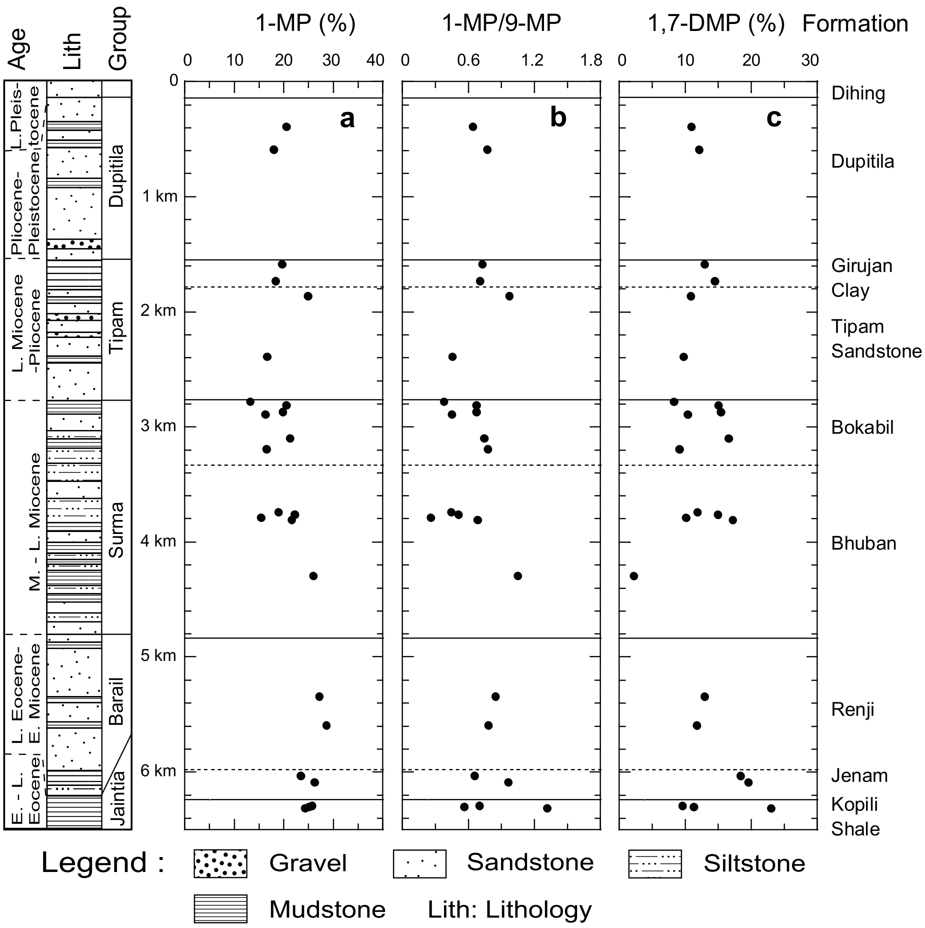

Fig. 6. Vertical distribution of 1-MP, 1MP/9MP and 1,7-DMP (pimanthrene) in the Sylhet mudstones. Abbreviations as in Fig. 3.

sequence, and that the depositional environment could be divided into three stages. In the first stage (lower part of the succession, middle Eocene to early Miocene Jaintia and Barail Groups), higher plant organic matter with abundant angiosperm material was deposited in seawater-dominated oxic environmental conditions. In the second stage (middle part, middle to late Miocene Surma Group), planktonic organic matter was deposited mainly in seawater-influenced, oxygen-poor freshwater conditions, with some transitions between anoxic and oxic environments. In the third stage (upper part, late Miocene to Pleistocene Tipam and Dupitila Groups) planktonic organic matter with a small angiosperm input was deposited in oxygen-poor freshwater conditions (Hossain et al., 2009). These variations in organic source and depositional environment could cause the observed abundances and stratigraphic variations of MA, pimanthrene and 1-MP. In the early stage of the oil window, data sets of MA, pimanthrene and 1-MP can be good indicators of the contribution of terrestrial organic matter, rather than of organic maturity.

