DISTRIBUTION AND CHARACTERIZATION OF HYDROCARBONS IN SEDIMENTS OF SETIU WETLAND, TERENGGANU: A PRELIMINARY STUDY

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ABSTRACT

Samples of surficial bottom sediment collected from 10 stations along Setiu Wetland (Terengganu) have been analysed and characterized in terms of biogenic and anthropogenic hydrocarbons. Sediment was extracted by using ultrasonic agitation methods with dichloromethane (DCM) as solvent. After removal of sulphur content using mercury treatment technique, the hydrocarbons were separated into fractions by silica-alumina column chromatography. Aliphatic and polycyclic aromatic hydrocarbons (PAHs) fractions were analysed using GC-FID and GCMS, respectively. The concentration of total identified n-alkanes in sediment ranged from 1.13 - 10.5 μg g^{-1} dry weight while total identified aromatic hydrocarbons ranged from 0.04 - 1.80 μg g^{-1} dry weight. Most of the stations exhibit the presence of C_{29} and C_{31} as C_{max} which are known to originate from epiticular waxes of higher (vascular) terrestrial plants. A distribution of n-alkanes in the range of C_{25} – C_{31} with odd carbon predominance and the absence of PAH's from anthropogenic sources (e.g. combustion process) in the sediments provide further evidence in support of terrigenous input of these hydrocarbons in the study area. It can thus be concluded that the sediments in the wetland is still in pristine condition.

Keywords: biogenic hydrocarbons, anthropogenic hydrocarbons, wetland, surface sediment, terrigenous input

ABSTRAK

Sampel enapan permukaan yang diambil dari sepuluh stesen pensampelan di Tanah Bencah Setiu (Terengganu) telah dikaji dan dicirikan kandungan hidrokarbonnya berdasarkan sumber biogenik dan antropogenik. Pengekstrakan hidrokarbon dari enapan dilakukan dengan menggunakan kaedah ultrasonik dan pelarut diklorometana. Raksa digunakan bagi menyingkirkan kandungan sulfur dalam enapan. Kemudiannya, hidrokarbon dalam ekstrak dipisahkan kepada pecahan hidrokarbon alifatik dan aromatik polisiklik dengan menggunakan turus silika-alumina dan penentuan sebatian hidorkarbon tersebut dilakukan dengan GC-FID dan GC-MS. Julat kepekatan jumlah n-alkana dalam enapan ialah dari 1.13 - 10.5 μg g^{-1} (berat kering) manakala jumlah PAHs ialah diantara 0.04 - 1.80 μg g^{-1} berat kering. Kebanyakan stesen menunjukkan kehadiran C_{29} dan C_{31} sebagai C_{max} di mana kehadiran sebatian ini sering dikaitkan dengan lilin epitikular dari tumbuhan daratan. Agihan n-alkana dalam julat C_{25} – C_{31} dengan kepilihan karbon ganjil dan ketiadaan sebatian PAHs dari sumber antropogenik (spt. proses pembakaran) menguatkan lagi keberangkalian hidrokarbon yang wujud dalam enapan tanah bencah Setiu adalah berasal dari sumber biogenik. Sebagai kesimpulan, enapan di Tanah Bencah Setiu boleh dianggap masih berada ditahap tidak tercemar.

INTRODUCTION

Contemporary sediments are considered as a 'sink' for hydrocarbons in the aquatic environment and their importance in pollution monitoring has been recognized by several authors [1,2]. In fact in the aquatic environment (lacustrine or marine) there is a net downward flux of hydrocarbons within the water column towards the sediment as result of the deposition of particulate materials, both organic (dead organism, fecal pellets, etc) and inorganic (dust, eroded soils, etc) that contains significant amount of biogenic and

anthropogenic hydrocarbons. Thus sediments are good sources of integrated samples, exhibiting levels of hydrocarbons several orders of magnitude higher than those found in water column.

