

DISTRIBUTION AND GEOCHEMICAL APPLICATIONS OF AROMATIC HYDROCARBONS IN CRUDE OILS

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Abstract

Distribution of aromatic hydrocarbons was studied in a set of crude oils, five from northern Indus basin of potwar area and two from southern Indus basin. Diaromatic and triaromatic hydrocarbons were separated from highly complex mixture of sedimentary organic matter by using liquid chromatography techniques such as column chromatography, TLC and GC-FID. These classes of compounds were identified to alkylated isomers of naphthalenes and phenanthrenes by using reference chromatograms and literature data. High concentration of di-, tri- and tetra-methyl naphthalenes was observed in all crude oils except Kal#1. The relative increase in concentration of alkyl naphthalenes was found as moved to higher methyl substituted isomers. This suggests that they are the product of sedimentary alkylation reactions during catagenesis and metagenesis. The significant concentration of methyl phenanthrenes indicated source of organic matter. High levels of both 1-MP and 9-MP showed marine and terrestrial source of organic matter except Umer crude oil which is most likely to have terrestrial origin. The ratios of β -substituted to the α -substituted isomers of both alkyl naphthalenes and alkyl phenanthrene were used to assess the thermal maturity of sedimentary organic matter, which revealed high maturity level of Dhurnal, Pindori, Badin and Toot crude oils.

Keywords: Aromatic hydrocarbons, crude oils, geosynthesis, organic matter.

INTRODUCTION

Aromatic compounds are the major constituents of petroleum and the organic extracts of ancient and recent sediments. Their occurrence and distribution has been discussed for shales [Radke *et al.* 1982a, b, Radke and Welete 1983, Alexander *et al.* 1993], coals [Radke *et al.* 1990, Miranda *et al.* 1999, Fazeelat and Asif 2005] and crude oils [Alexander *et al.* 1993, Ellis *et al.* 1995b, Bastow 1998]. Geochemical significance of aromatic biomarkers has been studied; including Different Classes of aromatic hydrocarbons have been correlated with biogenic source, For example, aromatic steranes originate from aromatization of both the regular and rearranged steranes [Villar and Puttmann 1990] under sedimentary conditions. Distribution of di- and Tri-aromatic hydrocarbons has been applied to assess the ages of sedimentary organic matter [Alexander *et al.*

1992]. The alkyl naphthalene and alkyl phenanthrene have widely been used as thermal maturation indicators [Radke 1987, Stojanovic *et al.* 2001] and however a few studies have used aromatic hydrocarbons for source correlation studies [Alexander *et al.* 1992, Jinggui *et al.* 2005].

In this study, seven crude oils from Indus basin having different geological ages were analyzed. Occurrence and distribution of di- and tri-aromatic hydrocarbons is described. Also reports the applications of alkyl naphthalenes and alkyl phenanthrenes are discussed in terms of their source organic matter, geosynthesis and thermal maturation studies.

MATERIALS AND METHODS

SAMPLES

Different sedimentary origin crude oils were selected for this study. Geological data is given in Table 1. Fimkassar and Kal#1 are older one generated from early Cambrian time's organic matter. Umer crude oil from lower Indus basin was generated cretaceous source rocks. Dhurnal and Pindori from upper Indus basin are tertiary age crude oils.

SAMPLE PREPARATION

Free sulfur from crude oils was removed by passing oil samples (~100mg) through column (diameter, 0.5cm; length, 5cm) of precipitated copper (~1g). Cyclohexane was used as solvent to elute the crude oils. Any free sulfur present in crude oils chemically reacted with activated copper and was converted to CuS. Evaporation of solvent from sulfur free crude oils performed under flow of nitrogen. The samples were quantified to determine the %S in crude oils.

Table 1: Geological Data of Analyzed Crude Oils.

Sample	Depth (m)	Basin	Probable age	Geological formation	Lithology
Dhurnal	4135	Upper Indus	Eocene	Chorgali/Sakesar	Carbonate
Badin	--	Lower Indus	-	-	-
Fimkassar	4165	Upper Indus	Early Cambrian	Tobra/Khewra	Coglomerate/ Sandstone
Kal#1	2660	Upper Indus	Early Cambrian	Khewra	Sandstone
Pindori	4283	Upper Indus	Early Eocene	Sakesar	Carbonate
Toot	4465	Upper Indus	Jurassic	Datta	Shale/ Sandstone
Umer	--	Lower Indus	Lower Cretaceous	Lower Goru	Shale

FRACTIONATION BY LIQUID CHROMATOGRAPHY

Sulfur free oil samples were fractionated by column chromatography. Activated Silica gel 60 (70-230 mesh, Merck, 5g) in n-hexane was used for column (diameter, 1cm; length, 30cm) packing. The crude oil (50mg) in n-hexane (500µL) was introduced onto the column. Saturated hydrocarbons were eluted with three bed volume of n-hexane. Second elution for aromatics was performed with three bed volume of mixture of n-hexane:diethyl ether (95:5) and NSOs were eluted with three bed volume of methanol. The fractions were dried under the flow of nitrogen to constant weigh and quantified.

