Journal of Petroleum & Environmental Biotechnology

Sangeetha et al., J Pet Environ Biotechnol 2017, 8:6
DOI: 10.4172/2157-7463.1000353

Research Article

Open Access

Hydrocarbon Exploration in Peninsular India by Advanced Biochemical Markers Method

Sangeetha T[1], Elumalai S[2]*, Roop Singh D[1] and Rajesh Kanna G[3]

[1]*Department of Chemistry, Presidency College (Autonomous), Chennai, India*
[2]*Department of Biotechnology, University of Madras, Guindy Campus, Chennai, India*
[3]*Department of Plant Biology and Plant Biotechnology, Presidency College (Autonomous), Chennai, India*

Abstract

Hydrocarbons are a linear chain of carbon and hydrogen rich molecules serve as fuel from fossil source from the deep underground. Due to rapid population explosion followed by dynamic development in the Industrial sector, the Indian sub-continent is spending lot of money on energy to the Middle East Countries. Therefore, exploration of hydrocarbon rich regions within our country is one of the needful mission to cut-short the cost of fuel. As a novel theme, the hydrocarbon exploration study was carried out at five different locations each for freshwater site (Cauvery Riverbed region) and Marine site (Chennai Coastal region). About 100 g of soil samples from ten different sampling sites were collected by digging the ground up to three feet deep in both the riverbed and marine coastal sites. Then the soil samples were analyzed for different physio-chemical parameters such as pH, moisture content, nitrogen, potassium, sodium, magnesium phosphorous, total organic carbon, Sulphur, manganese, zinc, copper, molybdenum and nickel. For hydrocarbon analysis, the soil samples were subjected to hydrocarbon extraction by Soxhlet extraction method and analyzed by GC-MS by using standards for polyaromatic hydrocarbons including Naphthalene, Acenaphthylene, 2-Bromo-Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Pyrene, Fluoranthene, Chrysene, Benz [a] anthracene, Benzo [b] fluoranthene, Benzo [ghi] perylene, Dibenz [a,h] anthracene and Indeno [1,2,3-cd] pyrene. The final result confirms that the hydrocarbon content was high in the soil samples of Chennai Coastal sites than the Cauvery freshwater riverbed regions. This may be due to high biochemical depositions of dead particles and algae in the sediments of marine coastal regions for a very long period. And this is a preliminary study to explore hydrocarbons in the soil sediments by exploring hydrocarbons from small pits as biochemical markers.

Keywords: Hydrocarbon; Exploration; Coastal; Riverbed

Introduction

Transportation is the basic need for every country to empower everyday economy of each by exporting and importing goods including foods, medicines, garments and raw materials to produce various other products. Petroleum based fuels are the only available energy source consumed enormously for transportation of about 97 %. The crude oil is one among the fossil fuels from which the petroleum products have been produced and are going to be exhausted within the next 30 to 40 years. Due to the depletion and unsustainability of fossil fuel, there will be a huge price hike and demand for fuel in the near future. The population explosion along with economic growth in the developing countries like India and China had led to rapid increase in demand for energy all over the world. Many governmental, non-governmental, private organizations and companies have assigned in search of alternate energy to be explored in the upcoming future.

The different types of hydrocarbon fractions have been discovered from aquatic depositions from freshwater and coastal regions in some parts of the world. The hydrocarbons are the long chain fatty acids with a long chain of carbon and hydrogen with it. Both aliphatic and aromatic hydrocarbons have been discovered from the underground soil where biological materials were deposited some million years back. The fossil fuels were also deposited in the same manner but the hydrocarbons can be used efficiently than the fossil fuel for conservation of energy because the fossil fuel requires pretreatment and refinement for further processes.

Especially, the hydrocarbons are one of the biochemical markers much useful for the exploration of hydrocarbons from soil. As described above, the hydrocarbon exploration has been done in some parts of the world by using hydrocarbons as a biochemical marker. The hydrocarbon may have changed in its structure due to long time pressure and high temperature under the earth. According to geochemistry, the petroleum and other ancient are rich in organic materials especially oil shales. The hydrocarbons are one of the organic complex materials rich in terpenoids and considered that they have been originated from ancient biological organisms. For example, pristane and phytane were the saturated hydrocarbon fractions seen in petroleum and oil shales [1]. Aliphatic polyaldehydes of high molecular weight occur in the three races of *B. braunii* [2,3].

This oil which deposits in Ethiopia can be used for the production of bio-fuel and gas [4]. Macrocyclic alkanes have been identified in two tertiary crude oils (Mianas and Duri, Indonesia) known to contain remains of the freshwater alga *B. braunii.* Coorongites are lamellae like deposits occur in the dried basins of ephemeral lakes and they yield high amount of aliphatic oils in Lake Balkash and Kazakhstan [5]. The grey and dark brown clay deposits were isolated from the Black Sea, offshore, Romania during the Pliocene period due to South Carpathians depression which is reported as a rich source of hydrocarbon [6]. The compounds

*Corresponding author: Elumalai S, Department of Biotechnology, University of Madras, Guindy Campus, Chennai, India, Tel: +91-9710116385; E-mail: dalbergia17@gmail.com

Received August 30, 2017; **Accepted** December 18, 2017; **Published** December 26, 2017

Citation: Sangeetha T, Elumalai S, Roop Singh D, Rajesh Kanna G (2017) Hydrocarbon Exploration in Peninsular India by Advanced Biochemical Markers Method. J Pet Environ Biotechnol 8: 353. doi: 10.4172/2157-7463.1000353

Citation: Sangeetha T, Elumalai S, Roop Singh D, Rajesh Kanna G (2017) Hydrocarbon Exploration in Peninsular India by Advanced Biochemical Markers Method. J Pet Environ Biotechnol 8: 353. doi: 10.4172/2157-7463.1000353

are the valuable biochemical markers by the contribution of the specific organisms to deposit of sediments and alternatively they can be an efficient marker for exploration of hydrocarbons from underground. The current study gives a preview on using the hydrocarbons as biochemical markers deposited long ago as sediments in the nearby aquatic resources for proposing large scale hydrocarbon exploration.

Materials and Methods

Field survey and sample collection

The field surveys were undertaken in the coastal and riverbed regions around Chennai coastal area and Cauvery delta river of Tamil Nadu, India between August 2012 and July 2014. The soil samples were collected by digging up to three feet small pits on the ground. A 100g of soil samples from each of about five different sampling sites were chosen randomly for each of the coastal and freshwater riverbed regions. Thus about ten soil samples were randomly collected and brought to the laboratory for further processes (Table 1).

