

**GEOCHEMICAL CHARACTERIZATION OF OIL
SEEPS FROM UPPER INDUS BASIN, PAKISTAN**



MIAN SAJJAD HUSSAIN

01-262162-046

BAHRIA UNIVERSITY, ISLAMABAD

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MIAN SAJJAD HUSSAIN

01-262162-046

A thesis submitted to Bahria University, Islamabad in partial fulfillment
of the requirement for the degree of MS in Geology

Department of Earth and Environmental Sciences

BAHRIA UNIVERSITY, ISLAMABAD

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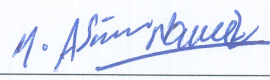

Bahria University

Department of Earth & Environmental Sciences
Islamabad Campus, Islamabad

Dated: 27/02/2020

Certificate

A thesis submitted by **Mian Sajjad Hussain** to the Department of Earth & Environmental Sciences, Bahria University, Islamabad in partial fulfillment of the requirements for the degree of **Masters in Geology** (Session 2016–2018).

Committee Member	Name	Signature
Supervisor	Mr. Saqib Mehmood	
Co-Supervisor	Dr. Samina Jahandad	
Internal Examiner	Prof. Dr. Muhammad Zafar	
External Examiner	Mr. Asim Nawaz	
Post Graduate Coordinator	Prof. Dr. Muhammad Zafar	
Head of Department (E&ES)	Prof. Dr. Tahseenullah Khan	

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Geochemical Characterization of Oil Seeps in Upper Indus Basin

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DEDICATION

I dedicate this research work to my sons Mohammad Bin Sajjad and Ahmad Bin Sajjad.

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ABSTRACT

This research was carried out to delineate the geochemistry of selected samples of the oil seeps. Research is aimed to investigate the source input, thermal maturity, age, lithology and depositional environment of the source rock of these seeps, and to evaluate the extent of biodegradation of the seeps. Samples from four oil seeps from Upper Indus Basin were collected for the geochemical characterization. These four seepages were Jaba Seep, Golra Seep, Kundal Seep and Panoba Seep. Kundal Oil Seep occurs at the contact of Khatriara Sandstone with Siwalik Group. Seepages of Jaba occur in the upper 250 feet area of Sakesar Limestone. Golra Oil Seep lies along the northern boundary of Sakesar Limestone. The detailed geochemical analyses were carried out in the laboratories of Hydrocarbon Development Institutes of Pakistan, Islamabad. The samples were first de-asphalted followed by column chromatography for the separation of samples into saturated hydrocarbons, aromatic hydrocarbons and polar compounds. Gas chromatography flame ionized detector (GC-FID) was used to confirm the separation of mixture of organic compounds, in GC-FID hydrocarbons are separated into individual components on the base of their molecular size. For detailed analysis of saturated hydrocarbons and aromatics hydrocarbons gas chromatography mass spectrometry (GC-MS) was used which is one of the modern and sophisticated analytical techniques.

Results show clear sign of biodegradation in almost all the studied samples. Marginal -highly maturity is noted for source rock of seeps being produced in different regions of Potwar. In Jaba Seep presence of Oleanane confirms Late Jurassic-Early Cretaceous age of source rock. Results show variation in depositional environment and source input. Kundal has anoxic depositional environment and carbonate lithology of the source rock. The source of Panoba was deposited in more of oxic environment that has received high deltaic input so high terrestrial input. The source rock of Jaba and Golra seeps appear to have moderate sub-oxic environment and shale lithology of the source rock.

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LIST OF ABBREVIATIONS

α	Alpha
β	Beta
C	Celsius
DBT	Dibenzothiophene
DCM	Dichloromethane
DH	Diahopane
FID	Flame ionization detector
G	Gammacerane
GCMS	Gas chromatography mass spectrometry
HH	Homohopanes
H	Hopane
m/e	mass over charge ratio
N	Naphthalenes
NSO	Nitrogen Sulfur Oxygen
nCx	Normal alkanes, x=carbon number
O	Oleanane
P	Phenanthrenes
Ph	Phytane
Pr	Pristane
SIM	Selective ion monitoring
TeCT	Tetracyclic Terpanes
TCT	Tricyclic terpane
UCM	Unresolved complex mixture
Vs.	Versus

CHAPTER 1

INTRODUCTION

1.1 Oil Seeps

Oil seeps are naturally leakages of liquid hydrocarbons which migrate up to the earth surface. Such seepages generally occur when seal is breached. Oil seeps are clues of the existing hydrocarbons in that area. These clues are then used to reach to the source rocks where oil was generated or to reservoir from where it leaked out and migrated up to earth surface. Across the world a huge number of wells are drilled in the response of seepages. Many great oil fields are the direct results of seepage drilling (Preston, 2009).



Figure 1.1. A photograph showing oil seep in Kundal area of Mianwali.

1.2. General Description of the Study Area

Upper Indus Basin is study area for this research or which is also known as Kohat-Potwar Basin. It is most northern side of large Indus Basin. Sedimentation in this area began in the Precambrian. Depositional record of Upper Indus Basin shows that it has complete depositional history in between Late Proterozoic and Holocene. In this the area basements rocks of Late Proterozoic which are metamorphic in nature and covered by oil-impregnated nature shales, interbedded type carbonates, sandstones and also evaporites belong to the Late Proterozoic duration. In these basement rocks another well-known formation is Lower Cambrian age Salt Range Formation (Shah, 1977). In this area oldest rock is Salt Range Formation. Both Kohat and potwar areas have undergone through similar tectonic activities and evolutionary history. There is a distinct difference in stratigraphy of both Kohat as well as Potwar regions (Wandrey *et al.*, 2004; Irfan *et al.*, 2010).

Samples for geochemical investigation were collected from four different locations; Jaba, Kundal, Panoba and Golra. Kundal and Jaba seeps both lie in district Mianwali. There are several seepages near to village kundal at the northern edge of the khisor Range. In this area one of the first exploratory well was drilled in 1866, known as Kundal-1 (Mudassar *et al.*, 2012). Seepages of Kundal exist near kundal-1. Seepages of Jaba lie near Jaba Village of Mianwali. This location is situated near to north-western end of Salt range and almost six miles away from Daud Khel railway station. Panoba Seep lies in the north of Khushalgarh railway station, beside the fampus River Indus in Kohat district. Golra seep is in Golra village of Islamabad which is north-eastern side of Kohat-Potwar Basin. The locations of collected samples are marked in figure 1.1.

1.2.1 Jaba Seep

In the Tredian Hills near the north-western end of the Salt Range the well-known oil seepages of Jaba occur 6 miles east-southeast of Daud Khel railway station. A mile and a half south of Jaba village is a small gorge called Chotta Khatta and 2/3 of a mile further upstream is another such gorge called Bara Khatta. The brooks from these two gorges unite and form the stream passing by Jaba.

The oil seepages occur on the west bank of the former and on the east one of the latter, i.e., on the two flanks of the prominence between the two gorges and both occurrences are less than 10 feet above the stream level. Stratigraphically, they occur in the upper 250 feet of the Sakesar Limestone. There are seven seepages in the Chotta and three in the Bara Khatta. The oldest rocks exposed here are Wargal Limestones. The Sakesar Limestone here consists of rubbly limestone, very light in colour and is succeeded by usual red series and olive gray clay and sandstone of the Siwalik Group.

The oil seepages occur in the subsidiary anticline of a larger irregular main anticline striking north-northwest/south-southeast. Both anticlines pitch towards the north-northwest with the main anticline disappearing obliquely beneath the alluvium.

In all the ten seepages, oil issues drop by drop from little crevices in the rock and collects in sumps and overflow into the streams where it is stopped by small dams, constructed by the local inhabitants. In addition, pits have been dug by the villagers to collect the oil. A gallon of oil per day is the normal production, though Pascoe (1920) reported that upto 50 gallons of thick greenish black sulphurous smelling oil had also been obtained in the past.

1.2.2 Kundal Seep

In the Kundal region there are several oil seepages close to the village of Kundal and to the region south of it. Most of these seepages occur in the stream valleys which enter the plain from the Khisor and Marwat ranges. Around each the seepage oil is left behind as asphalt layers upto five feet thick and covering an area of 2 to 5 square miles. In the past ten years several leases have been awarded to private mining companies for the development of asphalt deposits in this region.

The oil seepage opposite Dominiwala, occurs at the contact of the Khatkiara Sandstone with the Siwalik Group (Hussain, 1960). The seepage is located in a tributary Nala flowing due north along the north western flank of the Khisor Range. Hussain (1960) reported that the oil could be traced up dip to the Permian black shale occurring near the crest of the Khisor range. The oil seepage at Kundal occurs in the conglomerate bed at the base of the Siwalik Group.

According to Pinfold (Gee, 1938), the oil seepage near Kafir Kot about 10 miles south of Kundal, occurred in a faulted block and Gee believed that Pinfold had erroneously referred the sandstone host rock to be Jurassic in age. The Khisor structure is a large anticline plunging due north-northeast. The dips on the western side are about 35° - 45° and the eastern limb has been disrupted by several gravity faults. The Siwalik sandstone, siltstone, and clays overlie disconformably the Triassic and Permian rocks in this region.

Pascoe (1920), believed that the oil was possibly originating from Eocene rocks (Chharat and Sakesar Limestone) lying below the Siwaliks. Gee (in Pascoe 1920), has refuted this possibility since he believed the underlying rocks to be equivalent to the Kioto limestone of Upper Triassic or Jurassic age. Hussain (1960) confirmed the presence of Triassic rocks lying immediately below the Siwalik rocks and he believed that the oil here is not of Tertiary age but older (Permian).

Oil seepages here are marked by asphalt on the surface, and in the few pools of water asphaltic oil floats on top of the surface. The locality was unsuccessfully tested by shallow wells drilled during the latter part of the 19th Century.

1.2.3 Panoba Seep

Panoba is a small collection of farms up in the hills on the Afridi border, north of Kushhalgarh Railway Station (Kohat District) and is 13 km downstream along the right bank of the River Indus.

Three seepages are present in the Panoba valley; one consists of a group of three or four pools of water on which oil collects, associated with salt springs contaminated with hydrogen sulphide; the other two, some 20 yards further north are in outcrops of oil bearing sandstone. The crude oil, according to Pascoe (1920) 'gives a bad light and much smoke'. Locally, it is used to protect wood against white ants (termites).

Location of Seep Sample From Upper Indus Basin, Pakistan

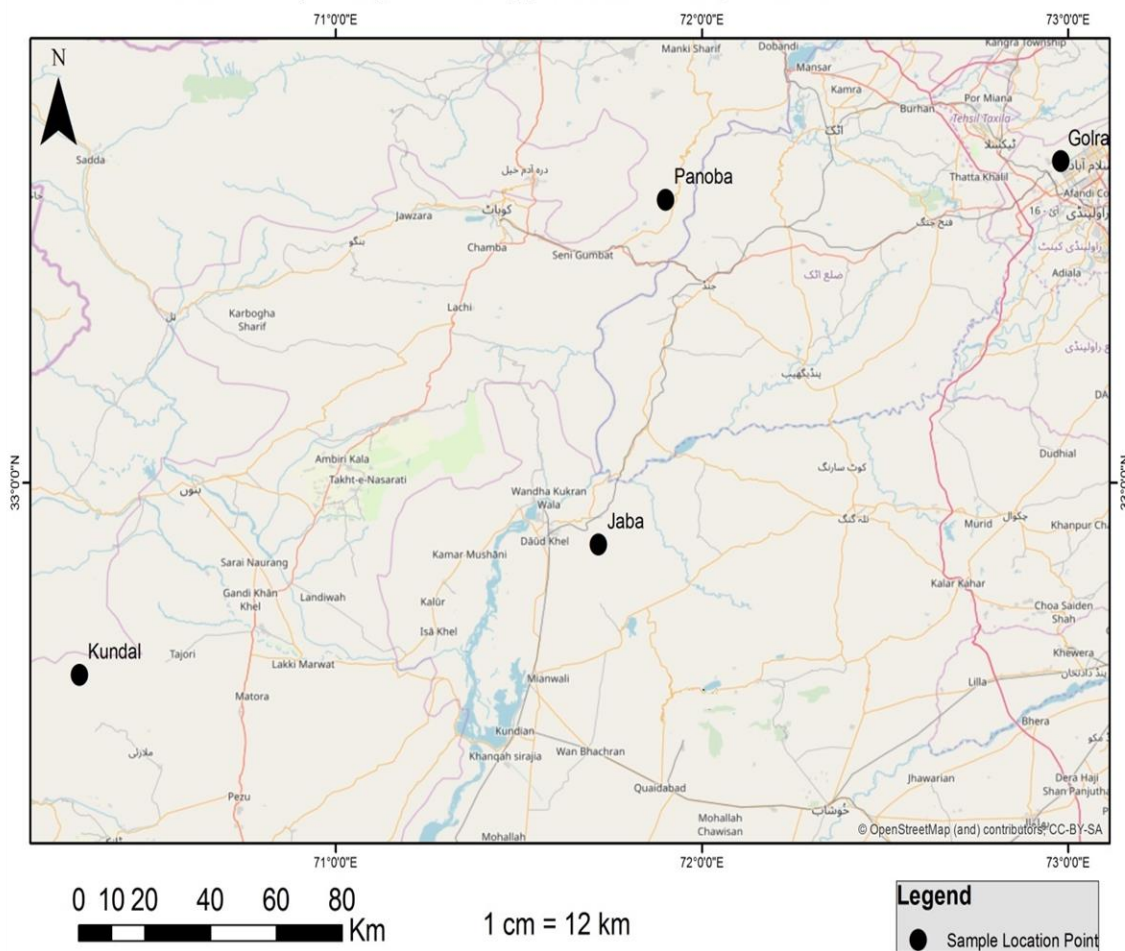


Figure 1.2. Map showing locations of the seep samples from Upper Indus Basin.

1.2.4 Golra Seep

Golra village lies in E-12 sector of Islamabad. Immediately north of Golra town is a long narrow outcrop of rocks of Sakesar age. Westwards, the outcrop of Sakesar Limestone can be traced continuously to the Shah Alladitta road. The basal Murree Formation with its derived Nummulites is present along the northern boundary of the Sakesar Limestone. The structure is of an anticlinal nature, but the fold is complicated by reverse faulting. Eastwards there is a distinct fork and the main anticline branches out into two anticlines.

Pascoe (1920) stated that shallow pits have been dug in which there was usually an accumulation of oil on the surface of the water and a distinct odour of hydrogen sulphide was noticeable. In 1913-1914, a well was drilled by the Indolex Petroleum Syndicate in the area lying between the two seepages and there was an oil show at the depth of 300 feet. In the northeast-southwest reach of the Jodh Kas, just below the Desi Shah Sikandarwali mosque, patches of bituminous earth have been seen, but there were no seepages of oil.

1.3 Petroleum System

Generally, a petroleum system is an assembly of few elements and mechanisms. Source rock, reservoir rock and seal rocks are essential elements. Generation, migration and accumulation or trapping are essential mechanisms. Specifically it includes all above mentioned major and also other minor geologic processes with associated elements which are essential for trapping or accumulation of hydrocarbons. Conversion of organic matter and accumulation of hydrocarbons need all these involving geological elements and related processes must be occurred in specific space and time. Kohat-Potwar Basin is the prolific hydrocarbon province and has number of proven petroleum systems.

1.3.1 Source Rocks

In this part of large Indus Basin hydrocarbons are produced from multiple sources. In this area the Paleocene age rock Patala Formation acts as main primary and well contributor source in the production hydrocarbons. There are many other source rocks with potential of hydrocarbons in this region of Indus Basin. These source rocks which are declared as primary source include rocks of Late Proterozoic to Lower Cambrian Salt Range Formation; Permian aged Wargal Formation, Sardhai Formation, and Chhidru Formation; Lockart Formation of Paleocene (OGDC, 1996; Quadri and Quadri, 1996). Other source rocks are Lower Goru Formation and Sembar Formation temporal equivalents the Lumshiwali and Chichali Formations almost the youngest mature strata having considerable hydrocarbons enrichment throughout the Kohat Plateau (Patala-Nammal TPS, 802601).

1.3.2 Reservoir Rocks

In this area reservoir rocks are belong to different time of deposition such as alluvial sandstones belong to Miocene, shelf carbonates lithology of Paleogene, also continental sandstones from Permian strata and Cambrian alluvial with shoreface natured sandstones (Iqbal and Shah, 1980; Shah *et al.*, 1977). In Potwar area, hydrocarbons have been generated from following Formations: Cambrian Kherwa, Kussak, and Jutana; Tobra, Amb, and Wargal Formations of Permian; Datta Formation of Jurassic; Lumshiwai Formation of Cretaceous; Khairabad Formation, Lockhart Formation, Patala Formation and Nammal Formation belongs to Paleocene; Bhadrar Formation, Chorgali Formation, and Margala Hill Limestone of Eocene; also Murree Formation of Miocene (Petroconsultants, 1996 and Khan *et al.*, 1986).

1.3.3 Traps and Seals

All production of oil or gas in this Kohat-Potwar Sub-Basin is obtained from structural nature of traps. Many fields which are existed in this basin are in overturned and faulted anticlines structure or in popup type structures and in existing faulted blocks type traps. Here in the region, it is observed that strike of those feathers which are belong to anticlinal structure is almost parallel to plate collisional zone with orientation generally east-northeast to west-southwest. Many structures of this region are amplified among these folds, or the occurrence of these structures is observed only at detachment zone in Eocambrian rocks (Jaswal *et al.*, 1997). In Kohat-Potwar Basin seals are present in the form of truncated faults and in the form of interbedded nature shales and also in the form of thick layers of shales and clays of the Siwalik strata (the Patala-Nammal TPS, 802601).

1.4 Geochemical Characterization

In this research the samples of oil seep are taken from four seepages of Upper Indus Basin. These samples are chemically characterized in detail. This geochemical characterization of crude oil is a tool which gives a compositional profile of crude oil.

Geochemical analysis tells crude oil is a mixture of different types of hydrocarbons as well as other compounds. This mixture has a wide range of compounds from a small volatile compound to a large non-volatile compound. Hundreds to thousands different compounds have been reported in the crude oil. Ultrahigh-resolution fourier transform ion cyclotron resonance mass spectrometry revealed that this crude oil contains organic compounds of hetero-atomic nature and their number is over twenty thousand with distinct elemental compositions. (Wang *et al.*, 2004) In general, petroleum components are classified in bulk groups of saturates, olefins, aromatics, resin and asphaltenes with minor amount of metal-porphyrine complexes and trace elements. The elemental composition of hydrocarbons with average percentage is 85% carbon, 13% hydrogen and 2% NSO compounds (Martinelli, 2009)

On the base of geochemical characterization many paleo and current information are obtained. Chemical composition of hydrocarbons is representative identity of source from which this was formed. However when this crude oil was interacted with different conditions, chemistry of crude oil is affected which results a slight change in chemistry of crude oil. Current geochemical analysis is focused on detail analysis of biomarkers present in oil samples.

1.4.1 Biomarkers

Biomarkers can be defined as “the naturally occurring ubiquitous and relatively more stable complexes which are indicators of different respective states. They give indication or information of specific state when they measured and analyzed for a particular objective (Moustafa *et al.*, 2012). There is a variety of biomarkers for respective field of study. However biomarkers of petroleum can be defined as “mixture of organic compounds having a wide range of constituents, derived or obtained from formerly living organisms found in oil (Mobarakabad *et al.*, 2011). Crude oil was formed from different sources such as somewhere it is result of marine life and somewhere it is product of terrestrial life, so there is a large classification exists of organism from which crude oil was formed. Crude oil generated in different environmental conditions and in different geological age. Source input, depositional

environment and age can be assessed with presence or absence of some particular compounds. These compounds or complexes are termed as biomarkers.

Biomarkers remain as indicators because with the passage of time many processes happen such as biodegradation, weathering and evaporation etc., however biomarkers offer resistance to this process. Here in this characterization different characteristics of crude oil samples are studied at different parameters. This study is done on abundance and patterns of biomarker with particular ratio between occurrence and abundance of biomarkers (Peters *et al.*, 2005).

To identify the source rock of seepage oil, generally a correlation is made between characteristics of these oil and source rocks of these areas. Samples from oil seeps are interpreted to know about the lithology of source rock, source input, and environment in which source rock was deposited, age and thermal maturity of source rock. A brief list of biomarker parameters is given in table 1.1 to table 1.4 those are generally used in such type of research.

Table 1.1. List of maturity parameters of geochemical characterization.

Characteristics	Biomarkers and Related Parameters
Maturity	Saturates/aromatics Pristane/phytane ; Pristane/ nC_{17} ; Phytane/ nC_{18} Diasteranes/(Dia + Ster) Steranes $\% C_{24}/(C_{24}+C_{27})$; $\% C_{27}/(C_{27}-C_{29})$; $\% C_{28}/(C_{27}-C_{29})$; $\% C_{30}/(C_{27}-C_{30})$ Diasteranes $\% C_{27}/(C_{27}-C_{29})$; $\% C_{28}/(C_{27}-C_{29})$ Monoaromatic steroids $\% C_{27}/(C_{27}-C_{29})$; $\% C_{28}/(C_{27}-C_{29})$ MA(I)/MA(I + II) Triaromatic steroids $C_{26}S/C_{28}S$; $C_{27}R/C_{28}R$ TA(I)/TA(I + II) Hopanes C_{35} homohopane index $22S/(22S + 22R)$ HH31; $22S/(22S + 22R)$ HH32 C_{29} moretane/ C_{29} hopane ; C_{30} moretane/hopane Steranes $\% 20S/(20S + 20R)$ C_{29} ; $\% \beta\beta/(\beta\beta + \alpha\alpha)$ C_{29}

Table 1.2. Depositional environment and source input parameters.

