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Petroleum pollution in surface sediments of Daya Bay, South China, revealed by chemical fingerprinting of aliphatic and alicyclic hydrocarbons

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ABSTRACT

Nine surface sediments collected from Daya Bay have been Soxhlet-extracted with 2:1 (v/v) dichloromethane-methanol. The non-aromatic hydrocarbon (NAH) fraction of solvent extractable organic matter (EOM) and some bulk geochemical parameters have been analyzed to determine petroleum pollution of the bay. The NAH content varies from 32 to 276 $\mu g\,g^{-1}$ (average 104 $\mu g\,g^{-1}$) dry sediment and accounts for 5.8–64.1% (average 41.6%) of the EOM. *n*-Alkanes with carbon number ranging from 15 to 35 are identified to be derived from both biogenic and petrogenic sources in varying proportions. The contribution of marine authigenic input to the sedimentary *n*-alkanes is lower than the allochthonous input based on the average n-C_{31}/n-C_{19} alkane ratio. 25.6–46.5% of the *n*-alkanes, with a mean of 35.6%, are contributed by vascular plant wax. Results of unresolved complex mixture, isoprenoid hydrocarbons, hopanes and steranes also suggest possible petroleum contamination. There is strong evidence of a common petroleum contamination source in the bay.

1. Introduction

Hydrocarbons are naturally occurring compounds and one of the important components of sedimentary organic matter in marine coastal areas. Their composition and distribution are significantly influenced by human activities especially in recent decades. Hydrocarbons as potential environmental contaminants are an assemblage of substances coming from various sources including biogenic, diagenetic, petrogenic and pyrogenic (Yunker et al., 1993; Page et al., 1996; Hostettler et al., 1999; Wu et al., 2001). Hydrocarbons generated by biological or diagenetic processes naturally occur at low content in sediments, and are part of the natural hydrocarbon baseline of an ecosystem (Commendatore and Esteves, 2004). However, human activities such as oil transportation and spill, shipping, and industrial, stormwater and domestic discharge are believed to be an important influence on hydrocarbons in marine sediments, especially in coastal areas (Zheng and Richardson, 1999; Commendatore and Esteves, 2004). Study of the composition of hydrocarbon compounds in different marine sediments can provide much information about their sources and diagenetic processes and reflect the extent of anthropogenic pressures on the environment (Hostettler et al., 1999; Medeiros et al., 2005; Zaghden et al., 2005).

Daya Bay is a subtropical drowned valley bay of northern South China Sea located in the eastern coast of Guangdong Province, southern China (Fig. 1). It covers an area of ~600 km^2 with a width of about 20 km and a north–south length of about 30 km. The water depth in Daya Bay generally ranges from 6 to 16 m, and the western part is deeper than the eastern part (Xu, 1989; Han, 1995). Although without any large river discharging into the bay, there are over 10 seasonal streams running into it in short distances along its coast (Han, 1995). In recent decades, the mean sedimentary rate of the bay is 0.9 cm $year^{-1}$ (Han, 1995). Daya Bay is a busy region greatly affected by human activities. Its surrounding area is in the important economic development district in Guangdong Province. Petrochemical, plastic, printing and other industries as well as a commercial shipping harbor are present (Song et al., 2004). Two nuclear plants, Daya Bay Nuclear Power Station and Ling'ao Nuclear Power Station, which came into operation in 1994 and 2002, respectively, are situated at its western coast. Fish, shrimp and shellfish aquaculture are well developed in Daya Bay profiting from its good water quality. Owing to its special status at both environmental and economic levels, Daya Bay has received much attention from many researchers in different fields since the 1980s and a national research station affiliated to the South China Sea Institute of Oceanology, Chinese Academy of Sciences, with emphasis on the marine biology of Daya Bay had been established in 1984 for regular monitoring (e.g. Pan and Cai, 1996; Pan and Wang, 1998; Zhou et al.,

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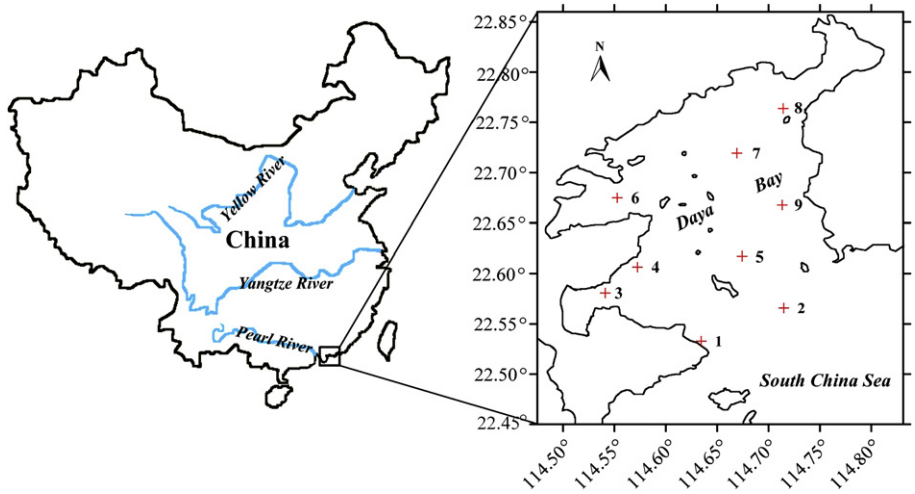

Fig. 1. Location of sampling sites in Daya Bay, northern South China Sea.

2001; Tang et al., 2003; Zhou and Maskaoui, 2003; Song et al., 2004; Wang et al., 2006c). However, reports related to quantification and characterization of lipids in Daya Bay are very scarce. The present work represents the first study on the composition, origin and distribution of non-aromatic hydrocarbons (NAH) in solvent extractable organic matter (EOM) from Daya Bay surface sediments, and provides a background estimation of the contamination of Daya Bay surface sediments with petroleum related hydrocarbons.