Physio-chemical analysis of soil samples

Soil sample: The Physio-chemical parameters were analyzed for all the soil samples collected from both the Coastal and Riverbed regions, which includes pH (Method 9040C, National Bureau of Standards, 2004), moisture content, nitrogen (N_2) (Kjeldahl method) and minerals such as potassium (K), sodium (Na), magnesium (Mg), phosphorous (P), total organic carbon (Walkley-Black wet combustion method, Walkley and Black, 1934), sulphur (S) (Method 9038, Standard methods for the examination of water and waste water, 1975; Annual book of ASTM standards, 1976), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo) and Nickel (Ni). All the Physio-chemical parameters mentioned above were analyzed by Chennai Testing Laboratory Pvt. Ltd., Industrial estate, Guindy, Chennai, Tamil Nadu, India.

S. No.	Coastal sampling sites (Chennai)	Freshwater riverbed sampling sites (Cauvery Delta River)
1.	Pazhaverkadu – Pulicat (PP)	Tiruchirappalli (TI)
2.	Ennore (EE)	Thiruvaiyaru (TU)
3.	Besant Nagar (BN)	Papanasam (PM)
4.	Muttukadu – Kovalam (MK)	Kumbakonam (KM)
5.	Mahabalipuram (MM)	Mayiladuthurai (MI)

Table 1: Sampling sites where soil samples were collected.

S. No.	Poly aromatic hydrocarbons	Target Ion	Reference Ions	
			I	II
1.	Naphthalene	128	127	129
2.	Acenaphthylene	152	151	150
3.	2-Bromo-Naphthalene	127	206	208
4.	Acenaphthene	153	154	152
5.	Fluorene	166	165	163
6.	Phenanthrene	178	176	179
7.	Anthracene	178	176	179
8.	Pyrene	202	200	203
9.	Fluoranthene	202	200	203
10.	Chrysene	228	226	229
11.	Benz [a] anthracene	228	226	229
12.	Benzo [a] pyrene	252	250	253
13.	Benzo [b] fluoranthene	252	250	253
14.	Benzo [ghi] perylene	276	250	253
15.	Dibenz [a,h] anthracene	278	250	253
16.	Indeno [1,2,3-cd] pyrene	276	277	274

Table 2: PAHs – GC-MS with target and reference ions.

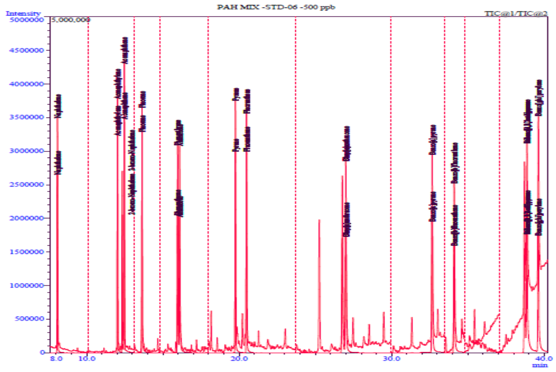

Figure 1: Standard peaks showing different polyaromatic hydrocarbons (PAH).

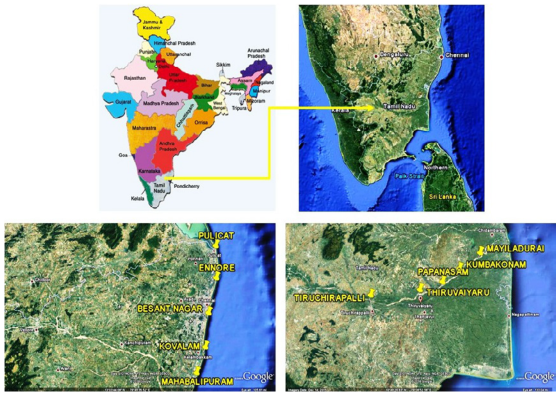

Figure 2: Map image showing areas of sample collection in Chennai coastal regions and Cauvery delta river of Tamilnadu.

Poly Aromatic Hydrocarbons (PAH) analysis of soil samples

The soil samples were allowed to extract hydrocarbons by means of solvent using Soxhlet extraction method. The extract was analyzed and determined by GC – MS. In this present investigation, a sum of ten soil samples were subjected to PAH analysis collected from different places of Chennai coastal regions and Cauvery delta river of Tamil Nadu. The different PAHs were analyzed including Naphthalene, Acenaphthylene, 2-Bromo-Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Pyrene, Fluoranthene, Chrysene, Benz [a] anthracene, Benzo [b] fluoranthene, Benzo [ghi] perylene, Dibenz [a,h] anthracene and Indeno [1,2,3-cd] pyrene by the use of standards (Table 2 and Figure 1).

Results

Field survey and sample collection

The images in Figures 2 and 3 show the topographical view of the sampling regions and sampling sites where samples were taken respectively.

Physio-chemical analysis of soil samples

The detail report on the Physio-chemical parameters of the soil samples was given in Table 3. The pH of soil samples ranged between 7.1 and 8.3 from the sampling sites BN and PP respectively. The average pH of coastal soil was 7.7 and riverbed soil was 7.96. The results revealed that the approximate pH occurred in all the soil samples were from 7.0 to 8.0 (Figure 4). The high soil moisture content was shown in the sampling site BN (19.52 %) and comparatively occurred low in the site

PM (12.38 %) (Figure 5). The sodium (Na) content present in the soil samples ranged from 0.12 mg/kg (BN and MK) to 1374 mg/kg (MM) relatively very high. The sodium content of the site MM was very high when compared with the other coastal soil samples but the riverbed soil samples have shown an average sodium content of 513.4 mg/kg was comparatively high in comparison with the average sodium content of coastal soil samples (288.34 mg/kg) (Figure 6). About 120 mg/kg of potassium (K) content was obtained in the sampling site PM which was low when compared with all the sites and the site KM have shown high amount of potassium in its soil with 388 mg/kg. Relatively, the average potassium content of coastal soil samples was low (181.4 mg/kg) in comparison with the riverbed soil samples (250.6 mg/kg) (Figure 7).

The occurrence of magnesium (Mg) content was high in the coastal soil samples when compared with the riverbed soil samples with an average of 137.4 mg/kg and 88 mg/kg respectively. The magnesium content present in the soil samples ranged between 10 mg/kg (TI and TU) and 216 mg/kg (MI) (Figure 8). The phosphorous (P) have occurred in a range between 82 mg/kg and 328.5 mg/kg with respect to the sampling sites MM and TI & TU. The average phosphorous content was high in the riverbed soil samples (219.01 mg/kg) and it was low in the coastal soil samples (177.18 mg/kg) (Figure 9). The total organic carbon in the soil samples have occurred low level in the

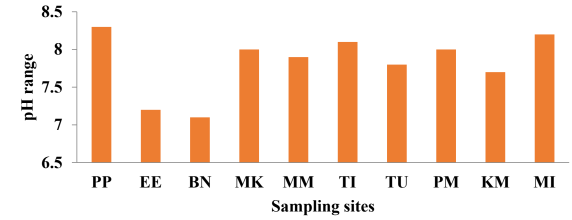

Figure 4: Analysis of soil pH.

