

SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS IN MANGROVE SEDIMENTS OF PULAU CIK WAN DAGANG, KEMAMAN.

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Abstract: In this study, the distributions of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of fifteen stations from a small mangrove island located within the estuary of Kemaman River were determined. Sediments were Soxhlet extracted using a 1:1 mixture of dichloromethane and hexane as solvent. Desulphurisation was done using mercury treatment while fractionation was done using silica-alumina column chromatography technique. The hydrocarbons were detected using Gas Chromatography-Mass Spectrometer (GCMS). Results showed that total identified PAHs (TIP) ranged between 0.12 – 1.42 mg g⁻¹. Regardless of site, the most common compounds detected were those of higher molecular weight largely known to be associated with combustion of fuel materials. A strong correlation exists between benzo[ghi] perylene and TIP suggested that combustion of fuel materials (vehicular emissions) could be a major contributor of PAHs to these sediments. Based on the strategic location of the island within the Kemaman estuary, it is postulated that the most likely sources of the PAHs compounds are runoffs and atmospheric deposition from various related activities from Chukai Township and from maritime sources such as discharges from ships and fishing boats.

KEYWORDS: South China Sea, river estuary, PAHs, fuel combustion, vehicular emission

Introduction

Occurrence of hydrocarbons in the marine environment comes from many different sources and can generally be classified into two major sources viz. biogenic and anthropogenic sources. Hydrocarbons of biogenic origin naturally occur at low concentrations in different substrates, such as water and sediments, and are part of the natural hydrocarbon baseline of an ecosystem. These hydrocarbons originate from terrestrial plant waxes, biosynthesis by marine organisms and diagenesis transformation of non-hydrocarbon biosynthetic natural products such as sterols and hopanols. Hydrocarbons of anthropogenic origin, on the other hand, are introduced into the environment as a result of activities related to oil exploration, maritime transport (operational discharges and tanker accidents), harbour activities and domestic and industrial effluents. Due to their hydrophobic nature, hydrocarbons, especially

polycyclic aromatic hydrocarbons (PAHs), in aquatic environment rapidly tend to be adsorbed onto particulate materials and then deposited in sediment as a final sink. Thus, it is not surprising that sediment is generally recognised as the most important reservoir of these contaminants [Culotta et al., 2006][Hwang et al., 2006]. Background values for PAHs in sediments are reported to be in the range of 0.01 to approximately 1 mgkg⁻¹ dry weight. However, there is a high probability of finding them higher in the river mouth, estuaries and bays, as well as in areas associated with ship traffic, oil production and transportation [Culotta et al., 2006]. It is generally accepted that the Malaysian marine environment is increasingly being threatened by oil pollution, namely oil and grease pollutants [DOE, 2008][Mohd Pauzi Zakaria et al., 2002][Mohd Tahir et al., 1999].

Consequently, mangrove forests, important nurseries and breeding grounds for a variety of living resources, being coastal ecosystems are therefore extremely vulnerable to the threats of

oil pollution. Few studies have been carried out to assess the distribution and accumulation of PAHs in mangrove forests and estuaries in certain regions. (Tam *et al.*, 2001) have reviewed the levels of PAHs observed in mangrove and marine sediments of Hong Kong, China and other areas in the tropical region; generally the values (Table 1) showed significant variation with locations and these differences could be related to variations in and the extent of activities in the areas of study.

Malaysia is estimated to have approximately 612,580 ha of mangrove forests, the bulk of which are located in Sabah and Sarawak. Peninsular Malaysia has an estimated 103,203.11 ha of mangrove forests, out of which only ca. 1987 ha. are found in Terengganu [Mohd Lokman & Sulong, 2001]. Kemaman estuary is unique in that not only it has the largest extent of mangrove forest in Terengganu, it is also in the vicinity of Kemaman supply base, the main supply port that services the oil and gas operation in the South China Sea. The estuary is also just ca. 20 km south

of the Kerteh crude oil terminal, which receives oil from the South China Sea oil wells. Studies [Mohd Tahir et al., 1999][Mohd Tahir et al., 1997][Hairunazifah, 2001] on the hydrocarbon distributions in this region suggested some indications of oil and grease contamination when compared to other areas in the east coast of the Peninsular [Mohamad Pauzi Zakaria et al., 2001] [Kuhan Chandru et al., 2008]. Kemaman estuary is well studied with respect to physical processes (e.g. sediment transport phenomenon) in the estuary [Abdul Khadir Ishak, 2003] and also the extent of mangrove forests [Mohd Lokman & Sulong, 2001] but studies on chemical transport and/or distribution of pollutants, particularly on hydrocarbons, are still limited. The definition of a baseline level of hydrocarbons is essential when attempting to determine chemical changes introduced by anthropogenic effects. Consequently, this study is initiated to provide the relevant and much needed information on current levels of polycyclic aromatic hydrocarbons as