2. Materials and methods

2.1. Sampling

Sediment samples were collected from nine sites in Daya Bay, northern South China Sea, using a stainless steel box grab sampler on 12 and 13 January 2006 (Fig. 1). The coordinates of sampling sites are given in Table 1. Undisturbed top 5 cm sediments were sampled and placed in pre-cleaned glass jars and stored at −20 °C in the dark until further analysis. Only one sample was collected from each sampling station.

2.2. Chemical analyses

After being freeze-dried, sediment samples were finely ground and homogenized with an agate pestle and mortar. Then, about 80 g of these pretreated samples were Soxhlet-extracted with a mixture of 2:1 (v/v) dichloromethane-methanol for 72 h (Duan, 2000; Duan and Ma, 2001). The extracts were treated with activated copper in order to remove elemental sulfur, weighed to determine EOM and fractionated by column chromatography on alumina over silica gel with different solvents sequentially. The column was packed with 8 g each of silica and alumina, which were activated at 120 and 350 °C for 12 h, respectively, and then deactivated with 5% water before use. A series of fractions, including non-aromatic hydrocarbons, aromatic hydrocarbons, ketones, alcohols, and fatty acids and asphaltenes, were obtained by successive elution with petroleum-ether, benzene, 10% ethyl acetate in hexane, 20% ethyl acetate in hexane and methanol (Lü and Zhai, 2006; Lü et al., 2006). The composition of EOM and major lipid components in ketones, alcohols and fatty acids has already been reported in our previous paper (Gao et al., 2008).

The non-aromatic hydrocarbon fractions were analyzed by gas chromatography–mass spectrometry (GC–MS), using an HP 6890N gas chromatograph equipped with an HP-5 fused silica capillary column (30 m, 0.25 mm inner diameter, and 0.25 μm film thickness) and interfaced to an HP 5973N mass selective detector (Agilent Technologies, Santa Clara, California, USA). The GC oven temperature was programmed to increase from 80 to 290 °C at 4 °C min^{-1}, and then kept constant for 30 min. Helium was used as a carrier gas. MS operating conditions were EI ionization, ion source 230 °C, electron energy 70 eV, and interface temperature 280 °C. Identification of the target compounds was based on the NIST mass spectral library supplied with the GC–MS instrument.

The sample granulometry was analyzed using a Mastersizer 2000 particle size analyzer (Malvern Instruments Ltd., Malvern, Worcestershire, UK) capable of analyzing particle sizes between 0.02 and 2000 μm. The percentages of three grain size groups were determined: <4 (clay), 4–63 (silt), and >63 μm (sand). Crushed and homogenized sediment samples were acidified with 10% HCl overnight to remove carbonates, rinsed with distilled water and dried before analysis of the total organic carbon (TOC) using a PE 2400 Series II elemental analyzer (Perkin–Elmer, Inc., Waltham, Massachusetts, USA) (Hedges and Stern, 1984).

3. Results and discussion

3.1. Bulk geochemical parameters

The bulk geochemical parameters of samples used in this study have been described in detail elsewhere (Gao et al., 2008), and the main findings are outlined here for a better understanding of this study. In summary, surface sediments collected from nine sites of Daya Bay are dominantly composed of clay and silt, and the highest and lowest TOC values are recorded at the sites located at the most extensive aquacultural region in the northwest part of Daya Bay – Aotou Cove (site 6) and the western nearshore part of the bay mouth (site 1), respectively (Table 1). EOM content in surface sediments of Daya Bay exhibits a clear spatial variation and accounts for <3% of the TOC in the dry sediments except at site 7 (Table 1). NAH is a major component of EOM in surface sediments of Daya Bay and its content varies in the range of 32–276 μg g^{-1} (average 104 μg g^{-1}) dry sediment and accounts for 5.8–64.1% (average 41.6%) of the EOM (Table 1). NAH content in surface sediments of Daya Bay is much higher at the present time than that of the northern South China Sea outer continental shelf (<10 μg g^{-1} dry sediment) (Gao et al., 2007) and comparable with other marine areas that receive important anthropogenic inputs such as Montevideo Harbor (Muniz et al., 2004), western north and south

Table 1
The coordinates of each sampling site and some bulk geochemical parameter values of the sediments sampled (Gao et al., 2008)

Site	Longitude (E)	Latitude (N)	TOC[a] (%)	EOM_1[b] ($\mu g\,g^{-1}$)	EOM_2[c] (%)	NAH[d] ($\mu g\,g^{-1}$)	Clay (%)	Silt (%)	Sand (%)
1	114°38.06′	22°31.97′	0.86	130.0	1.52	54.7	4.3	93.8	1.9
2	114°42.89′	22°33.95′	1.08	163.9	1.51	51.8	5.7	86.9	7.4
3	114°32.46′	22°34.85′	1.40	284.7	2.04	182.4	5.8	89.1	5.1
4	114°34.35′	22°36.39′	0.87	197.8	2.28	123.5	15.6	73.5	10.9
5	114°40.46′	22°37.03′	1.06	88.1	0.83	31.9	28.9	55.6	15.5
6	114°33.17′	22°40.49′	1.60	436.1	2.72	275.8	34.6	65.3	0.1
7	114°40.15′	22°43.16′	1.42	1637.4	11.53	95.2	31.7	66.3	2.0
8	114°42.86′	22°45.82′	1.53	202.4	1.32	52.3	36.8	61.8	1.4
9	114°42.79′	22°40.06′	1.46	168.3	1.15	72.5	34.5	63.4	2.1

[a] TOC: total organic carbon content in dry sediment sample.
[b] EOM_1: extractable organic matter content in dry sediment sample evaluated by gravimetry.
[c] EOM_2: extractable organic matter relative to TOC.
[d] NAH: non-aromatic hydrocarbon content in dry sediment sample evaluated by gravimetry.