THIN LAYER CHROMATOGRAPHY

The aromatic hydrocarbons were further fractionated to di- and tri- aromatic fractions by thin layer chromatography (TLC) on neutral alumina by using method elsewhere [Asif and Fazeelat 2006].

Application of Sample and Development of TLC Plate

The plate was divided to 2-compartments for sample and internal standards (naphthalene and phenanthrene). The sample (30mg in 300 μ L n-hexane) of aromatic fraction was applied parallel to the Standards (naphthalene and phenanthrene) for reference to identification of di- and tri-aromatic regions.

n-hexane: Dichloromethane (9:1) was used as solvent in the tank for development of the plate. The solvent impregnated filter paper was used to ensure that the atmosphere inside is saturated with solvent vapors. The solvent level in the tank was kept ~1.0cm from bottom of the tank. TLC plate was developed through solvent move by capillary action moving the components at different rates on the basis of their distribution coefficients between the stationary and mobile phase. When solvent front reached about 2cm below the top, the plate was removed and air dried.

Plate was observed under UV long and short wavelength lamp. The di- and tri-aromatic fraction was marked reference to standards used. The marked portions of plate were scratched off and extracted with Dichloromethane in ultrasonic bath for 10 minutes. These fractions were recovered by filtration and evaporation of solvent and quantified.

CAPILLARY GAS CHROMATOGRAPHY

The sample dilution and internal standard preparation were made as follows:

Sample aromatic fraction (8mg) was dissolved in 400 μ L of n-hexane. Each microliter of sample solution contains 20ng of aromatic hydrocarbons. β -sitosterol (10mg) was dissolved in 10mL of n-hexane, so that each μ L contains 1ng of β -sitosterol. To above prepared sample solution (8mg/400 μ L) 100 μ L of β -sitosterol solution was added as internal standard for quantification of aromatic hydrocarbons. 1 μ L from this mixture was injected for GC which contained 0.8 μ L (16ng) aromatic sample and 0.2 μ L (0.2ng) of standard.

Analysis of aromatic fractions was carried out by using a Shimadzu GC-14B series Gas Chromatograph, with fused Silica capillary column (dimensions 30m \times 0.25mm \times 0.25 μ m film) coated with methyl silicone (OV-1). The sample (1 μ L) was injected in splitless mode at 60°C. Detector (FID) and injector temperatures were 280°C and 250°C, respectively. The oven temperature was programmed from 60°C to 290°C at 4°C min⁻¹ and hold at final for 10 min. Nitrogen at a linear velocity of 2 cm/s was used as the carrier gas. The data was collected from retention time 0-70min.

RESULTS AND DISCUSSION

The crude oils were fractionated to saturates, aromatics and NSOs by column chromatography using silica gel. The relative percentages of each fraction were measured and asphaltenes was calculated by difference method. Table 2 shows the results. The relative percentages of sats, aros, and polars were plotted on ternary diagram for crude oils of each basin (see Fig. 1), which revealed closed

relationship between Fimkassar and Kal#1, both oils are generated from same source of organic matter which is supported by their geological formations (Table 1). Similarly Dhurnal, Pindori and Toot might have similar or very similar source, however in terms of hydrocarbon composition Umer and Badin are different.

Table 2: Geochemical Data of Crude Oils.