In addition, P/MP and MP/DMP ratios increase in the lower part of the succession, and there is a good correlation between Pr/Ph (pristane/phytane) and MP/DMP ratios (Fig. 7). This could depend on supply of abundant terrestrial organic matter and deposition under oxic environmental conditions. High Pr/Ph ratios (>3) signify high input of terrestrial organic matter, and are characteristic of oxic environments (Didyk et al., 1978; Powell, 1988). Pr/Ph ratios in the Jaintia and Barail

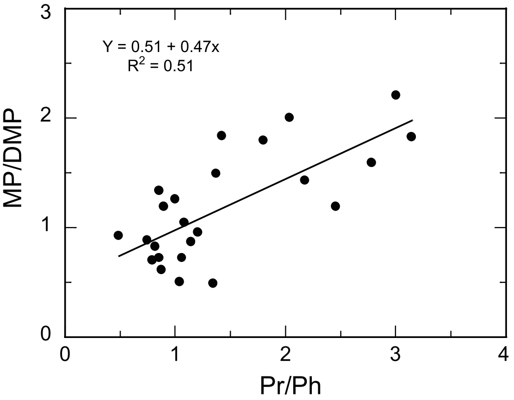

Fig. 7. Relationship between Pr/Ph and MP/DMP ratios in the Sylhet mudstones. Abbreviations as in Fig. 5. Pr/Ph data from Hossain et al. (2009).

Group mudstone suggest oxic environmental conditions with high influx of terrestrial organic matter (Hossain et al., 2009). Progressive aerial oxidation may increase phenanthrene/alkylphenanthrene values (Ahmed and Smith, 2001).

In this way variability in the P, MP and DMP values (Table 2 and 3) is probably controlled by the sources of the organic matter rather than by thermal maturity.

6. Conclusions

The overall distributions of tri-aromatic hydrocarbons investigated in the Sylhet mudstones are characterized by higher abundances of P relative to MP and DMP in most samples. MA and A were also present in small amounts. In this sedimentary succession T_{max} and R_{o} are restricted to a range of 426 – 449 °C and 0.51 – 0.66%, respectively, and MPI 3 shows poor correlation with T_{max}. This suggests MPI 3 was influenced by organic matter type, rather than by thermal maturity. Relative abundances of MA, pimanthrene and 1-MP are high in the lower part of the Sylhet succession, implying that data set of MA, pimanthrene and 1-MP are good indicators for terrestrial organic matter in the early stage of the oil window. High relative concentrations of the 1,7-DMP isomer suggests biogenic sources such as pimaric acids. High ratios of phenanthrene/alkylphenanthrenes may be due to oxic depositional environment. The variability in P, MP and DMP values is probably controlled by organic matter sources, rather than by thermal maturity in the early stage of the oil window.

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References

Ahmed M. and Smith J. W. (2001) Biogenic methane generation in the degradation of eastern Australian Permian coals. *Organic Geochemistry* **32**, 809-816.

Angelin M. L., Collignan A., Bellocq J., Oudin J. L. and Ewald M. (1983) Investigation of polycyclic aromatic hydrocarbons in source rock bitumens and petroleums by high pressure liquid chromatography. *Comptes Rendues de I'Académie des Sciences Paris, Series II* **296**, 705-708.

Armstroff A., Wilkes H., Schwarzbauer J., Littke R. and Horsfield B. (2006) Aromatic hydrocarbon biomarkers in terrestrial organic matter of Devonian to Permian age. *Palaeogeography, Palaeoclimatology, Palaeoecology* **240**, 253-274.

Budzinski H., Garrigues P., Connan J., Devillers J., Domine D., Radke M. and Oudin J. L. (1995) Alkylated phenanthrene distributions as maturity and origin indicators in crude oils and rock extracts. *Geochimica et Cosmochimica Acta* **59**, 2043-2056.

Didyk B. M., Simoneit B. R. T., Brassell S. C. and Eglinton G. (1978) Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature* **272**, 216-222.

Garrigues P., De Sury R., Angelin M. L., Bellocq J., Qudin J. L. and Ewald M. (1988) Relation of the methylated aromatic hydrocarbon distribution pattern to the maturity of organic matter in ancient sediments from the Mahakam delta. *Geochimica et Cosmochimica Acta* **52**, 375-384.

Garrigues P., Qudin, J. L., Parlantini E., Monin J. C. Robcis S. and Bellocq J. (1990) Alkylated phenanthrene distribution in artificially maturated kerogens from Kimmeridge clay and the Brent Formation (North Sea). *Organic Geochemistry* **16**, 167-173.