Mediterranean (Zaghden et al., 2005) and the Bay of Fort de France (Mille et al., 2006).

3.2. n-*Alkanes, unresolved complex mixture and isoprenoid hydrocarbons*

A representative total ion chromatogram of non-aromatic hydrocarbon fraction is shown in Fig. 2. Based on mass fragmentogram of $m/z = 85$, *n*-alkanes in the carbon number ranging from C_{15} to C_{35} are detected. Bimodal distributions of *n*-alkanes are observed (Fig. 3). Such a distribution pattern of sediment *n*-alkanes is similar to those reported for other China marine areas such as the subtropical Changjiang Estuary and tropical Nansha Sea (Duan, 2000; Lü and Zhai, 2006).

The phenomenon that *n*-alkanes maximized at C_{18} is characteristic of most crude oil samples (Jacquot et al., 1999). In contrast, marine phytoplankton synthesizes *n*-alkanes having chains of $<C_{23}$ and presenting odd carbon numbers predominance (Blumer et al., 1971). *n*-Alkanes in algae and aquatic photosynthetic bacteria are often dominated by the C_{17} homologue (Blumer et al., 1971; Giger et al., 1980; Cranwell et al., 1987); *n*-alkanes in submerged and floating macrophytes commonly maximize at C_{21}, C_{23} or C_{25} (Ficken et al., 2000). Unlike these, land vascular plants generally contain large proportions of C_{27}, C_{29} and C_{31} *n*-alkanes in their epicuticular waxy coatings (e.g. Cranwell, 1973; Rieley et al., 1991; Yamamoto et al., 2003). In general, *n*-alkanes in woody land plants display a carbon number distribution dominated by C_{27} or C_{29} homologue while herbaceous land plants display a carbon number distribution dominated by their C_{31} homologue (Schwark et al., 2002; Xie et al., 2002). For surface sediments of Daya Bay, the dominant peaks occur at C_{17} or C_{18} and C_{29} or C_{31} for the short chain (C_{15}–C_{20}) and long chain (C_{21}–C_{35}) *n*-alkanes, respectively (Fig. 3 and Table 2). At some sites, such as sites 3 and 9, *n*-C_{21} is also present in high abundance. These indicate that surface sediments in different regions of Daya Bay have different sources of dominant *n*-alkanes.

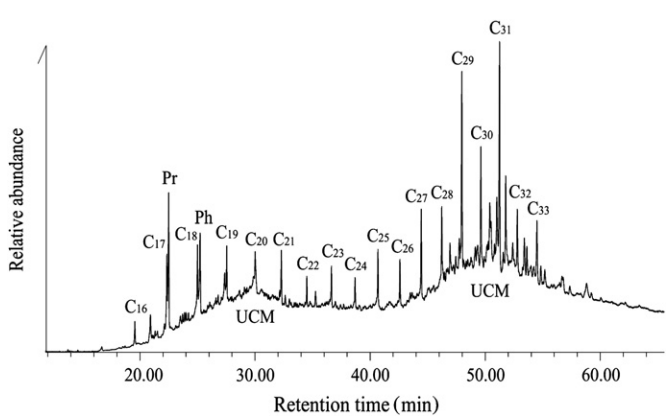

Fig. 2. The representative total ion chromatogram of non-aromatic hydrocarbon fraction from surface sediment at site 5.

The ratio of $\sum$*n*-alkanes/*n*-C_{16} can be used as an index indicating oil pollution and its value smaller than 30 in sediments indicates pollution with crude oil, whereas a value greater than 50 suggests unpolluted sediments receiving significant input from biogenic-derived alkanes (Colombo et al., 1989). The values calculated for this ratio in Daya Bay are in the range of 30.3–143.1 (Table 2). Based on this criterion, surface sediments at the northeast part and the mouth of the bay are unpolluted by crude oil while at the part near west coast run risk of crude oil pollution especially for sites 4 and 6.

The carbon preference index (CPI) is a parameter that has frequently been used as a source indicator of *n*-alkanes in marine sediments (e.g. Bray and Evans, 1961; Boehm and Requejo, 1986; Colombo et al., 1989). *n*-Alkanes from various sources have CPI values with different ranges. In land plant epicuticular waxes, typical CPI values of *n*-alkanes range from 4 to 10 (Tulloch, 1976); CPI values of *n*-alkanes from petroleum and anthropogenic activities such as vehicular emissions, fossil fuel combustion and biomass combustion are close to 1 (Simoneit, 1984; Seki et al., 2006). Higher CPI values indicate greater biogenic contribution (Rieley et al., 1991). In this study, calculated by the method put forward by Bray and Evans (1961), *n*-alkanes in surface sediments of Daya Bay show CPI values ranging from 1.94 to 3.36 with an average of 2.71 (Table 2), which are lower than those from typical terrigenous plant inputs while higher than those from fossil fuel related inputs. This reflects the admixture of fossil *n*-alkane series with those of higher land plants in varying proportions. Compared with other Chinese seas, CPI values of *n*-alkanes in surface sediments of Daya Bay are lower than those of Bohai Sea sediments' 4.0–5.9 while higher than those of Yellow Sea sediments' 1.9 on average (Li, 2000; Wu et al., 2001). Calculated by the method put forward by Boehm and Requejo (1986), Jiaozhou Bay, another important bay in China whose original characteristics are dramatically altered by human activities like Daya Bay, possesses CPI values of *n*-alkanes in its surface sediments ranging from 0.9 to 2.0 with an average of 1.3 (Wang et al., 2006), which are as a whole lower than the Daya Bay's range of 1.6–2.9 with an average of 2.4 calculated by the same method. This indicates the proportion of *n*-alkanes from petroleum contamination in surface sediments of Daya Bay is lower than that of Jiaozhou Bay.