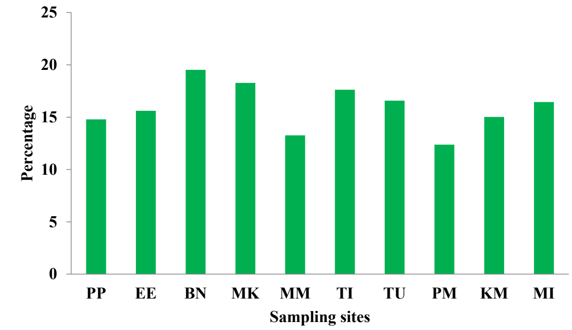

Figure 5: Analysis of soil moisture.

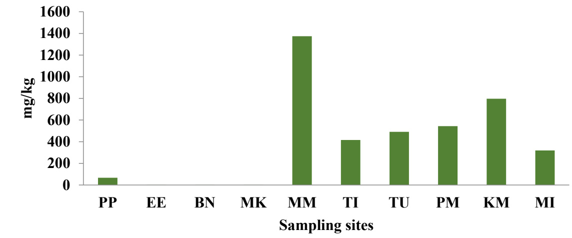

Figure 6: Analysis of Sodium (Na).

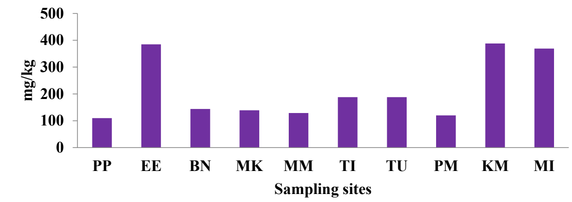

Figure 7: Analysis of Potassium (K).

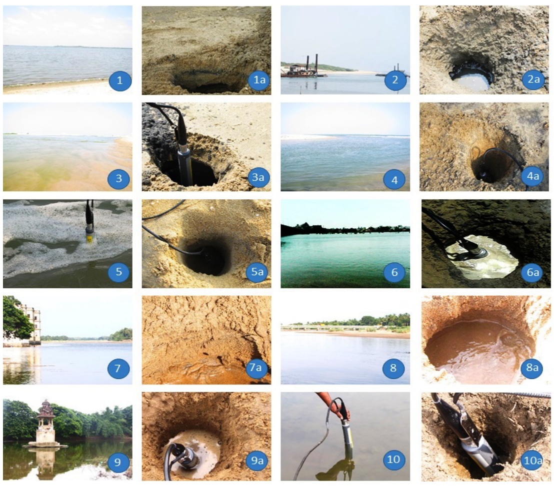

Figure 3: Sampling sites: 1 and 1a. Pazhaverkadu, Pulicat (PP); 2 and 2a. Ennore (EE); 3 and 3a. Besant Nagar (BN); 4 and 4a. Muttukadu, Kovalam (MK); 5 and 5a Mahabalipuram (MM); 6 and 6a. Tiruchirappalli (TI); 7 and 7a. Thiruvaiyaru (TU); 8 and 8a. Papanasam (PM); 9 and 9a. Kumbakonam (KM); 10 and 10a. Mayiladuthurai (MI).

Soil sampling sites	pH	Temperature (ºC)	Specific conductivity (ms/cm^2)	Conductivity (mg/L)	Total dissolved solids (TDS g/t)	Salinity (sal.)	Dissolved O_2 (mg/L)	Oxidation reduction potential (ORP)
Pazhaverkadu – Pulicat (PP)	7.05	32.18	38.27	43.94	24.93	24.15	1.53	-122.0
Ennore (EE)	7.20	31.78	48.51	57.32	12.93	11.77	-0.34	-184.3
Besant Nagar (BN)	7.09	31.91	23.74	26.88	15.41	14.19	-1.74	-176.7
Muttukadu – Kovalam (MK)	7.27	30.88	15.60	17.35	10.14	9.03	3.63	-131.3
Mahabalipuram (MM)	7.05	32.22	17.84	20.30	11.59	10.42	5.17	-135.7
Tiruchirappalli (TI)	7.05	30.87	0.734	0.821	0.484	0.36	-0.51	-160.9
Thiruvaiyaru (TU)	7.47	32.46	0.151	0.173	0.098	0.07	1.97	-163.5
Papanasam (PM)	7.56	32.74	0.314	0.361	0.204	0.15	3.16	-142.0
Kumbakonam (KM)	7.12	30.23	0.146	0.160	0.095	0.07	2.59	-165.3
Mayiladuthurai (MI)	6.75	32.35	0.329	0.375	0.214	0.15	0.51	-51.8

Table 3: Physio-chemical analysis of soil samples collected from different sampling sites.

sampling site EE and high level in the sampling site MM with 0.02 % and 0.96 % respectively. All the coastal soil samples have shown very low percentage of total organic carbon except the site MM. The average total organic carbon was doubled in the riverbed soil samples (0.61 %) when compared with coastal soil samples (0.338) (Figure 10).

The sulphur (S) content in the soil samples were ranged between 0.10 mg/kg and 592 mg/kg in the sampling sites EE and BN respectively. Although the low amount of sulphur was recorded in the coastal soil sample EE the average sulphur content was high in the coastal water samples (171.02 mg/kg) when compared with the riverbed soil samples (78.2 mg/kg) (Figure 11). The manganese (Mn) content present in the soil samples ranging from 8.5 mg/kg to 94.8 mg/kg in the sampling sites PP and KM respectively. Comparatively, the average manganese content of the riverbed soil samples (67.2 mg/kg) was three times more than that of the average of the coastal soil samples (20.72 mg/kg) (Figure 12). The average zinc (Zn) content was high in the riverbed soil samples (32.94 mg/kg) in comparison with the coastal soil samples (17.5 mg/kg) which was doubled in the case of riverbed soil samples. Otherwise, the zinc content present in the soil samples ranged from 7.7 mg/kg in PP and 56.8 mg/kg in MI (Figure 13).

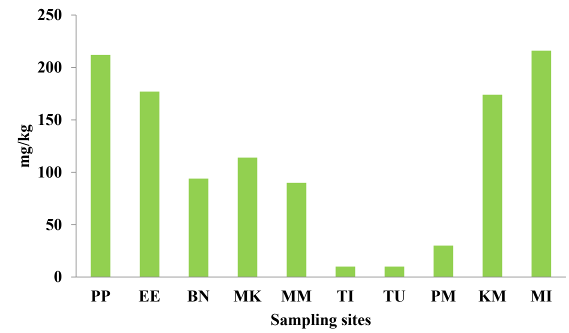

Figure 8: Analysis of Magnesium (Mg).