Hydrocarbons enter into the marine environment by both aquatic and atmospheric pathways, the latter consisting of dry and wet deposition. The relative importance of the two main input pathways for a given environment depends on the geographical setting of the later [3,4,5]. Among hydrocarbons, the polycyclic aromatic ones (PAH's) have received special attention since they have long been recognized as hazardous environmental chemicals [6]. Aside from anthropogenic sources, hydrocarbons also come from natural sources, such as terrestrial plant waxes, marine phytoplankton and bacteria, biomass combustion and digenetic transformation of biogenic precursors. As a result of the variety of their sources, hydrocarbons occur as complex mixtures in environment samples.

The research site, Setiu Wetland is a unique area which covers many ecosystems such as estuary, mangrove, wetland and lagoon. It is said to be the only area with such diverse ecosystems in the east coast of Peninsular Malaysia, offering a vast array of biological diversity and many utilizable natural resources. Main economic activities in the area centred around coastal and riverine fishing with some fish and prawn culture activities. However at present, the number of cultures in the area is rapidly increasing causing fears of the potential increase in the disturbance to the pristine environment. Until recently, the only research that has been carried out in the area was on the nesting density of marine turtles and painted terrapin [7]. Owing to the importance of the area, efforts are now underway by KUSTEM's researchers to study the various aspects of the wetland. The results of a preliminary study on the hydrocarbon in the surficial sediment of the Setiu Wetland are discussed in this paper. The study focused on the characterization of aliphatic hydrocarbons and PAH's in an attempt to asses their origin, distribution and concentration in the sediment.

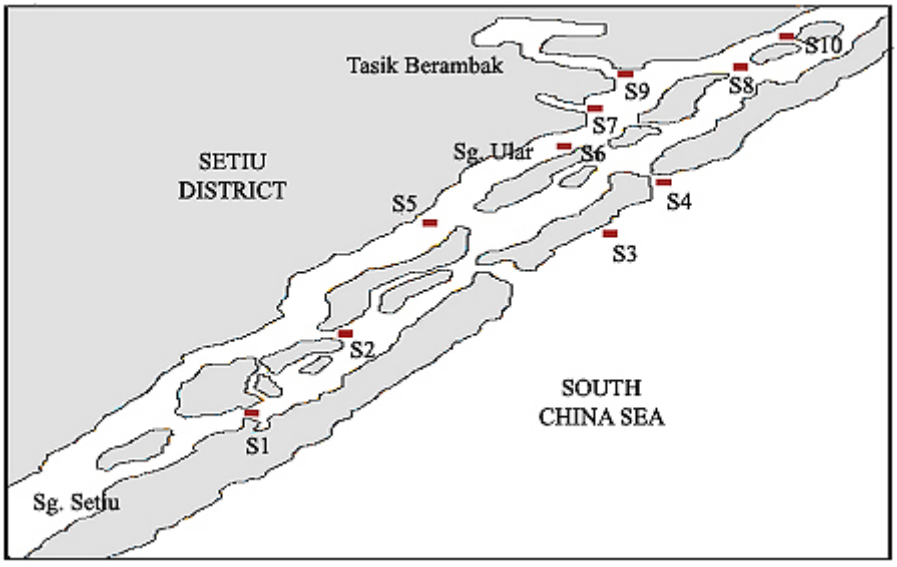

Figure 1 : Location of the sampling stations

EXPERIMENTAL PROCEDURE

Sampling

In this study, 10 sampling sites (S1 – S10) were selected along Setiu Wetland covering an area from Setiu River to Beting Lintang. Figure 1 shows the location of the sampling stations whilst Table 1 gives the detailed (longitude and latitude) of these stations. Surficial sediment samples for hydrocarbon analysis were collected using a grab sampler (Eekman Grab Sampler) in March 2001. The undisturbed surface sediment was recovered, wrapped with aluminium foil, frozen and stored at -30°C until analysis.

Sample Treatment

The sediments were freeze dried and sieved using 500 μm sieve. Analysis was carried out in the fraction < 500 μm.