Besides CPI, many other indices have been put forward and employed by researchers to differentiate the *n*-alkane inputs from different sources, including *n*-alkane C_{31}/C_{19} ratio, the contribution of *n*-alkanes from plant wax, the ratio of low molecular weight

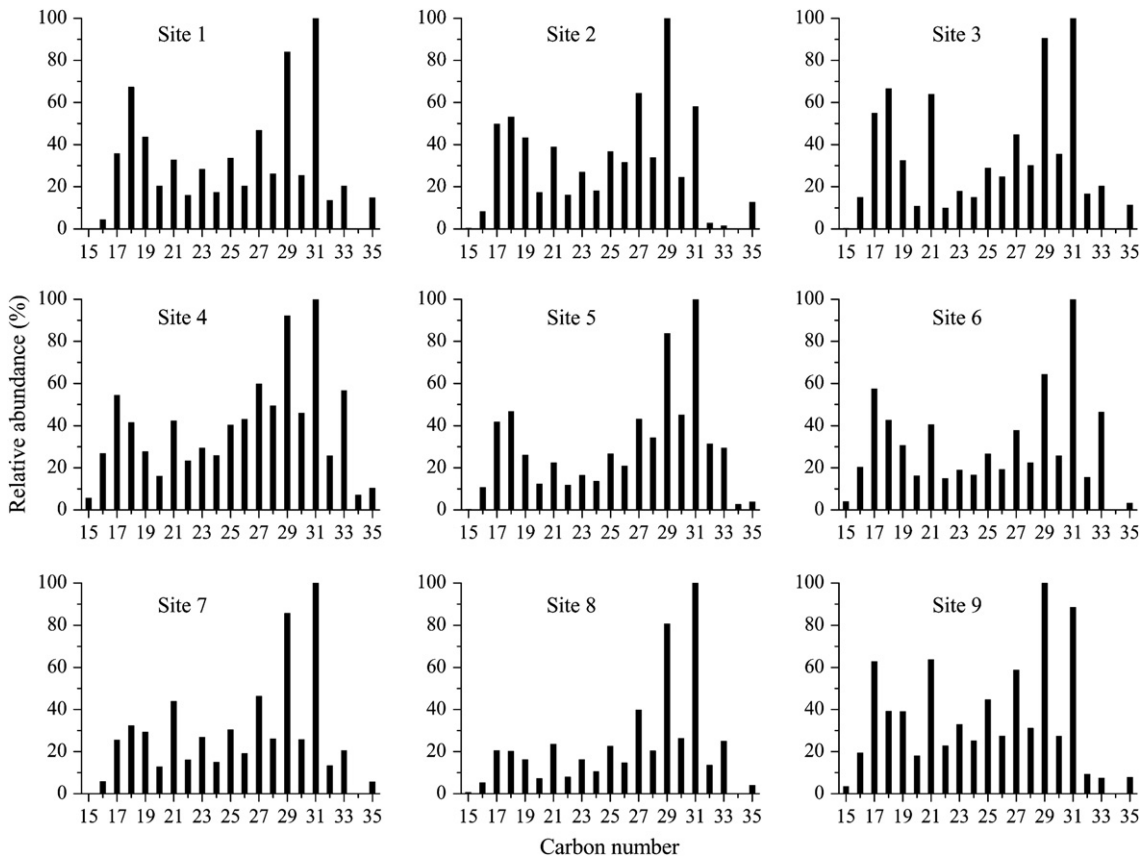

Fig. 3. Distribution patterns of *n*-alkanes from surface sediment samples of Daya Bay, normalized to the most abundant components.

n-alkanes (LMW) to high molecular weight ones (HMW) and so on (e.g. Gearing et al., 1976; Moldowan et al., 1985; Simoneit et al., 1990).

The *n*-alkane C_{31}/C_{19} ratios can serve as a measure of the relative proportions of allochthonous and autochthonous hydrocarbon inputs. The *n*-alkane C_{31}/C_{19} ratios are low in all kinds of marine sedimentary environments and values >0.4, as those obtained in this study, are thought to be diagnostic of non-marine sources (Moldowan et al., 1985).

The contribution of *n*-alkanes from plant wax was estimated following the approach put forward by Simoneit et al. (1990). The result shows that epicuticular waxes of plants are an important source of sedimentary *n*-alkanes and account for 25.6–46.5% of the total *n*-alkanes with a mean of 35.6% (Table 2).

It has been reported that LMW/HMW ratios that are <1 usually represent *n*-alkanes produced by higher plants, marine animals and sedimentary bacteria, LMW/HMW ratios close to 1 suggest that *n*-alkanes are mainly from petroleum and plankton sources, while LMW/HMW ratios >2 often indicate the presence of fresh oil in sediments (Gearing et al., 1976; Commendatore et al., 2000). Some petroleum distillates are also reported to have the LMW/HMW value significantly smaller than 1 (Stout et al., 2002; Wang and Fingas, 2005). In surface sediments of Daya Bay, the high molecular weight *n*-alkanes (HMW, C_{21}–C_{35}) obviously outweigh low

Table 2
Analytical data of *n*-alkanes and isoprenoid hydrocarbons

Site	*n*-Alkanes							Isoprenoid hydrocarbons		
	CPI[a]	$\sum n$-alkanes/n-C_{16}[b]	LMW/HMW[c]	n-C_{31}/n-C_{19}	Wax C_n (%)[d]	Dominant peaks	U/R	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}
1	3.09	143.1	0.35	2.29	33.5	C_{18}, C_{31}	1.3	0.62	1.22	1.04
2	2.57	74.8	0.36	1.34	33.4	C_{18}, C_{29}	2.5	1.24	1.16	0.88
3	2.49	45.3	0.35	3.08	35.2	C_{18}, C_{31}	2.3	0.85	1.11	1.07
4	1.94	30.3	0.26	3.61	25.6	C_{17}, C_{31}	1.7	1.46	1.10	0.98
5	1.96	57.7	0.27	3.84	25.8	C_{18}, C_{31}	3.6	0.92	1.12	1.09
6	3.04	30.5	0.38	3.25	38.3	C_{17}, C_{31}	4.1	1.64	1.14	0.94
7	3.10	98.3	0.22	3.41	42.2	C_{18}, C_{31}	0.9	1.09	1.36	0.98
8	3.36	90.4	0.17	6.16	46.5	C_{17}, C_{31}	0.8	0.94	1.02	1.10
9	2.85	37.1	0.30	2.45	39.9	C_{17}, C_{29}	1.1	1.37	0.88	0.92