Samples	Relative percentages			
	Saturates	Aromatics	NSOs**	Asphaltene+Resin*
Dhurnal	62.9	19.1	4.3	13.7
Badin	55.5	24.6	11.7	8.2
Fimkassar	59.4	19.2	13	8.4
Kal#1	57.3	14.9	12.8	15
Pindori	61.8	17.9	6.9	13.4
Toot	62.1	20	10.2	7.7
Umer	67.4	13	8	11.6

* by difference method,

** NSOs, nitrogen, sulfur and oxygen containing compounds.

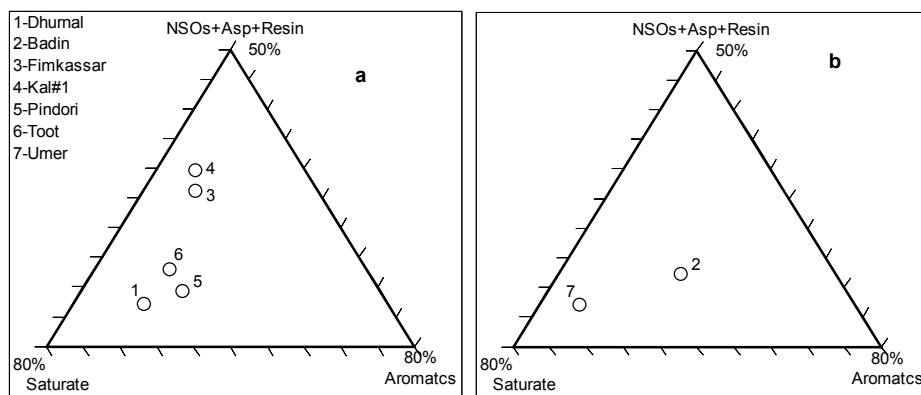


Fig. 1: Ternary diagram of relative %ages of Saturates, aromatics and polar hydrocarbons for crude oils from upper Indus basin (a) and lower Indus basin (b).

IDENTIFICATION AND QUANTIFICATION

Temperature programmed Gas Chromatography with medium polarity capillary column shows the best resolution of aromatic hydrocarbons on the basis of their molecular structures and type of alkylation. By using isothermal, non-isothermal or both oven heating programs, each compound elutes at specific retention time. In the present study, aromatic fractions of all crude oils are analyzed by capillary GC-FID by using same temperature program. Known amount of internal standard of aromatics (naphthalene and phenanthrene) was injected to differentiate between di- and tri-aromatic regions of the Gas chromatograms. The alkylated regions of naphthalene and phenanthrenes are identified by using reference GC-FID chromatograms [Chakhmakhchev and Suzuki 1995] and specific isomers of methyl naphthalenes and phenanthrenes are identified by using kovat indices [Kovats 1958, Asif and Fazeelat 2006] and literature data [Stojanovic *et al.* 2001].

Concentrations of aromatic hydrocarbons are calculated by using FID peak areas reference to internal standard peak area. Peak area of internal standard indicates their known weight and related to identified aromatic hydrocarbons for the calculation of their concentration by following formula:

$$\text{Conc. of compound (ng)} = \frac{\text{Conc. of Std.} \times \text{Peak area of desired compd.}}{\text{Peak area of Std.}}$$

Concentration of identified naphthalenes and phenanthrenes hydrocarbons are shown in Table 3.

Table 3: Concentration (ng) of Identified Aromatic Hydrocarbons from Crude Oils.

Peak No. from Fig. 1	Identified aromatic hydrocarbons	Dhurnal	Badin	Fimkassar	Kal#1	Pindori	Toot	Umer
1	naphthalene	0.02	0.05	0.02	0.02	0.03	-	0.01
2	2,6+2,7-DMN	0.30	0.61	0.13	-	0.99	0.73	1.10
3	1,3+1,7+1,6-DMN	0.17	0.30	0.07	-	0.48	0.37	0.54
4	1,3,7-TMN	0.09	0.11	-	-	0.18	-	-
5	1,3,6-TMN	0.24	0.30	0.07	-	0.50	0.50	1.02
6	1,4,6+1,3,5-TMN	0.27	0.36	0.12	-	0.57	0.35	0.67
7	1,3,5,7-TeMN	0.52	0.52	0.23	-	0.50	0.54	1.21
8	1,3,6,7-TeMN	0.53	0.48	0.23	-	0.63	0.50	1.12
9	1,2,4,6+1,2,4,7+1,4,6,7-TeMN	0.20	0.19	0.16	-	0.18	0.37	0.44
10	2,3,6,7-TeMN	0.10	0.12	0.07	-	0.13	0.17	0.24
11	1,2,6,7-TeMN	0.15	0.11	0.09	-	0.22	0.22	0.40
12	Phenanthrene	0.29	0.31	0.33	0.17	0.46	0.55	0.17
13	Anthracene	0.10	0.04	0.09	-	0.09	0.06	0.11
14	3-MP	0.30	0.34	0.25	0.03	0.42	0.35	0.36
15	2-MP	0.44	0.44	0.32	0.03	0.55	0.47	0.43
16	9-MP	0.27	0.31	0.25	0.03	0.39	0.32	0.41
17	1-MP	0.36	0.35	0.27	0.03	0.39	0.30	0.54
18	1,3+3,9+2,10-DMP	0.63	0.77	0.53	0.05	0.83	0.11	0.86
19	1,6+2,9+2,5-DMP	0.49	0.50	-	0.07	0.49	0.49	-
20	1,7-DMP	-	0.22	0.52	0.04	0.23	0.42	0.78