Extraction and Fractionation

The analytical procedure summarized below followed the protocol described by (UNEP) [8]. TOC (total organic carbon) of the sediment were analysed using Wakley's and Black titration method [9] Freeze-dried sediment were extracted ultrasonically using dichloromethane (DCM) as a solvent. Before extraction, two internal standard (n-C_{32} for aliphatic fraction (fraction 1) and 9,10 – Dihydroanthracene for PAH's fraction (fraction 2)) were spiked into the sediment for recovery assessment. Sulphur content in the sediment is removed using mercury treatment. The extracts were concentrated to about 1 ml using rotary evaporator (at temperature <35°C) and then fractionated into subfractions on silica-alumina column with silica gel (230-400 mesh) and alumina (70- 30 mesh) which was deactivated with 1% deionized water. 25ml of n- hexane was then used to elute the n-alkanes followed by 25ml 50% DCM in hexane to eluted the second fraction.

GC-FID/GCMS analysis

Aliphatic fractions were analysed using GC-FID while PAH's fraction with GC-MS. Gas chromatographic anayses were performed with a Trace GC 2000 (GC-FID) equipped with an on column injector, HP-5 fused silica capillary column (25 m x 0.32 mm i.d; 0.52 μm filmed thickness) and flame ionization detector (FID). Helium was used as carrier gas and the oven temperature was programmed from 50°C (1.5 min) to 300°C (80 min) at 5°C/min. PAH's fraction were injected in the GCMS fitted with a fused silica column (30m x 0.25 mm i.d; 0.25μm filmed thickness). The column temperature was programmed as follows: - hold at 50°C for 1 min; 50 - 140°C at 5°C min^{-1}; 140 - 290°C at 4°C min^{-1} and maintained at 290°C for 13 min. Helium was used as the carrier gas with a flow rate at 1.0ml min^{-1}. The GC injection port temperature was set at 290°C and sample injections were made using a splitless mode. GC-MS interface was set at 300°C. Hydrocarbons were identified by comparing their retention time with those of unknown standards injected under the same conditions and quantified. In the case of PAH compounds, verification of peaks was also carried out using the MS library.

RESULT AND DISCUSSION

Table 1: Coordinate of the chosen sampling station

	Sampling Site	Latitude	Longitude
S1	Kg. Kuala Baharu	N 05° 38′ 25.1″	E 102° 48′ 37.5″
S2	Kg. Telaga Papan	N 05°40′ 02.2″	E 102°44′ 13.4″
S3	Kg Kuala Setiu Baharu	N 05°40′ 27.2″	E 102°44′01.3″
S4	Pulau Sotong	N 05°40′15.7″	E 102°43′49.1″
S5	Pulau Gemia	N 05°40′00.1″	E 102°43′49.2″
S6	Pulau Tok Aji	N 05°39′15.8″	E 102°44′46.9″
S7	Kg.Pengkalan Gelap	N 05°40′38.6″	E 102°43′03.2″
S8	Pulau Che Him	N 05°40′49.9″	E 102°42′51.7″
S9	Pulau Wan Embong	N 05°40′23.0″	E 102°42′58.0″
S10	Pulau Telaga Tujuh	N 05°41′18.1″	E 102°42′25.5″

TOC

Surface sediment in the study area contained relatively low organic carbon, with values ranging between 0.2% anf 2.2%. Samples from the station 7 (S7), which received direct riverine influence, exhibit highest

OC contents [10]. Samples from station 5 (S5) and station 6 (S6) where fine sediment accumulate, exhibit relatively high OC values. This is most likely due to the increase in biological activities at S5 and S6, since those two stations are in close vicinity of prawn culture cages. The results obtained (Table 2) are slightly higher than values reported for the estuary of another major river in China, the Huang He (0.06%-0.39%), [9] and Yangtze River (0.11% -0.65%), [11].