[a] $CPI = 1/2[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})]$ (Bray and Evans, 1961).
[b] $\sum n\text{-alkanes}/n\text{-}C_{16} = \sum n\text{-}C_{15-35}/n\text{-}C_{16}$.
[c] $LMW/HMW = \sum n\text{-}C_{15-20}/\sum n\text{-}C_{21-35}$.
[d] Wax $n\text{-}C_m$ (%) $= \sum(n\text{-}C_m - 0.5(n\text{-}C_{m-1} + n\text{-}C_{m+1}))/\sum C_{15-35} \times 100\%$, where m is an odd number between 15 and 35, negative values of wax n-C_m were replaced by zero (Simoneit et al., 1990).

molecular weight ones (LMW, C_{15}–C_{20}). LMW/HMW varies in a narrow range of 0.17–0.38 with an average of 0.30 (Table 2). Combining the data of LMW/HMW ratio with *n*-alkane C_{31}/C_{19} ratio and the contribution of plant wax *n*-alkanes, it suggests a predominant contribution of *n*-alkanes from allochthonous petrogenic sources to Daya Bay surface sediments. This seems inconsistent with the result of $\sum n$-alkanes/n-C_{16}. Weathering processes, which can lead to significant loss of lighter end *n*-alkanes, may be a reason causing $\sum n$-alkanes/n-C_{16} ratio to be overestimated. Distinct petroleum contamination can be further proved by the parameters that will be discussed below. Compared with the data obtained from Jiaozhou Bay (Wang et al., 2006), LMW/HMW values of this study are in general much lower indicating the different sources and proportions of *n*-alkanes in surface sediments of these two areas.

Besides *n*-alkanes, the presence of unresolved complex mixture (UCM) of branched and cyclic hydrocarbons, which has a well-known linkage to degraded or weathered petroleum residues (Venkatesan et al., 1980; Readman et al., 2002), is another characteristic of Daya Bay surface sediments and present in all samples. Compared to *n*-alkanes, UCMs are more resistant to biodegradation and thus have a greater tendency to remain and accumulate in the environment (Aboul-Kassim and Simoneit, 1995). In this study, UCMs appear in the gas chromatograms as two raised baseline humps eluted between n-C_{16} and n-C_{35}, and center around n-C_{20} and n-C_{30}, respectively (see Fig. 2 for example). The peaks around n-C_{20} are all smaller than those around n-C_{30}. Although some UCMs, mainly in the lower molecular weight range, can also be the products of bacterial degradation of natural organic matter such as algal detritus (Venkatesan and Kaplan, 1982), for a bay facing serious anthropogenic influences like Daya Bay, these bimodal UCMs in all probability suggest the presence of both light and heavy petroleum-derived compounds and this can be further suggested by the ratio between unresolved to resolved (U/R) hydrocarbons. U/R ratios can be used as a criterion to assess anthropogenic input. Some researchers suggested that a U/R value ≥ 2 reflects significant contamination by petroleum products (Simoneit, 1986), while others suggested a U/R value >1 can be taken as a threshold of such significant contamination (Aboul-Kassim and Williamson, 2003). Anyway, contamination by petroleum products can be diagnosed with confidence at some sampling sites by U/R ratios and is found to be lower in surface sediments from the northeast part of Daya Bay than that from the other parts at present (Table 2).

The detection of a large number of aliphatic isoprenoid hydrocarbons in oils, coals, shales, and dispersed organic materials was thought to be one of the most important discoveries in petroleum chemistry and organic geochemistry (Wang et al., 2006a). Pristane (Pr) and phytane (Ph) are the two most abundant isoprenoid hydrocarbons and are identified in all samples of this study. These two compounds are considered to originate primarily from the phytyl side chain of chlorophylls during diagenesis. In uncontaminated recent sediments, phytane is practically absent and high pristane content can be derived from zooplankton and some other marine animals (Blumer et al., 1963; Volkman et al., 1992), leading to the pristane/phytane (Pr/Ph) ratio higher than 1, typically between 3 and 5 (Steinhauer and Boehm, 1992). A Pr/Ph value close to or lower than 1 suggests petroleum contamination (Broman et al., 1987; Steinhauer and Boehm, 1992). The Pr/Ph ratios obtained for Daya Bay surface sediments are between 0.62 and 1.46 with an average of 1.13, indicating petroleum contamination (Table 2).

In addition to their use as petroleum contamination markers, the Pr/n-C_{17} and Ph/n-C_{18} ratios are often used for evaluating the extent of biodegradation on oils (Commendatore and Esteves, 2004). Comparatively, isoprenoid hydrocarbons are more resistant to biodegradation than *n*-alkanes, leading to the increase of Pr/n-C_{17} and Ph/n-C_{18} ratios to a value of much higher than 1 when they have been deeply degraded (UNEP, 1995; Hwang et al., 2002; González-Vila et al., 2003). Petroleum contamination in Daya Bay sediments is relatively fresh because, as shown in Table 2, both Pr/n-C_{17} and Ph/n-C_{18} ratios are around 1. The distribution of Pr/n-C_{17}, Ph/n-C_{18} and Pr/Ph ratios for all samples points to a common petroleum contamination source in Daya Bay (Table 2).