Characteristics	Biomarkers and Related Parameters
Depositional Environment and Source Input	<p> <i>nC</i>₁₅, <i>nC</i>₁₇, <i>nC</i>₁₉ <i>nC</i>₂₇, <i>nC</i>₂₉, <i>nC</i>₃₁ <i>nC</i>_{23–nC}₃₁ (odd) 2-Methyldocosane monomethylalkanes Pristane/phytane C₂₀ HBI Diatoms C₂₅ HBI Diatoms C_{31–C}₄₀ isoprenoids 16-Desmethylbotryococcane) Polymethylsqualanes <i>Saturates</i> C_{25–C}₃₄ macrocyclic alkanes C_{15–C}₂₃ cyclohexyl alkanes (odd) β-Carotane Phyllocladanes 4β-Eudesmane C_{19–C}₃₀ tricycliterpanes C₂₄ tetracyclic terpane C_{27–C}₂₉ steranes 23,24-Dimethylcholestanes C₃₀ 24-<i>n</i>-propylcholestanes 4-Methylsteranes Pregnane, homopregnane Diasteranes Dinosteranes 25,28,30-trisnorhopane 28,30-Bisnorhopane C₃₅ 17α,21β(H)-hopane Norhopane (C29 hopane) 2-Methylhopanes 3β-Methylhopanes Bicadinanes 23,28-Bisnorlupanes Gammacerane T 18α-Oleanane Hexahydrobenzohopanes Benzothiophenes, alkyldibenzothiophenes </p>

Table 1.3. Parameters to detect the age of hydrocarbons.

Characteristics	Biomarkers and Related Parameters
Age	<i>nC</i> ₁₅ , <i>nC</i> ₁₇ , <i>nC</i> ₁₉ Botryococcane 24-Isopropylcholestane Oleananes, lupanes Dinosterane, triaromatic dinosteroids Triaromatic 23,24-dimethylcholesteroids 24-Norcholestane, 24-nordiacholestanes C ₂₀ , C ₂₅ , C ₃₀ highly branched isoprenoids C ₂₈ –C ₂₉ tricyclic C ₂₈ /C ₂₉ steranes Beyerane, kaurane, Cadinanes

Table 1.4. Lithology parameters for rocks where hydrocarbons were generated.

Characteristics	Biomarkers and Related Parameters
Lithology	Pristane/phytane Phytane/ <i>nC</i> ₁₈ Steranes/17 α -hopanes Diasteranes/steranes C ₂₄ tetra-/C ₂₆ tricyclic diterpanes C ₂₉ /C ₃₀ hopane C ₃₅ homohopane index Hexahydrobenzohopanes and benzohopanes Dia/(Reg + Dia) monoaromatic steroids Ts/(Ts + Tm) C ₂₉ monoaromatic steroids

1.5 Applications of Hydrocarbon Composition

The occurrence of hydrocarbon seeps in an area replicates either migration fairway or the failure of development of good seal to preserve the accumulated hydrocarbons and it could result from fault/fractures etc. Therefore, the relationship

between hydrocarbon migration and presence of seep is considerably complex (Abrams, 2006; Escobar et al., 2011). The study of composition of seeps can give valuable information which help to know about the feasible petroleum system, and biomarkers are the evidence of its source rock for source input of organic matter, environment of deposition, biodegradations and extent of organic matter transformations (diagenetic impact) related to its maturity (Peters et al., 2005; Rogers et al., 1999). In fact oil seeps have been serving as a guide for discovery of the oilfields during early ages of exploration (Sutton, 1946; Stalder, 1981). The existing biodegradation scales applied to the assessment of the level of biodegradation process in crude oils are based on the extent of degradation of classes of hydrocarbons (Larter et al., 2012).

1.5.1 Source and Depositional Environment

The hydrocarbon composition of the seeps tells volume about the source, e.g. the light oils with API 40 from Amana Field showing bimodal distribution of alkanes in chromatograms, having predominance in area of nC_{12} - nC_{20} and nC_{25} - nC_{33} ; and pristane/phytane value of 2.5 indicate that oil is derived from siliciclastic source rocks with continental organic matter (Escobar, 1987).

The hydrocarbons derived from specific lithology represents some of the important features, biomarkers record representing the processes or activities that happening at the seep venting sites (Martin *et al.*, 2004; Feng *et al.*, 2008) therefore, a probable link between the macroscopic seeps and those of its reservoirs can be suggested like those of hydrocarbon seeps detected from the well-known site Gulf of Mexico (Roberts and Aharon, 1994 and Brooks *et al.*, 1986;). And seeps from region of the North Sea (Mazzini *et al.*, 2003), and the Sea of Marmara (Cremiere *et al.*, 2012). In case seep is from limestone then limestone precipitation will be associated with the hydrocarbon fluids released as observed at the Messinian Salinity Crisis (Clari *et al.*, 2009; Natalicchio *et al.*, 2013).

The parameters associated with source input and depositional environment include isoprenoid ratio, pristane/phytane, homohopane index and relative occurrence or abundance of regular steranes in saturate hydrocarbons fraction of oil/seep and source rock extract while aromatic fraction includes dibenzothiophene/phenanthrene (DBT/P).

GC–MS analyses have been used for detailed hydrocarbon composition applying selective ion monitoring (SIM), method for the selected classes of hydrocarbons which included m/z 57 & 85 for n-alkanes, m/z 183 for isoalkanes, m/z 191 for terpane, and m/z 217, 218 for sterane biomarkers in saturated hydrocarbons.

The abundance of regular steranes C_{27} , C_{28} and C_{29} is applied to evaluate the type of organic matter input (Huang and Meinschein, 1979) although these biomarkers are affected by the extent of biodegradation in the seep (Seifert and Moldowan, 1979). The cross plot on the base of isoprenoids versus aromatics, Pr/Ph vs DBT/P, and DBT/P vs. the sulfur content, the plot of C_{24}/C_{23} and C_{22}/C_{21} tricyclic terpane (TCT) these ratios are all used for the identification of depositional environment of source rock (Hughes *et al.*, 1995; Peters *et al.*, 2005).

1.5.2 Thermal Maturity

The seep samples commonly show biodegradation of varying extent, the level is reflected by the total decomposition or partial disintegration of class of hydrocarbons, the hydrocarbons least resistant to biodegradation are n-alkanes which appear in low abundance in m/z 57 or 85 and a major shift in baseline. The shift in baseline is due to unresolved complex mixture (UCM) that results from the biodegradation and could not be resolved on nonpolar column used for hydrocarbon study (Peters *et al.*, 2005).

Most of the studied seep samples from Upper Indus Basin are characterized by dominance of isoprenoids, iso-alkanes particularly pristane and phytane. Therefore CPI i.e. carbon preference index, Ph/ nC_{18} , OEP i.e. odd-even predominance and Pr/ nC_{17} could not be used to know about the maturity of seeps.

Quantitatively high relative presence of thermally stable compounds like C_{27} pentacyclic terpane, 18a(H)-22,29,30 Trisnorneohopane over its biological isomer 17a(H)-22,29,30 trisnorhopane will result from high thermal maturity in rocks that generated these hydrocarbons (Seifert and Moldowan, 1981). Similarly thermodynamically stable S isomer of C_{27} - C_{29} regular steranes and C_{31} - C_{32} homohopanes will be in more quantity as compared to R isomer that has biological precursor (Seifert and Moldowan, 1978). Among steranes the abundance of thermally

stable $\beta\beta$ isomer will increase compared to $\alpha\alpha$ isomer of steranes with increasing thermal maturity and can therefore be applied as maturity indicator.

1.5.3 Biodegradation of Oil Seeps

The biomarker parameters are applied for the assessment of thermal maturity of the source rock and determination of source rock type (marine, terrestrial etc.) and depositional environment may become problematic in case of severely biodegraded oil seeps where n-alkanes, iso-alkanes and cyclic alkanes biomarkers are effected by the biodegradation (Bennett and Larter, 2008; Escobar, 2011).

The studied seep samples rank 2-3 on Peters and Moldowan biodegradation scale, seeps at PM biodegradation level 3 have almost total loss or the absence of n-alkanes type in saturate hydrocarbons of seep samples (Peters *et al.*, 2005).

1.5.4 Aromatic Hydrocarbons

Aromatic hydrocarbons include mono-, di- and triaromatic ringed structures such as substituted benzenes, naphthalenes, phenanthrenes which are produced through aromatization of saturate hydrocarbon precursors at high thermal maturity.

Naphthalenes are common constituents of organic matter in sediments as well as crude oils (Tissot and Welte, 1984; Alexander *et al.*, 1985; Strachan *et al.*, 1988; Budzinski *et al.*, 1993b) and studied by SIM-GCMS analysis of aromatic fraction using m/z-128 ion chromatogram to study naphthalene while m/z 142 chromatogram for methylnaphthalenes (MNs), m/z 156 ion chromatogram dimethylnaphthalenes (DMNs), m/z 170 ion chromatograms for trimethylnaphthalenes (TMNs) and m/z 184 ion chromatograms for tetramethylnaphthalenes (TeMNs).

The high abundance of some of the substituted naphthalenes have been observed in rock extracts and oils of low thermal maturity including 1,6-DMN (van Aarssen *et al.*, 1992), 1,2,5-TMN (Strachan *et al.*, 1988; Heppenheimer *et al.*, 1992), 1,2,7-TMN (Püttmann and Villar, 1987) and 1,2,5,6-TeMN (Killops *et al.*, 1991; Heppenheimer *et al.*, 1992). These are suggested to have originated from the triterpenoids, triterpane

precursors which are derived from the microbial and terrestrial sources (Püttmann and Villar, 1987; Forster *et al.*, 1989a). The other substituted isomers which show increased concentrations with thermal maturity are considered to have originated from the isomerization of these aromatic with natural precursor or through methyl group transfer to more of the stable position on naphthalene

Phenanthrene is abundant in the source and crude oil that was dominated by terrestrial input. Phenanthrene (P) is quantified from m/z 178 ion chromatogram, methylphenanthrenes (MPs) from m/z 192, and dimethylphenanthrenes (DMPs) from m/z 206 ion chromatograms in aromatic fractions of the oil seeps. Phenanthrene hydrocarbons have been detected in shales (Radke *et al.*, 1982a; Garrigues *et al.*, 1987), coals (Radke *et al.*, 1990b; Garrigues *et al.*, 1987) and crude oils (Melikadze *et al.*, 1985; Boreham *et al.*, 1988; Radke *et al.*, 1993; Fisher *et al.*, 1996b). 1-MP, 1,7-DMP have been observed to be produced from the resins (Radke *et al.*, 1982b; Alexander *et al.*, 1992b). Methylphenanthrenes are particularly applied as maturity indicators and for calculation of equivalent vitrinite reflectance.

Dibenzothiophene (DBT) is class of aromatic hydrocarbons containing sulfur and its resistance is high against biodegradation while naphthalenes and phenanthrenes have comparatively low resistance. DBT is abundant in sulfur rich depositional environment, thereby DBT/P vs sulfur content serves as parameter of depositional environment. The cross-plot which was generated from the ratios of Pr/Ph vs DBT/P (fig 4.23) and it is used to predict the lithology of the source and to distinguish depositional environment as well (Hughes *et al.*, 1995).

1.6 Aim and Objectives

This geochemical investigation of oil seeps is aimed mainly to infer the source rock based on the geochemical parameters. This study has following specific objectives:

- To understand the geochemical composition of seep samples to the related characteristics.
- To make assessment of that specific source rock.

- To evaluate the depositional environment, source input and age of the source.
- To investigate thermal maturity of that source rock from where seeped oil was generated and also level of biodegradation.

CHAPTER 2

REGIONAL GEOLOGY AND STRATIGRAPHY

2.1 Regional Geology and Tectonics Setting

Study area is from the large Indus Basin, which is located in north western area of Pakistan. Tectonics and geology of this area is associated with the events which occurred in the formation of Himalaya's discovery; the collision of Indian Eurasian plates 40-50 Ma ago.

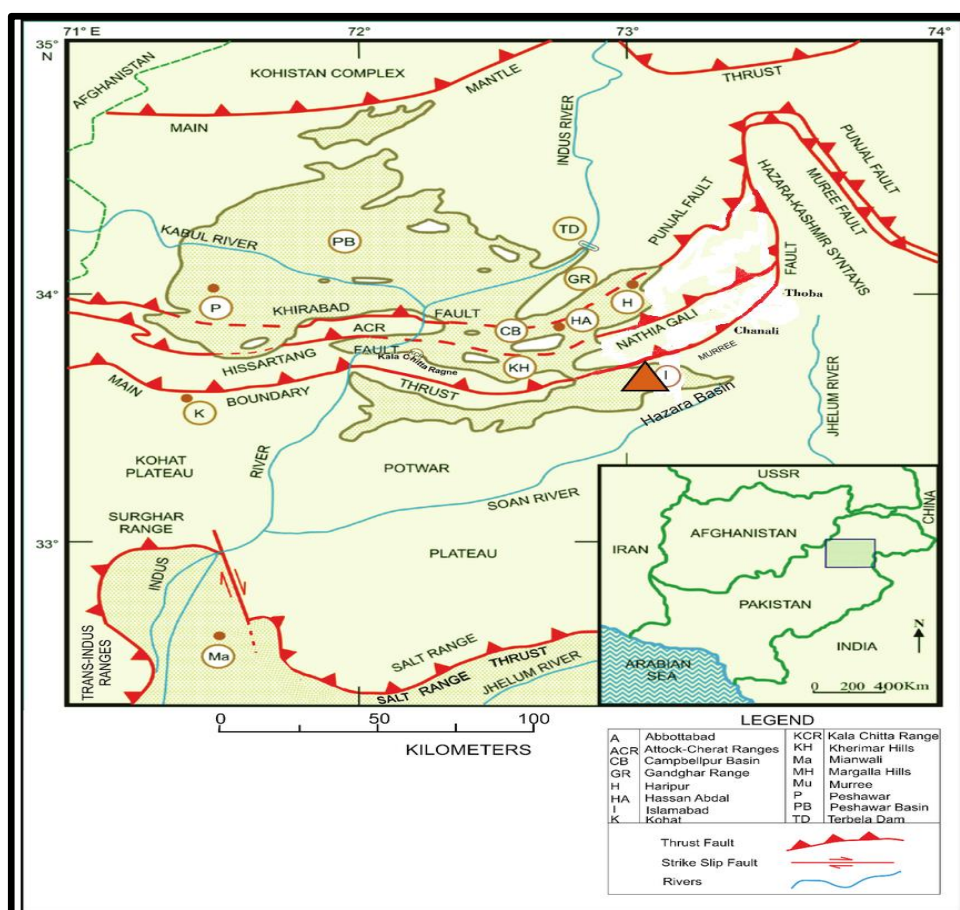


Figure 2.1. Map showing tectonics in Upper Indus Basin of Pakistan (modified after Pogue et al., 1999).

Sedimentation in study area is also related to the uplifting of Himalayas. In this regard it can be stated that structural features in Indus Basin are associated with two major tectonic activities; one is rifting of Indian tectonic plate from the Gondwanaland and its collision with Eurasian plate (Nazir, 2013).

2.1.1 Evolution and Geology of Himalayas

In mid Triassic Pangaea had split into two super continents which were Luanussia and Gondwanaland. After this separation some fragments of Gondwanaland were detached from their parent supercontinent, and these detached fragments drifted towards Luanussia where they collided and assembled. One of these fragments was Indian plate which was once located with Australian plate, African plate and Antarctic plate, in Jurassic to Early Cretaceous Indian plate was rifted and moved northward (Wandrey *et al.*, 2004). The Indian and Eurasian plate collision was brought about after reaching of Indian plate to the Luanussia. In this collision 100-500 kilometers of Indian passive continental margin has been under thrust beneath Eurasian plate (Keerey *et al.*, 2013). This collision is concern with geology and tectonics of Himalaya Mountains range and Indus Basin. Himalayas form a 2500 kilometers long and 160-400 kilometers wide mountains belt. Himalaya is not a single straight mountain instead of this, it comprised of series of mountain ranges with extensive intervening valleys (Kazmi and Qasimjan 1998).

The Himalayas are combination of three huge imprecated thrust slices and many related folds which are separated by four major fault systems. As Himalayas were formed in the result of continent-continent collision, obviously besides uplifting of mountains subduction occurred too, in both uplifting and subduction shortening of plates in considerable amount was occurred and imbricated thrusts, having an area about 250 to 350 kilometers in width, that shows the accommodation of approximately one-third to one-half of that shortening which happened between Indian Plate and Eurasian Plate (DeCelles *et al.*, 1998). In mountains Himalayas at the stack's base the Main Frontal Thrust exists which is mostly buried however topographic fronts of mountains are exposed. Main Frontal Thrust is the most active fault and the youngest of this thrust system and carries rock of the Himalaya mountains in the direction of south into a basin

called the Ganga Basin. This basin contains an area of over 5 km of Miocene–Pliocene terrigenous sedimentary sequences which are overlain by late Pleistocene alluvium (DeCelles *et al.*, 2001). The Sub Himalaya is the northern part of this basin, which forms the Himalayan foothills; its area is 10 to 25 km in width. At above Main Frontal Thrust (MFT) and to the north of it, there is another thrust which is known as MBT i.e. Main Boundary Thrust. This fault system goes gradually downward in the north side and also indicated that it remained active mostly in the Pleistocene age, although slip on it may have initiated during the Late Miocene– Pliocene. This fault threw low-grade schist of Precambrian– Mesozoic and unmetamorphosed rocks of Lesser Himalaya above the Sub-Himalaya. Above the Lesser Himalaya granitic rocks of the Higher Himalayas and high-grade gneisses are moved with MCT. The MCT a significant accommodation of shortening process in the time of Early Miocene and Pliocene, and it is inactive in most places today (Keerey *et al.*, 2013).

The Higher Himalaya consists of Precambrian gneiss overlain by the sedimentary rocks Paleozoic as well as Mesozoic. These rocks have been thrust southward for a distance of 100 kilometers. When these all faults go down at a depth all these three faults merge into a common system mean decollement is formed there called Main Himalayan Thrust (Keerey *et al.*, 2013).

2.2 Indus Basin

Among the all well-known sedimentary basins of our country Indus Basin is the largest basin. Indus Basin is a sedimentary depression basin with area of 533500 square kilometers in north western side of Pakistan (Zahid *et al.*, 2014). Indus Basins contains sediments of Precambrian to recent age. Sedimentation in Indus Basin is associated with Himalayan's uplift (Nazir, 2013.) With respect to tectonic point of view the Indus Basin is considered very stable in the comparison with other basins or tectonic zones of Pakistan (Shazia *et al.*, 2014). From late Cretaceous through middle of Paleocene many features were developed in this area, in that duration accumulation of trap deposits and also basal sands remained continue to the direction of north, west and east of the Indian plate. When convergence of Indian Plate and Eurasian Plate happened in this geological event not only some micro plates were merged also this collision

resulted the formation of regional arches like, in Indus basin Sargodha and Jacobabad highs. These are markers of tectonic activities of that time (Wandrey *et al.*, 2004).

Being a large basin the well-known Indus Basin is further partitioned into 3 relatively small parts or sub basins, these are named on the base of their location from north to South; Upper Indus Basin is located in most northern side, Central Indus Basin is an area between southern and northern edges as clear from its name and Lower Indus Basin. In the north Upper Indus Basin is bounded by well-known MBT thrust while Sargodha High is the mark that separates it from Central Indus Basin in southward. Area between Sargodha High and Sukkar Rifts comprises the Central Indus Basin. The most southern part of Indus Basin comprising area of Marith Khandot horst, Jacobabad-Khiarpur High, Kirthar Fold Belt with its depression and monoclines is termed as Lower Indus Basin (Kazmi and Qasimjan 1998; Kadri, 1995).

2.2.1 Upper Indus Basin

Indus Basin is oriented a basin, its northern side is eastward while southern side is westward. The northern part of the basin is known as Upper Indus Basin. From the MBT which is part of Himalayas towards south to Sargodha High is the Upper Indus Basin which comprising Kohat Plateau, Potwar Plateau, Bannu Depression, Cis and Trans Indus Salt range and northern Punjab monoclines. This region has complex pattern in its structural style as well as stratigraphy of Precambrian to recent time. Also many petroleum fields are in the area (Kadri, 1995; Kazmi and Qasimjan 1998). Kohat Plateau bounds Bannu Depression in north, in the east by Surghar Range while Khisor range bounds it from southern east side. Bhattani range marks Bannu Depression from southern west while Kurram Fault lies in the west of Bannu Depression. This depression was formed due to southward thrusting of Trans Indus range (Kadri, 1995).

Kohat-Potwar plateaus region dominates the upper part of Indus Basin. Due to this dominated area Upper Indus Basin is commonly known as the Kohat-Potwar Basin. Kohat and Potwar area has hydrocarbon potential. North of Potwar region is proven and declared the main producing area of hydrocarbons while the tectonic pattern and structure record of Kohat area show there is also potential for oil and gas. Both Kohat and Potwar areas had experienced similar tectonic activities and evolutionary history

however stratigraphy made considerable difference between both plateaus (Irfan *et al.*, 2010). Kohat is one of the complex plateaus and there are a number of asymmetrical structures due large number of wrench tectonic thrusts, rejtunal and normal faulting (Paracha, 2004). Bannu plane and Salt Range bound the Kohat Plateau from south while famous MBT is northern marker of kohat Plateau. Axial Belt and Indus River are boundaries of western and eastern sides respectively (Nazir, 2013).