Total n-alkanes

N-alkanes dominated the aliphatic hydrocarbon fraction. Total n-alkanes (TNA) obtained ranged from 1.35 to 10.5 μg/g dry weight. Although the TNA concentration does not differentiate between natural (biogenic) and anthropogenic sources of hydrocarbons, its values usually reflect the degree of pollution within a certain area; the concentrations of biogenic hydrocarbons are usually small relative to the contaminant concentration in polluted samples. It has been reported that levels of biogenic hydrocarbons average about 5-10 μg/g dry weight. in coastal sediments [8]. Results in Table 2 clearly indicate that, with exception of S7 which exhibited a TNA value marginally above 10 μg/g dry weight, all other remaining stations showed TNA values in the natural range. Comparison with other studies in the region showed that the concentration observed in this study were generally lower than those reported in the sediment collected from Taman Negara (9.0 - 26.5 μg/g dry weight) [12], Pulau Cik Wan Dagang located at Kemaman estuary (5.5 – 22.0 μg/g dry weight) [13] and from sediments collected along the West Coast of Peninsular Malaysia: 2.85 - 17.6 μg/g dry weight) [14].

Table 2: Concentration of aliphatic hydrocarbons and selected finger printing parameters in surface sediments of Setiu Wetland, Terengganu

Sampling Sites	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Parameter						μg/g				
OC (%)	1.4	0.4	0.2	0.5	1.6	2.1	2.2	2.1	1.3	1
TNA	6.06	3.23	1.35	3.13	4.63	6.88	10.5	3.48	2.47	1.50
$CPI_{(25-33)}$	2.92	1.75	5.0	2.96	3.56	1.80	3.58	5.3	2.88	1.22
$CPI_{(15-23)}$	0.35	2.02	0.91	0.06	0.74	0.08	0.34	0.37	0.41	0.24
ALK (ter)	3.56	0.29	0.14	1.61	2.32	3.61	6.03	1.68	1.16	0.45
C_{29}	1.29	0.14	0.06	0.07	0.66	1.81	2.99	0.68	0.44	0.21
C_{31}	1.24	0.10	0.08	0.11	0.95	1.41	2.44	0.87	0.33	0.24

OC: organic carbon; TNA: Total n-alkanes; $CPI_{(25-33)}$: Carbon Preference index in the carbon range C_{25}-C_{33}; $CPI_{(15-23)}$: Carbon Preference index in the carbon range C_{15}-$c_{23;}$ ALK (ter): C_{27} + C_{29} + C_{33} n-alkanes.

Normal n-alkanes ranging from $C_{14} – C_{34}$ were detected in the sediment. Their molecular distribution show an odd carbon number predominance with C_{max} generally at C_{29} and C_{31} with no clear dominance of one species over another (Table 2 and Figure 2); others studies have also found that in some cases, there exist a shift in C_{max} between C29 and C_{31} [14]. The n-alkanes compositional profile showed a high predominance of long chain homologues ($\Sigma C_{25} – C_{31}$) with an elevated odd to even carbon number preference as reflected in the CPI values ($C_{25} – C_{31}$) greater than 1.0 (Table 2). This distribution pattern is indicative of prominent terrigenous inputs derived from higher plant waxes [15, 16] and their occurrence reveals the importance of terrestrial input in study area. Figure 3(a) and 3(b) show typical chromatograms of the aliphatic fractions from two sediment samples (S7 and S1, respectively). The sum of the most abundant n-alkanes related to biogenic terrestrial sources (C_{27}, C_{29} and C_{31}) [10] is referred in Table 2 as ALK (ter) and account for 40%-65% of the total alkanes; the high contribution of the ALK (ter) reflects the importance of terrestrial plant input into the sediments of Setiu Wetland.

UCM

UCM consist of complex mixture of polycyclic aliphatic hydrocarbons [17] and has a well-known linkage to biodegraded petroleum residues [18, 19]. The absence of UCM in this study strongly suggests that there is no petroleum residue input observed from this study.