DISTRIBUTION AND GEOCHEMICAL SIGNIFICANCE

Naphthalenes

Naphthalenes are known to be widespread constituents of geological materials and believed to have been derived partly from non-aromatic natural precursor such as terpenoids [Starchan *et al.* 1988].

Gas chromatograms of aromatic fractions of all samples showed absence of monoaromatic hydrocarbons (Fig. 2). Diaromatic region start from naphthalene present in low relative concentration ($\sim 0.02 \text{ ng g}^{-1}$) in Fimkassar, Kal#1 and Umer while a comparatively high concentration was observed in Badin oil (0.05 ng g^{-1} , Table 3). Monomethyl naphthalenes were absent or present in very low concentration. Dimethyl naphthalenes (DMN), particularly 2,6+2,7-DMN are present in higher concentration than other dimethyl naphthalenes isomers (Table 3).

Almost double concentration of these isomers (2,6 and 2,7-DMN) was observed than 1,3+1,7+1,6-DMN in all crude oils. The most pronounced concentration of β,β -substituted isomers (2,6 and 2,7-DMN) was present in Pindori (0.99 ng g^{-1}), Toot (0.73 ng g^{-1}) and Badin (0.61 ng g^{-1}) which is attributed to more stability of β,β -isomers than α,α -dimethyl substituted isomers. The origin of these structurally simple alkyl aromatics is the topic of many studies; for example 1,7-DMN

is suggested to be derived from diterpenoid acid like agathic acid by reduction and aromatization through maturation processes. Mostly during sediment maturation processes the degradation of biogenic precursors, largely by thermal bond breaking and dehydrogenation reactions followed by aromatization, are generally accepted reactions responsible for the distribution of these alkyl aromatics in petroleum [Alexander *et al.* 1992]. It has also been shown that significant quantities of alkyl aromatic hydrocarbons in sedimentary organic matter may be derived by methylation of parent aromatic hydrocarbons [Radke *et al.* 1982a].