Table1. Concentration of total polycyclic aromatic hydrocarbons (PAH; ngg⁻¹ d.w.) in mangrove sediments and marine sediments in Hong Kong and other cities in China.

Sites	Mean	S.E.	Range	Sample Stations	Reference
Mangrove sediments in Puerto Rico	1820	2349	500-6000	14	Klekowski et al. (1994)
Mangrove sediments in Carribean Island	502	554	103-1657	13	Bernard et al. (1996)
Mai Po mudflat in Hong Kong	547	142	400-831	3	Zheng (unpublished)
Marine coastal sediments in Hong Kong	553	253	7-4420	20	Zheng and Richardson (1999)
Marine bottom sediments in Hong Kong					Connell et al. (1998)
Background			40-60	66	
Eastern buffer	94	93	40-230	4	
Deep bay	99	89	47-231	4	
Tolo Harbour	42	4	39-50	4	
Victoria harbour			66-116	6	
Typhoon shelter			42-1159	9	
Marine sediments in Pearl River Estuary	2196	3087	408-10 811	10	Mai et al. (2000)
Marine sediments in South China Sea	146		25-275	16	Yung et al. (2000)
Marine sediments in Xiamen Harbour	367	87	247-480	9	Zhou et al. (2000)

Source: Tam *et al.*, 2001;

well as fingerprinting sources of these compounds in the area.

Methodology

Figure 1 shows the location of Pulau Cik Wan Dagang which is located in the Kemaman estuary. The island is not populated and is actually a mangrove island which is subjected to tidal influence. Also included in the diagram are potential sources of hydrocarbon input into the estuary: Sg. Limbong is actually a small river which is now turned into a concrete channel and the domestic sewerage system (*sistem peparitan*) of Chukai town actually drains into this channel bringing possible wastes into the estuary; jetties and KSB are potential sources as fishing boats and supply ships uses these facilities, respectively. A total of 15 stations were selected for the collection of surface sediments on the island (Figure 2). Sediments were collected using an Ekman grab sampler, wrapped in pre-cleaned aluminum foil and transported to the laboratory in an ice chest packed with ice. Once in the laboratory, samples

were frozen until further analysis. These samples were later freeze-dried followed by sieving using a 500 μ m sieve. Only the fraction < 500 μ m were used in the analysis.

Analytical methodology

The analytical procedure adopted for the extraction of hydrocarbon compounds was based on standard method proposed by UNEP [UNEP, 1992]. Briefly, sediments were soxhlet-extracted using DCM:hexane (1:1) mixture for eight hours. Prior to the extraction, an internal surrogate standard (9,10 – Dihydroanthracene) was spiked into the sediment for recovery assessment; this procedure typically yields recoveries of PAHs in the region of 55 - 80%. PAHs concentration was recovery-corrected using the spiked surrogates. Removal of sulphur from the extract was done by using mercury treatment. The sulphur-free extracts were then concentrated to about 1 ml using a combination of rotary evaporator (<35°C) and nitrogen blow-down followed by fractionation on partially-deactivated (5%) silica-alumina column. The PAHs fraction was eluted using a combination of 30 ml 10% DCM and 20 ml 50% DCM in hexane respectively and the extracts collected in one fraction. Procedural blanks were run throughout the study to ensure there was little or no detectable contamination of the samples.

GCMS analysis

Identification and quantification of PAH's fraction were carried out using GC-MS by comparing the retention times compared to that of external PAHs standards. Confirmation of peaks was also carried out using the MS library. Sixteen USEPA priority PAHs compounds were analysed in this study. These compounds were as follows: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FTH), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k) fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DA), benzo(g,h,i)perylene (BgP) and indeno(1,2,3,cd)pyrene (IP). Sums of these 16 compounds were collectively known as total identified PAHs (TIP).