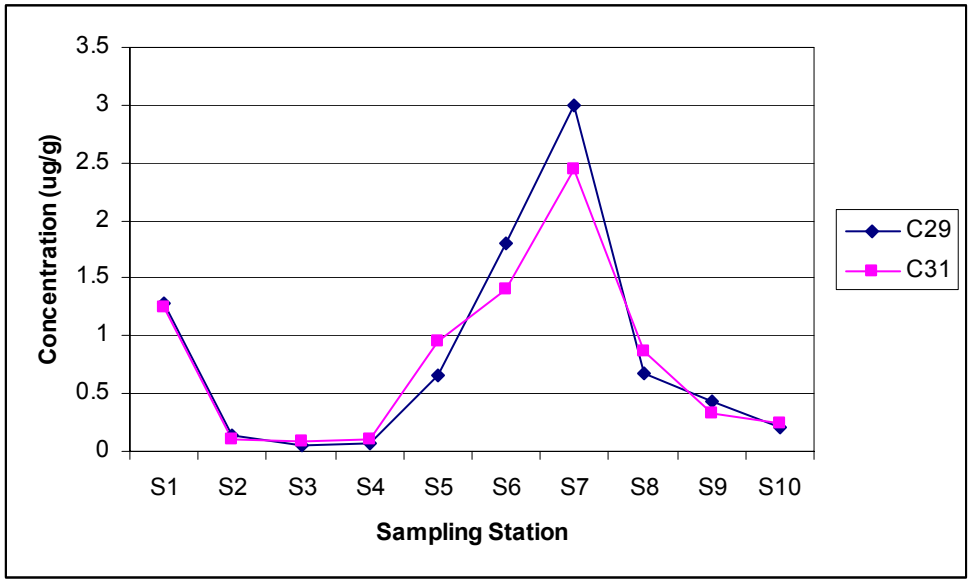

Figure 2: Comparison of C_{29} and C_{31} concentration in sediment

Polycyclic Aromatic Hydrocarbon (PAH's)

Individual PAH compound identified and quantified in the study area listed in Table 3. Total identified aromatic compound observed in the study area ranged from 0.04 to 1.80 µg/g dry weight. Out of 16 PAH's listed, only anthracene was found in all the samples with S9 exhibiting the highest concentration whilst the lowest concentration of identified aromatic hydrocarbon was observed in station 4. Figure 4(a) and 4(b) show the typical chromatograms of the PAHs fractions as typified by sample from S6 and S7, respectively.

Previous study has shown that phenanthrene and anthracene were produced from pyrolysis of organic materials by various processes, including incomplete fossil fuel burning and can also exist as trace concentration in petroleum [20]. The high abundance of coronene and benzo [g,h,i] perylene is an indicative of gasoline vehicular emission [21]. The absence of PAH's associated with combustion sources in the present study further support the contention that anthropogenic sources input in the area is limited.

CONCLUSION

The results of this study clearly indicate that the sources of hydrocarbons in Setiu Wetland are mainly derived from biogenic inputs viz. from epiticular plant waxes associated with terrestrial plants. It is speculated that these natural hydrocarbons are primarily delivered by riverine discharges and also from terrestrial plants that exists in the lagoon such as mangroves. It can thus be concluded that Setiu Wetland sediments are still in pristine condition.