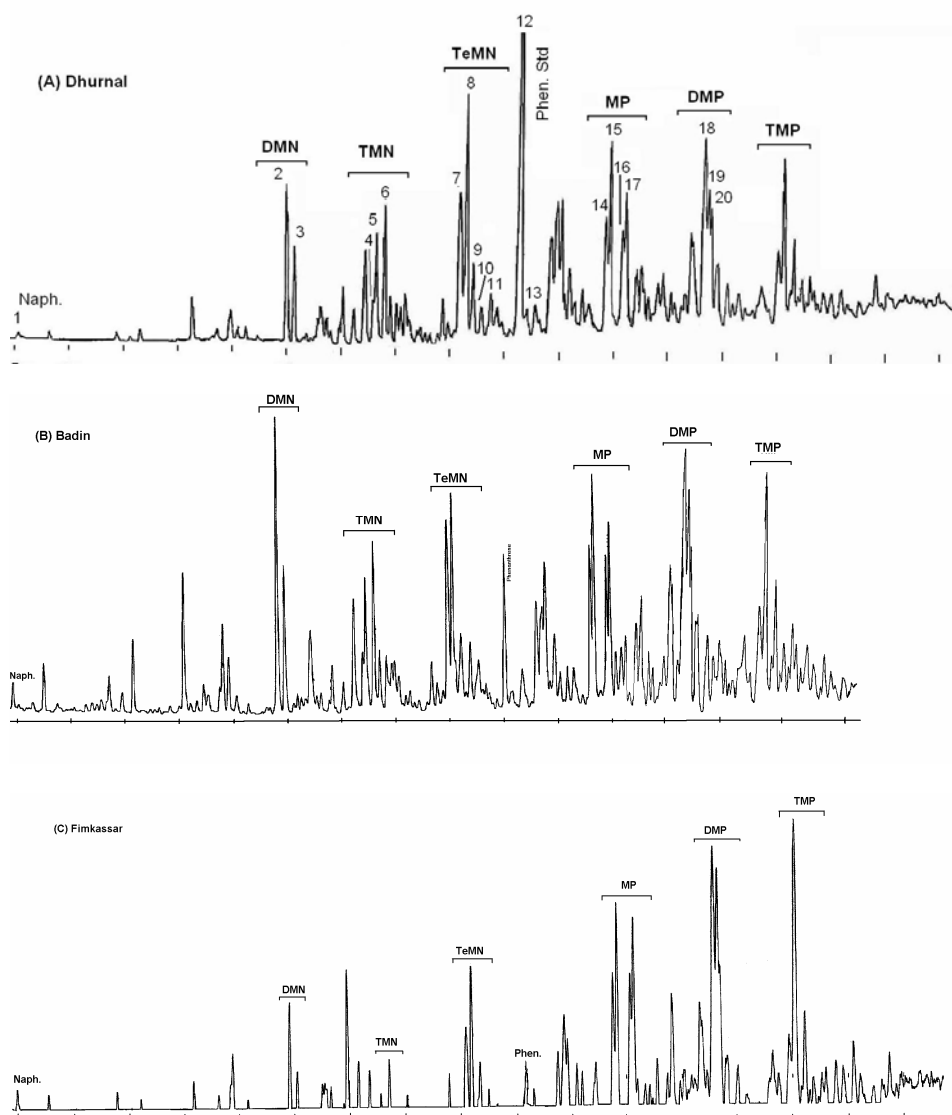


Fig. 2: FID Chromatograms of Aromatic Fraction of Analyzed Crude Oils, peak number refers to Table 3.