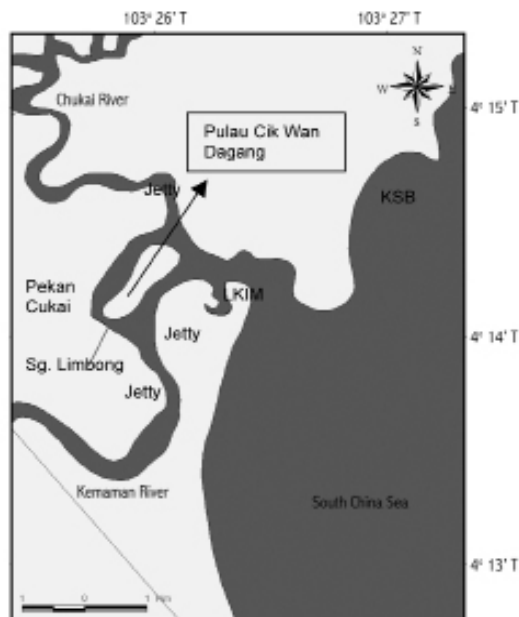


Figure 1. Location of Pulau Cik Wan Dagang and possible sources of hydrocarbon inputs.

Legend: KSB – Kemaman Supply Base

LKIM – Jetty (Lembaga Kemajuan Ikan Malaysia)

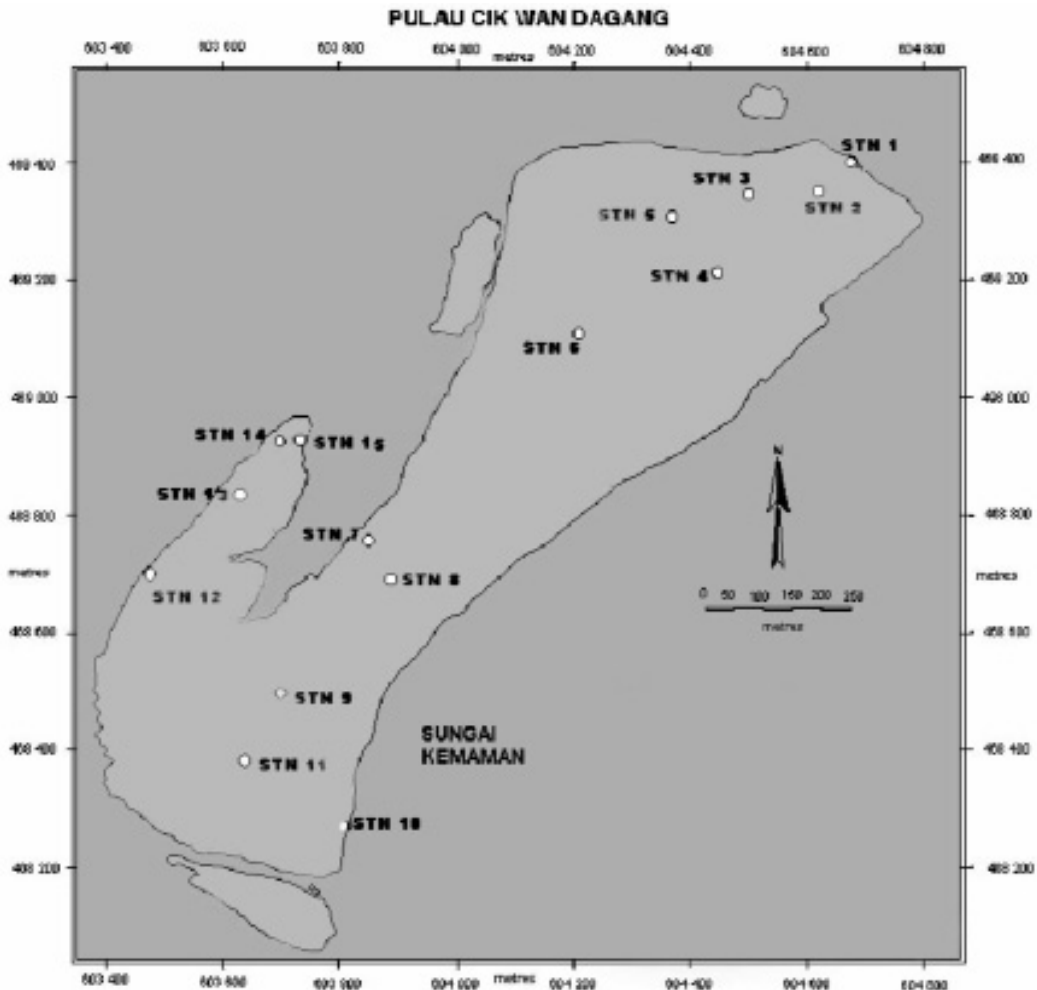


Figure 2. Map showing the location of sampling stations.