Garrigues P., Saptorahardjo A., Gonzalez C., Wehrung P., Albrecht P., Saliot A. and Ewald M. (1985) Biogeochemical aromatic markers in the sediments from Mahakam Delta (Indonesia). In: Leythaeuser D., Rullkötter J. (Eds.), *Advances in Organic Geochemistry 1985.* John Wiley and Sons, New York, pp. 959-964.

Heppenheimer H., Steffens K., Püttmann W. and Kalkreuth W. (1992) Comparison of resinite-related aromatic biomarker distributions in Cretaceous-Tertiary coals from Canada and Germany. *Organic Geochemistry* **18**, 273-287.

Hiller K. and Elahi M. (1984) Structural development and hydrocarbon entrapment in the Surma Basin, Bangladesh (northwest Indo-Burman fold belt). *Fifth Offshore South East Asia Conference*, Singapore, pp. 650-663.

Hossain H. M. Z., Sampei Y. and Roser B. P. (2009) Characterization of organic matter and depositional environment of Tertiary mudstones from the Sylhet Basin, Bangladesh. *Organic Geochemistry* **40**, 743-754.

Hughes W. B. and Dzou L. I. P. (1995) Reservoir overprinting of crude oils. *Organic Geochemistry* **23**, 905-914.

Khan F. H. (1991) Geology of Bangladesh. The University Press Limited, Dhaka, Bangladesh, 207 p.

Kaneko N. and Takeda N. (1995) Application of alkylated phenanthrene maturity parameters to the Miocene source rock from the Niigata Basin, central Japan. *Journal of the Japanese Association for Petroleum Technology* **60**, 285-292. (Japanese with English abstract).

Mair B. J. (1964) Terpenoids, fatty acids and alcohols as materials for petroleum hydrocarbons. *Geochimica et Cosmochimica Acta* **28**, 1303-1321.

Najman Y., Bickle M., BouDagher-Fadel M., Carter A., Garzanti E., Paul M., Wijbrans J., Willett E., Oliver G., Parrish R., Akhter S. H., Allen R., Ando S., Chisty E., Reisberg L. and Vezzoli G. (2008) The Paleogene record of Himalayan erosion: Bengal Basin, Bangladesh. *Earth and Planetary Science Letters* **273**, 1-14.

Powell T. G. (1988) Pristane/phytane ratio as environmental indicator. *Nature* **333**, 604.

Radke M. (1987) Organic geochemistry of aromatic hydrocarbons. In: Brooks J., Welte D. (Eds.), *Advances in Petroleum Geochemistry*. Academic Press, London, pp. 141-205.

Radke M. and Welte D. H. (1983) The Methylphenanthrene Index (MPI): a maturity parameter based on aromatic hydrocarbons. In: Bjorøy M. et al. (Eds.), *Advances in Organic Geochemistry 1981*. John Wiley and Sons, New York, pp. 504-512.

Radke M., Welte D. H. and Willsch H. (1982a) Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta* **46**, 1-10.

Radke M., Willsch H. and Leythaeuser D. (1982b) Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta* **46**, 1831-1848.

Radke M., Welte D. H. and Willsch H. (1986) Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. In: Leythaeuser D., Rullkötter J. (Eds.), *Advances in Organic Geochemistry 1985.* John Wiley and Sons, New York, pp. 51-63.

Reimann K. -U. (1993) Geology of Bangladesh. Gebrüder Borntraeger, Berlin, 160 p.

Sampei Y., Suzuki N., Mori K., Nakai T. and Sekiguchi K. (1994) Methylphenanthrenes from MITI Takadaheiya well and thermally altered Kusanagi shales by dolerite intrusion in Northeast Japan. *Geochemical Journal* **28**, 317-331.

Simoneit B. R. T., Grimalt J. O., Wang T. G., Cox R. E., Hatcher P. G. and Nissenbaum A. (1986) Cyclic terpenoids of contemporary resinous plant detritus and of fossil woods, ambers and coals. *Organic Geochemistry* **10**, 877-889.

Stout S. A. and Emsbo-Mattingly S. D. (2008) Concentration and character of PAHs and other hydrocarbons in coals of varying rank – Implications for environmental studies of soils and sediments containing particulate coal. *Organic Geochemistry* **39**, 801-819.

Streibl M. and Herout V. (1969) Terpenoids – especially oxygenated mono-, sesqui-, di-, and triterpenes. In: Eglinton G., Murphy M. T. J. (Eds.), *Organic Geochemistry*. Springer Verlag, Berlin, pp. 401-424.