River Indus separates the Kohat and Potwar plateaus. Potwar plateau is a region east of river Indus while Kohat Plateau lies in the west. The Potwar Plateau region is broad segment of the fold-and-thrust zone; the foreland basin area comprises a basement with meta-sedimentary rocks and metavolcanic rocks belong to the Indian part of Indian-Australian plate. This basement is overlain by alluvial deposits of Pleistocene to Holocene. In Potwar Plateau main structural features of foreland basin area are faults and possibly stock in basement rocks (Drewes, 1995). MBT bounds the Potwar Sub-Basin in the north while Salt Range is its southern boundary. Indus River separates it in the west from Kohat Plateau where across the river Indus Kalabagh Fault also lies and Jhelum fault is in east of Potwar sub-Basin (Nazir, 2013).

2.3 Stratigraphy

2.3.1 Stratigraphy of Upper Indus Basin

The study area is Kohat-Potwar Sub-basin and this basin has relatively complete depositional history from Late Proterozoic to Holocene (Asim, 2006). The sedimentation which was started in Late Precambrian to Pleistocene having following well-known unconformities; first one is Ordivician-Carbonateferous, second unconformity is Late Permian-Mesozoic while Oligocene is the third one (Nazir, 2013). In this the area basements rocks of Late Proterozoic which are metamorphic in nature and are covered by oil-impregnated nature shales, interbedded type carbonate rocks, sandstones and evaporate of the time of Late Proterozoic. In basements rocks also well-known formation i.e. Salt Range Formation of Lower Cambrian age is existing (Shah, 1977). Salt Range Formation is not uniform or near to uniformity in thickness, it varies from 50 meters to 1000 meters and even more in somewhere. Its upper part is consists of thick

carbonates and above these evaporates are present which are in contact with almost 150 meters of shales of marine nature and massive sandstones belong to Jhelum Group's Khewra Formation of Lower Cambrian. Above Khewra Formation there are glauconitic shore face sand stones and siltstones of Kussak Formation as much as 180 meters in thickness are deposited. Khewra and Kussak formations have produced oil in different fields. Overlaying Jutana Formation that consists of near shore sandstones and sandy carbonates. Cambrian aged stratigraphic strata or sequence is marked by Baghanwala Formation having lithology Shales and Interbedded type sandstones (Wandrey *et al.*, 2004).

The lower Cambrian age's Jhelum Group (Khewra, Kussak, Jutana and Baghanawal) is recorded in the Potwar region. However these successions are not reported in Kohat region. Lower Permian strata that constitutes Tobra Formation which is buried under Warcha whose lithology is sandstones and clay stones, Dandot, Sardhai, Chidru and Wargal formations present on the Precambrian and also on Cambrian age rocks in the Kohat-Potwar Forebelt (Fazeelat *et al.*, 2010).

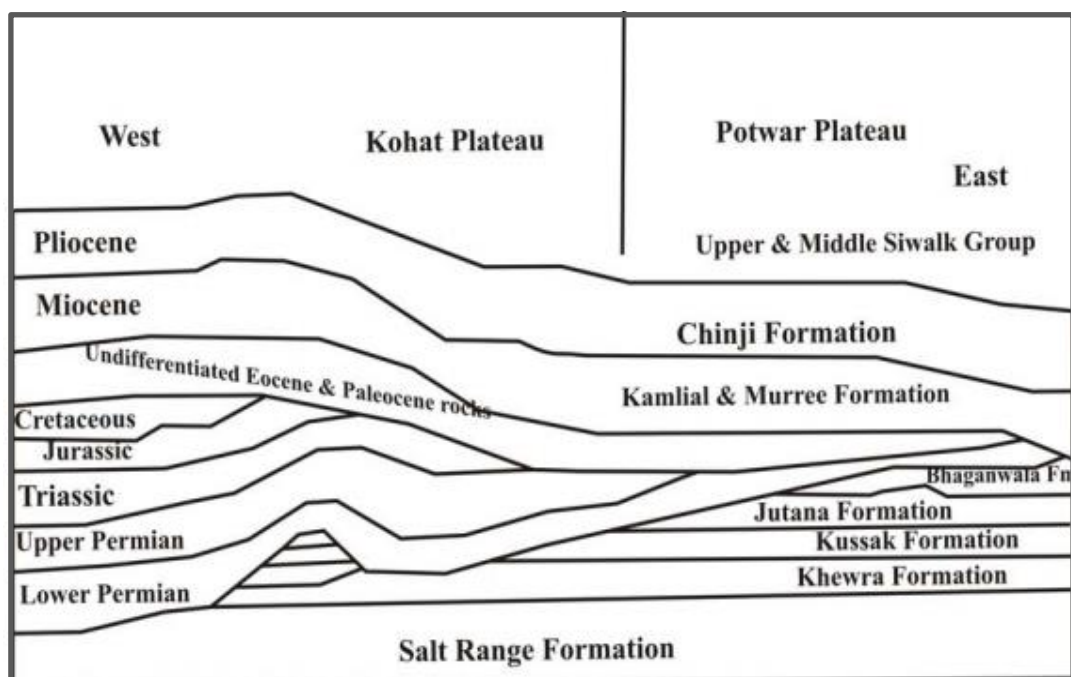


Figure 2.2. Cross section of stratigraphic sequence in Upper Indus Basin of Pakistan (Law *et al.*, 1998)

Stratigraphy of Kohat-Potwar Sub-basin has a change towards west; the Precambrian age basement rocks are clearly exposed in the area of eastern side of Potwar, Tertiary rocks are directly contacted with Precambrian strata. In this region the Permian strata consists of Nilawahan Group and Zaluch Group. The Nilawahan Group of Lower Permian comprising the Tobra Formation with lithology silt stones, glacial natured tillites and also shales, the Warcha and Sardhai Formations are similar in composition having sand stones of argillaceous nature with occasional shales however the Sardhai Formation has also fine grained sand stones intervals (Shah *et al.*, 1977; Wandrey *et al.*, 2004).

Zaluch Group of Upper Permian has Amb and Wargal Formations with lithology shelf carbonates sequence while Chidru Formation of same group has marls and stones (Wandrey *et al.*, 2004). Triassic and Jurassic strata is bounded to western side of Kohat area and absent or poorly deposited in Potwar region. Erosions here explain the missing of Cretaceous, so non-deposition concept is not in business here in this case. In this region Mesozoic aged rocks are buried in Salt Range as well as southeast Potwar Sub-Basin, part of section or complete section shows absence in the Kohat area and also in the northwestern Potwar area, which is deformed region (Jaswal *et al.*, 1997). There is a thinning in deposition toward the western side which may gathered with erosional process is the reason of missed rocks. Lithological compositions sandstones with course to fine sized grain, carbonates and shales of the Triassic age Musa Khel Group rocks are deposited over unconformable Permian strata. Shelf carbonates belong to Triassic aged Kingriali Formation present over Tredian. Triassic age carbonates of Kingriali Formation overlie the Tredian. Shinawari and Datta formations of Jurassic having lithology of near shore siliciclastics containing non marine sandstones interval overlie the carbonates of Samana Suk Formation (Khan *et al.*, 1986). Then next section is of Lower Cretaceous age where shales of Chichali Formation along with Sembar and Lower Goru. This strata is deposited under the Lumshiwai Formation which is lithological a sandstone. In the south east of the Salt Range, Upper Goru, Kawagarh and Mughal Kot formations are deposited moreover these are also representatives of Cretaceous lowstand activities and events. In Potwar plateau these rocks are absent in the stratigraphy (Wandrey *et al.*, 2004).

Above the eroded surface of Lumshiwai Formation, Hangu Formation was deposited; contact between these two formations is a transitional in nature. Overlying

Lockart Formation's carbonates contacting with Patala Formation. Patala Formation has shale marine shales and carbonates of subordinate nature. This contact is also of transitional nature. Above Patala Formation Nammal and Panoba formations are present, again contact nature is transitional. Lithology of these rocks comprising of shales and limestones; shallow marine to lagoonal shales and interbedded lime stones. Nammal has its upper contact with Margalla Hill Formation or Sakesar .Margalla Hill has shales with marine limestone (Wandrey *et al.*, 2004).

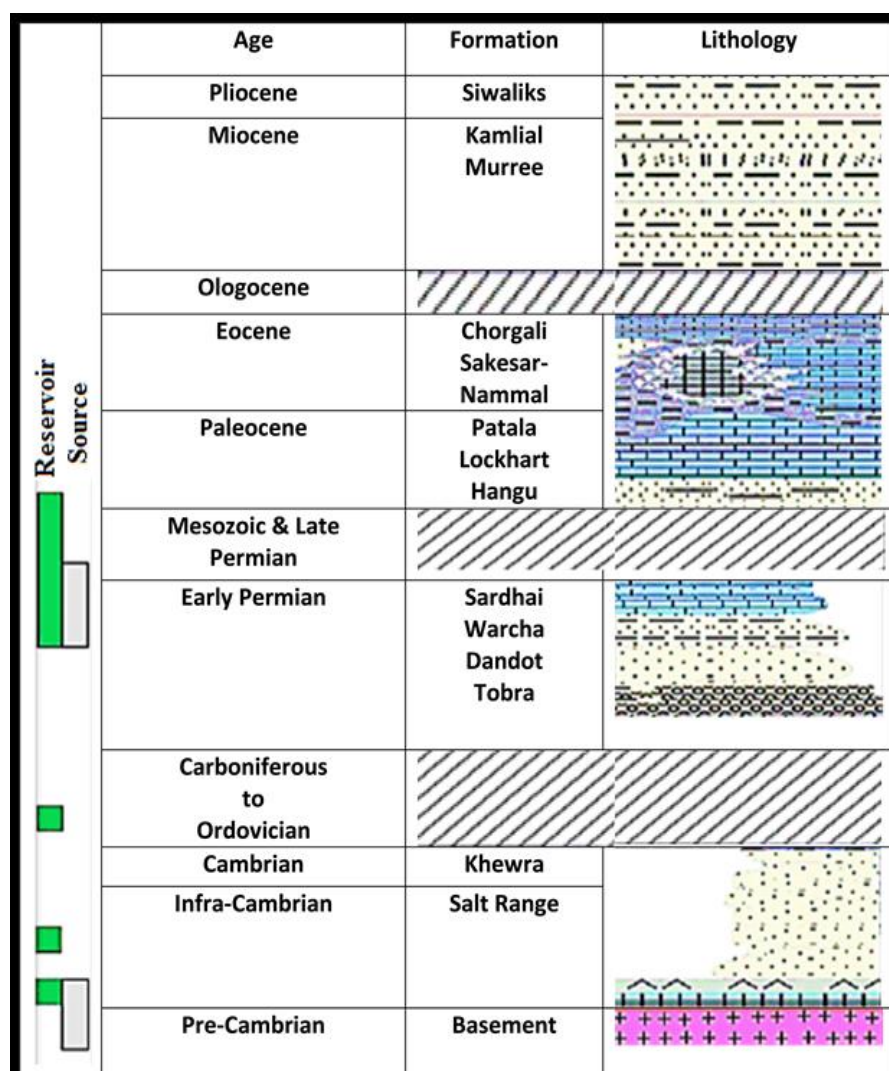


Figure 2.3. Stratigraphic column of Upper Indus Basin of Pakistan (modified from OGDC, 1996; Quadri, 1996; Iqbal and Shah, 1980).

Next strata is in the form of Cherat Group. It includes the interbedded lime stones and shales of Chorgali Formation of lower Eocene, upper Eocene Kohat Formation and ramp carbonates along with highstand shales of Oligocene's Kirthar Formation. Most of Oligocene rocks are missing in mostly parts of basin (Nazir, 2013). Fluvial sandstones and siltstones of Murree Formation, same type of sand stones of Kamliyal Formation and the clays of Rawalpindi Group is the upper region deposition. The top of stratigraphic column is marked by Pliocene and Pleistocene rocks of Siwalik Group (Wandrey *et al.*, 2004).

CHAPTER 3

METHODOLOGY

Methodology of this research work is divided methodology for field work and methodology for laboratory work.

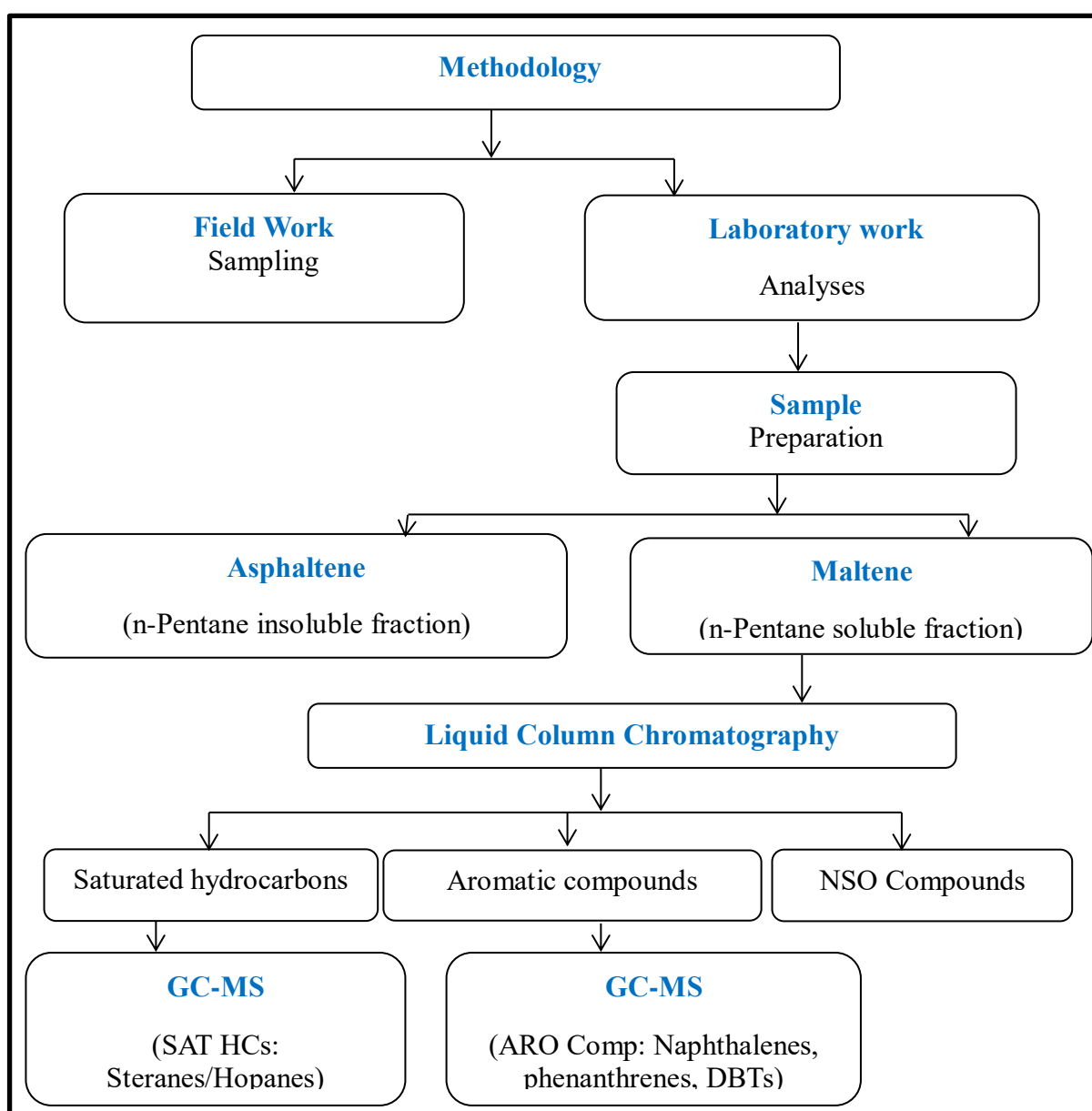


Figure 3.1. Representation of flow chart for research work.

3.1 Methodology for Field Work

Field activities of this research comprises of physical observations of study area, taking of photographs of seeps and collection of samples. Physical observation is very important to develop concepts and imagination about the site of oil seeps, which is consequently helpful in study and learning process. Besides these most important job in field is sample collection.

During collection of samples a greater degree of care was taken because the whole research work is dependent upon the analysis of the samples which were collected in the field. For these geochemical analyses oil samples were collected with uncontaminated spatula/syringe from the bottom of the seepages. The mean to collect samples from bottom is that at bottom the most recent oil is present which is comparatively unaffected by environment factors. These oil samples; one from each location, were kept in small glass containers which were already labeled. These containers were then stored in bag and brought to the laboratory for detail geochemical analysis.

3.2 Methodology for Laboratory Work

In the laboratory the detailed geochemical analysis of collected oil samples were carried out to determine the composition of biomarkers for characterization. There were a number of analytical techniques which were used for geochemical analysis. In this research following analytical techniques were used for analyses which were; liquid chromatography, gas chromatography and gas chromatography mass spectrometry.

3.3 Sample Preparation

3.3.1 Deasphaltation

Liquid chromatography is one of the basic techniques used for the fractionation of oil/extract samples after deasphaltation. The process of deasphaltation involved taking approximately 1 gram of sample using analytical balance (figure 3.2) followed by the addition of n-pentane in ratio of 40:1 in a glass tube that was capped and refrigerated

overnight (figure 3.3). The asphaltene being insoluble in n-pentane precipitated out while hydrocarbons (saturated & aromatic) and polar compounds remained in solution form (maltene).

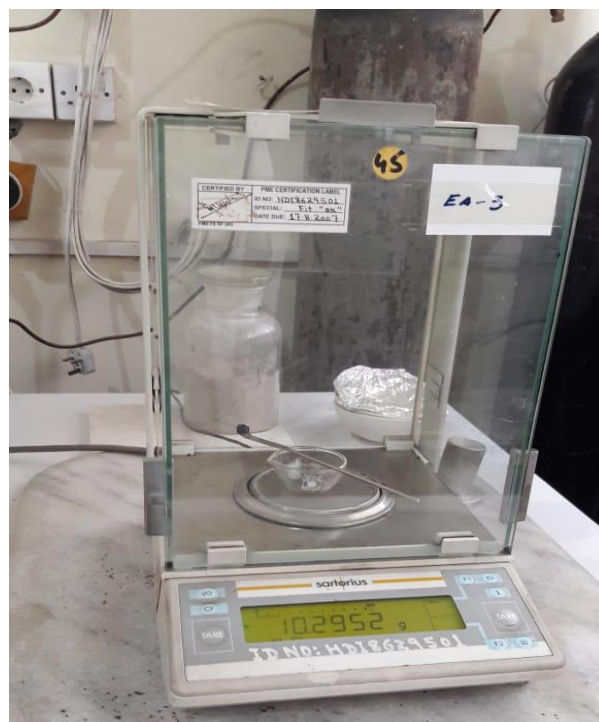


Figure 3.2. Seep samples were weighed using analytical balance.



Figure 3.3. Addition of n-pentane and refrigeration of samples for precipitation.

The samples were centrifuged to separate the asphalt content (figure 3.4). Maltene fractions of seep samples were subjected to Rotavapor to remove solvent and finally transferred to pre-weighed and cleaned glass vials. Rotavapor was operated with vacuum and water was heated to temperature of 45-48 °C (Figure 3.5). The samples were weighed till constant weight of maltene fraction was achieved.

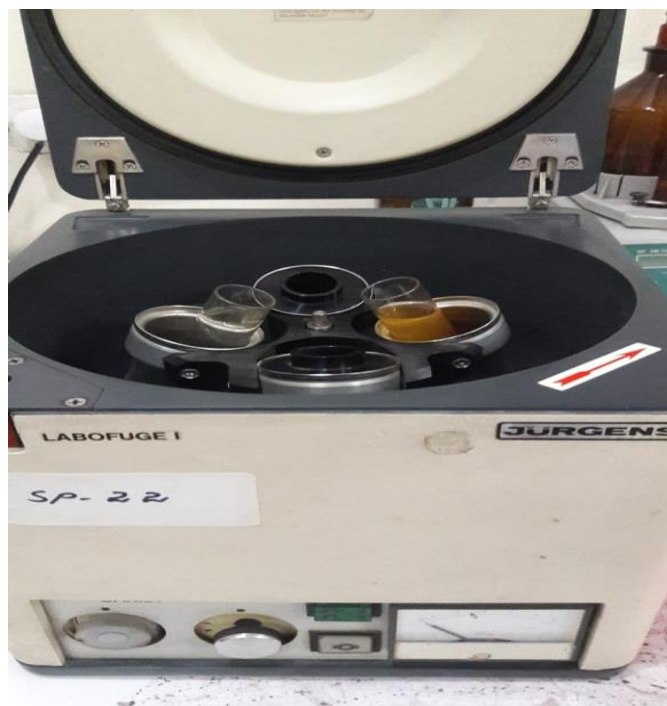


Figure 3.4. Samples centrifuged to separated precipitated asphaltenes.



Figure 3.5. Evaporation of excess of organic solvent rotavapor.

3.3.2 Liquid Chromatography

The stabilized maltene fractions of seep samples were separated into different fractions; such as saturated hydrocarbons, aromatic hydrocarbons, and polar compounds by this column chromatography. Activated silica and alumina were used to pack glass column, slurry of silica in n-hexane was used to pack two third of column while rest of one third was packed alumina slurry in the same solvent (Figure 3.6).



Figure 3.6. Glass column packed with silica and alumina for the separation of maltene fractions

The samples were loaded at the top of column and eluted by using 30 ml of n-hexane to get saturated hydrocarbon fraction followed by 30 ml dichloromethane to elute aromatic hydrocarbons. The polar fraction, containing compounds of nitrogen, sulfur and oxygen was eluted with 30ml mixture of ethanol and ethyl acetate. The excess of solvent was evaporated and fractions transferred to pre-weighed vials.



Figure 3.7. Aromatic fractions (pale color) of maltenes being eluted by DCM.



Figure 3.8. Evaporation of solvent in nitrogen stream.