In the GC-MS analysis, the GC operating condition was as follows: HP-5 fused-silica column (30 m x 0.25 mm i.d; 0.25 mm film thickness); injection temperature was set at 290°C using a splitless mode; column temperature was programmed in the following manner: hold at 50°C for 1 min, first temperature ramp of 50 - 140°C at 5°C min⁻¹ followed by the second temperature ramp of 140 - 290°C at 4°C min⁻¹ and then maintain at 290°C for 13 min resulting in a total run time of 82 mins; helium was used as the carrier gas with a flow rate at 1.2ml min⁻¹. The GCMS interface was set at 300°C.

Result and Discussion

Polycyclic aromatic hydrocarbon distribution

Table 2 shows the distribution of TIP and selected fingerprinting parameters in surface sediments of Pulau Cik Wan Dagang. TIP found in these sediments ranged from 0.12 to 1.42 µg/g dry wt with mean of 0.60 ± 0.45 µg/g dry wt. Regardless of sampling sites, it is interesting to note that most common PAHs detected were those of higher molecular weight, largely known to be associated with combustion of fuel materials viz. DA, BgP and IP. CHR was another compound

quite commonly detected in the samples. The combustion of fuels generates a compositionally characteristic series of primarily non-alkylated PAHs, regardless of the fuel type burned [Lee et al., 1977]. The following nine compounds are often the most dominant members of this series viz. FTH, PYR, BaA, CHR, BbF, BkF, BaP, DA, BgP and IP. These primarily combustion-derived PAHs are referred quantitatively in the following section as a composite term Σ Comb (Table 2), defined as the sum of the concentrations of these nine compounds in each sample. The results (Table 2) show that Σ Comb represent almost 41 to 93% of the total PAHs identified in the samples, indicating the important contribution of this source of input into the area under study. Another interesting feature is that for some stations (e.g. stations 1, 4 and 5), despite the relatively low TIP, Σ Comb represent extremely high proportions (>80%) of the TIP.

An association of BgP with vehicular emission source has long been established [Zheng et al., 2000]; in this study, almost all stations

showed the presence of BgP in their sediments. A strong correlation between BgP compound with the TIP (Figure 3) ($r=0.91$) indicates that vehicular emission could be a major source of PAHs found in these sediments. Exhaust emissions from road transports could be deposited onto soils and enter the estuary through run-offs from nearby Chukai township via Sg Limbong or through direct atmospheric deposition into the estuarine and marine environment. A major road runs across Chukai and Kemaman rivers; emissions from vehicles plying the route could potentially contribute to the PAHs content through atmospheric deposition into these river systems. Equally important, emissions from maritime activities, such as from ships and fishing boats using the jetties located along the estuary and supply vessels anchoring and /or using the Kemaman Supply Base (KSB) facilities in the area, could also deposit the PAHs into the marine environment.

Review of the distribution pattern of the individual PAHs compounds found in this study

Table 2. Distribution of total identified PAHs and selected fingerprinting parameters in surface sediments of Pulau Cik Wan Dagang, Kemaman Estuary.

Sampling station	TIP ($\mu\text{g/g}$)	Σ Comb ($\mu\text{g/g}$)	% Comb	BgP ($\mu\text{g/g}$)
1	0.241	0.215	89.2	0.042
2	1.133	0.513	45.3	0.218
3	0.413	0.236	57.1	0.132
4	0.158	0.137	86.7	nd
5	0.124	0.104	83.9	nd
6	0.274	0.192	70.1	nd
7	0.141	0.081	57.4	nd
8	0.261	0.215	82.4	0.042
9	0.231	0.215	93.1	0.996
10	0.657	0.317	48.2	0.204
11	0.908	0.419	46.1	0.116
12	1.417	0.587	41.4	0.362
13	1.135	0.723	63.7	0.397
14	0.918	0.571	62.2	0.320
15	1.042	0.515	49.4	0.355