Uddin A. and Lundberg N. (1998) Cenozoic history of the Himalayan-Bengal system: Sand composition in the Bengal basin, Bangladesh. *Geological Society of America Bulletin* **110**, 497-511.

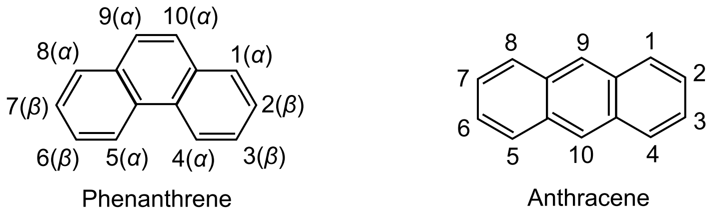
Uddin A. and Lundberg N. (1999) A paleo-Brahmaputra? Subsurface lithofacies analysis of Miocene deltaic sediments in the Himalayan–Bengal system, Bangladesh. *Sedimentary Geology* 123, 239-254.

Wakeham S. G., Schaffner C. and Giger W. (1980) Polycyclic aromatic hydrocarbons in Recent lake sediments–II. Compounds derived from biogenic precursors during early diagenesis. *Geochimica et Cosmochimica Acta* **44**, 415-429.

Yunker M. B., Macdonald R. W., Vingarzan R., Mitchell R. H., Goyette D. and Sylvestre S. (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* **33**, 489-515.

Appendix

A.1. Structures of phenanthrene and anthracene



Phenanthrene

Anthracene

A.2. Definition of parameters

$$\mathrm{MPI\ 3} = \frac{[2-\mathrm{MP}]+[3-\mathrm{MP}]}{[1-\mathrm{MP}]+[9-\mathrm{MP}]}$$

$$\mathrm{MPR} = \frac{[2-\mathrm{MP}]}{[1-\mathrm{MP}]}$$

$$\mathrm{MPDF} = \frac{[2-\mathrm{MP}]+[3-\mathrm{MP}]}{[2-\mathrm{MP}]+[3-\mathrm{MP}]+[1-\mathrm{MP}]+[9-\mathrm{MP}]}$$

$$\mathrm{DMPR} = \frac{[2,6-\mathrm{DMP}]+[2,7-\mathrm{DMP}]+[3,5-\mathrm{DMP}]}{[1,3-\mathrm{DMP}]+[1,6-\mathrm{DMP}]+[2,5-\mathrm{DMP}]+[2,9-\mathrm{DMP}]+[2,10-\mathrm{DMP}]+[3,9-\mathrm{DMP}]+[3,10-\mathrm{DMP}]}$$

Appendix A. 1. Structures of phenanthrene and anthracene, 2. Definition of parameters.

Appendix B. Raw data (height of mass chromatogram) of investigated aromatic hydrocarbons in the Tertiary mudstones, Sylhet Basin, Bangladesh.