3.4 Analysis

3.4.1 Gas Chromatography- Flame Ionized Detector

This technique or method or process separates the mixture of organic compounds into individual molecules based on their molecular sizes. In this technique, 1.0 μl of the sample which is dissolved hydrocarbon mixture in the organic solvent is injected into preheated injector maintained at a temperature of 300°C. The sample is volatilized in this section and gaseous sample is flushed with an inert gas onto DB-1 column that has temperature programming and initial temperature is 100°C which is increased to 300°C @ 5°C/minute and then it was kept isothermal for next five minutes. The hydrocarbons, both saturated and aromatics get separated on non-polar column according to their molecular weight. Hydrogen gas (H_2) was used as a carrier as well as fuel for the Flame ionization Detector. Certified standards like those of saturated hydrocarbons mixture: n-alkane +isoalkane (nC_{17} & pristine) were used to judge the working of column and detector's sensitivity. The aromatic and saturated fraction hydrocarbons were diluted with dichloromethane.

The lighter components elute at low retention time. All the hydrocarbons are subjected to flame ionization detector (FID) and signal is generated that is proportional to the quantity of analyte. FID is also maintained at 300 °C (Stashenko, Elena E. et al., 2004).



Figure 3.9. Auto XL Gas chromatograph at the top used to study seeps and GC oven housing column in bottom figure.

3.4.2 Gas Chromatography Mass Spectrometry

One of the modern and sophisticated analytical techniques is GCMS which is used for detailed analysis of saturated hydrocarbons and aromatics hydrocarbons. In GC-MS, a gas chromatography is combined with a mass spectrometry. In this combination the function of gas chromatography is the separation of different compounds which is further enhanced by second stage of separation of particular ions produced in the ion source of the mass spectrometer. Mass spectroscopy works on ionization and mass analysis. The separated components are bombarded by a beam of electrons. This bombardment breaks the components into some small fragments and some fragments which retain their structure and shape. Mass analyzer of mass spectroscopy measures the mass of ions by mass to charge ratio (Stashenko and Elena et al., 2004). In this analysis the time from injection of sample to detection of component is called retention time. (Iadanza et al., 2015) The temperature programming for GCMS remains the same as that of GC, carrier gas used was helium while DB-5MS was the column used for separation.

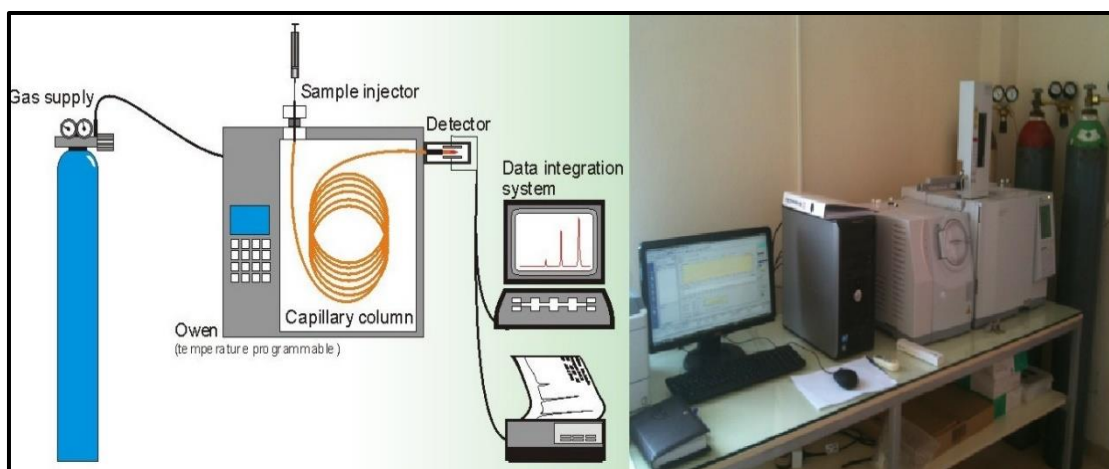


Figure 3.10. Shimadzu QP 2010 mass spectrometer coupled with Shimadzu GC2010 (right) used for biomarkers study while schematics of GCMS are displayed on the left side.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Jaba Seep

Total ion chromatogram of the saturate fraction of hydrocarbons show major shift in baseline which is indicator of biodegradation, unresolved complex mixture, UCM in figure 4.1. The extent of biodegradation is level 4 of Moldowan Biodegradation Scale (Peters *et al.*, 2005) where the n-alkanes have almost completely disappeared and isoalkanes are slightly affected. In non-biodegraded oil, the chromatogram is dominated by n-alkanes followed by iso- and cycloalkanes. The figure shows presence of iso-alkanes at low retention time including pristane and phytane which elute at retention time of 10.5 and 12.4 seconds. There are cyclic alkanes, the biomarkers at higher retention time.

Pristane and phytane isoprenoids are product of chlorophyll of bacteria and phototropic organisms during the catagenesis stage of organic matter transformation. Didyk *et al.* (1978) has made the interpretation of redox parameter of depositional environment; Pr and Ph ratio greater than 1 in oil is an indication of anoxic environment of deposition of the source rock, value > 3 shows oxic environment while 1-3 reflects suboxic condition of depositional environment.

In this sample, isoprenoid pristane and phytane predominate and therefore isoprenoid/n-alkane ratio considerably high due to loss of n-alkane which reflects biodegradation. This ratio is expected to increase with increase in thermal maturity since thermal cracking releases abundant amount of n-alkanes and Ph/nC₁₈ and Pr/nC₁₇ ratio decrease. The well-known Pr/Ph ratio is also used to study and guess the environment in which deposition was occurred and another characteristic the source input, since assemblage of the organism contributing to organic matter in sedimentary rocks will depend upon the environment of that time (Didyk *et al.*, 1978; Haven *et al.*, 1987; Fu *et al.*, 1990).

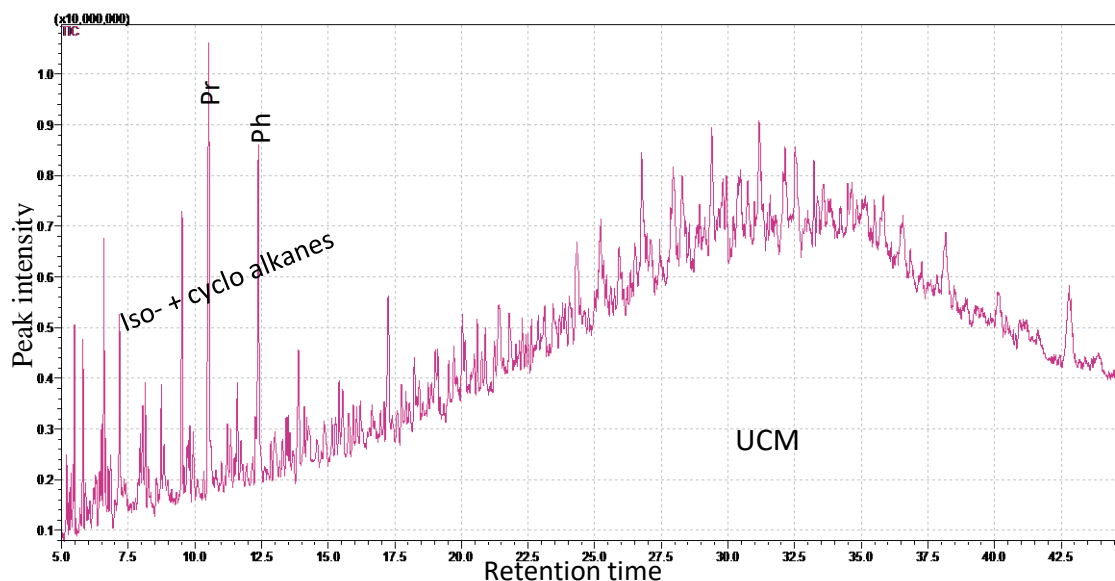


Figure 4.1. Total ion chromatogram of Jaba seep showing UCM and absence of n-alkanes.

Pr/Ph ratio for Jaba seep was calculated from integration of peaks in m/z 85 and 183 ions chromatograms and it has value of 1.4 that shows suboxic type environment when the source rock was deposited and is expected to have received the mixed source organic matter, marine as well as terrestrial during deposition, though $Pr/Ph < 1$ in non-biodegraded oils is generally considered as marine (Peters and Moldowan, 1993). It is also useful parameter to indicate the terrestrial versus marine source input in sedimentary rocks (Talukdar *et al.*, 1986; Peters *et al.*, 2005).

The distribution of biomarkers is obtained by fragmentograms of saturate fraction of all the seep samples; terpanes by m/z 191, steranes by m/z 217 and 218. Jaba seep terpane distribution is represented by figure 4.2. The ion chromatogram is dominated by hopanes, pentacyclic terpanes compared to tricyclic terpanes.

The series of tricyclic terpanes has three six membered rings and starts from nC_{19} and extends upto C_{54} due to side chain (Moldowan *et al.*, 1983). The origin of tricyclic terpanes has been considered a precursor in prokaryotic membranes (Ourisson *et al.*, 1982), while some have even suggested that high concentrations associated with *Tasmanites* rich source rocks could even be related to algae (Azevedo *et al.*, 1992). The extended tricyclic terpanes, C_{28} and C_{29} are applied for the oil-oil and oil-source correlations (Seifert *et al.*, 1980; Seifert and Moldowan, 1981).

The lowest member of the tricyclics, C_{19} and C_{20} has been considered as terrestrial source indicators (Noble, 1986). Figure 4.2 shows low abundance of tricyclic

terpanes, the most abundant is C₂₃ among series while C₁₉ and C₂₀ show low abundance. Tetracyclic terpanes are produced from degradation of hopanes and have higher resistance to process of biodegradation and maturation than the hopanes.

Pentacyclic terpanes have precursors in prokaryotes, even in the higher plants however there appears no precursor in eukaryotic algae. Since bacteria are very common in sedimentary rock, the hopanes are generally present in oil and source rock extracts. Hopanes contain 27 to 35 atoms of carbon arranged in such way that there are four 6-membered rings and one 5-membered ring (Van Dorsselaer *et al.*, 1977; Peters and Moldowan, 1993).

The source related biomarkers in Jaba seep include presence of Oleanane which shows the source input from flowering plants (Ekweozor and Udo, 1988; ten Haven and Rullkotter, 1988) and here Oleanane index is 18%. The Oleanane is also used as age biomarker and Late Cretaceous to Younger source rock have oleanane index > 20% (Moldowan *et al.*, 1994a). However, absence of oleanane is not the evidence that oil has been produced from Early Cretaceous or the older sedimentary rocks. Small quantity of oleanane has been observed in sediments from Jurassic time period source rock extracts and crude oils with oleanane index <20% (Moldowan and others, 1994a; Peters *et al.*, 1999b; Taylor *et al.*, 2004). Based on this fact, the source rock for Jaba seep appears to be Jurassic to Early Cretaceous.

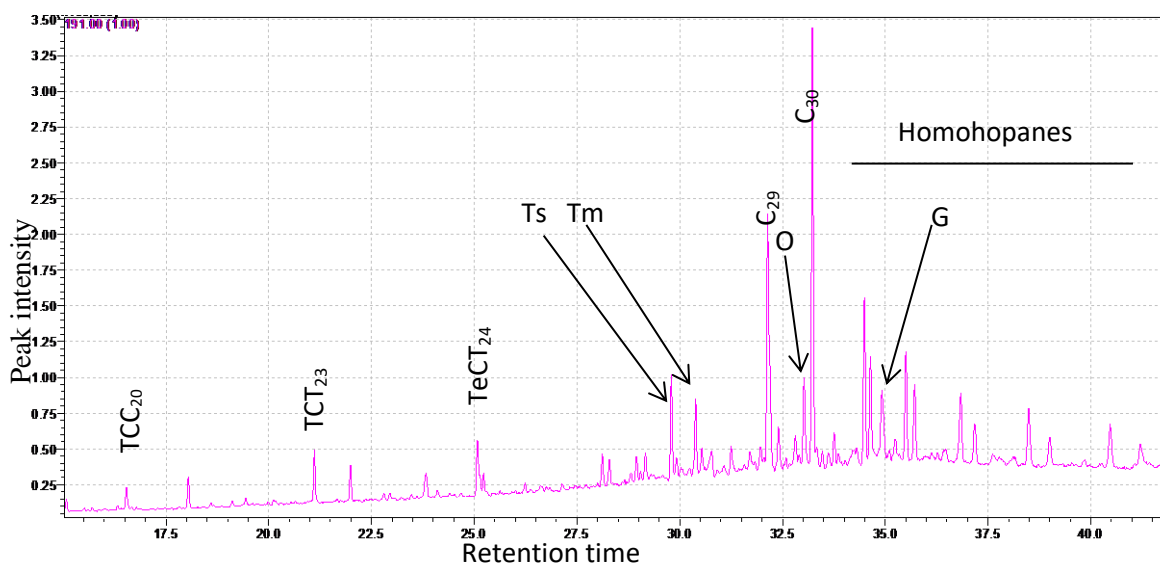


Figure 4.2. Ion chromatogram 191 representing tri-, tetra- and pentacyclic terpanes in Jaba Seep.

The environment when source rock was deposited is also detected by gammacerane, high abundance relative to C_{31} homohopanes in oil/seep indicates the source was deposited during hypersaline conditions (Sinninghe Damste *et al.*, 1995). It shows water column stratification was formed in marine as well as non-marine type environment of deposition. Presence of gammacerane in Jaba seep shows water column stratification during deposition of its source rock.

Another source indicator is sterane distribution represented by ion chromatograms m/z 217 and 218 (figures 4.3 and 4.4 respectively). Both of fragmentograms show dominance of C_{29} steranes, C_{29} is 55% while C_{27} is 28% (Table 4.1). C_{27} sterane has marine input while abundance of C_{29} reflects terrestrial input (Moldowan and Peters 1993). Jaba seep with dominance of C_{29} sterane reflects considerable terrestrial input in accordance with oleanane.

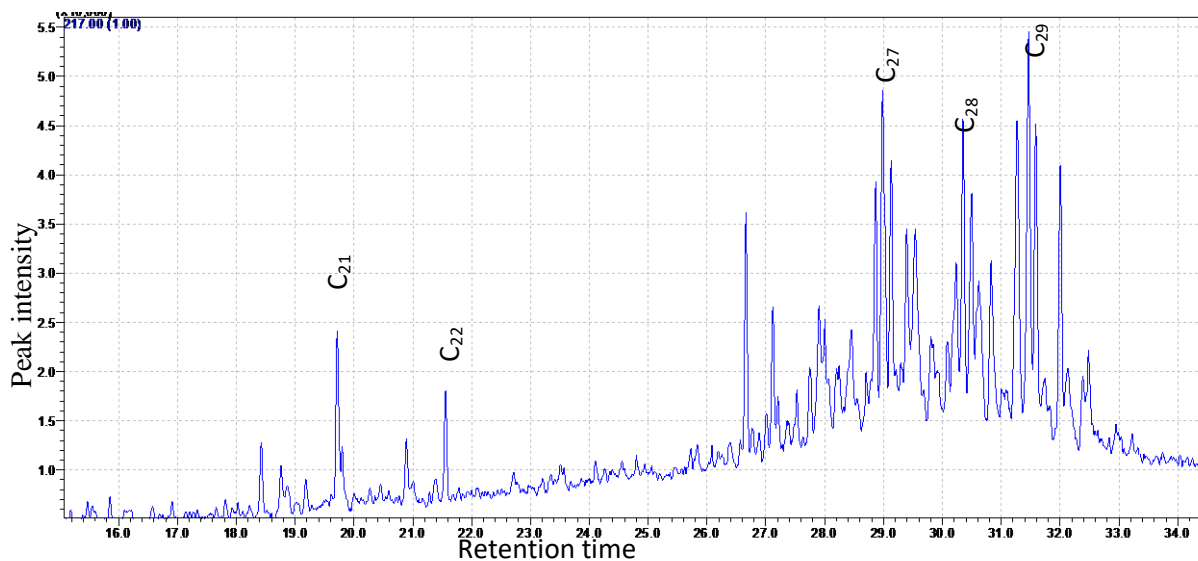


Figure 4.3. Chromatogram m/z 217 showing composition of diasteranes and regular steranes in Jaba seep.

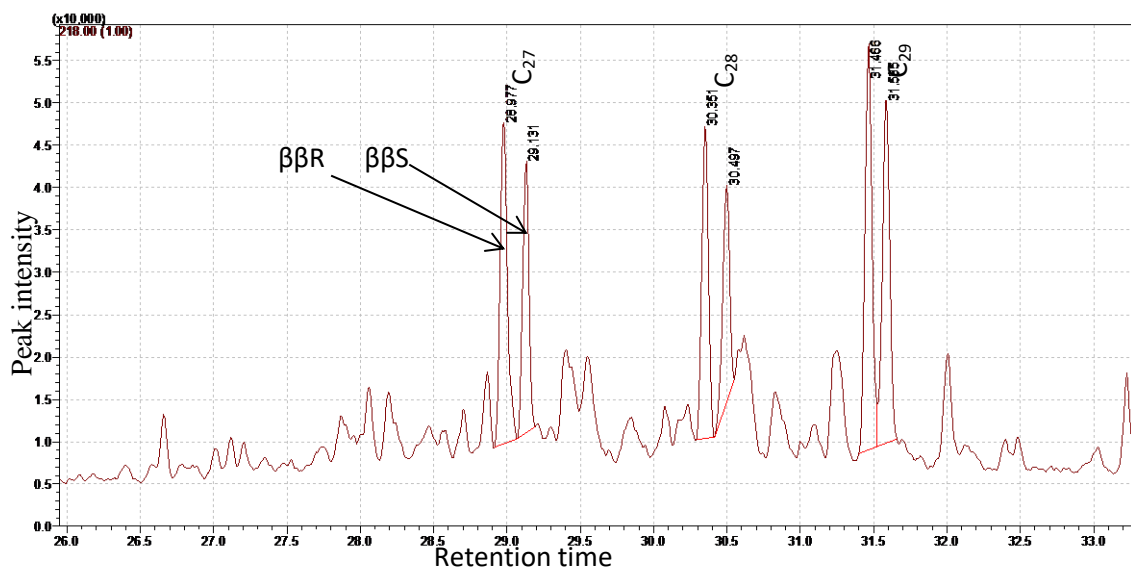


Figure 4.4. Chromatogram m/z 218 showing distribution of $\beta\beta$ C₂₇-C₂₉ steranes in Jaba Seep.

There is a consistent increase in the ratio of C₂₈ to C₂₉ sterane ratio in marine petroleum due to diversifications of phytoplanktons throughout the geological time (Moldowan *et al.*, 1985; Grantham and Wakefield, 1988) as presented in figure 4.5. The ratio calculated from m/z 218 has value of 0.7 which represents Jurassic-Cretaceous aged source rock for the Jaba seep oil.

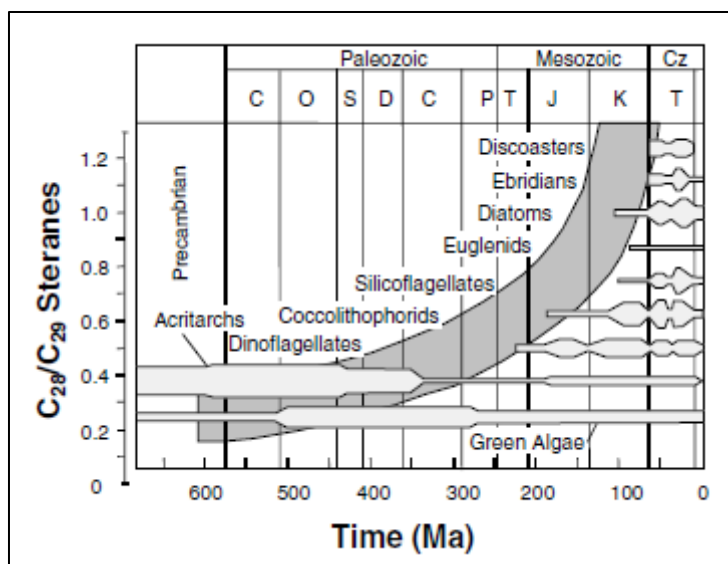


Figure 4.5. C₂₈/C₂₉ steranes ratio of crude oils from the marine source rocks (Grantham and Wakefield 1988).

4.2 Kundal Seep

The oil seep from Kundal represented in figure 4.6 shows have biodegradation where all the n-alkanes and iso-alkanes have been completely removed and total ion chromatogram shows clear distribution of cyclic biomarkers.

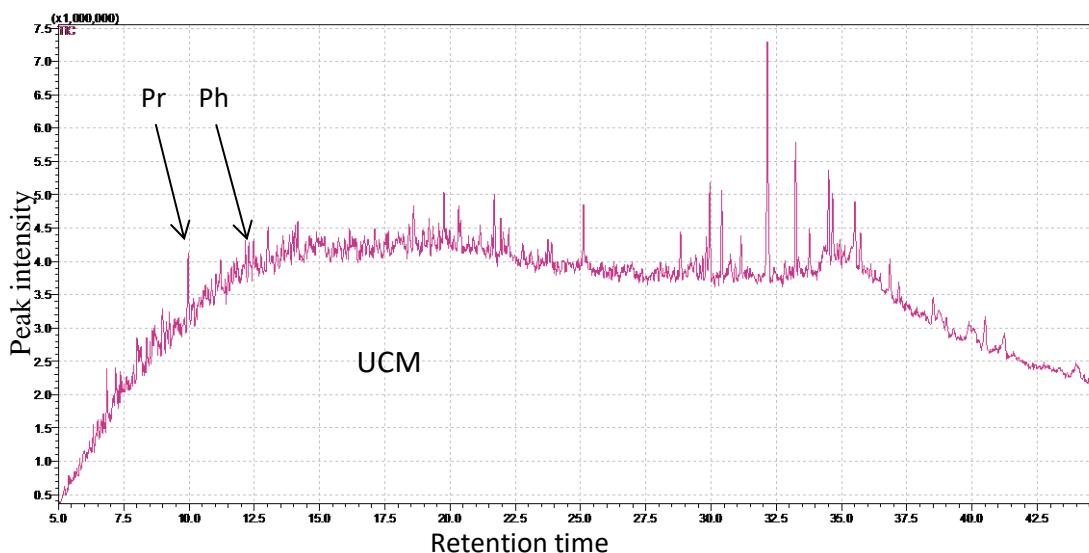


Figure 4.6. Total ion chromatogram of Kundal seep oil.