TIP: total identified PAHs; Σ Comb: sum of total combustion-derived PAHs;
nd: not detected

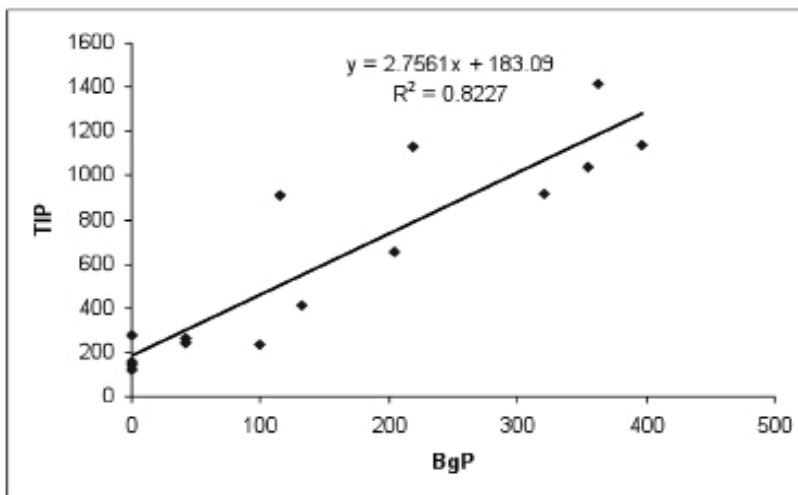


Figure 3. Correlation between benzo(g,h,i) perylene and total identified PAHs.

showed the depletion of low molecular weight PAHs compounds such as ACE, ACY, PHEN, ANT, PYR from majority of the sediment samples. It is uncertain at present whether the absence is actually inherent to these samples or because of a possible technical problem occurring in the analysis of PAHs compounds. Thus, it is conceded that further study is needed to verify these findings. Nonetheless, present results clearly show that PAHs compounds were present in these samples and, based on the present observation, they were of anthropogenic source probably resulting from combustion of fuel materials.

Admittedly, it is difficult to accurately identify PAHs origins based on the fact that these analytes could be emitted by a number of possible sources or undergo various processes before being deposited into the sediments. Nonetheless, previous researchers [e.g. Culotta et al., 2006] [Mohamad Pauzi Zakaria et al., 2001] [Kuhan Chandru et al., 2008] [Zhang et al., 2004] [Mille et al., 2006] have evaluated possible sources of PAHs found in sediments by employing individual ratios of selected PAHs compounds molecular markers in their source apportionment (Table 3). The abundance ratio of two-and-three-ring to four-to-six-ring PAHs (LMW/HMW) can be used to evaluate the petrogenic and pyrolytic sources. Ratio between benzo(ghi)perylene and indeno(1,2,3,cd)pyrene suggests combustion

input sources, either from gasoline or diesel exhaust, while ratio between Benzo[a]anthracene and the sum of Benzo[a]anthracene and chrysene can potentially differentiate between general combustion process with grass, wood and coal combustion sources. However, a degree of caution is needed when using the latter ratio, a value of > 0.5 generally favours grass, wood and coal combustion sources but Yunker *et al.*, (2002) as cited by Mille *et al.*, (2006), has reported that combustion residues from airport and automobile traffics and nautical activities sometimes yield values in excess of this ratio and thus cannot totally be excluded. In addition to ratios listed in Table 3, methyl phenanthrene to phenanthrene (MP/P) ratio of < 1 is also taken as an indication of combustion sources while a value of > 1 is indicative of petrogenic origin (Zakaria *et al.*, 2002).

Table 4 shows the ratios of selected PAHs compound in mangrove sediment of Pulau Cik Siti Wan Dagan. All the values of LMW/HMW were lower than 1, indicating significant PAHs input from pyrolytic sources which are a common cause of contamination, such as atmospheric deposition that might have introduced PAHs into water bodies. The ratios of BgP/IP for stations 3, 13, 14 and 15 were approximately 3.5, suggesting combustion input of gasoline, while stations 2, 10, 11 and 12 were approximately 1.1, showing that these PAHs were derived from diesel combustion

Table 3: Suggested PAHs sources based on the ratios of some PAH compounds.