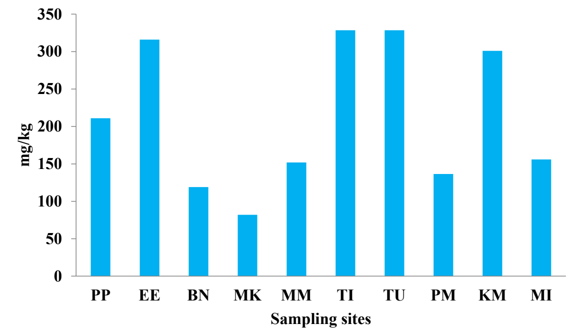

Figure 9: Analysis of Phosphorous (P).

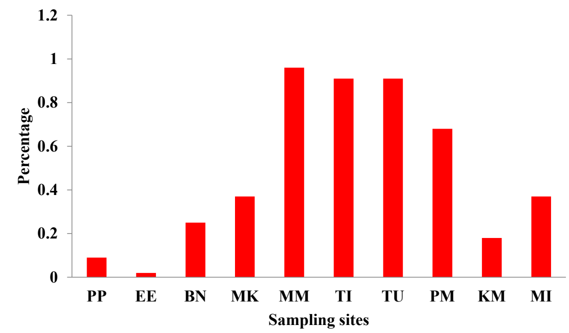

Figure 10: Analysis of total organic carbon.

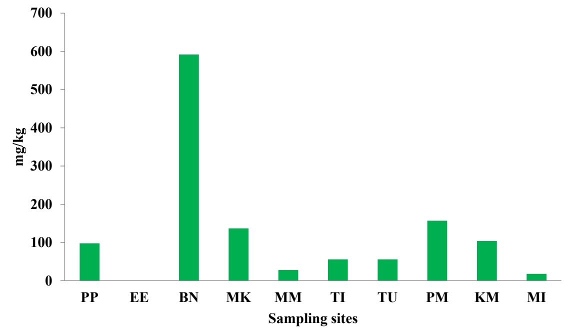

Figure 11: Analysis of Sulphur (S).

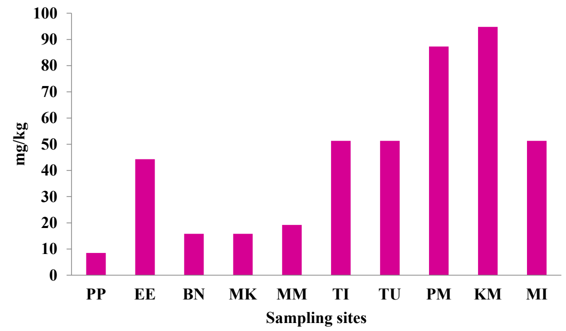

Figure 12: Analysis of Manganese (Mn).

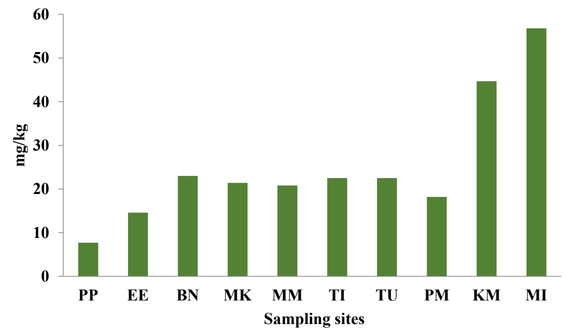

Figure 13: Analysis of Zinc (Zn).

The soil sampling site MI have recorded high amount of copper (Cu) content with 89.14 mg/kg and which was comparatively low in the case of PP with only 1.9 mg/kg. The average copper content of coastal soil samples (49.3 mg/kg) was relatively low in contrast to riverbed soil samples (79.6 mg/kg) (Figure 14). The nitrogen (N_2) content has not shown any considerable differences in their amount between the different soil samples. But it was occurred between the range from 150 mg/kg to 242 mg/kg in the soil sampling sites PM and KM respectively. The average nitrogen content between the coastal soil (169.8 mg/kg) and riverbed soil (189.2 mg/kg) samples also have not shown any considerable differences (Figure 15).

The soil analysis of both the Coastal regions and Riverbed regions resulted that the presence of minerals including sodium (Na), phosphorous (P), total organic carbon (TOC), manganese (Mn), zinc (Zn) and Copper (Cu) were higher in the case of Riverbed regions when compared to the Coastal regions. The magnesium (Mg) content alone

Citation: Sangeetha T, Elumalai S, Roop Singh D, Rajesh Kanna G (2017) Hydrocarbon Exploration in Peninsular India by Advanced Biochemical Markers Method. J Pet Environ Biotechnol 8: 353. doi: 10.4172/2157-7463.1000353

occurred high in the Coastal regions in comparison with the Riverbed regions.

Poly aromatic hydrocarbon analysis of soil samples

All the analyzed poly aromatic hydrocarbons from different soil samples of both riverbed regions and coastal regions were illustrated in Tables 4a and 4b, Figures 16-25. The naphthalene was recorded in the soil samples EE, MM, TU, PM and MI ranges from 0.07 mg /kg to 0.14 mg/kg in soil samples TU and MM respectively. The naphthalene was not occurred in the soil samples PP, BN, MK, TI and KM. The soil sample PP has shown low amount of acenaphthylene (0.082 mg/kg) and occurred high in sample MI (1.15 mg/kg) when compared with other soil samples. The hydrocarbon 2-bromo-naphthalene was not recorded in any of the samples from riverbed regions but present highly in the samples of coastal regions PP (7.5 mg/kg) and meagerly present in MK (0.49 mg/kg).

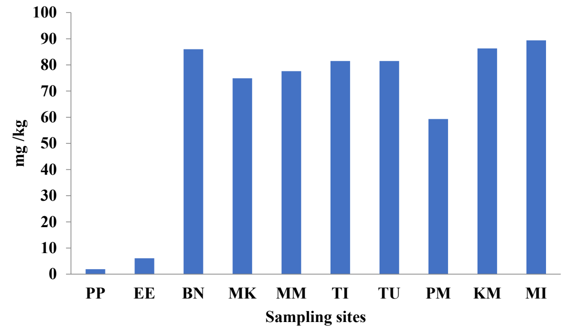

Figure 14: Analysis of Copper (Cu).

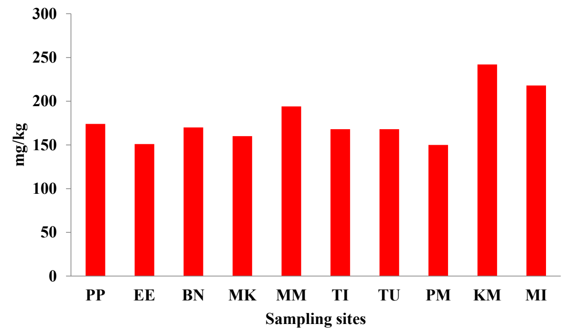

Figure 15: Analysis of Nitrogen (N_2).