According to Peters and Moldowan biodegradation scale (figure 4.7) Kundal seep falls in category of PM-5 scale where alkane and isoprenoid classes of hydrocarbons have been completely removed. Therefore the information about source input, thermal maturity and environment of deposition based on distribution of alkanes and isoprenoids could not be made.

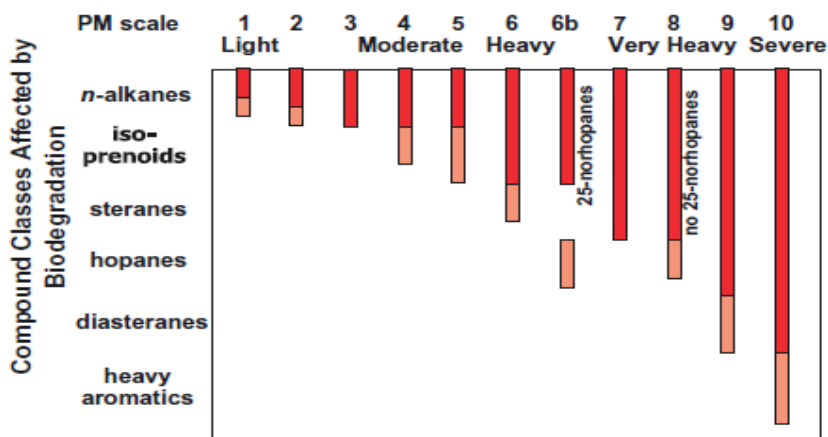


Figure 4.7. Modified Peters and Moldowan (1993) biodegradation scale (Larter et al., 2012).

The distribution of terpanes is presented for Kundal seep in figure 4.8 that shows dominance of hopanes over tricyclic terpanes and among hopanes, C₂₉ hopane is most dominant which represents carbonate source rock (Fan et al., 1987; Subroto *et al.*, 1991; Peters *et al.*, 2005). Among homohopanes C₃₅ has high relative abundance over C₃₄ which is an indicator of anoxic depositional environment of the source rock of Kundal seep (Dhal *et al.*, 1994). The Oleanane biomarker, a well-known age as well as source input indicator is absent in this seep oil sample.

The maturity indicator Ts/Tm shows dominance of thermodynamically stable isomer Ts over biological isomer Tm, thereby representing high thermal maturity of the source rock.

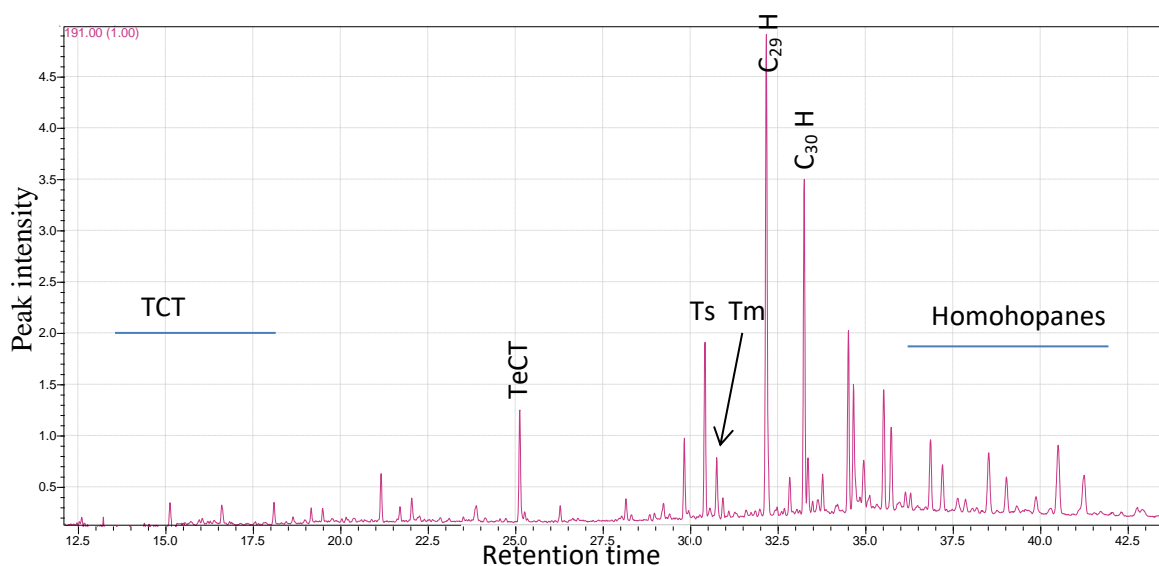


Figure 4.8. Ion chromatogram m/z 191 showing predominance of the tricyclic terpanes in Kundal Seep.

The thermal maturity characteristic of the source rock from where Kundal seep is produced, based on homohopanes biomarkers; C₃₁ S/S+R is 0.58 (Table 4.2) which indicates peak oil maturity for producing rock a corresponds to 0.7 to 0.8 of vitrinite reflectance (Peters *et al.*, 2005). Other maturity indicators based on C₂₉ steranes are S/S+R and $\beta\beta/\beta\beta+\alpha\alpha$ with values of 0.59 and 0.54 respectively. It was observed by Seifert and Moldowan (1981) that oil formation takes place at maturity of S/(S +R) value of 0.23–0.29 and reaches equilibrium at 0.5 (Seifert and Moldowan, 1986). The biogenic precursor has R isomer that is converted into S with increasing thermal maturity for homohopanes and steranes. Low maturity source has dominant $\alpha\alpha$ isomer that is transformed into thermally stable $\beta\beta$ isomer during organic matter transformation at

catagenesis stage (Peters and Moldowan, 1993). This transformation attains equilibrium at late stage of thermal maturity of the source with value of 0.67-0.7 (Seifert and Moldowan, 1986).

Table 4.1. Source and depositional environment related biomarkers based on terpanes in Seep samples

PARAMETERS	JABA	PANOBA	KUNDAL	GOLRA
C ₁₉ /C ₂₀ TCT	0.5	1.2	1.0	0.8
C ₂₀ /C ₂₃ TCT	0.5	---*	0.5	0.8
C ₂₅ /C ₂₆ TCT	0.8	---	3.6	1.4
C ₂₄ TeT/C ₂₆ TCT	1.6	---	19.6	3.6
C ₂₄ TeT/C ₃₀ H	0.1	0.1	0.3	0.3
C ₂₃ TCT/H	0.1	0.0	0.1	0.3
C ₂₃ /C ₂₁ TCT	1.6	---	2.2	1.1
C ₁₉ +C ₂₀ /C ₂₃ TCT	0.8	---	0.9	1.5
C ₂₄ /C ₂₃ TCT	0.8	---	0.5	0.7
C ₂₆ /C ₂₅ TCT	1.3	---	0.3	0.7
C ₃₀ H/C ₃₁ R HH	4.4	3.9	2.3	3.4
Pr/Ph	1.4	3.5	0.9	1.3
H ₂₉ /H ₃₀	0.6	0.5	1.5	0.8
HH ₃₅ /HH ₃₄	0.7	0.3	1.3	0.6
HHI	0.1	0.0	0.2	0.1
GI=G/G+30H	0.2	0.1	0.2	0.1
OI=O/(O+30H)%	18.0	0.0	0.0	0.0

★ Parameter couldn't be evaluated due to absence of biomarker in sample

The short chain steranes, not common in young Phanerozoic petroleum systems were studied by GCMS in the petroleum from the Siberian platform (Nepa-Botuoba anticline) and Arabian platform (Southern Oman Salt Basin) and these steranes appeared to be thermodynamically more stable than regular steranes (Kashirtsev *et al.*, 2015). Kundal seep shows high abundance of C₂₁ and C₂₂ (short

chain) steranes over C_{27} - C_{29} steranes which is hint of the high thermal maturity level in the source rock as displayed in figure 4.9 (Peters et al., 2005).

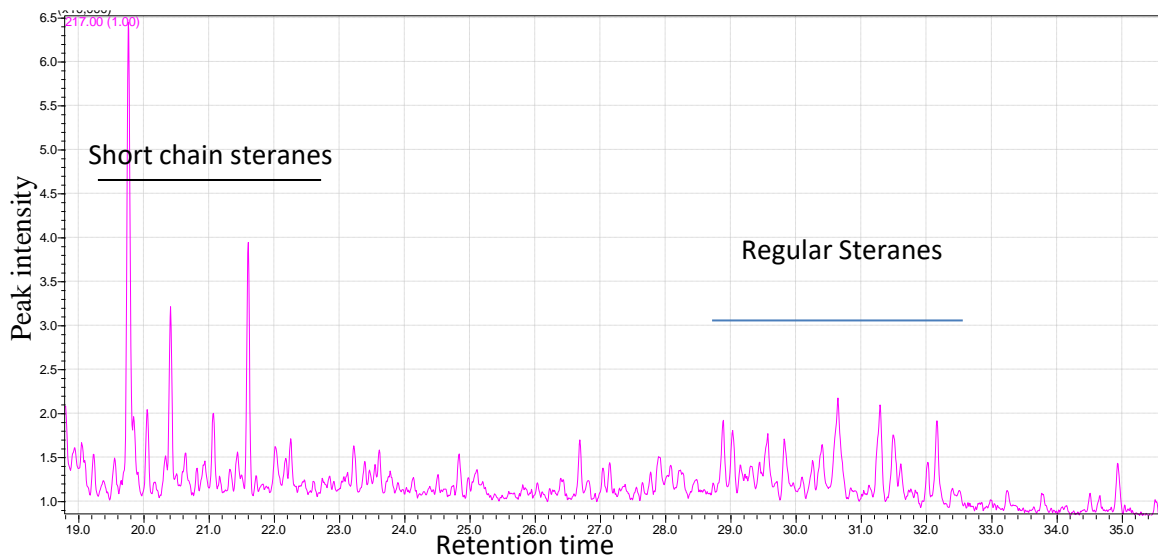


Figure 4.9. m/z 217 presenting sterane distribution in Kundal seep.

The relative abundance of sterane shows high relative concentration of C_{29} sterane (figure 4.9) while C_{28}/C_{29} sterane has value of 0.47 which corresponds to high abundance of dinoflagellates (figure 4.5; table 4.2).

4.3 Panoba Seep

Panoba seep is characterised by low level of biodegradation, scale 2 of Peters and Modowan Biodegradation scale as reflected by figure 4.10 which shows biodegradation of n-alkanes though not completely removed. The short chain alkanes have been almost removed from the seep oil of Panoba. The chromatogram shows high abundance of isoprenoids pristane and phytane. There is also a shift in baseline which represents biodegradation products in the form of unresolved complex mixture. The predominance of pristane over phytane is an indication for oxic nature of environment during the deposition of source rock of the seep sample. The value of Pr/Ph is 3.5 (Table 4.1) which falls in category of oxic depositional environment and is expected to have received predominant terrestrial input (Peters *et al.*, 2005).

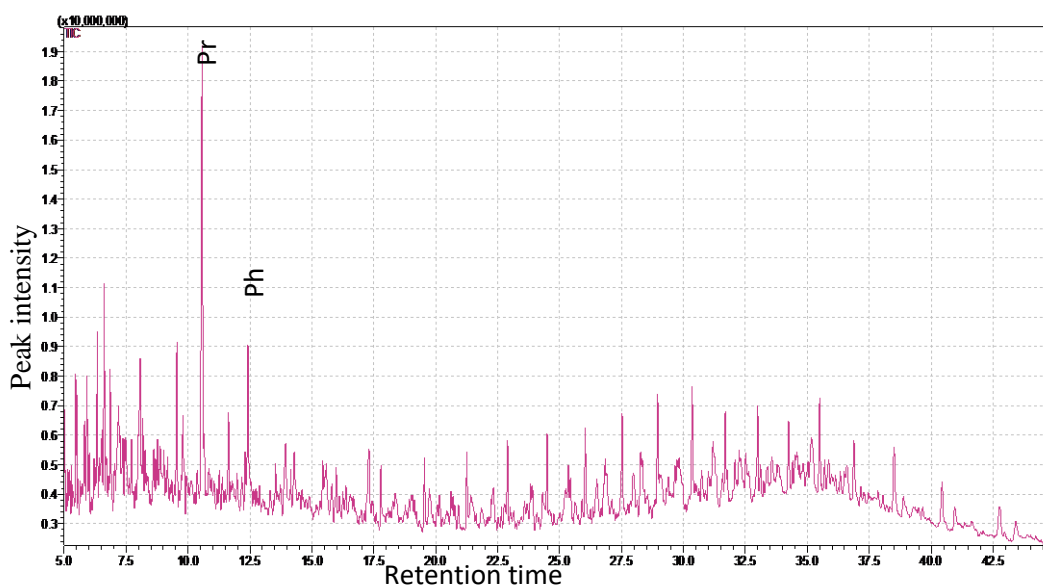


Figure 4.10. Total ion chromatogram of Panoba oil seep.

The n-alkanes upto nC_{37} are observed in m/z 57 ion chromatogram (figure 4.11) with odd to even predominance in higher alkanes with $nC_{29} > nC_{30} < nC_{31}$, $nC_{31} > nC_{32} < nC_{33}$ and $nC_{33} > nC_{34} < nC_{35}$ which are characteristics of terrestrial source input and low thermal maturity of the source rock. In the chromatogram the most abundant of n-alkanes is nC_{27} .

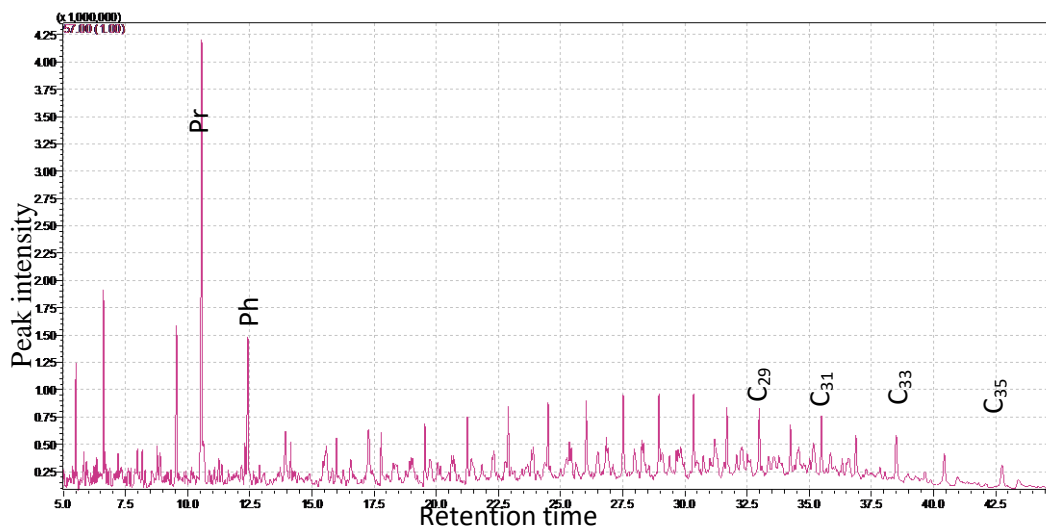


Figure 4.11. m/z 57 showing n-alkane and iso-alkane distribution in Panoba seep.

The distribution of terpanes is displayed in figure 4.12 which have an abundance of pentacyclic terpanes. Among tricyclic terpanes there is presence of C_{19} and C_{20} TCT which are contributed by the terrigenous organic matter as expected for the oxic depositional environment. Hopanes are dominated by C_{30} hopane; high ratio of C_{30}/C_{29} hopane indicates shale lithology of the source rock. The high abundance of diahopane (eluting next to C_{29} hopane) reflects presence of clay minerals which catalyze the conversion of hopane precursor into C_{30} diahopane.

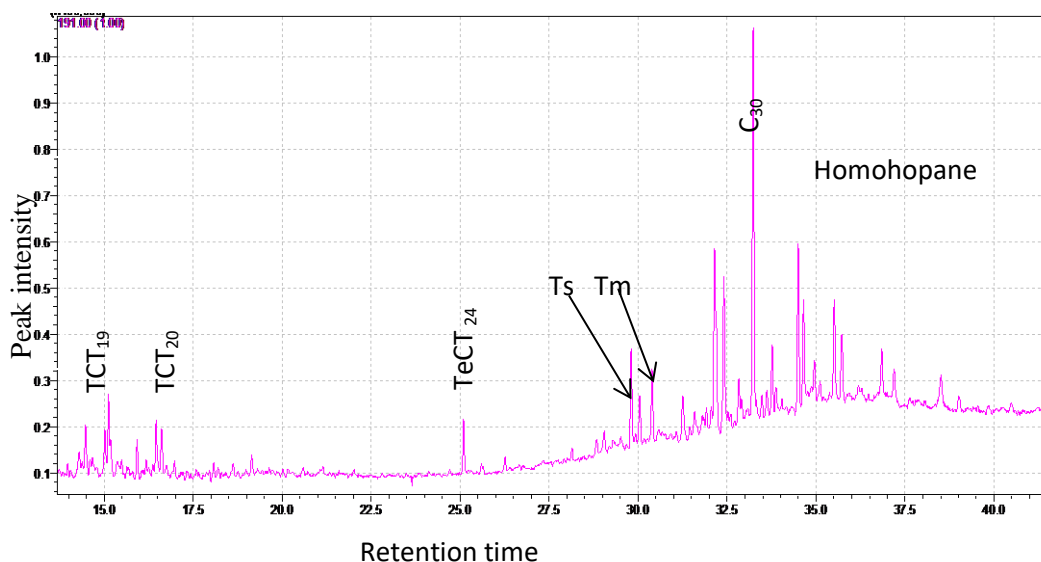


Figure 4.12. m/z 191 displaying terpanes distribution in Panoba seep.

Among homohopanes C_{35} has almost disappeared owing to oxic depositional environment and biodegradation. S/S+R 32 homohopane shows abundance of stable S isomer compared to R isomer of biological origin and has value of 0.55. Another

thermal maturity parameter $T_s/T_s + T_m$ has value of 0.68 (figure 4.12), both of which show thermally mature source rock. It is expected that source rock has not attained peak thermal maturity as reflected by odd to even predominance in higher n-alkane series. Panoba seep has series of sesquiterpanes among which drimane and homodrimane (figure 4.13) and dominant the ratio of drimane/homodrimane is 0.87 which again shows the source rock has not attained peak maturity.

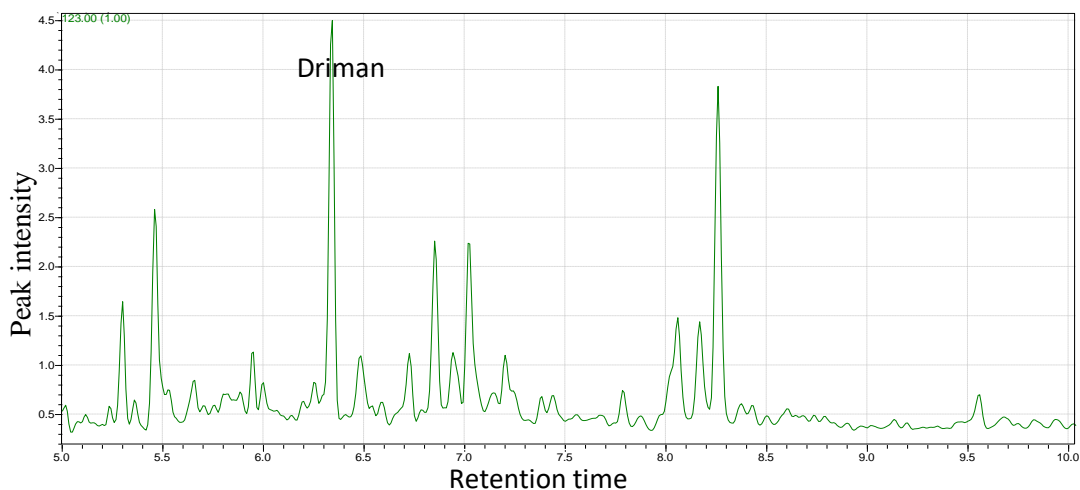


Figure 4.13. m/z 123 showing relative abundance of sesquiterpanes in Panoba seep.

The m/z 217 ion chromatogram shows high diasteranes abundance as compare to compare to regular steranes as C_{27} sterane shows co-eluting C_{28} and C_{29} diasteranes.