Ratio PAHs source	LMW/HMW	BgP/ InP	BaA/Σ228
Pyrolytic	<1 ^a		
Petrogenic	>1 ^a		
Gasoline exhaust		3.5 ^a	
Diesel exhaust		1.1 ^a	
Combustion			>0.35 ^b
Grass/ wood/ coal combustion			>0.5 ^b

LMW/HMW: ratio between the sum of two and three-ring PAHs and the sum of four to six-ring PAHs. BgP/InP: ratio between benzo(g,h,i)perylene and indeno(1,2,3,cd)pyrene. BaA/Σ228: ratio between benz[a]anthracene and the sum of benz[a]anthracene and chrysene.

^aZhang *et al.* (2004); ^bMille *et al.*, (2006)

Table 4: Ratios of some PAH compounds in the mangrove sediments.

Station	LMW/HMW	BgP/InP	BaA/Σ228
1	0.12	na	na
2	0.03	1.5	0.32
3	0.18	4.8	na
4	0.15	na	0.28
5	0.2	na	na
6	na	na	na
7	0.74	na	0.48
8	0.21	na	na
9	0.07	na	0.5
10	na	2.31	na
11	0.03	1.13	0.39
12	na	2.82	0.31
13	0.02	4.35	0.73
14	0.07	4.71	0.6
15	0.02	3.46	na

na: not available

(Figure 4). BaA/Σ228 ratios of stations 7 and 11 were over 0.35, suggesting that they were from combustion sources. The ratios in excess of 0.5 as exhibited by stations 9, 13 and 14 are indicative of combustion of grass, wood or coal.

The concentration of PAHs analysed in this study were compared with the effects-based guideline values such as the effects range-low (ERL) and effects range-median (ERM) values provided by the US National Oceanic and Atmospheric Administration (Long *et al.*, 1995 as cited by Zhang *et al.*, 2004). This comparison shows that PAHs level from these stations (0.124-1.396 μg g⁻¹) does not exceed the level of the ERL value (4.022 μg g⁻¹), suggesting the PAHs found in the study area are not likely to cause any biological effect. However, it must be noted that the levels of PAHs in mangrove sediments

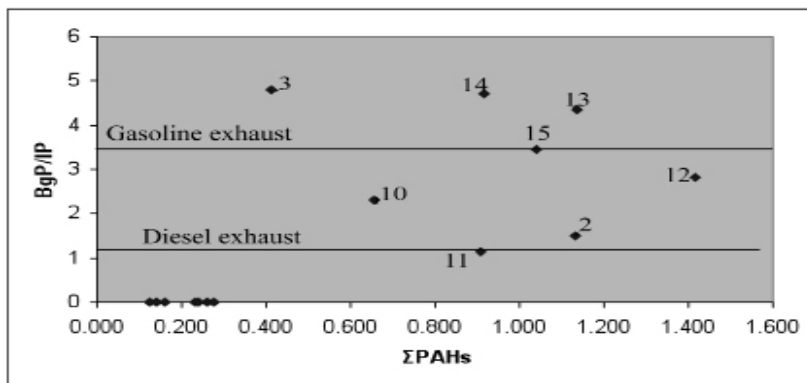


Figure 4: Plot of BgP/IP versus ΣPAHs for the sediments collected from Pulau Cik Wan Dagang Mangrove forest.

of some stations on Pulau Cik Wan Dagang have exceeded the background level of PAHs found in uncontaminated sediments ($0.01-1 \mu\text{g g}^{-1}$), indicating that some parts on the island are showing sign of contamination.

Conclusion

Data obtained from the PAHs analyses revealed the presence of PAHs compounds generally associated with the combustion of fuels materials i.e. pyrolytic sources. Analysis of diagnostic molecular markers suggest that the most likely sources of these compounds were of mixed origin, namely runoffs and atmospheric deposition from Chukai Township and also maritime sources such as discharges from ships and fishing boats. From the toxicity point of view, present levels of PAHs in these sediments are not likely to cause any serious biological effects. However, it must be conceded that a follow-up study is timely and very needed since the results discussed in the present article are based on sampling carried out in year 2001. In future, organic-carbon analysis should be conducted for the sediments. Normalisation of PAHs to organic carbon is necessary since it is an important controlling factor of sorption of PAHs on sediment [Karickhoff et al., 1979].

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