3.3. Hopanes and steranes

Alicyclic hydrocarbons are known to be more resistant to biodegradation than aliphatic hydrocarbons are. Hopanes and steranes are representatives of these compounds, and can be used as source and/or maturity indicators to identify the nature of the fossil materials from which petroleum originate.

Hopanes and steranes in sediments are converted from corresponding biogenic precursors, and exist as many stereoisomers with different α/β and/or *R*/*S* configurations that have different thermodynamic stability. During sedimentary burial, the thermodynamically unstable isomers are gradually replaced by the geologically stable isomers reaching a known equilibrium point and providing a measure of the maturity of organic matter (Seifert and Moldowan, 1986; Peters and Moldowan, 1991). These processes are combinations of a series of bacteriological actions and low-temperature reactions generally referred to as diagenesis, catagenesis, and metagenesis (Wang et al., 2006a).

Fig. 4 shows the representative mass fragmentograms of *m*/*z* 191 and 217 of non-aromatic hydrocarbon fraction from surface sediment at site 5 in the elution region of hopanes (Fig. 4a) and steranes (Fig. 4b) respectively. A series of C_{27}–C_{35} hopanes are identified in all sediment samples. The extended 17α,21β-hopane series (C_{31}–C_{35}) occur as 22*S* and 22*R* epimers. Based on mass fragmentograms of *m*/*z* 217, in addition to the presence of diasteranes and C_{30} steranes, the dominance of C_{27}, C_{28}, and C_{29} ααα- and αββ-regular steranes with their 20*S* and 20*R* epimers is observed and presents a V-shape.

In surface sediments of Daya Bay, hopanes with ≥ 29 carbon atoms exhibit the predominance of 17α,21β-configurations with maximization at the C_{30} homologue. Hopanes with 17α,21β-configuration in the range of 27–35 carbon atoms are characteristic of petroleum because of their greater thermodynamic stability compared with other epimeric series (Wang et al., 2006b). Like hopanes, isomerization at the C-14 and C-17 positions in the 20*S* and 20*R* C_{29} steranes causes the αββ/(αββ + ααα) ratio to rise from zero to the equilibrium value of about 0.8 with increasing maturity (Seifert and Moldowan, 1986). The C_{29} sterane αββ/(αββ + ααα) ratios are below the equilibrium value in surface sediments of Daya Bay (Table 3).

During maturation, besides the shift of α/β configurations, the biological 22*R* configuration of extended C_{31}–C_{35} hopanes and 20*R* configuration of C_{27}–C_{29} steranes decrease in favor of their thermodynamically more stable 22*S* and 20*S* epimers, respectively. The point of thermal equilibrium is 0.57–0.62 during early oil generation at low thermal maturity for the hopane $22S/(22S+22R)$ ratio and 0.52–0.55 at low thermal maturity for the sterane $20S/(20S+20R)$ ratio (Peters et al., 2005). The C_{31} hopane $22S/(22S+22R)$ and C_{29} sterane $20S/(20S+20R)$ ratios in Daya Bay sediments are close to or within the range of the thermal equilibrium values (Table 3), indicating that the hopanes and steranes are close to or have reached low thermal maturity.

The relationship between the two C_{27} hopanes 18α(*H*)-22,29,30-trinorhopane (Ts) and 17α(*H*)-22,29,30-trinorhopane (Tm), expressed as Ts/(Ts + Tm), is one of the indices that have been used for the purposes of source identification and differentiation of oils, monitoring and evaluation of oil weathering, and degradation under a variety of conditions (Wang et al., 1998). Although the exact value is strongly dependent on original facies, the Ts/(Ts + Tm) ratio reaches equilibrium at intermediate to later thermal maturity