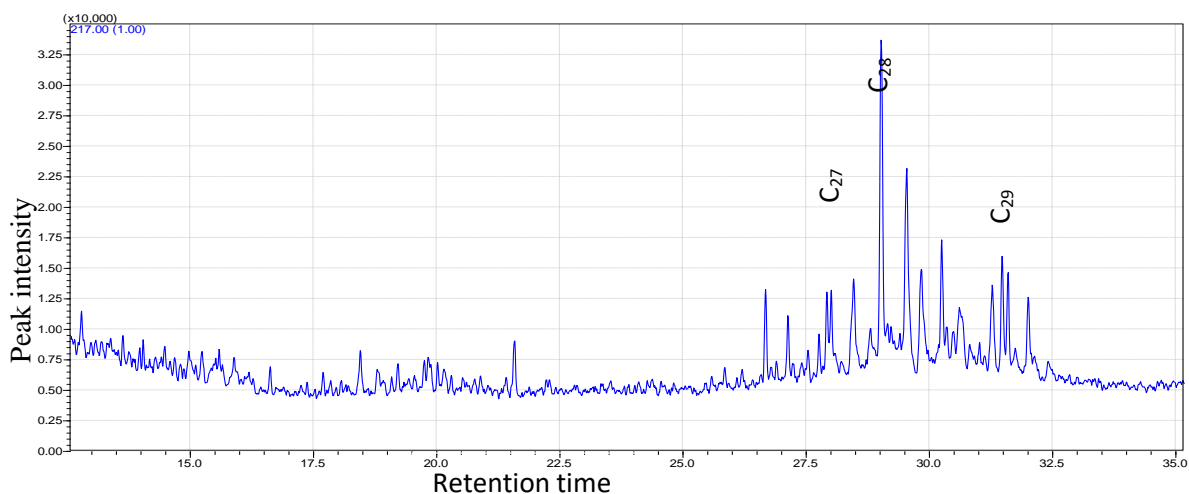


Figure 4.14. m/z 217 showing abundance of diasteranes in Panoba seep

This is very similar to high concentration of diahopane C_{30} . Both types of products are enhanced by clay minerals in source rock (figure 4.14). In both m/z 217 and 218 ion chromatograms the high concentration of C_{29} steranes is an evidence of

terrestrial input in Panoba seep (figure 4.14 and 4.15 respectively). The percentage composition of C_{27} and C_{29} is 36% and 57% respectively which is evidence of terrigenous input to source rock. Thermal maturity based on $S/S+R$ and $\beta\beta/\beta\beta+\alpha\alpha$ C_{29} sterane parameters has values 0.6 and 0.58 respectively. The equilibrium value of $\beta\beta/\beta\beta+\alpha\alpha$ at late maturity of 0.67-0.7 and therefore source rock has not attained this equilibrium. The values show peak maturity of the source.

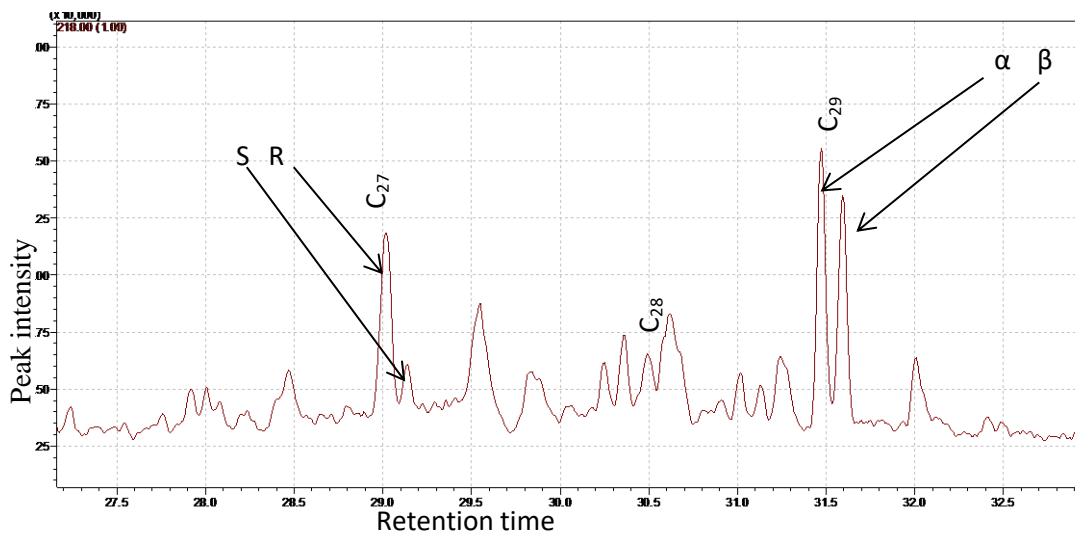


Figure 4.15. m/z 218 ion chromatogram showing relative abundance of $\beta\beta$ steranes in Panoba seep.

Table 4.2. Maturity related biomarkers based on terpanes in Seep samples

PARAMETERS	JABA	PANOBA	KUNDAL	GOLRA
Ts/Ts+ Tm	0.6	0.7	0.3	0.5
29Ts/29Ts+29H	0.2	0.3	---	0.0
M29/H29	0.1	0.8	0.0	0.2
M30/H30	0.1	0.2	0.1	0.1
HH31S/S+R	0.6	0.6	0.6	0.6
HH32S/S+R	0.6	0.6	0.6	0.6

4.4 Golra Seep

Golra seep has characteristic chromatogram of biodegraded oil, n-alkanes have disappeared and has predominant peaks of iso-alkanes in which pristane (retention time 10.518) is most abundant followed by phytane (having retention time of 12.382) as presented in figure 4.16. This stage of biodegradation corresponds to level 2 of Peters and Moldowan Scale and slightly degraded on Wanger (2002) scale. The extent of biodegradation is reflected by UCM from region of light to heavy n-alkanes. Pr/Ph has value of 1.3 which indicates sub-oxic environment of deposition with mixed, marine and terrestrial source input.

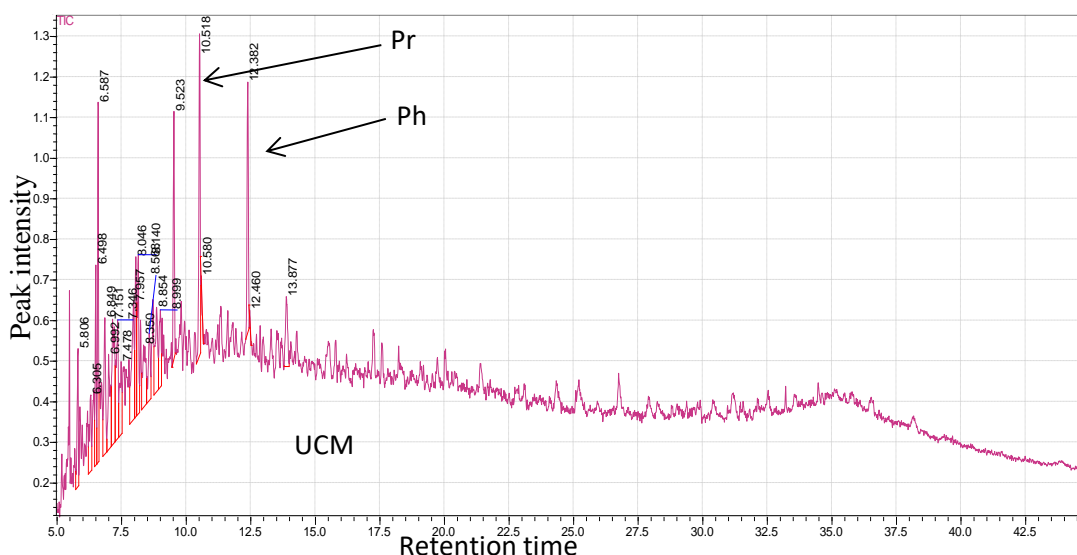


Figure 4.16. Total ion chromatogram of Golra seep dominated by isoprenoids.

The biomarkers among terpane series are dominated by hopanes (figure 4.17), tricyclic terpanes extend from C₁₉ to C₂₉ with nC₂₃ being the most abundant (retention time 21.116). High value for (C₁₉+C₂₀)/C₂₃ tricyclic terpane (1.52) shows terrestrial input.

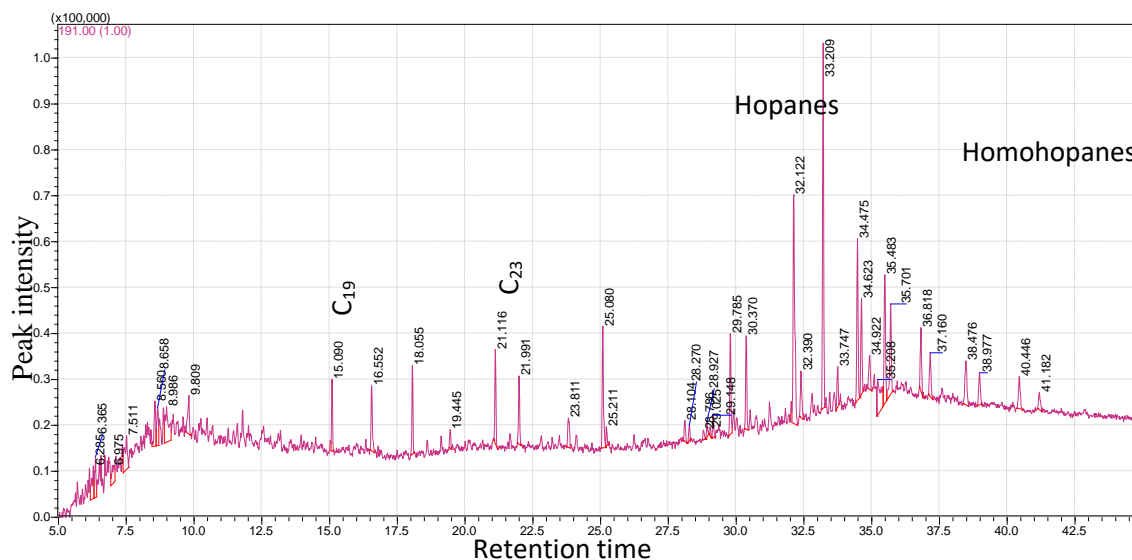


Figure 4.17. m/z 191 showing relative abundance of terpanes in Golra Seep.

$C_{19}/(C_{19} + C_{23})$ TCT ratio has been applied as an indicator of organic matter source and has high values for seeps terrigenous sourced rocks while low values are observed marine source (Zumberge, 1987). Tetracyclic terpanes are dominant in the petroleum whose depositional environment associated with carbonate or evaporite (Palacas *et al.*, 1984; Clark and Philp, 1989). The value of C_{24} TeCT/(C_{24} TeCT + C_{23} TCT) with value of 0.56 reflects influence of mixed source input (Figure 4.18) for Golra Seep. However due to unavailability of biomarkers in Panobal sample it could not be seen in figure 4.18.

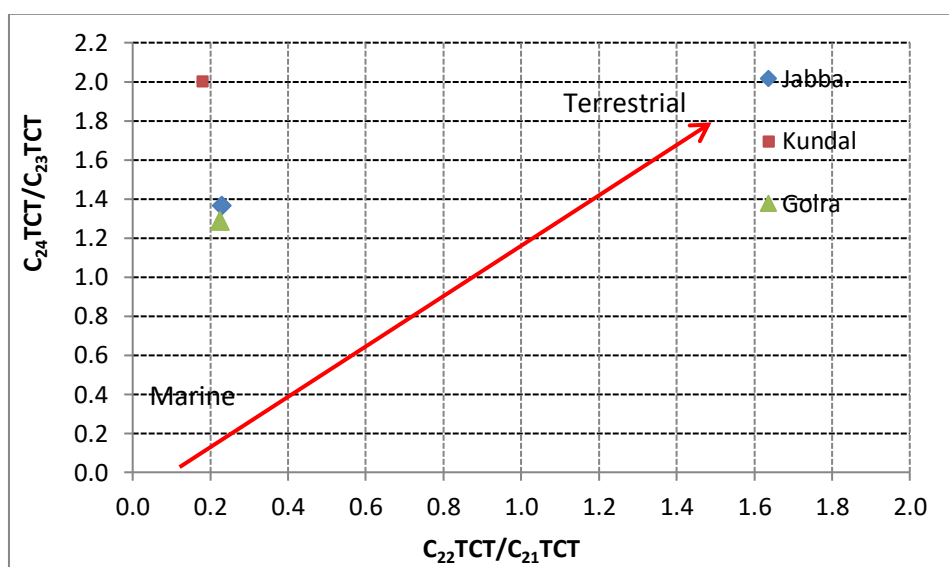


Figure 4.18. Figure showing source matter for oil seeps from Upper Indus Basin.

The distribution pattern of doublet series of homohopanes in ion chromatogram m/z 191 is applied for the assessment of redox conditions of the source sediment. High relative presence of C_{29} compared to C_{30} is applied for the carbonate source as well, therefore high ratio C_{29}/C_{30} will be an indication of carbonate lithology as a source input (Machihara and Waples, 1991). Based on study of (Peters et al., 2005) the correlation $C_{29}/C_{30} > 0.6$ with C_{35}/C_{34} homohopane ratios >0.8 are applied as indications lithology of marine carbonate rocks which appear to be 0.82 and 0.60 for Golra seep doesn't not support carbonate source, however values of C_{29}/C_{30} hopane and C_{35}/C_{34} homohopane 1.54 and 1.30 for Kundal seep reflects carbonate source rock (figure 4.19, Table 4.2).

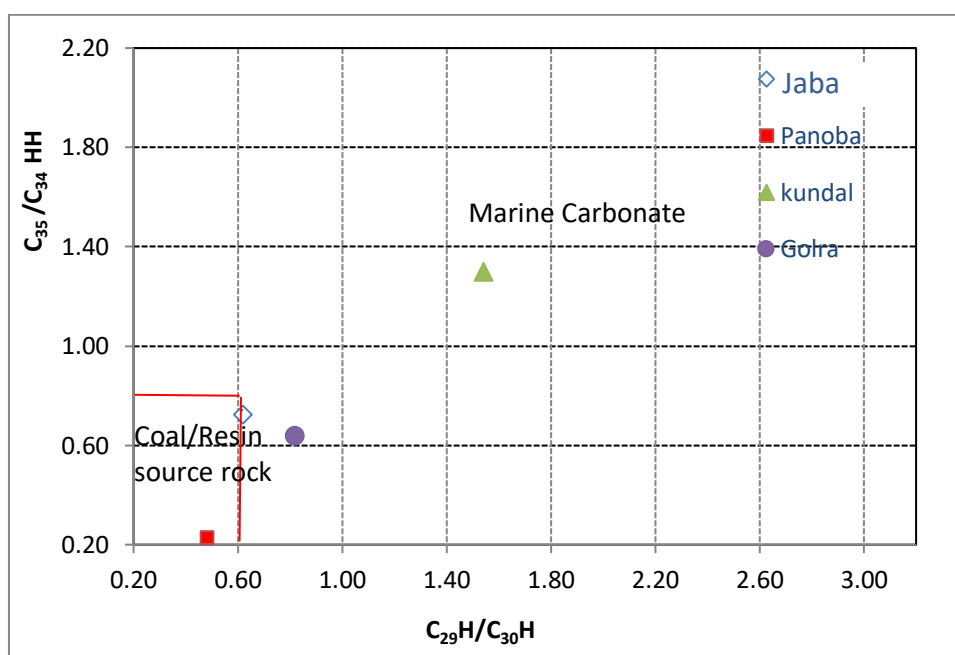


Figure 4.19. Cross Plot of $C_{29}/C_{30} H$ vs. $C_{35}/C_{34} HH$ for evaluation of source facies for oil seeps.

Steranes are the saturated hydrocarbons having precursors derived from a number of organisms, including dinoflagellates, algae, phytoplanktons, and higher plants and studies from m/z 218 and 217 ion chromatograms which are dominated by C_{29} sterane (55%, Table 4.3) in figure 4.20 and 4.22. The relative abundance of sterols plotted on a ternary diagram can be used to determine the source input as well as environment of deposition (Moldowan *et al.*, 1985; Huang and Meinschein, 1979). The ternary plot for Golra seep based on steranes distribution gshows higher plant input (figure 4.21).

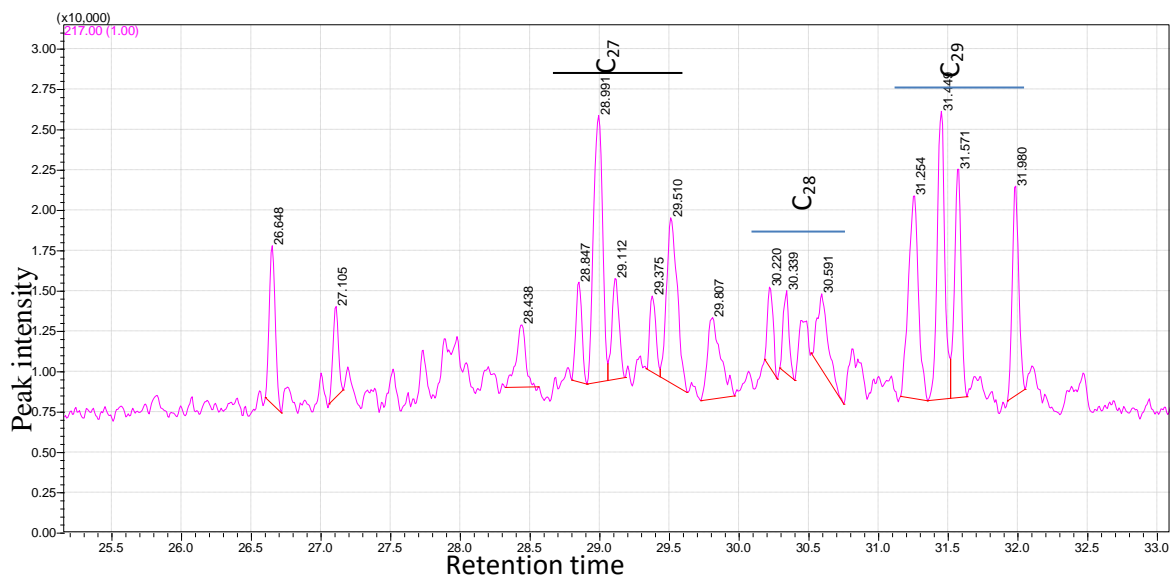


Figure 4.20. m/z 217 showing sterane distribution in Golra seep.

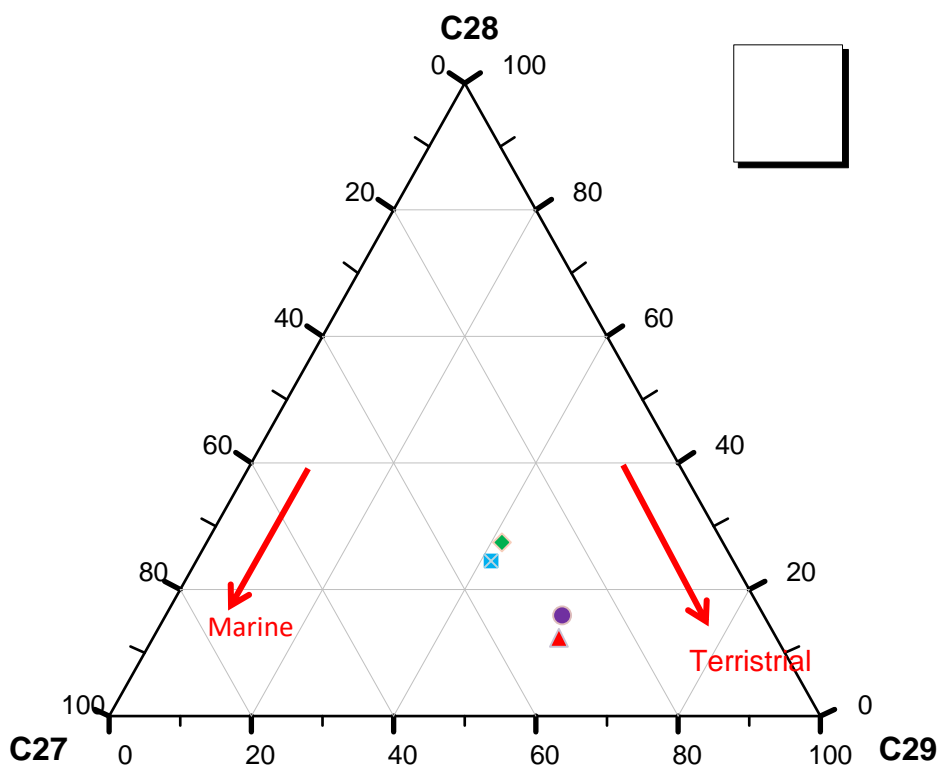


Figure 4.21. Ternary diagram displaying regular steranes distribution of oils and source rock extracts.

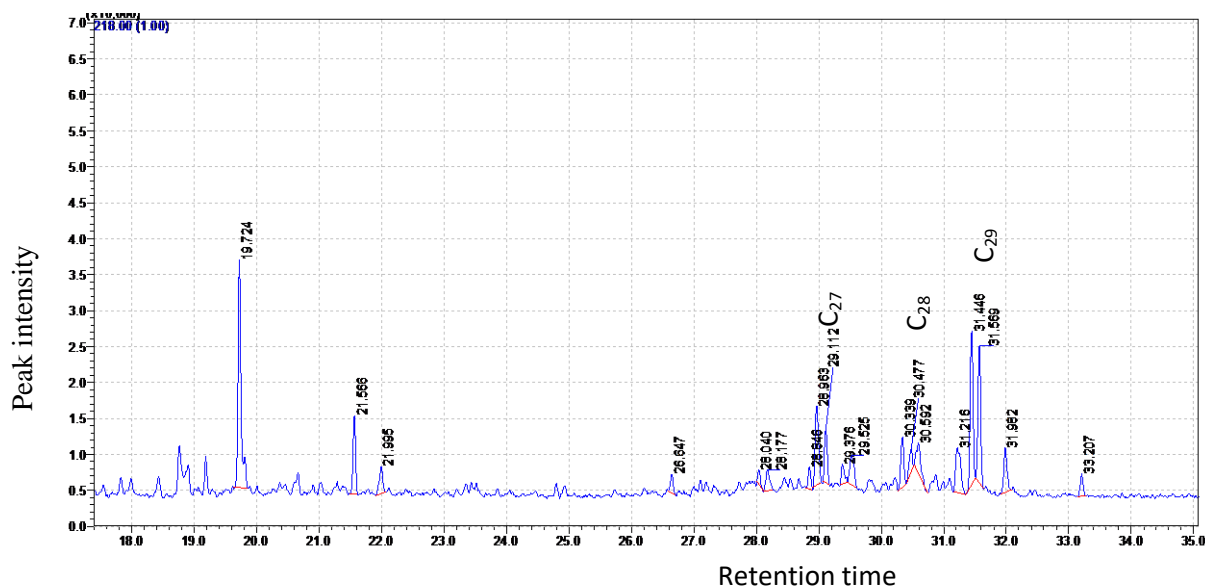


Figure 4.22. m/z 218 showing distribution of $\beta\beta$ steranes.