(D) Kal#1

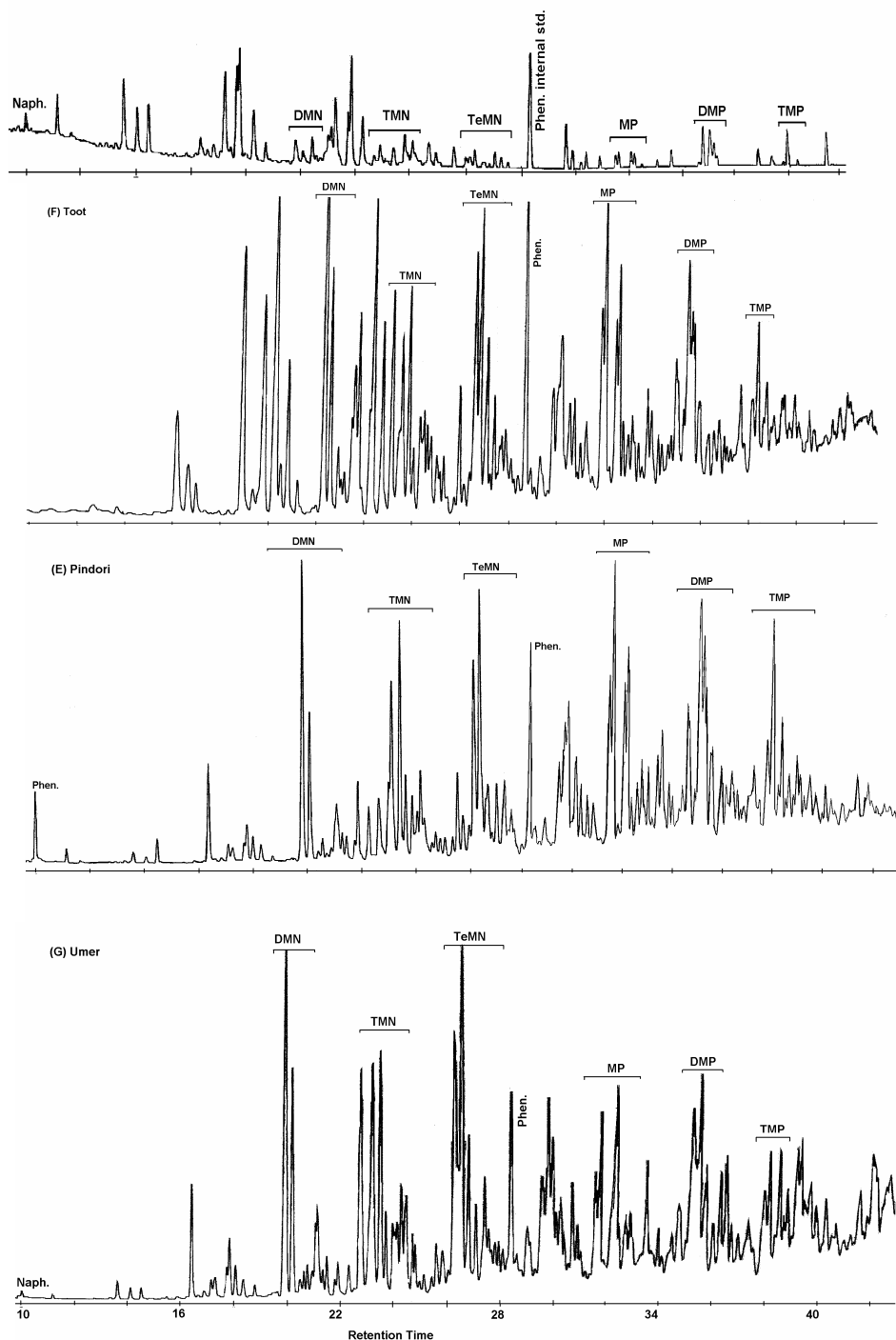


Fig. 2 (continued): FID Chromatograms of Aromatic Fraction of Analyzed Crude Oils, peak number refers to Table 3.

Trimethyl naphthalenes (TMNs), e.g. 1,3,6; 1,4,6; 1,3,5-TMN ($\sim 0.60 \text{ ng g}^{-1}$) are present in significant concentration while 1,3,7-TMN is present in small concentration ($\sim 0.1 \text{ ng g}^{-1}$) in all crude oils while Fimkassar and Kal#1 show absence of later (Table 3, Fig. 2C&D). Almost same isomers of TMN are present in all oils however their relative abundances show variation. Pindori and Umer show high concentration of 1,4,6-TMN along with 1,3,5-TMN, it has been proposed through laboratory heating experiments that (1,4,6-TMN) is the methylation product of 1,6-DMN by clay catalyzed reactions [Bastow 1998], while 1,6-DMN is not significantly present in these samples due to co-presence of 1,3+1,7-DMN. It is suggested that high clay content in case of umer and Pindori oil might have resulted to enhance the concentration of 1,4,6-TMN.

Tetramethyl naphthalenes (TeMNs) concentration is highest of all methyl naphthalenes, which show the continued methylation reactions of naphthalenes with passage of time. Presence of 1,2,4,7-TeMN has been correlated with 1,2,7-TMN. It has been suggested that (1,2,7-TMN) is readily methylated when heated with methyl donor species, this was interpreted as evidence for sedimentary methylation reactions. 1,3,5,7-TeMN and 1,3,6,7-TeMN are the most abundant isomers in TeMNs region and these compounds are suggested to be formed from 1,2,5,6-TeMN and 1,2,3,5-TeMN [9] therefore latter compounds are totally absent in all crude oil. Low mature samples have these 1,2,5,6-TeMN and 1,2,3,5-TeMN isomers in abundance and supposed to be derived from bicyclic compounds of microbial origin or their precursors. These precursors might undergo aromatization processes commonly observed in migration of one *gem-dimethyls* to the adjacent ring position during aromatization under laboratory conditions in sediments [Villar And Puttmann 1990].

The distribution of both stable isomers, 1,3,5,7-TeMN and 1,3,6,7-TeMN is linear in all analyzed crude oils except Kal#1 crude oil (Table 3). The relative abundance of certain isomers with time has been attributed to ring isomerisation and transalkylation processes [Alexander *et al.* 1993, Smith *et al.* 1994, Smith *et al.* 1995].

Phenanthrenes

Phenanthrene shows the significant concentration in all analyzed samples except Kal#1 and Umer. In Kal#1, it may be due to lower relative percentage of aromatic fraction while Umer showed strongly paraffinic in nature with higher waxy contents. Phenanthrene concentration was used to differentiate between fresh and marine water deposition of organic matter [Fan *et al.* 1990]. The source of phenanthrenes is ambiguous but supposed to be derived from terpenoids and steroids. It has been also reported that phenanthrene and methylphenanthrenes are degradative product followed by aromatization of β -amyrines [Budzinski *et al.* 1997].