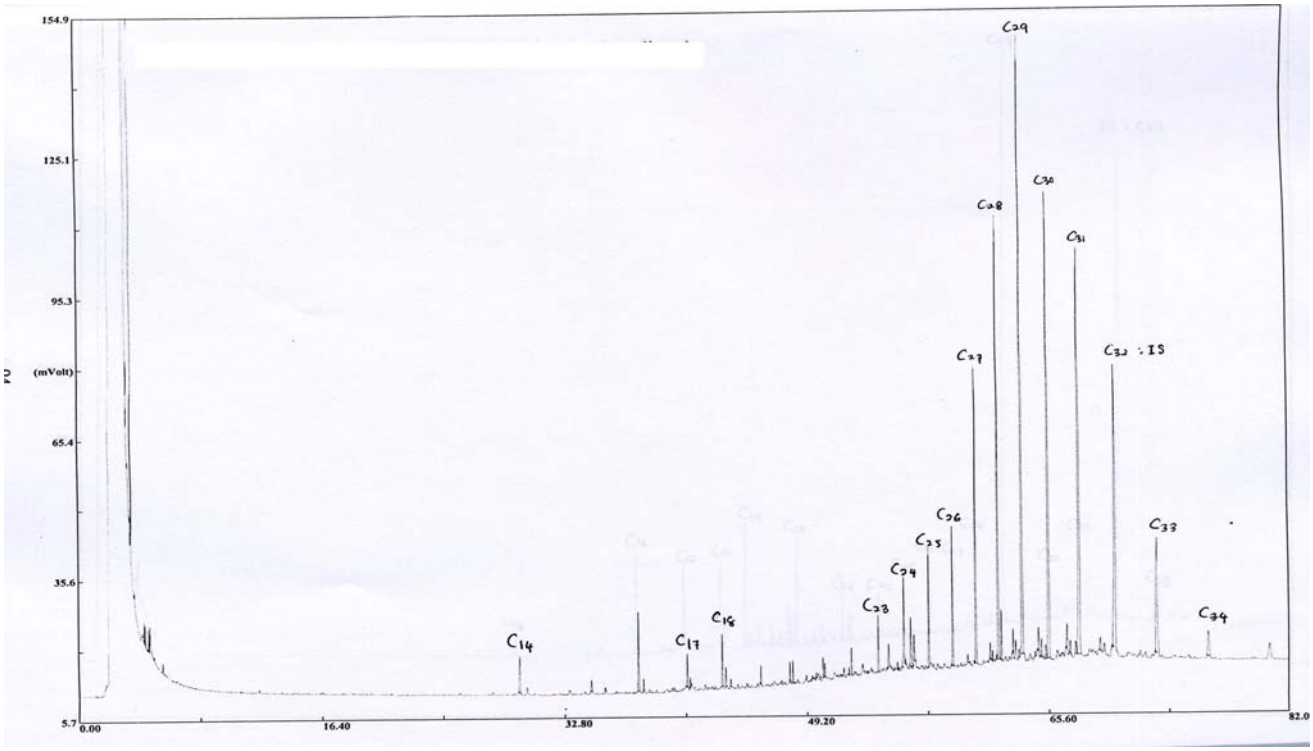

Figure 3 (a)