Sample No	Group	Formation	Phenanthrene and anthracene (*m/z*=178)		Methylphenanthrene and methylanthracene (*m/z*=192)					Ethylphenanthrene and dimethylphenanthrene (*m/z*=206)											
			P	A	3-MP	2-MP	MA	9-MP	1-MP	3-EP	2-EP	3,6-DMP	9+1-EP	3,5+2,6-DMP	2,7-DMP	1,3+2, 10+3, 9+3, 10-DMP	1,6+2, 9+2, 5-DMP	1,7-DMP	2,3+1, 9+4, 9+4, 10-DMP	1,8-DMP	1,2-DMP
Z-02-surface	Dupitila	Dupitila	697	b.d.l.	2426	3189	b.d.l.	3799	2464	875	852	767	1760	2951	1910	7376	3999	3021	2187	574	887
Z-03-surface	Dupitila	Dupitila	1386	b.d.l.	2716	3648	b.d.l.	2530	1975	351	437	1328	b.d.l.	2359	1389	4130	1872	1954	1297	319	416
Z-14-surface	Tipam	Girujan	2825	749	4121	5043	b.d.l.	4672	3437	676	682	903	1959	3450	2388	9313	4214	4149	2141	1197	658
Z-15-surface	Tipam	Girujan	2358	b.d.l.	1266	1848	b.d.l.	1450	1037	397	132	537	855	1604	1061	3427	1494	1890	856	332	352
Z-20-surface	Tipam	Tipam	33800	1756	59212	60796	1071	62775	61518	5883	4037	4888	9637	12865	7983	44407	20752	16704	12480	7952	5050
Z-28-surface	Tipam	Tipam	27139	2444	23463	24666	1852	38862	17908	4184	4456	3706	9042	13200	7594	49940	20266	14390	11432	3989	3262
ZH-122-well1-1085.4m	Surma	Bokabil	487133	b.d.l.	181040	274243	b.d.l.	280473	191809	12646	13420	21509	36259	80585	57836	229728	111298	115293	43154	16594	19707
ZH-126-well1-1249.7m	Surma	Bokabil	109079	b.d.l.	95896	172689	b.d.l.	155664	106163	8690	9735	14710	29832	71767	51777	203220	87560	100994	37477	14939	17987
ZH-128-well1-1827.9m	Surma	Bokabil	49981	956	55585	91717	b.d.l.	83869	63032	6040	9296	18155	b.d.l.	45230	35208	130368	65147	73284	29317	12297	13397
ZH-55-well2-2198.0m	Surma	Bokabil	2497568	b.d.l.	1520185	2084279	b.d.l.	1244100	974435	105593	46191	480376	b.d.l.	983654	566817	1389952	597226	470382	327774	57758	33388
Z-31-surface	Surma	Bokabil	25843	2008	33963	33144	b.d.l.	45532	17573	6720	5696	4733	11540	19208	10762	54892	23144	14795	14971	4657	3568
Z-35-surface	Surma	Bokabil	55071	3554	47570	46106	b.d.l.	71096	32664	6762	6968	6232	14608	21476	13347	77160	30964	24888	19862	6704	6422
ZH-59-well2-2459.0m	Surma	Bhuban	11287	b.d.l.	15531	18790	b.d.l.	37692	17032	2824	3802	3551	8077	13207	9524	43159	19129	16621	10965	3513	4232
ZH-88-well2-3770.0m	Surma	Bhuban	64087	1170	35568	45375	642	101963	53082	4138	5203	4312	8866	13270	9300	50224	24092	26604	15016	8497	6900
ZH-14-well3-961.1m	Surma	Bhuban	102117	b.d.l.	74931	107067	b.d.l.	123789	85416	5141	5594	20145	b.d.l.	41597	29189	114366	53582	67224	26286	11941	12511
ZH-32-well3-2829.0m	Surma	Bhuban	972811	b.d.l.	720108	1154616	b.d.l.	950396	1003668	103467	395564	367181	21400	216439	118396	1257934	366848	112498	715451	831979	155365
Z-43-surface	Surma	Bhuban	40351	3044	17863	21040	1016	92339	24487	4694	9599	3120	6818	6246	12758	44776	18534	14908	14353	6972	2327
Z-55-surface	Barail	Renji	4656499	578961	1251276	1966277	378856	2851618	2437629	303478	265011	515470	b.d.l.	286464	141124	1359491	528771	696308	750033	225734	243450
Z-57-surface	Barail	Renji	3978747	334899	948465	1396606	187536	2651504	2102325	208802	205291	359432	b.d.l.	186653	97168	1051594	406560	471529	588286	217630	169079
ZH-11-well4-4733.0m	Barail	Jenam	1365021	47625	478212	696984	57344	1074506	713006	67077	57138	74019	119520	152784	87901	525961	230496	391626	212593	91125	99835
ZH-12-well4-4735.0m	Barail	Jenam	4835872	103726	1965964	2997073	62639	2966166	2877885	232422	158502	493186	b.d.l.	798773	599957	1928658	738022	1567401	831579	336449	268768
Z-70-surface	Jaintia	Kopili	1273407	88632	521708	961190	77838	1524033	1078505	110051	86554	162291	186832	141681	79821	672951	300399	255814	350259	118003	157417
Z-72-surface	Jaintia	Kopili	1922384	86019	465442	835165	43675	1939756	1110936	132693	116890	160123	171603	99233	60268	617995	275038	273195	288328	110468	87237
Z-74-surface	Jaintia	Kopili	1522415	415564	888584	1234006	779016	935739	1239904	91766	61494	147343	b.d.l.	234659	154949	859003	298440	873945	465027	264349	325811

P, phenanthrene; A, anthracene; MP, methylphenanthrenes; MA, methylanthracene; EP, ethylphenanthrenes; DMP, dimethylphenanthrenes; b.d.l., below detection limit.