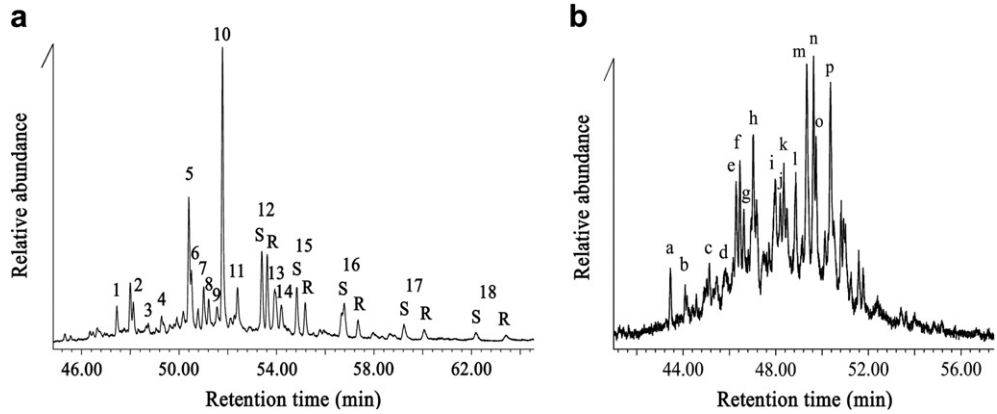

Fig. 4. Representative mass fragmentograms of $m/z = 191$ (a) and 217 (b) of non-aromatic hydrocarbon fraction from surface sediment at site 5. Main compounds identified include 1: 18α(*H*)-22,29,30-trisnorhopane (Ts); 2: 17α(*H*)-22,29,30-trisnorhopane (Tm); 3: 17β(*H*)-22,29,30-trisnorhopane; 4: norlupane; 5: 17α(*H*),21β(*H*)-30-norhopane; 6: 18α(*H*),21β(*H*)-30-norneohopane; 7: lupane; 8: 17β(*H*),21α(*H*)-30-norhopane; 9: 18α(*H*)-oleanane; 10: 17α(*H*),21β(*H*)-hopane; 11: 17β(*H*),21α(*H*)-hopane; 12: 17α(*H*),21β(*H*)-homohopane(22*S* + 22*R*); 13: gammacerane; 14: 17β(*H*),21β(*H*)-hopane; 15: 17α(*H*),21β(*H*)-bishomohopane(22*S* + 22*R*); 16: 17α(*H*),21β(*H*)-trishomohopane(22*S* + 22*R*); 17: 17α(*H*),21β(*H*)-tetrakishomohopane(22*S* + 22*R*); 18: 17α(*H*),21β(*H*)-pentakishomohopane(22*S* + 22*R*); a–d: diasteranes; e: C_{27} 5α(*H*),14α(*H*),17α(*H*)-cholestane(20*S*); f: C_{27} 5α(*H*),14β(*H*),17β(*H*)-cholestane(20*R*); g: C_{27} 5α(*H*),14β(*H*),17β(*H*)-cholestane(20*S*); h: C_{27} 5α(*H*),14α(*H*),17α(*H*)-cholestane(20*R*); i: C_{28} 5α(*H*),14α(*H*),17α(*H*)-ergostane(20*S*); j: C_{28} 5α(*H*),14β(*H*),17β(*H*)-ergostane(20*R*); k: C_{28} 5α(*H*),14β(*H*),17β(*H*)-ergostane(20*S*); l: C_{28} 5α(*H*),14α(*H*),17α(*H*)-ergostane(20*R*); m: C_{29} 5α(*H*),14α(*H*),17α(*H*)-stigmastane(20*S*); n: C_{29} 5α(*H*),14β(*H*),17β(*H*)-stigmastane(20*R*); o: C_{29} 5α(*H*),14β(*H*),17β(*H*)-stigmastane(20*S*); p: C_{29} 5α(*H*),14α(*H*),17α(*H*)-stigmastane(20*R*).

(Peters et al., 2005). Under most natural weathering conditions, this ratio suffers little change and remains characteristic of the source oil (Wang et al., 1998). In Daya Bay surface sediments, the ratios of Ts/(Ts + Tm) vary from 0.39 to 0.54 (Table 3), and are much close to the 0.41 to 0.66 of five representative lubricating oils (Wang et al., 2006a), suggesting a possible source of petroleum contamination to the bay.

Based on the analysis mentioned above, the hopane and sterane fingerprints of Daya Bay surface sediments are on the whole of moderately mature oils. In recent sediments with little thermal action such as those studied in this research, organic matter with greater maturity can most likely be attributed to petroleum contamination. The Ts/(Ts + Tm), C_{31} hopane 22S/(22S + 22R) and C_{29} sterane 20S/(20S + 20R) ratios all vary within narrow ranges indicating probably a common petrochemical source in the area.

17β(*H*),21α(*H*)-hopane is present in all samples. Its abundance is relatively high accounting for, on average, about 20% of the most abundant constituent 17α(*H*),21β(*H*)-hopane. This feature is quite unique and has rarely been seen in crude oils and petroleum products (Wang et al., 2001), further indicating that the petroleum contaminants in surface sediments of Daya Bay come from the same source. A similar pattern has been found in surface sediments of the northern South China Sea outer continental shelf (Gao et al., 2007).

Some biomarker compounds are found to exist only in certain oils and can therefore be used to identify the source of petroleum contamination by events such as oil spills (Wang et al., 2006b). Oleanane and gammacerane are among these unique biomarkers. 18α(*H*)-Oleanane, the thermodynamically more stable configuration of its two isomers, is highly specific for angiospermous plant input and is found only in Tertiary and Cretaceous (<130 million years) rocks and oils (Riva et al., 1988; Wang et al., 2006b). Gammacerane, which is thought to originate from protozoa or bacteria (ten Haven et al., 1989; Venkatesan, 1989), has frequently been associated with hypersaline depositional environments and its structures were shown to be reliable geochemical indicators of water column stratification in marine deposits (Sinninghe Damsté et al., 1995). 18α(*H*)-Oleanane and gammacerane have been identified in all nine surface sediments from Daya Bay. Besides 18α(*H*)-oleanane, other higher plant biomarkers including C_{24} tetracyclic terpane and lupane have also been detected. The presence of these biomarkers clearly exhibits the geochemical characteristics of petroleum contaminants in surface sediments of Daya Bay.

Steranes in sediment or oils are derived from the transformation of biological sterol precursors. In general, C_{27} and C_{29} steranes are indicative of algae and higher plant source of organic matter respectively. So, the ratio of C_{27}/C_{29}-steranes >1 specifies the predominance of organic matter input from marine algae, while <1 indicates a preferential higher plant input (Peters and Moldowan, 1993; Gürgey, 2002). In surface sediments of Daya Bay, the ratios of C_{27}/C_{29}-steranes are in the range of 0.45–0.72 and lowest at site 1 and highest at site 6 (Table 3), further indicating an abundance of organic matter with higher plant origin in the source rocks for these petroleum contaminants.

4. Conclusions

This work represents the first study of the composition and sources of solvent extractable non-aromatic hydrocarbons in surface sediments of Daya Bay.

Table 3
Hopane and sterane biomarker ratios used for oil identification

Compound	Index	Site								
		1	2	3	4	5	6	7	8	9
Hopanes	Ts/(Ts + Tm)	0.45	0.44	0.54	0.52	0.46	0.46	0.42	0.40	0.39
	C_{31} αβ 22*S*/(22*S* + 22*R*)	0.50	0.49	0.57	0.55	0.52	0.55	0.48	0.54	0.48
Steranes	C_{29} ααα 20*S*/(20*S* + 20*R*)	0.60	0.58	0.61	0.62	0.51	0.56	0.52	0.56	0.59
	C_{29} αββ/(αββ + ααα)	0.47	0.45	0.45	0.48	0.42	0.48	0.44	0.46	0.45
	C_{27}/C_{29}[a]	0.49	0.56	0.67	0.69	0.50	0.72	0.54	0.57	0.62

[a] $C_{27}/C_{29} = C_{27}$-sterane (αββ + ααα)/C_{29}-sterane (αββ + ααα).