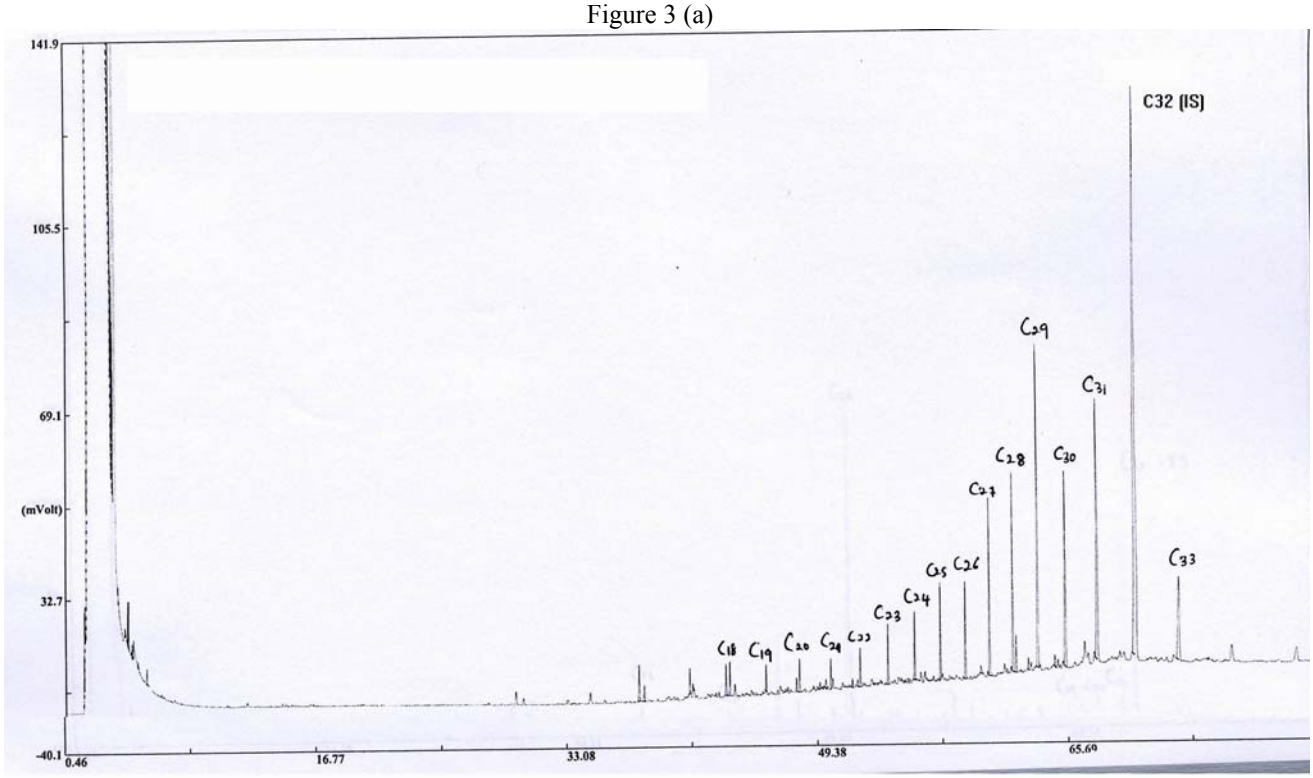

Figure3(b)

Fig. 3: Typical example of fraction 1 chromatogram obtained in this study. (a) : S7 and (b) S1