The acenaphthene content was found very meagerly in four of the riverbed soil samples including TI, TU, PM and MI and absent in KM but it has occurred high in the coastal soil samples BN and absent in EE, MK and MM. The hydrocarbon fluorene was present high in the coastal soil sample BN (0.29 mg/kg) and relatively low in the riverbed soil sample PM (0.07 mg/kg) when compared with other soil samples. The fluorine has not recorded in both the coastal soil samples (PP and EE) and riverbed soil samples (TI and MI). Henceforth, the fluorine content was comparatively high in the coastal soil samples than the riverbed soil samples by analyzing the average amount of fluorene content extracted (0.07 mg/kg for riverbed soil samples and 0.29 mg/kg of coastal soil samples).

About an average of 1.185 mg/kg and 0.37 mg/kg of phenanthrene was extracted from the coastal soil and riverbed soil samples respectively. But it was absent in the coastal soil sample BN. Both the low profile (0.17 mg/kg) and high profile (2.14 mg/kg) of phenanthrene was found in the coastal soil samples with respect to EE and MK. At last, the result obviously evident that the phenanthrene was found high in the coastal soil samples. Comparatively, the same type of results was expressed for the hydrocarbon anthracene as in phenanthrene. In case of pyrene about 1.14 mg/kg was accumulated in the coastal soil sample MM and very low (0.23 mg/kg) in riverbed soil sample TU. The results have shown that the pyrene was not occurred in the two coastal soil samples BN and MK but the average accumulation was higher (0.77 mg/kg) than that of the riverbed soil samples (0.58 mg/kg).

The hydrocarbon fluoranthene has occurred in high amount in all the coastal soil samples but absent in BN. High amount of fluoranthene was reported in the coastal soil sample MK with 3.27 mg/kg and comparatively low in riverbed soil sample TU with 0.34 mg/kg. The average fluoranthene content was high (2.03 mg/kg) in coastal soil samples when compared with the riverbed soil samples but absent in the coastal soil sample BN. Both the hydrocarbons chrysene and benzo [a] anthracene was found only in the riverbed soil samples TI (0.28 mg/kg) and TU (0.43 mg/kg) and absent in all the soil samples analyzed. About 0.12 mg/kg and 2.32 mg/kg of benzo [b] fluoranthene was recorded in each of the sampling sites MM and TU respectively and absent in rest of the soil samples. The hydrocarbon benzo [ghi] perylene was found in two riverbed soil samples TU and KM and one coastal soil sample MM. From which, high amount of benzo [ghi] perylene was recorded in the soil sample TU (0.75 mg/kg).

The hydrocarbon dibenzo [a,h] anthracene was found only in two of the riverbed soil samples TU (0.25 mg/kg) and PM (0.16 mg/kg) while in case of Indeno [1,2,3-cd] pyrene, occurred in both the coastal

Sampling sites	Naphthalene mg/kg	Acenaphthylene mg/kg	2-Bromo-Naphthalene mg/kg	Acenaphthene mg/kg	Fluorene mg/kg	Phenanthrene mg/kg	Anthracene mg/kg	Pyrene mg/kg
Pazhaverkadu – Pulicat (PP)	-	0.082	7.5	0.06	-	1.67	1.70	0.89
Ennore (EE)	0.076	0.13	1.01	-	-	0.17	0.17	0.29
Besant Nagar (BN)	-	1.13	1.25	0.58	0.29	-	-	-
Muttukadu – Kovalam (MK)	-	0.25	0.49	-	0.3	2.14	2.13	-
Mahabalipuram (MM)	0.14	0.15	-	-	0.22	0.76	0.75	1.14
Tiruchirappalli (TI)	-	0.22	-	0.22	-	0.51	0.51	0.96
Thiruvaiyaru (TU)	0.07	0.16	-	0.07	0.13	0.39	0.38	0.23
Papanasam (PM)	0.095	0.17	-	0.05	0.07	0.20	0.21	0.25
Kumbakonam (KM)	-	0.13	-	-	0.08	0.48	0.48	0.69
Mayiladuthurai (MI)	0.09	1.15	-	0.05	-	0.27	0.28	0.77

Table 4a: Polyaromatic hydrocarbons (PAHs) of soil samples.

Citation: Sangeetha T, Elumalai S, Roop Singh D, Rajesh Kanna G (2017) Hydrocarbon Exploration in Peninsular India by Advanced Biochemical Markers Method. J Pet Environ Biotechnol 8: 353. doi: 10.4172/2157-7463.1000353

Sampling sites	Fluoranthene mg/kg	Chrysene mg/kg	Benz [a] anthracene mg/kg	Benzo [b] fluoranthene mg/kg	Benzo [ghi] perylene mg/kg	Dibenz [a,h] anthracene mg/kg	Indeno [1,2,3-cd] pyrene mg/kg
Pazhaverkadu – Pulicat (PP)	1.87	-	-	-	-	-	-
Ennore (EE)	0.47	-	-	-	-	-	-
Besant Nagar (BN)	-	-	-	-	-	-	-
Muttukadu – Kovalam (MK)	3.27	-	-	-	-	-	-
Mahabalipuram (MM)	2.51	-	-	0.12	0.11	-	0.82
Tiruchirappalli (TI)	2.35	0.28	0.28	-	-	-	-
Thiruvaiyaru (TU)	0.34	0.43	0.43	2.32	0.75	0.25	0.07
Papanasam (PM)	0.36	-	-	-	-	0.16	-
Kumbakonam (KM)	1.41	-	-	-	0.13	-	-
Mayiladuthurai (MI)	2.36	-	-	-	-	-	-

Table 4b: Polyaromatic hydrocarbons (PAHs) of soil samples.

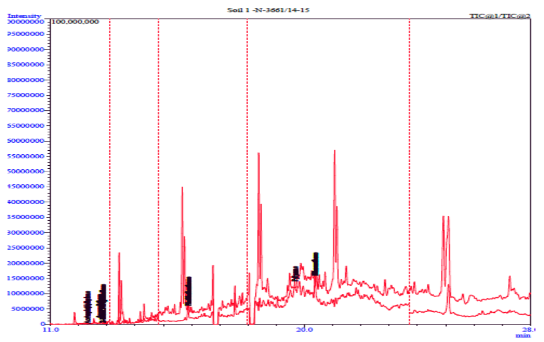

Figure 16: Poly-aromatic hydrocarbons of soil from Pazhaverkadu -Pulicat (PP).