Table 4.3. Sterane Biomarker Parameters of Seep samples.

Parameters	Jaba	Panoba	Kundal	Golra
%C27	31.0	30.6	23.8	28.3
%C28	27.5	12.4	24.5	15.8
%C29	41.5	57.0	51.7	55.9
C29 $\beta\beta/(\beta\beta+\alpha\alpha)$	0.5	0.6	0.5	0.5
C29 S/S+R aa	0.6	0.6	0.6	0.6
C28/C29	0.7	0.2	0.5	0.7
C29/C27	1.3	1.9	2.2	2.0

The environment of deposition predicted from correlation of DBT/P and Pr/Ph shows marine carbonate for Kundal seep, the source rock for Jaba and Golra seeps appear to be Marine shale and other lacustrine while that of Panoba is paralic/deltaic source rock as displayed in figure 4.23.

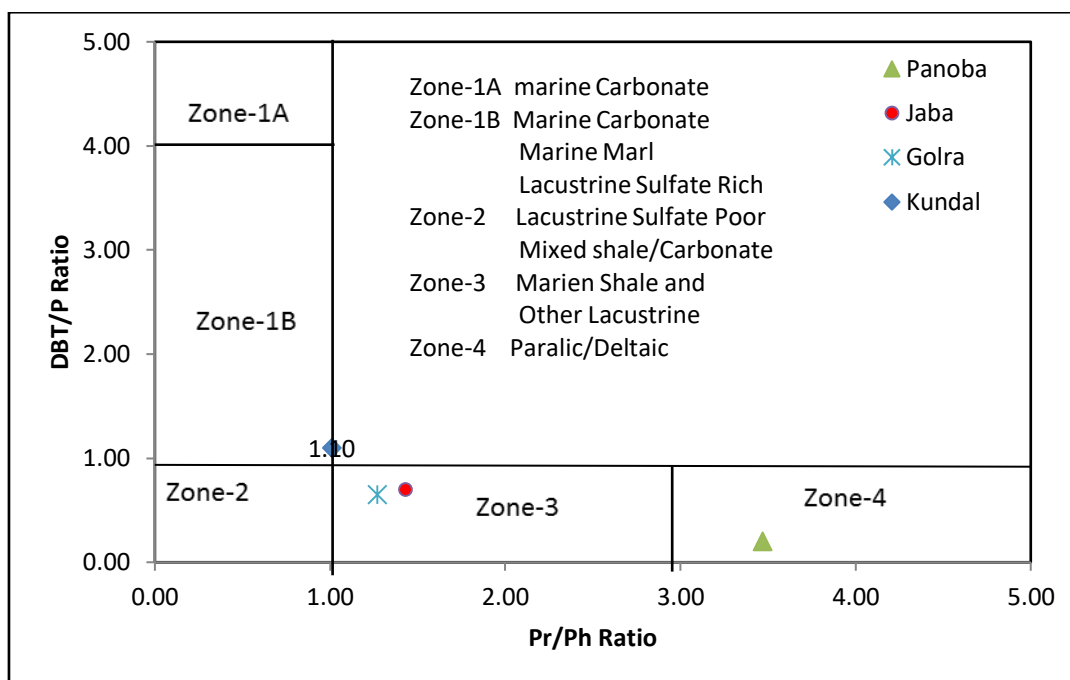


Figure 4.23. Cross plot of DBT/P versus Pr/Ph for seep samples of Uper Indus Basin.

Table 4.4. Aromatic hydrocarbons based thermal maturity parameters and their results.

Parameters	Jaba	Panoba	Kundal	Golra
$DNR-1 = [2,6+2,7-DMN]/1,5-DMN$	4.8	---	2.5	1.5
$Rca = 0.49 + (0.09 \times DNR-1)$	0.9	---	0.7	0.6
$TMN-2 = 2,3,6-+1,3,7-(1,4,6-+1,3,5-+1,3,6-TMN)$	1.0	0.7	0.5	0.5
$Rcb = 0.4 + (0.6 \times TMN-2)$	1.0	0.8	0.7	0.7
$Rmpdf = (2.2424 \times MPDF) - 0.166$	1.3	1.3	1.1	1.1
$MPI = 1.5 \times [3-+2-MP]/[P+1-+9-MP]$	1.2	0.9	0.7	1.0
$Rc = -0.4 + (0.6 \times MPI)$	1.1	0.9	0.8	1.0

The calculated vitrinite reflectance based on trimethyl naphthalenes and phenanthrenes: Rca and Rcb respectively are given in Table 4.4 and have been plotted (figure 4.24) to predict the thermal maturity of the source. Source rock of Kundal and Golra seeps have peak maturity (oil window) while Jaba seep was produced from such rock which has attained late thermal maturity. Parameters for Panoba seep could not be found.

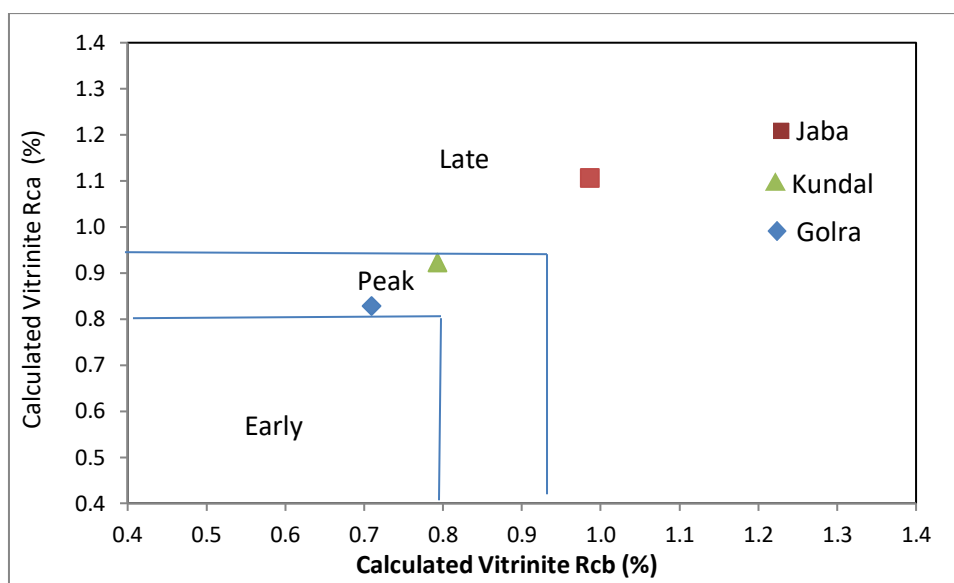


Figure 4.24. Plot of Rca versus Rcb showing thermal maturity for the source rock of seeps.

4.5 Recommendations

In exploration of hydrocarbons surface geochemical prospecting is an important part of the whole exploration process and study. Oil seeps are very informative clues from where we can get information of source rock. As in this research age, lithology and environment of depositions are found out, if these characteristics of source rocks of the area study by other geological methods and parameters then a correlation between seeps and source rocks will confirm the respective source rock of each seep.

The confirmation of source rock will open a window for research about migration of hydrocarbons. Location of oil seep and existing of its source rock will define the mechanism of migration of hydrocarbons up to the surface. The effect of migration on hydrocarbons can be studied by comparing characteristics of those hydrocarbons which are trapped in reservoir with these studied seeps. Hydrocarbons migrate or escape up to surface through fault system or due to absence of seals. Migration path study will be helpful in research of fault system of the area.

CONCLUSIONS

- The study of seep samples shows clear signs of biodegradation, with visible shift in baseline in the form of UCM.
- In almost all the studied samples short and long chain hydrocarbons have been degraded and chromatograms are dominated by isoprenoids.
- The seep samples fall in category of waxy/heavy oils with the exception of Kundal seep.
- The seeps show marginal-highly maturity of the source. There is evidence of secondary transformation, predominantly biological degradation in the form of high percentage of the polar fraction which constitutes asphaltenes and NSO compounds (nitrogen-sulfur-oxygen containing compounds) and loss of n-alkanes.
- The thermal maturity of source rock based on biomarker related maturity parameters indicates oil window, organic matter transformation into liquid hydrocarbon.
- The lithology of the source rock is shale for Panoba, Jaba and Golra while Kundal shows evidence of carbonate source.
- The presence of oleanane biomarker in Jaba seep indicates Late Jurassic-Early Cretaceous age of the source rock.
- The environment of deposition and accordingly source input show variation, Panoba having Pr/Ph ratio > 3 and DBT/P < 1 which shows deltaic depositional environment, Kundal seep shows signature of marine carbonate while Jaba and Golra show marine shale/other lacustrine lithology of the source rock.

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APPENDIX

A. Following are the tables and figures which were used for Identification of hydrocarbons.

Figure/Table	Description	Page
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Table A1	Tricyclic, Tetracyclic and Pentacyclic Terpanes in fragmentogram 191	67
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A1 Terpanes

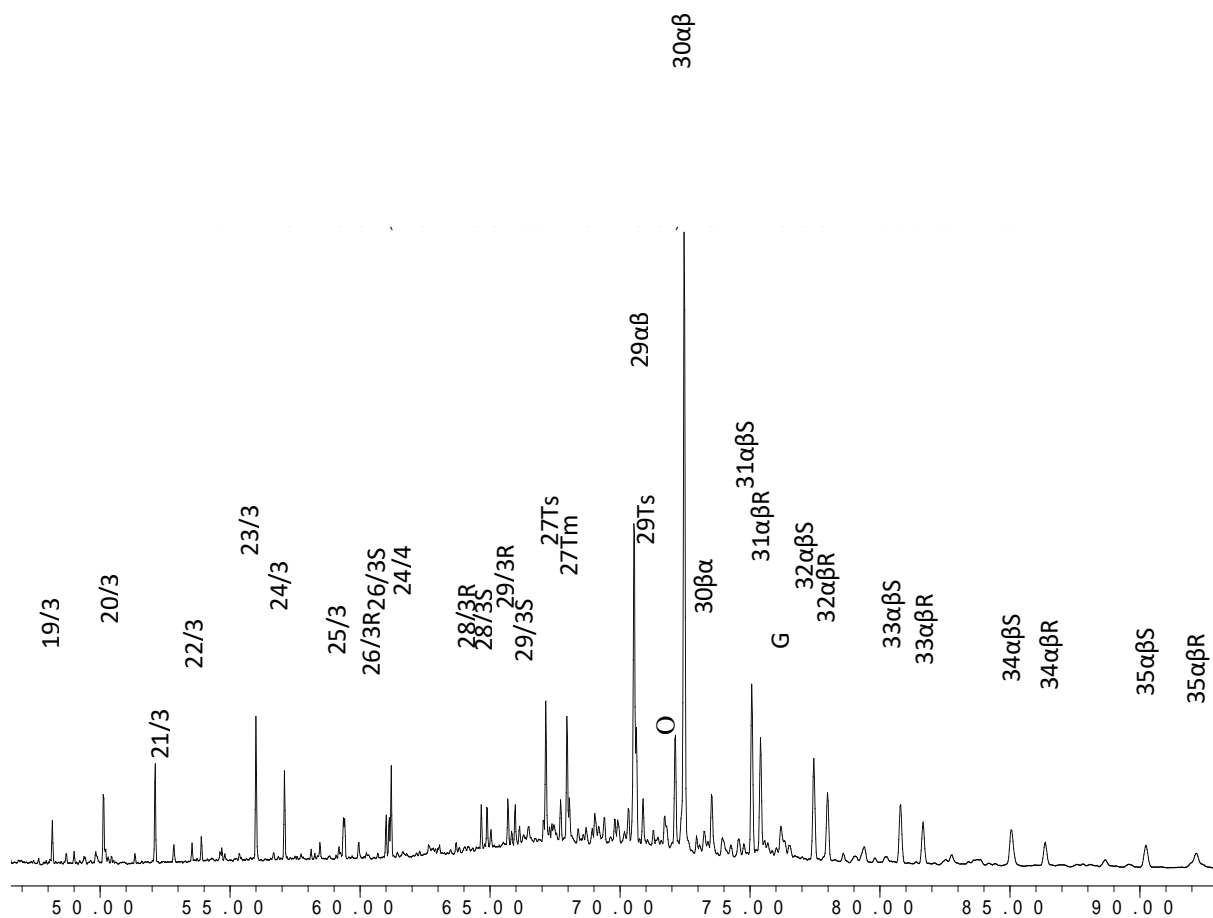


Fig. A1 m/z 191 ion chromatogram displaying relative abundance of tricyclic, tetracyclic and pentacyclic terpanes. The terpanes peak identified are described in Table A1.

Table A1 Tricyclic, Tetracyclic and Pentacyclic Terpanes in fragmentogram 191

Peak ID	COMPOUND
C19/3	C ₁₉ Tricyclic Terpene
C20/3	C ₂₀ Tricyclic Terpene
C21/3	C ₂₁ Tricyclic Terpene
C23/3	C ₂₃ Tricyclic Terpene
C24/3	C ₂₄ Tricyclic Terpene
C25/3	C ₂₅ Tricyclic Terpene
C24/4	C ₂₄ Tetracyclic Terpene
C26/3S	C ₂₆ Tricyclic Terpene/S
C26/3R	C ₂₆ Tricyclic Terpene/R
C28/3S	C ₂₈ Tricyclic Terpene/S
C28/3R	C ₂₈ Tricyclic Terpene/R
C29/3S	C ₂₉ Tricyclic Terpene/S
C29/3R	C ₂₉ Tricyclic Terpene/R
Ts	C ₂₇ 18 α (H)-22,29,30-trisnorneohopane (Ts)
Tm	C ₂₇ 17 α (H)-22,29,30-trisnorhopane (Tm)
BHN	C ₂₇ 28,30-bisnorhopane
C30*	C ₃₀ Diahopane
C29M	C ₂₉ 17 β (H),21 α (H)-moretane
O	Oleanane
C30	C ₃₀ 17 α (H),21 β (H)-hopane
C30M	C ₃₀ 17 β (H),21 α (H) Moretane
C31S	C ₃₁ 17 α (H),21 β (H)-30-homohopane (22S)
C31R	C ₃₁ 17 α (H),21 β (H)-30-homohopane (22R)
G	Gammacerane
C32S	C ₃₂ 17 α (H),21 β (H)-30-bishomohopane (22S)
C32R	C ₃₂ 17 α (H),21 β (H)-30-bishomohopane (22R)
C33S	C ₃₃ 17 α (H),21 β (H)-30-trishomohopane (22S)
C33R	C ₃₃ 17 α (H),21 β (H)-30-trishomohopane (22R)
C34S	C ₃₄ 17 α (H),21 β (H)-30-tetrakishomohopane (22S)
C34R	C ₃₄ 17 α (H),21 β (H)-30-tetrakishomohopane (22R)
C35S	C ₃₅ 17 α (H),21 β (H)-30-pentakishomohopane (22S)
C35R	C ₃₅ 17 α (H),21 β (H)-30-pentakishomohopane (22R)

A2 Steranes

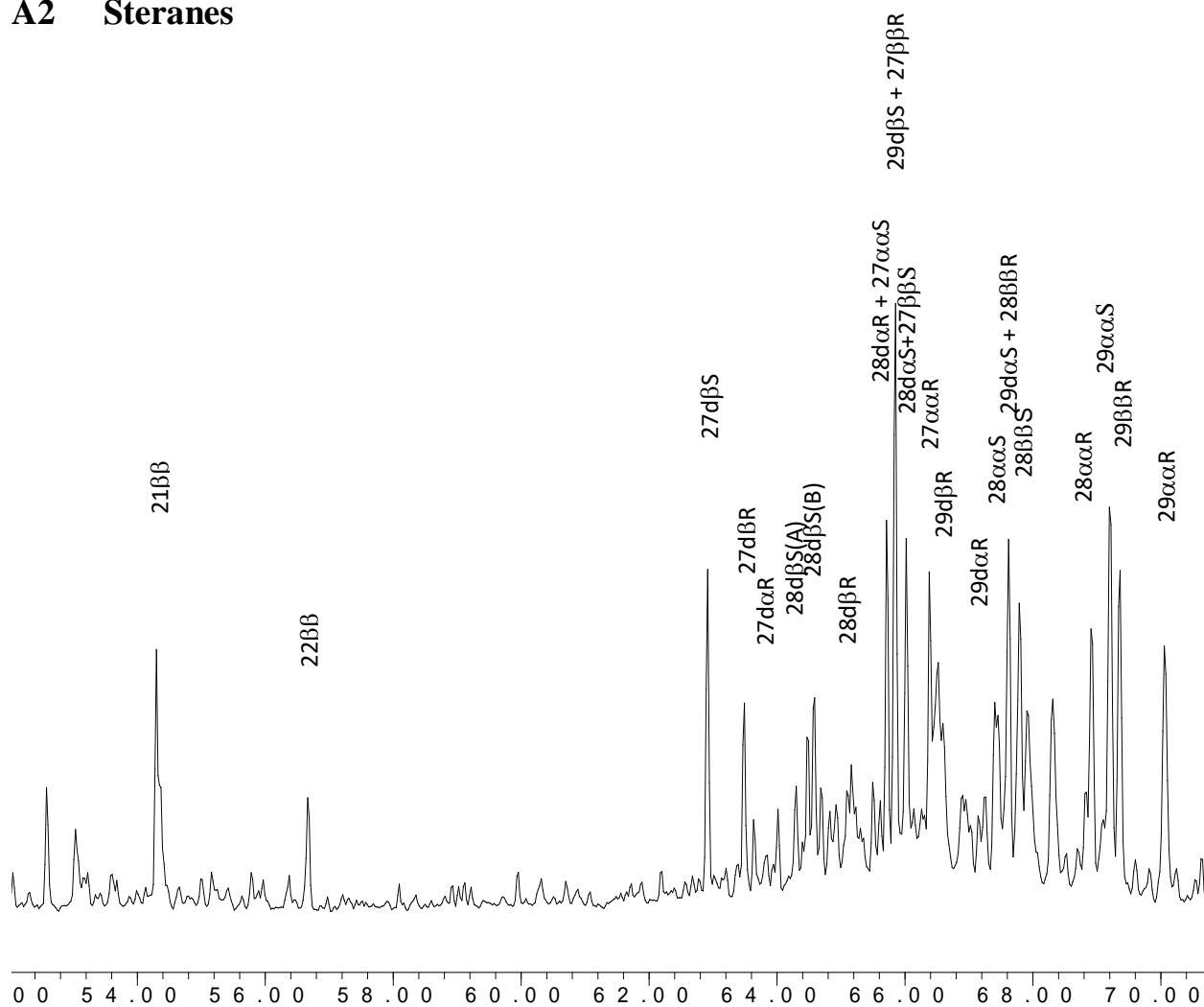


Fig. A2 m/z 217 fragmentogram showing steranes and diasteranes. The peaks of steranes described in Table 4.2.

Steranes ($\beta\beta$)

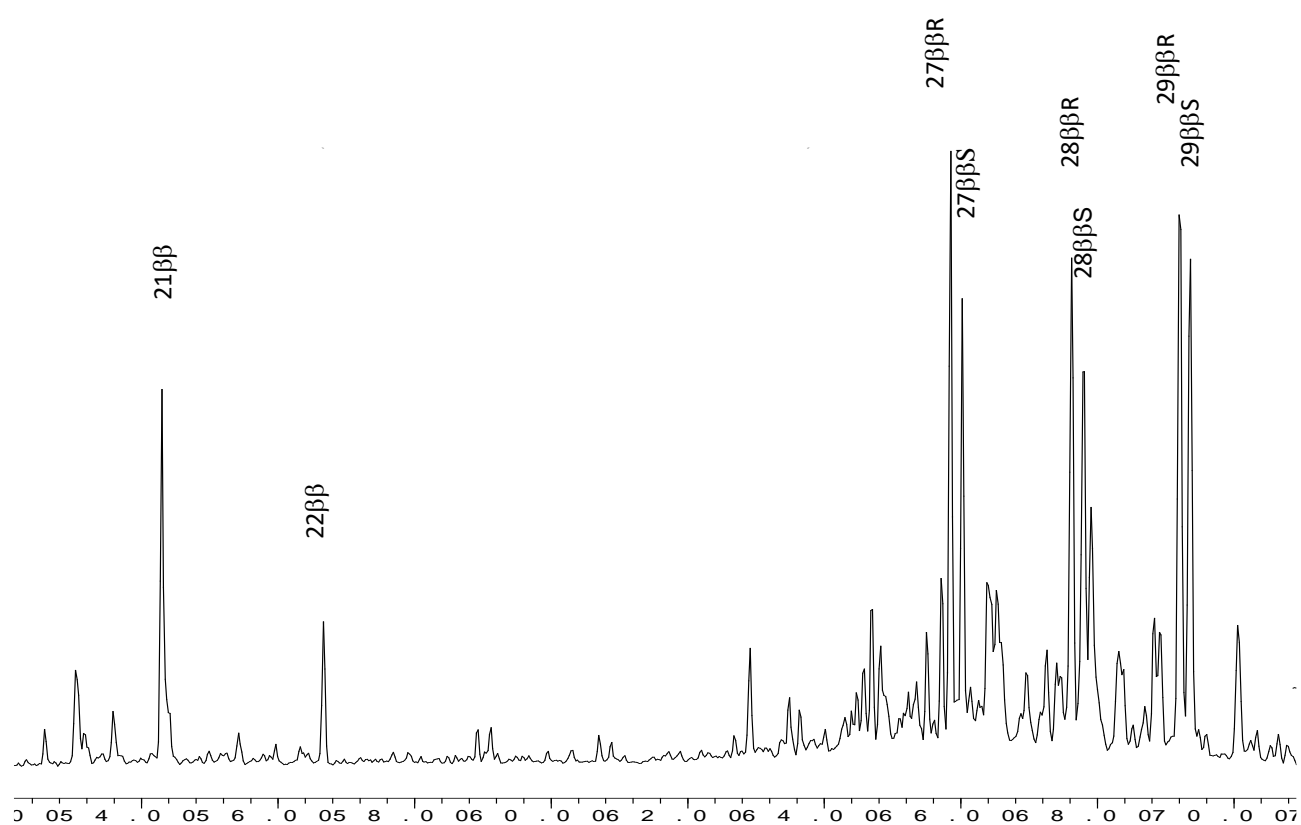


Fig. A3 m/z 218 ion chromatogram showing relative abundance of C₂₇-C₂₉ $\beta\beta$ steranes. The peaks are described in Table A2.