Polymethyl phenanthrenes are the common constituents of sedimentary organic matter. They have been reported in shales [Radke *et al.* 1982a, Fisher *et al.* 1996a, Borrego *et al.* 1997], coals and crude oils [Fisher *et al.* 1996a, Requejo *et al.* 1996a]. Methylphenanthrenes (MP) are predominantly observed in all crude oil samples. 2MP and 3MP are present in some extent higher concentration than 1MP and 9MP (Table 3). 1MP is suggested to be produced from diterpenoid acids specifically dehydroabietic acid and podocarpic acid through reduction

followed by aromatization [Alexander *et al.* 1992]. Budzinski *et al.* [1997] has tentatively related 1MP to terrestrial origin and 9MP to marine origin. In the present study, all samples show the same trend for distribution of 1MP and 9MP with respect to 2MP and 3MP indicate the same source of origin except Umer oil. At the early stage of diagenesis the 1 and 9 position of phenanthrene is more active for electrophilic substitution than 2 and 3 position, but with passage of time the heating increase transalkylation reactions for formation of 2MP and 3MP. The higher concentration 2MP and 3MP show the sedimentary methylation of parent phenanthrene and unstable α -isomers (1 and 9MP) have occurred in early stage of diagenesis.

In Dimethylphenanthenes (DMP), due to larger number of isomers, co-elution of identified isomers is observed. This one cause the higher concentration of individual peaks refers to corresponding isomers. DMPs are also suggested to be the product of methylation reactions of phenanthrene and methylphenanthenes in the presence of methyl donor clay catalyst [Radke 1987, Fisher 2002].

SOURCE OF AROMATIC BIOMARKERS

Aromatic hydrocarbons have been described to originate from aromatization of natural product precursors in higher plant and algal/bacterial source [Radke 1987, Starchan *et al.* 1988]. 1,2,5-TMN and 1,2,5,6-TeMN; 1-MP and 1,7-DMP have been reported both in coals [Shimoyama *et al.* 2000] and crude oils [Alexander 1992]. It has been suggested that higher plant as well as algal/bacterial are the source of these aromatics while 1,2,7-TMN, Cadalene and Retene are higher plant specific biomarkers [Starchan 1988].

In this study, all crude oil gas chromatograms show eo-elution of 1,7-DMN with 1,6- and 1,3-DMN while 1,2,5-TMN and 1,2,5,6-TeMN are totally absent. In TeMN, 1,3,5,7-TeMN and 1,3,6,7-TeMN as described in previous section formed from 1,2,5,6 and 1,2,3,5-TeMN by different thermal alterations which have been reported as indicator of higher plant and algal organic matter. The presence of 1,3,5,7- and 1,3,6,7-TeMN in analyzed samples show that the origin of organic matter is both higher plant and algal/bacterial matter.

Moreover, the widespread occurrence of biomarkers which are derived from natural product precursors by loss of an isopropyl or more generally by loss of 1-methylalkyl substituent, suggests that 1-MP is likely aromatic biomarker for abietic acid type natural products. Another likely source of 1-MP is the momo-aromatic podocarpic acid, which is also a common constituent of conifer resin. While the 9-MP has been suggested the marine source origin [Budzinski *et al.* 1997]. In the present study, 1MP show similar trend relative to 9MP. That proved the source of organic matter is both terrestrial as well as marine origin. While in case of Umer crude oil significance presence of 1MP (0.54ng) relative to 9MP (0.41ng), 2MP (0.43ng) and 3MP (0.36) strongly indicate the input of higher plant organic matter.

THERMAL MATURATION

The C₁₀+ aromatic hydrocarbons are principally used to study the thermal maturity of sedimentary organic matter [Radke 1982a, Radke 1987, Chakhmakhchev and Suzuki 1995, Wilhelms *et al.* 1998]. As we discussed, polycyclic aromatic hydrocarbons are not biological compounds, they are formed by different chemical reactions brought by heating effects. At the early stage of

aromatic hydrocarbons evolution from biogenic matter or from kerogen produced certain classes of compounds. With increase in thermal maturation of organic matter, these classes have been changed to most stable compounds. This change in relative concentration of aromatic hydrocarbons and their alkyl isomers has been observed to demonstrate the thermal maturation of organic matter.

Naphthalene concentration in all analyzed samples is quite low (Table 3). In alkylation naphthalenes, it has been observed that with increasing maturity the relative abundance of structurally stable β -isomers increases compares to less stable α -substituted isomers in methyl naphthalenes [Bastow 1998]. In dimethylnaphthalenes (DMN), the β,β - isomers 2,6+2,7-DMN are present in higher concentration (Table 3) than less stable α,β - isomers, 1,3+1,7+1,6-DMN. The 1,5- DMN and 1,8-DMN (both α,α - isomers) are absent or present in very low concentration. This shows that oils have reached their higher stage of thermal maturation.