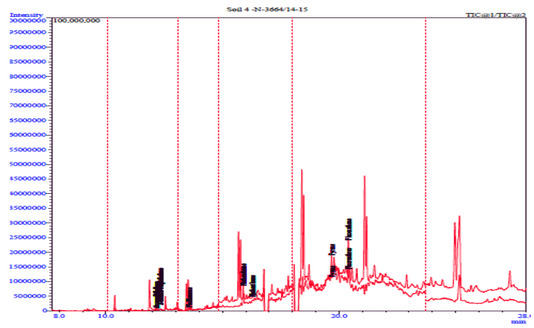

Figure 19: Polyaromatic hydrocarbon analysis of soil from Muttukadu–Kovalam (MK).

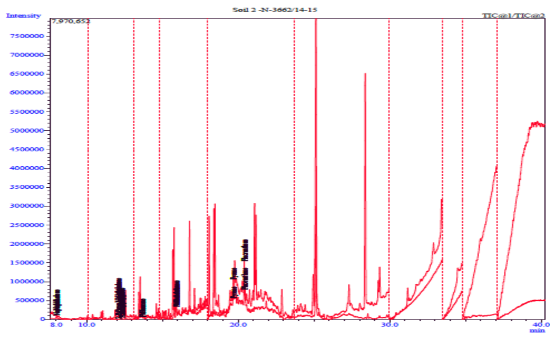

Figure 17: Polyaromatic hydrocarbon analysis of soil from Ennore (EE).

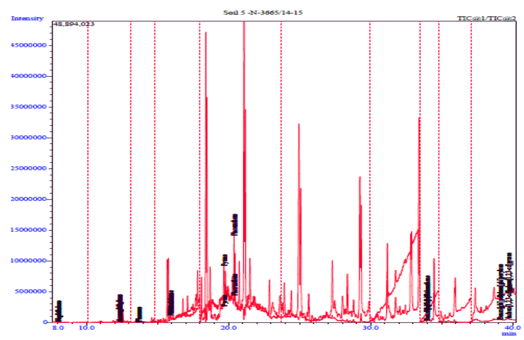

Figure 20: Polyaromatic hydrocarbon analysis of soil from Mahabalipuram (MM).

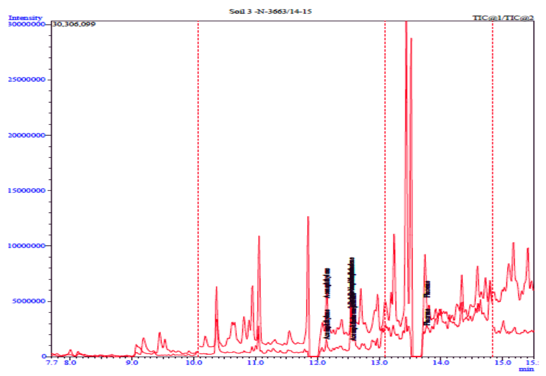

Figure 18: Polyaromatic hydrocarbon analysis of soil from Besant Nagar (BN).

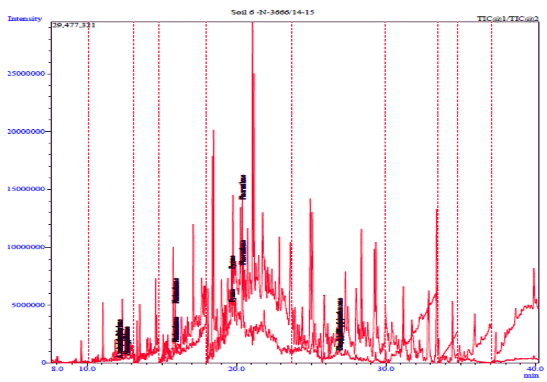

Figure 21: Polyaromatic hydrocarbon analysis of soil from Tiruchirappalli (TI).

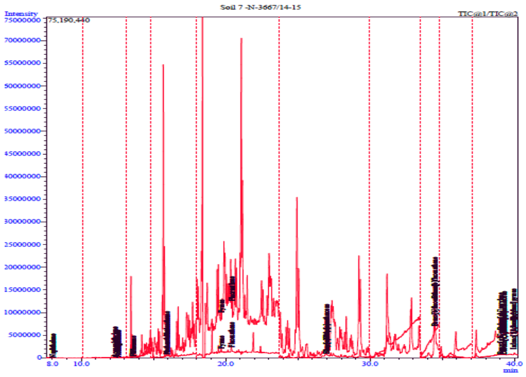

Figure 22: Polyaromatic hydrocarbon analysis of soil from Thiruvaiyaru (TU).

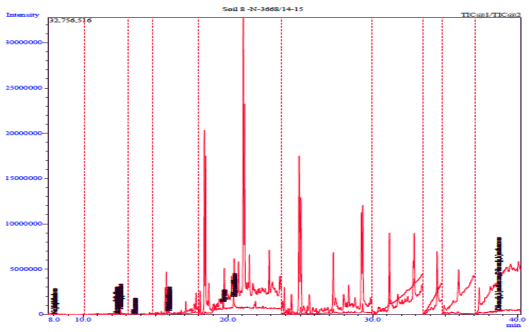

Figure 23: Polyaromatic hydrocarbon analysis of soil from Papanasam (PM).

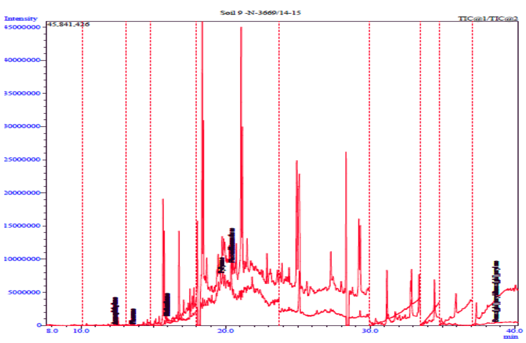

Figure 24: Polyaromatic hydrocarbon analysis of soil from Kumbakonam (KM).