Table A2 Peaks of steranes in m/z 217 and 218 chromatograms identified in seep samples.

Peak I.D.	Sterane
21 $\beta\beta$	C ₂₁ Pregnane
22 $\beta\beta$	C ₂₂ Homopregnane
27d β S	C ₂₇ 13 β (H),17 α (H)-Diacholestane 20S
27d β R	C ₂₇ 13 β (H),17 α (H)-Diacholestane 20R
27 α S	C ₂₇ 13 α (H),17 β (H)-Diacholestane 20S
27 α R	C ₂₇ 13 α (H),17 β (H)-Diacholestane 20R
28d β S	C ₂₈ 24 methyl-13 β (H),17 α (H)-Diacholestane 20S
28d β R	C ₂₈ 24 methyl-13 β (H),17 α (H)-Diacholestane 20R
28d β S+	C ₂₈ 24 methyl-13 β (H),17 β (H)-Diacholestane 20S +
C27 $\alpha\alpha$ S	C ₂₇ 14 α (H),17 α (H)-Cholestane 20S
28 α R+	C ₂₈ 24 ethyl-13 β (H),17 α (H)-Diacholestane 20R +
C27 $\beta\beta$ R	C ₂₇ 14 β (H),17 β (H)-Cholestane 20R
28 α R+	C ₂₈ 24 methyl-13 α (H),17 β (H)-Diacholestane 20R +
C27 $\beta\beta$ S	C ₂₇ 14 β (H),17 β (H)-Cholestane 20S
C27 $\alpha\alpha$ R	C ₂₇ 14 α (H),17 α (H)-Cholestane 20R
29 α R	C ₂₉ 24 ethyl-13 β (H),17 α (H)-Diacholestane 20R
29d β S	C ₂₉ 24 ethyl-13 α (H),17 β (H)-Diacholestane 20S
C28 $\alpha\alpha$ S	C ₂₈ 24 methyl-14 α (H),17 α (H)-Cholestane 20S
C28 $\beta\beta$ R+	C ₂₈ 24 methyl-14 β (H),17 β (H)-Cholestane 20R +
29d β R	C ₂₉ 24 ethyl-13 α (H),17 β (H)-Diacholestane 20R
C28 $\beta\beta$ S	C ₂₈ 24 methyl-14 β (H),17 β (H)-Cholestane 20S
C28 $\alpha\alpha$ R	C ₂₈ 24 ethyl-14 α (H),17 α (H)-Cholestane 20R
C29 $\alpha\alpha$ S	C ₂₉ 24 ethyl-14 α (H),17 α (H)-Cholestane 20S
C29 $\beta\beta$ R	C ₂₉ 24 ethyl-14 β (H),17 β (H)-Cholestane 20R
C29 $\beta\beta$ S	C ₂₉ 24 ethyl-14 β (H),17 β (H)-Cholestane 20S
C29 $\alpha\alpha$ R	C ₂₉ 24 ethyl-14 α (H),17 α (H)-Cholestane 20R

A3 Naphthalene and Substituted Naphthalenes

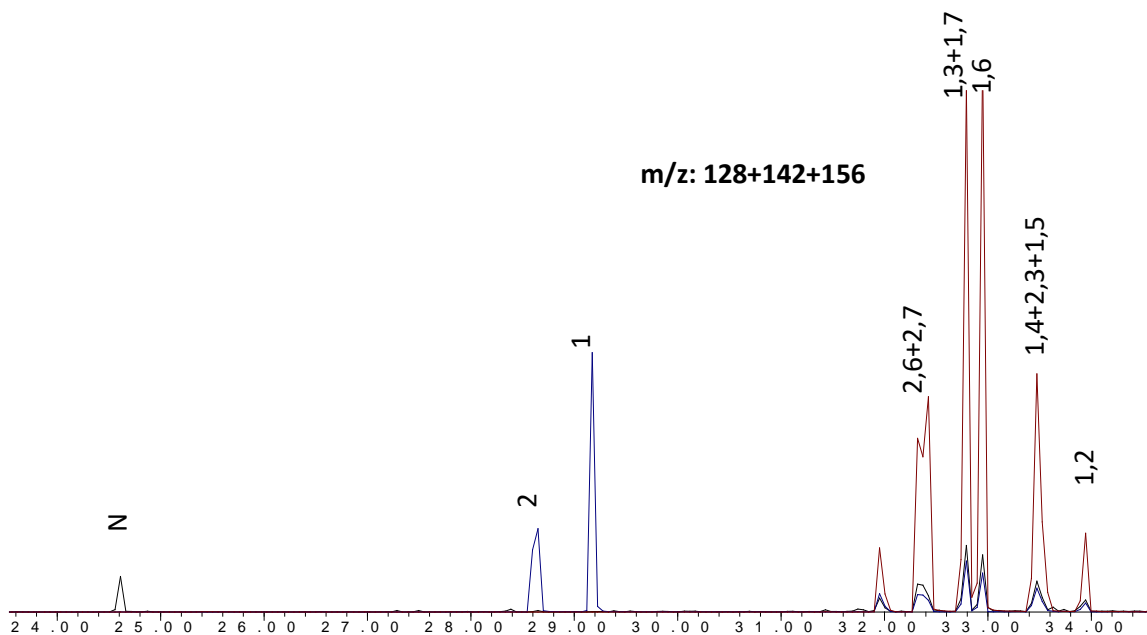


Fig. A4 Merged ion chromatograms, m/z 128+142+156 presenting naphthalene (N), methylnaphthalenes and dimethylnaphthalenes .

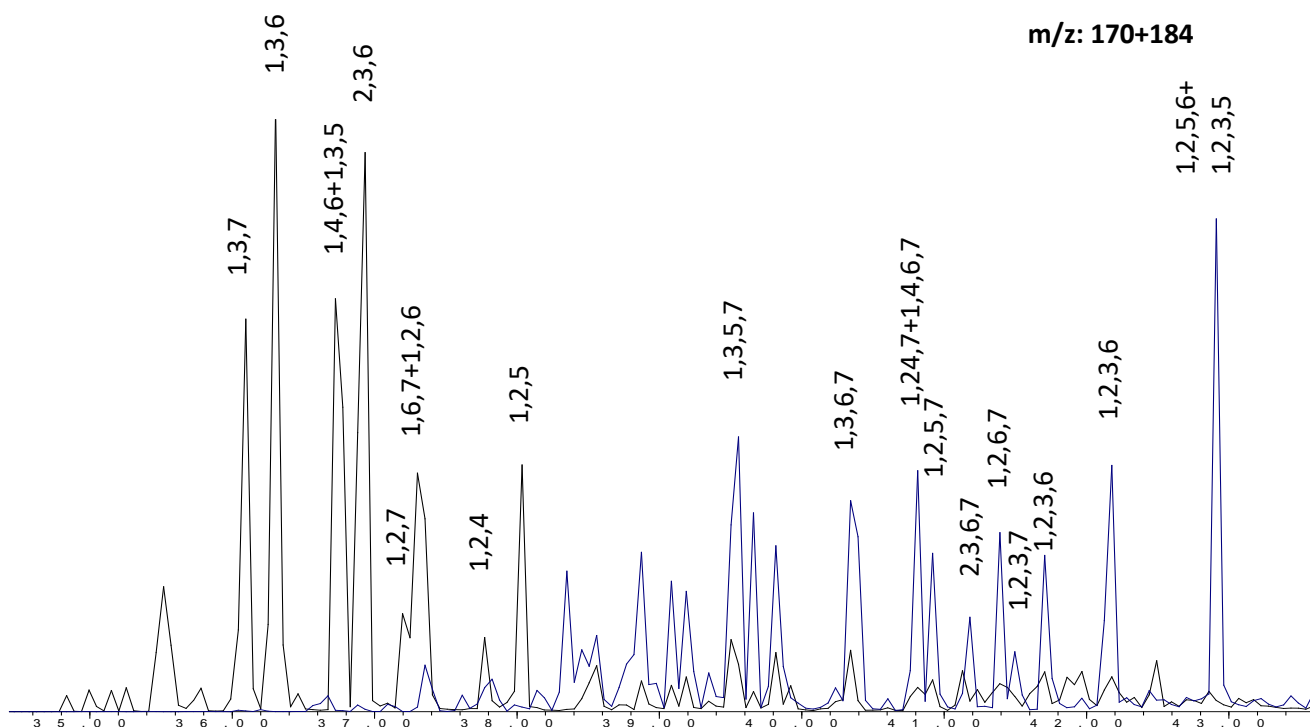


Fig. A5 Combined mass chromatograms, m/z 170+184 for trimethyl- & tetramethylnaphthalenes. The peaks are described in Table A3.

Table A3 Identification of naphthalenes in Seep samples

Peak	m/z	Compound
N	128	Naphthalene
2-MN	142	2-methylnaphthalene
1-MN	142	1-methylnaphthalene
2-EN	156	2-ethylnaphthalene
1-EN	156	1-ethylnaphthalene
2,6-DMN	156	2,6-dimethylnaphthalene
2,7-DMN	156	2,7-dimethylnaphthalene
1,3-DMN	156	1,3-dimethylnaphthalene
1,7-DMN	156	1,7-dimethylnaphthalene
1,6-DMN	156	1,6-dimethylnaphthalene
2,3-DMN	156	2,3-dimethylnaphthalene
1,4-DMN	156	1,4-dimethylnaphthalene
1,5-DMN	156	1,5-dimethylnaphthalene
1,2-DMN	156	1,2-dimethylnaphthalene
1,3,7-TMN	170	1,3,7-trimethylnaphthalene
1,3,6-TMN	170	1,3,6-trimethylnaphthalene
1,3,5-TMN	170	1,3,5-trimethylnaphthalene
2,3,6-TMN	170	2,3,6-trimethylnaphthalene
1,2,7-TMN	170	1,2,7-trimethylnaphthalene
1,2,6-TMN	170	1,2,6-trimethylnaphthalene
1,4,6-TMN	170	1,4,6-trimethylnaphthalene
1,6,7-TMN	170	1,6,7-trimethylnaphthalene
1,2,4-TMN	170	1,2,4-trimethylnaphthalene
1,2,5-TMN	170	1,2,5-trimethylnaphthalene

4A Phenanthrene and Substituted Phenanthrenes

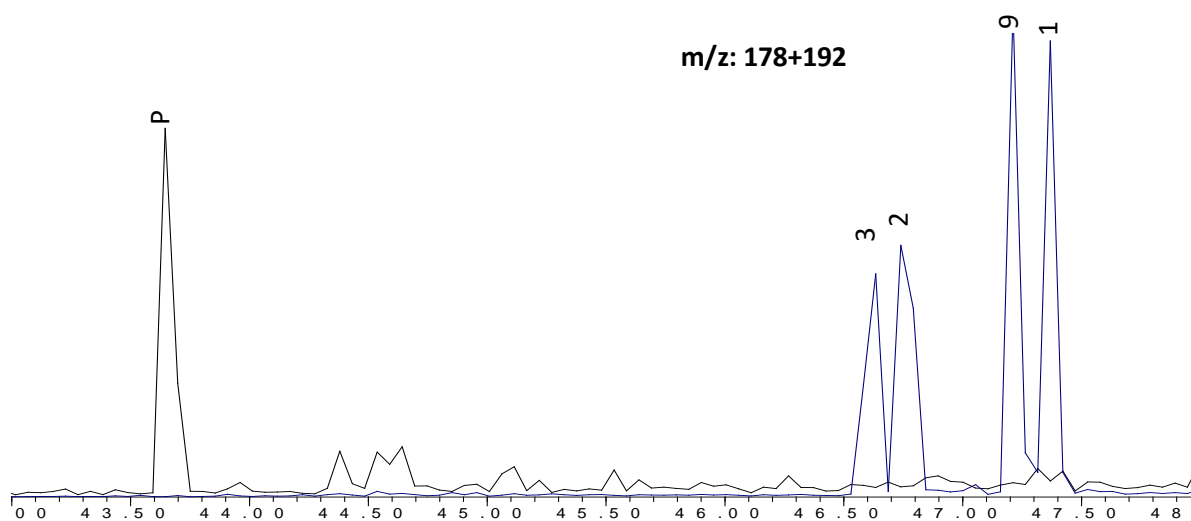


Fig. A6. Combined ion chromatograms m/z 178 and 192 presenting phenanthrene (p) and methylated phenanthrenes (indicated by substituent position) in Kundal Seep.

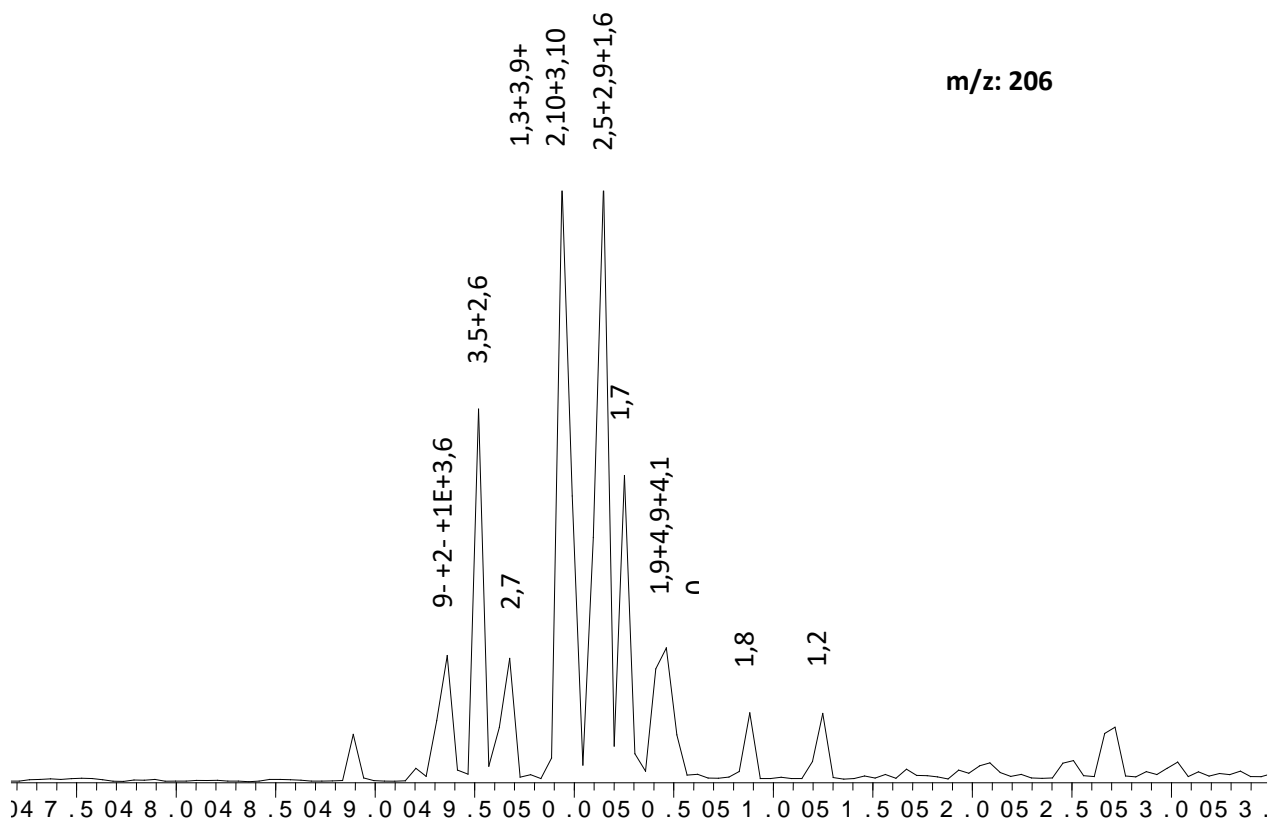


Fig.A7 Ion chromatogram m/z 206 showing distribution of dimethylphenanthrenes. The peak identification is given in Table A4.

Table A4 Peaks identified in m/z 178, 192 and 206 for phenanthrenes.

Peak	m/z	Compound
P	178	Phenanthrene
3-MP	192	3-methylphenanthrene
2-MP	192	2-methylphenanthrene
9-MP	192	9-methylphenanthrene
1-MP	192	1-methylphenanthrene
2-EP	192	2-ethylphenanthrene
9-EP	192	9-ethylphenanthrene
3,6-DMP	206	3,6-dimethylphenanthrene
1,3-DMP	206	1,3-dimethylphenanthrene
2,10-DMP	206	2,10-dimethylphenanthrene
3,9-DMP	206	3,9-dimethylphenanthrene
3,10-DMP	206	3,10-dimethylphenanthrene
1,6-DMP	206	1,6-dimethylphenanthrene
2,5-DMP	206	2,5-dimethylphenanthrene
2,9-DMP	206	2,9-dimethylphenanthrene
1,7-DMP	206	1,7-dimethylphenanthrene
2,3-DMP	206	2,3-dimethylphenanthrene
1,9-DMP	206	1,9-dimethylphenanthrene
4,9-DMP	206	4,9-dimethylphenanthrene
4,10-DMP	206	4,10-dimethylphenanthrene
1,8-DMP	206	1,8-dimethylphenanthrene
1,2-DMP	206	1,2-dimethylphenanthrene

A5 Dibenzothiophene and Substituted Dibenzothiophenes

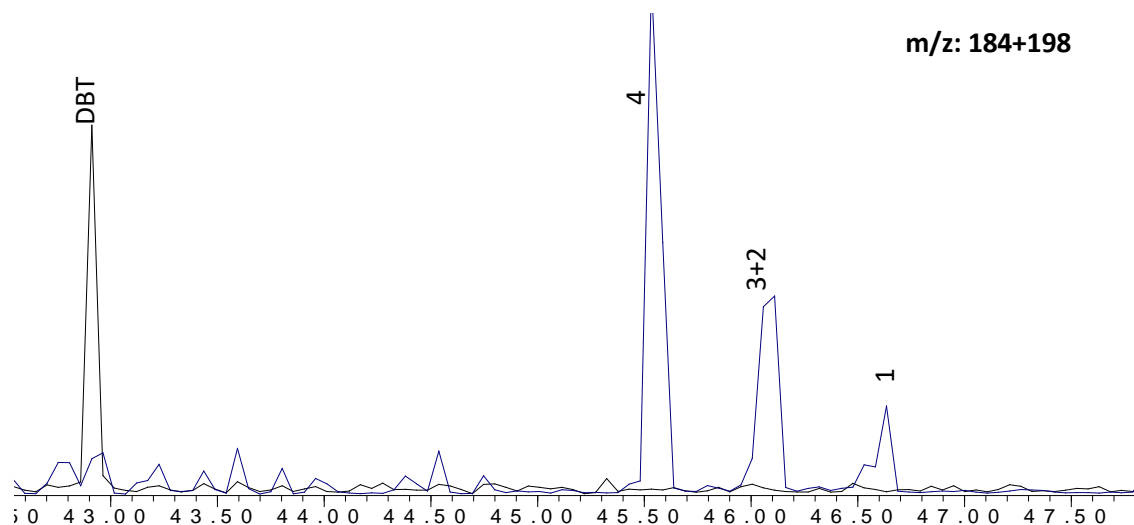


Fig.A8 Merged ion chromatograms, m/z 184+198 presenting dibenzothiophene (DBT) and methylthiophenes in Golra Seep. The peaks identified are enlisted in Table A5.

Table A5 Identification of dibenzothiophenes in seep samples from Upper Indus Basin

Peak	m/z	Compound
DBT	184	Dibenzothiophene
4-MDBT	198	4-Methyldibenzothiophene
3+2-MDBT	198	4-Methyldibenzothiophene
1-MDBT	198	4-Methyldibenzothiophene
4-E	212	4-Ethyldibenzothiophene
4,6-DMDBT	212	4,6-Dimethyldibenzothiophene
2,4-DMDBT	212	2,4-Dimethyldibenzothiophene
2,6-+3,6-	212	2,6-Dimethyldibenzothiophene
DMDBT		3,6-Dimethyldibenzothiophene
3,7-DMDBT	212	3,7-Dimethyldibenzothiophene
1,4-DMDBT	212	1,4-Dimethyldibenzothiophene
1,6 + 1,8-	212	1,6-Dimethyldibenzothiophene
DMDBT		1,8-Dimethyldibenzothiophene
1,3-+3,4-+1,2-	212	1,4-Dimethyldibenzothiophene
DMDBT		3,4-Dimethyldibenzothiophene
		1,2-Dimethyldibenzothiophene

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