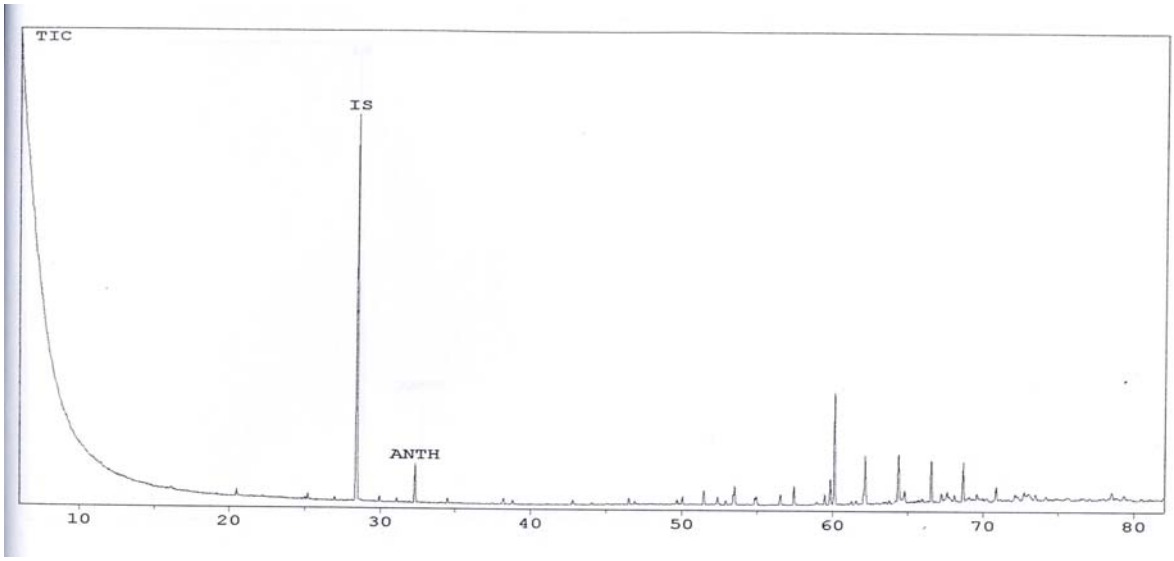

Figure 4a

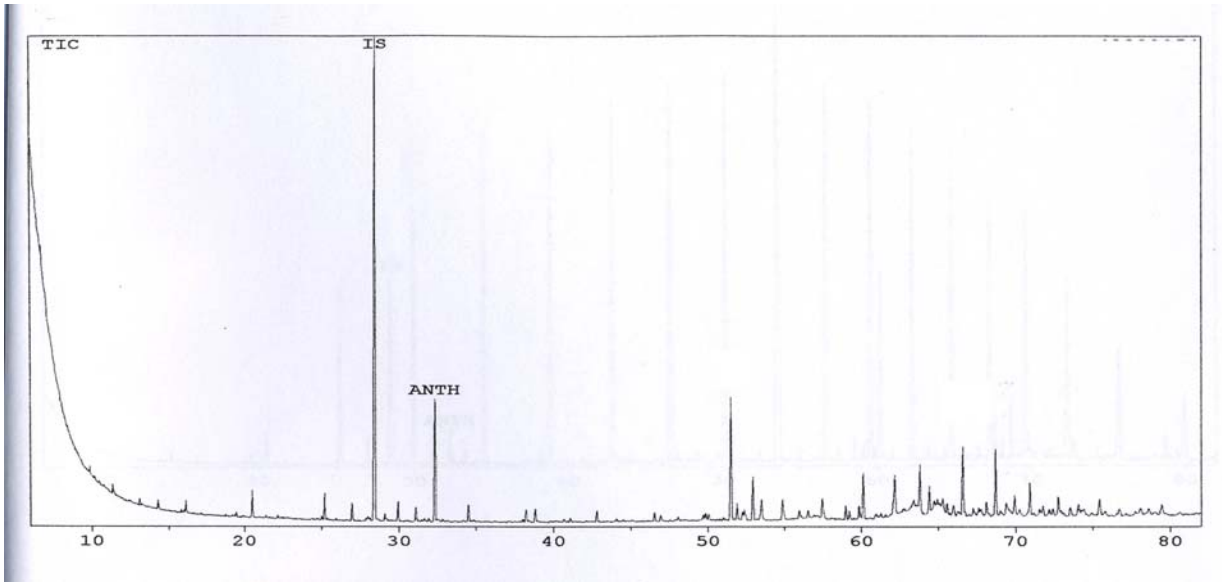

Figure 4(b)

Fig. 4: Typical example of fraction 2 chromatogram obtained in this study. (a): S6 and (b): S7

Table 3: Concentration of PAH's compound of Setiu Wetland Terengganu

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
PAH's Compound						μg/g				
Naphthalene	-	-	-	-	-	-	-	-	-	-
Acenapthalene	-	-	-	-	-	-	-	-	-	-
Acenapthene	-	-	-	-	-	-	-	-	-	-
Fluorene	-	-	-	-	-	-	-	-	-	-
Anthracene	0.35	0.31	0.70	0.04	0.30	0.23	0.92	0.24	1.80	0.50
Phenanthrene	-	-	-	-	-	-	-	-	-	-
Fluoranthene	-	-	-	-	-	-	-	-	-	-
Pyrene	-	-	-	-	-	-	-	-	-	-
Chrysene	-	-	-	-	-	-	-	-	-	-
Benzo [a]anthracene	-	-	-	-	-	-	-	-	-	-
Benzo [k]fluorantene	-	-	-	-	-	-	-	-	-	-
Indenol[1,2,3-CD]pyrene	-	-	-	-	-	-	-	-	-	-
Dibenz [a,h] anthracene	-	-	-	-	-	-	-	-	-	-
Benzo[g,h,l] perylene	-	-	-	-	-	-	-	-	-	-

- : not detected

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