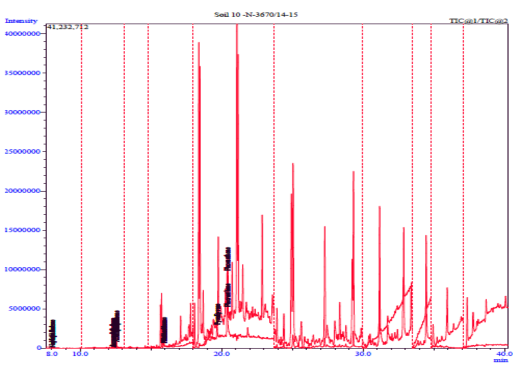

Figure 25: Polyaromatic hydrocarbon analysis of soil from Mayiladuthurai (MI).

and riverbed soil samples MM (0.82 mg/kg) and TU (0.07 mg/kg) respectively and both are absent in rest of the soil samples. There were about 12 hydrocarbons from coastal soil samples and 14 hydrocarbons from riverbed soil samples recorded in this study. The MM and BN were the coastal soil sample sites with more number of hydrocarbons (10) and least number (4) of hydrocarbons reported respectively. Likewise, TU was the riverbed soil sample site with more number of hydrocarbons (14) present in it and the least number of hydrocarbons (7) were recorded in both KM and MI. Among all the poly aromatic hydrocarbons studied, the acenapthylene is the only hydrocarbon present in all the soil samples of both the coastal and riverbed regions. The hydrocarbons including chrysene, benzo [a] anthracene, benzo [b] fluoranthene, dibenzo [a,h] anthracene and indeno [1,2,3-cd] pyrene were found only in two of the studied soil sampling sites. Fluoranthene was found high in most of all the riverbed soil samples, same way 2-bromo-naphthalene content was high in coastal soil samples.

The hydrocarbon content of all the soil sampling sites results that the high amount of hydrocarbon was accumulated in the site PP (1.967 mg/kg) of coastal soil and MI (0.71 mg/kg) of riverbed soil. Same way the low amount of hydrocarbon was reported from site EE (0.330 mg/kg) of coastal soil and PM (0.173 mg/kg) of riverbed soil. From the overall studies, it has been revealed that the coastal soil samples have high amount of hydrocarbon (1.042 mg/kg) content than the riverbed soil samples (0.492 mg/kg).

Discussion

The samples are collected using a hollow metal pipe by manual hammering. The soil samples about 100 g each was collected in pre-sterilized whirl-pack bags under aseptic conditions from a depth of about 0.5 to 1 m [7] and preferably on a grid pattern with a spacing of 200 m. With reference to our soil analysis of both the coastal soil and riverbed soil samples resulted that the presence of minerals including sodium (Na), phosphorous (P), total organic carbon (TOC), manganese (Mn), zinc (Zn) and Copper (Cu) which were higher in the case of riverbed soil samples than the coastal soil samples. The magnesium (Mg) content alone occurred high in the coastal soil samples in comparison with the riverbed soil samples.

Over recent years, many new compounds have been identified in sediments deposited in coastal and lacustrine environments. Despite the fact that our knowledge of algal lipids is still far from comprehensive, microalgal sources have now been identified for many of the lipids that are widely distributed in recent sediments [8,9]. Some of these compounds are only slowly degraded or transformed to more stable chemical structures [10,11], and thus they can be used as biomarkers for assessing the sources of the organic matter in sediments. However, it is also apparent that some compounds are more widely distributed in the biosphere than previously thought and thus their value as specific fossil biomarkers has diminished. Sterols provide a good example of this, some sterols are found only in a few classes while others are now known to be quite widely distributed [12]. The identification of several distinctive types of aliphatic biopolymer in some classes of microalgae [13,14] provides a new type of biomarker and highlights the value of studies of the bound lipids and macromolecular organic matter in organisms and sediments.

A common feature of the fatty acid distributions in sediments is the presence of C_{20}-C_{30} saturated straight-chain fatty acids that show a strong predominance of even chain-lengths. In many types of sediment, particularly those from lacustrine environments, these are probably derived from the surface waxes of higher plants [15]. However, an increasing body of analytical data suggests that microalgae [16,17] and perhaps bacteria [18] can also produce these fatty acids albeit in small amounts (typically <2%) relative to C_{14}-C_{20} fatty acids.

More widely distributed lipid classes, such as sterols and fatty acids, can still be useful indicators of carbon sources. However, it is becoming increasingly apparent that some sterols are widely distributed, and that care must be exercised when using these compounds to infer sources. Hydroxy fatty acids appear to have considerable potential as biomarkers, but information on their occurrence in organisms and sediments is still limited and as shown here for the riverbed eustigmatophytes, some surprising results are still being obtained. Since many of the simple lipids found in sediments are those that have escaped degradation because they were originally bound to resistant organic matrix, John [19] suggest that hydrolysates of the extractable and non-extractable fractions of algal cultures should be systematically examined for the presence of new biomarkers.

Polyaromatic hydrocarbon analysis of soil samples was analyzed and the results revealed that the poly aromatic hydrocarbons from different soil samples of both riverbed soil and coastal soil. The naphthalene was recorded in the soil samples EE, MM, TU, PM and MI ranges from 0.07 mg /kg to 0.14 mg/kg in soil samples TU and MM respectively. The naphthalene was not occurred in the soil samples PP, BN, MK, TI and KM. The soil sample PP has shown low amount of acenaphthylene (0.082 mg/kg) and occurred high in sample MI (1.15 mg/kg) when compared with other soil samples. The hydrocarbon 2-bromo-naphthalene was not recorded in each the riverbed soil samples but present high in the coastal soil sample PP (7.5 mg/kg) and meagerly low in MK (0.49 mg/kg).

The acenaphthene content was found very meagerly in four of the riverbed soil samples including TI, TU, PM and MI and absent in KM but which has occurred high in the coastal soil sample BN and absent in EE, MK and MM. The hydrocarbon fluorene was present high in the coastal soil sample BN (0.29 mg/kg) and relatively low in the riverbed soil sample PM (0.07 mg/kg) when compared with other soil samples. The fluorine has not recorded in the both the coastal soil (PP and EE) and riverbed soil samples (TI and MI). Henceforth, the fluorine content was comparatively high in the coastal soil samples than the riverbed soil samples by analyzing the average amount of fluorene content extracted (0.07 mg/kg for riverbed soil samples and 0.29 mg/kg of coastal soil samples).

About an average of 1.185 mg/kg and 0.37 mg/kg of phenanthrene was extracted from the coastal soil and riverbed soil samples respectively. But it was absent in the coastal soil sample BN. Both the low profile (0.17 mg/kg) and high profile (2.14 mg/kg) of phenanthrene was found in the coastal soil samples with respect to EE and MK. At last, the result obviously evident that the phenanthrene was found high in the coastal soil. Comparatively, the same type of results was expressed for the hydrocarbon anthracene as in phenanthrene. In case of pyrene about 1.14 mg/kg was accumulated in the coastal soil sample MM and very low (0.23 mg/kg) in riverbed soil sample TU. The results have shown that the pyrene was not occurred in the two coastal soil samples BN and MK but the average accumulation was higher (0.77 mg/kg) than that of the riverbed soil samples (0.58 mg/kg).