Tetramethylnaphthalenes (TeMNs) are the most abundant of all methylated naphthalenes (Table 4) in analyzed crude oils. Organic matter from low mature samples have 1,2,5,6-TeMN and 1,2,3,5-TeMN as the most abundant isomers where as with increase in maturity the 1,3,5,7-TeMN and 1,3,6,7-TeMN isomers showed greater abundance [Bastow 1998]. In high concentration of 1,3,5,7-TeMN and 1,3,6,7-TeMN in all crude oils reveals conversion of less stable isomers to stable isomers.

Table 4: Thermal Maturation Parameters.

Parameters	Concentration (ng g ⁻¹)						
Naphthalene	0.02	0.05	0.02	0.02	0.03	-	0.01
Total DMN	0.40	0.91	0.20	-	1.46	1.09	1.64
Total TMN	0.6	0.77	0.19	-	1.26	0.85	1.69
Total TeMN	1.5	1.43	0.79	-	1.65	1.8	3.41
Parameters	Ratios						
$\Sigma MP^a/P$	4.67	4.59	3.30	0.70	3.79	2.61	10.11
MPR 1: 1MP/9MP	1.23	1.12	1.08	1.0	1.0	0.94	1.32
MPR 2: 2MP/1MP	1.21	1.26	1.21	1.01	1.40	1.55	0.79
MPI 3: 3MP/1MP	0.83	0.97	0.93	1.0	1.08	1.16	0.67
MPI 2 ^b	1.43	1.34	1.15	0.39	1.33	1.21	1.15
MPI 3 ^c	1.17	1.18	1.12	0.90	1.24	1.33	0.83

^a $\Sigma MP = 1MP + 2MP + 3MP + 9MP$

^b $MPI\ 2 = 3(2MP)/P + 1MP + 9MP$ ()

^c $MPI\ 3 = 2MP + 3MP / 1MP + 9MP$ ()

Other TeMNs isomers particularly α substitution are in low concentration or absent especially compounds with substitution at position 1 and 8. Both these positions in DMN and TMN are also absent shows the unfavorable substitutions during sedimentary processes.

Phenanthrene showed significant concentration in all crude oil samples (Table 3). The relative abundance of methylphenanthrene (MP) to phenanthrene ($\Sigma MP/P$, Table 4) reflects the diagenetic evolution of methylated phenanthrenes and supports the arguments that mostly alkylphenanthrenes are formed from parent phenanthrene. In immature sedimentary organic matter the α -position (1 and 9) of phenanthrene is more active for methyl substitution than β -position (2 and 3). Smith *et al.* [1995] carried out methylation of phenanthrene in laboratory heating experiments; they observed that at lower temperature 9MP was present in higher concentration than 2MP and 3MP but with increase in temperature 2MP and 3MP

showed predominance. In the case of present study, 2MP show predominance (Table 3) over all other MP isomers in all samples except Umer crude oil which indicate the input of organic matter from different sources. Concentration of other methyl phenanthrene for all the samples are similar e.g. 3MP (0.25-0.42ng), 9MP (0.25-0.4ng) and 1MP (.27-0.4ng) which reveals the progress of transalkylation reactions with time.

Different ratios of methyl phenanthrenes have been used by petroleum geochemists as thermal maturity indices [Radke 1987]. The different maturity of oils has been assessed applying these parameters (Table 4.) Methyl-phenanthrene ratio (MPR) more than 1 (Table 4) reveals the predominance of most stable 2MP over 1MP in all samples which indicate the higher level of thermal maturity. MPI is dependent on phenanthrene and methylphenanthrene homologues with increasing maturity; α -methylphenanthrenes are gradually converted to more stable β -methylphenanthrenes. MPI 2 values greater than 1 for all oils except Kal#1 indicate that all samples have reached at higher stage of thermal maturation.

In all analyzed samples, Kal#1 (Fig. 2D) showed significant deviation in all geochemical parameters from other crude oils. The total absence of alkyl naphthalene and very low concentration of alkylphenanthrene was observed. In the case of thermal maturity parameters its values are quite different far away from other samples. This sort of observation relates to higher asphaltic oils suffered from water washing or biodegradation. Moreover it shows presence of dead organic carbon.

CONCLUSIONS

Alkyl naphthalenes and alkyl phenanthrenes are present in significant concentrations in all crude oils except Kal#1. Higher concentration of stable isomers presence revealed the Sedimentary reactions are responsible for the formation during metagenesis and catagenesis. Organic matter source was deposited both from land plants and marine life except Umer crude oil where higher plants presence is prominent. Thermal maturation of Dhurnal, Badin, Pindori and Toot has revealed that they were generated from mature source rocks.

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