The hydrocarbon fluoranthene has occurred in high amount in all the coastal soil samples but absent in BN. High amount of fluoranthene was reported in the coastal soil sample MK with 3.27 mg/kg and comparatively low in riverbed soil sample TU with 0.34 mg/kg. The average fluoranthene content was high (2.03 mg/kg) in coastal soil samples even absent in the coastal soil sample BN but which was low (1.36 mg/kg) in riverbed soil samples where it was present in all the soil samples. Both the hydrocarbons chrysene and benzo [a] anthracene was found only in the riverbed soil samples TI (0.28 mg/kg) and TU (0.43 mg/kg) and absent in all the soil samples analyzed. About 0.12 mg/kg and 2.32 mg/kg of benzo [b] fluoranthene was recorded in each of the sampling sites MM and TU respectively and absent in rest of the soil samples. The hydrocarbon benzo [ghi] perylene was found in two riverbed soil samples TU and KM and one coastal soil sample MM. From which, high amount of benzo [ghi] perylene was recorded in the soil sample TU (0.75 mg/kg).

The hydrocarbon dibenzo [a,h] anthracene was found only in two of the riverbed soil samples TU (0.25 mg/kg) and PM (0.16 mg/kg) while in case of Indeno [1,2,3-cd] pyrene which was occurred in both the coastal and riverbed soil samples MM (0.82 mg/kg) and TU (0.07 mg/kg) respectively and both are absent in rest of the soil samples. There were about 12 hydrocarbons from coastal soil samples and 14 hydrocarbons from riverbed soil samples recorded in this study. The MM and BN were the coastal soil sample sites with more number of hydrocarbons (10) and least number (4) of hydrocarbons reported respectively. Likewise, TU were the riverbed soil sample site with more number of hydrocarbons (14) present in it and the least number of hydrocarbons (7) were recorded in both KM and MI. Among all the poly aromatic hydrocarbons studied, the acenapthylene is the only hydrocarbon present in all the soil samples of both the coastal and riverbed. The hydrocarbons including chrysene, benzo [a] anthracene, benzo [b] fluoranthene, dibenzo [a,h] anthracene and indeno [1,2,3-cd] pyrene were found only in two of the soil sampling sites studied. Fluoranthene was found high in most of all the riverbed soil samples, same way 2-bromo-naphthalene content was high in coastal soil samples.

The mean hydrocarbon content of all the soil sampling sites results that the high amount of hydrocarbon was accumulated in the site PP (1.967 mg/kg) of coastal soil and MI (0.71 mg/kg) of riverbed soil. Same way the low amount of hydrocarbon was reported from site EE (0.330 mg/kg) of coastal soil and PM (0.173 mg/kg) of riverbed soil. From the overall studies, it has been revealed the coastal soil has high amount of hydrocarbon (1.042 mg/kg) than the riverbed soil sample (0.492 mg/kg).

Conclusion

In this study, the extracted and analyzed hydrocarbons from small content of soil from a small pit serves as a biochemical markers for hydrocarbon exploration as deposited several thousands of years ago as sediments. As they are the indicators for the high deposition of hydrocarbons along the coastal line. It gives a preliminary view on the occurrence and the availability of hydrocarbon for energy. The results of this study reveal that the hydrocarbon depositions were comparatively high in the case of coastal regions than the freshwater riverbed regions.

Acknowledgements

The authors have no conflict of interest.

References

1. Dean RA, Whitehead EV (1961) The occurrence of phytane in petroleum. Tetrahedron Letters 21: 768-770.
2. Metzger P (1993) n-heptacosatrienes and tetraenes from a Bolivian strain of *Botryococcus braunii*. Phytochemistry 33: 1125-1128.
3. Metzger P, Rager MN, Largeau C (2007) Polyacetals based on polymethylsqualene diols, precursors of algaenan in *Botryococcus braunii* race B. Org Geochem 38: 566-581.

4. Wolela A (2006) Fossil fuel energy resources of Ethiopia: Oil shale deposits. J African Earth Sci 46: 263-280.

5. Gatellier JPLA, De Leeuw JW, Sinninghe Damste JS, Derenne S, Largeau C, et al. (1993) A comparative study of macromolecular substances of a Coorongite and cell walls of the extant alga *Botryococcus braunii.* Geochim Cosmochim Acta 57: 2053-2068.

6. Demetrescu E (1998) The chloroccalean alga *Botryococcus* and its significance in hydrocarbon exploration. Proc. Intern. Workshop on "Modern and Ancient Sedimentary Environments and Processes" in Moeciu, Romania pp. 155-160.

7. Davis JB (1967) Petroleum microbiology. Elsevier Publishing Company, The Netherlands. p. 197-245.

8. Volkman JK, Barrett SM, Blackburn SI, Sikes EL (1995) Alkenones in *Gephyrocapsa oceanica*: implications for studies of paleoclimate. Geochim. Cosmochim. Acta 59: 513−520.

9. Conte MH, Volkman JK, Eglinton G (1994) Lipid biomarkers of Haptophyta. In Green JC, and Leadbeater BSC (Eds.), The Haptophyte Algae: Oxford (Clarendon Press) pp. 351-377.

10. Gagosian RB, Smith SO (1979) Steroids ketones in surface sediments from the south-west African Shelf. Nature 277: 287-289.

11. Kohnen MEL, Sinninghe Damsté JS, Kock-Van Dalen AC, Ten Haven HL, Rullkötter J, et al. (1990) Origin and diagenetic transformations of C_{25} and C_{30} highly branched isoprenoid sulphur compounds: further evidence for the transformation of organically bound sulphur during early diagenesis. Geochim Cosmochim Acta 54: 3053-3063.

12. Volkman JK (1986) A review of sterol markers for marine and terrigenous organic matter. Org Geochem 9: 83-99.

13. Gelin F, Volkman JK, Largeau C, Derenne S, Damste JS, et al. (1999) Distribution of aliphatic nonhydrolyzable biopolymers in marine microalgae. Org. Geochem. 30: 147-159.

14. De Leeuw JW, Largeau C (1993) A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal and petroleum formation. Engel MH and Macko SA (eds.), Plenum, Organic Geochemistry 11: 23-72.

15. Eglinton G, Hamilton RJ (1967) Leaf epicuticular waxes. Science 156: 1322-1335.

16. Rezanka T, Podojil M (1986) Identification of wax esters of the fresh-water green alga *Chlorella kessleri* by gas chromatography-mass spectrometry. J Chromatogr 362: 399-406.

17. Dunstan GA, Volkman JK, Jeffrey SW, Barrett SM (1992) Biochemical composition of microalgae from the green algal classes Chlorophyceae and Prasinophyceae 2: Lipid classes and fatty acids. J Exp Mar Biol Ecol 161: 115-134.

18. Volkman JK, Barrett SM, Blackburn SI, Mansour MP, Sikes EL, et al. (1998) Microalgal biomarkers: A review of recent research developments. Organic Geochemistry 29: 1163-1179.

19. John TG (1993) US Patent 5266685 - Non-bitter protein hydrolyzates.