Bulk parameters show that, in surface sediments of Daya Bay, NAH is much higher at the present time than that of the northern South China Sea outer continental shelf and comparable with other marine areas that receive significant anthropogenic inputs such as the Montevideo Harbor, western north and south Mediterranean and the Bay of Fort de France.

Multiple indices have been used to evaluate the extent of contamination by non-aromatic hydrocarbons, most of which suggest that petrogenic input is a predominant contribution of *n*-alkanes. *n*-Alkanes from vascular plant wax account for 25.6–46.5% of the total *n*-alkanes, with a mean of 35.6%. The $\sum n$-alkanes/n-C_{16} ratio seems to be unfit for estimating crude oil pollution in this study. Weathering processes may be a reason causing the $\sum n$-alkanes/n-C_{16} ratio to be overestimated. Results of unresolved complex mixture and isoprenoid hydrocarbons also suggest possible petroleum contamination. Hopanes and steranes show characteristics of higher maturity, suggesting that they are mainly from petroleum contamination. There is strong evidence of a common petroleum contamination source in Daya Bay.

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References

Aboul-Kassim, T.A.T., Simoneit, B.R.T., 1995. Petroleum hydrocarbon fingerprinting and sediment transport assessed by molecular biomarker and multivariate statistical analyses in the eastern harbour of Alexandria, Egypt. Marine Pollution Bulletin 30, 63–73.

Aboul-Kassim, T.A.T., Williamson, K.J., 2003. Forensic analysis and genetic source partitioning model for Portland harbor contaminated sediments. Journal of Environmental Informatics 1, 58–75.

Blumer, M., Guillard, R.R.L., Chase, T., 1971. Hydrocarbons of marine plankton. Marine Biology 8, 183–189.

Blumer, M., Mullin, M.M., Thomas, D.W., 1963. Pristane in zooplankton. Science 140, 974.

Boehm, P.D., Requejo, A.G., 1986. Overview of the recent sediment hydrocarbon geochemistry of Atlantic and Gulf coast outer continental shelf environments. Estuarine, Coastal and Shelf Science 23, 29–58.

Bray, E.E., Evans, E.D., 1961. Distributions of *n*-paraffins as a clue to recognition of source beds. Geochimica et Cosmochimica Acta 22, 2–15.

Broman, D., Colmsjö, A., Ganning, B., Näf, C., Zebühr, Y., Östman, C., 1987. Fingerprinting petroleum hydrocarbons in bottom sediment, plankton, and sediment trap collected seston. Marine Pollution Bulletin 18, 380–388.

Colombo, J.C., Pelletier, E., Brochu, C., Khalil, M., Catoggio, J.A., 1989. Determination of hydrocarbon sources using *n*-alkane and polyaromatic hydrocarbon distribution indexes. Case study: Río de la Plata estuary, Argentina. Environmental Science and Technology 23, 888–894.

Commendatore, M.G., Esteves, J.L., 2004. Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina). Marine Pollution Bulletin 48, 910–918.

Commendatore, M.G., Esteves, J.L., Colombo, J.C., 2000. Hydrocarbons in coastal sediments of Patagonia, Argentina: levels and probable sources. Marine Pollution Bulletin 40, 989–998.

Cranwell, P.A., Eglinton, G., Robinson, N., 1987. Lipids of aquatic organisms as potential contributors to lacustrine sediments. Organic Geochemistry 11, 513–527.

Cranwell, P.A., 1973. Chain-length distribution of *n*-alkanes from lake sediments in relation to post-glacial environmental change. Freshwater Biology 3, 259–265.

Duan, Y., 2000. Organic geochemistry of recent marine sediments from the Nansha Sea, China. Organic Geochemistry 31, 159–167.

Duan, Y., Ma, L., 2001. Lipid geochemistry in a sediment core from Ruoergai Marsh deposit (Eastern Qinghai-Tibet plateau, China). Organic Geochemistry 32, 1429–1442.

Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. Organic Geochemistry 31, 745–749.

Gao, X., Chen, S., Long, A., 2008. Composition and sources of organic matter and its solvent extractable components in surface sediments of a bay under serious anthropogenic influences: Daya Bay, China. Marine Pollution Bulletin 56, 1066–1075.

Gao, X., Chen, S., Xie, X., Long, A., Ma, F., 2007. Non-aromatic hydrocarbons in surface sediments near the Pearl River estuary in the South China Sea. Environmental Pollution 148, 40–47.

Gearing, P., Gearing, J., Lytle, T.F., Lytle, J., 1976. Hydrocarbons in 60 northeast Gulf of Mexico shelf sediments: a preliminary survey. Geochimica et Cosmochimica Acta 40, 1005–1017.

Giger, W., Schaffner, C., Wakeham, S.G., 1980. Aliphatic and oleanic hydrocarbons in recent sediments of Greifensee, Switzerland. Geochimica et Cosmochimica Acta 44, 119–129.

González-Vila, F.J., Polvillo, O., Boski, T., Moura, D., Andrés de, J.R., 2003. Biomarker patterns in a time-resolved Holocene/terminal Pleistocene sedimentary sequence from the Guadiana river estuarine area (SW Portugal/Spain border). Organic Geochemistry 34, 1601–1613.

Gürgey, K., 2002. An attempt to recognize oil populations and potential source rock types in Paleozoic sub- and Mesozoic–Cenozoic supra-salt strata in southern margin of the Pre-Caspian basin, Kazakhstan republic. Organic Geochemistry 33, 723–741.

Han, W.Y., 1995. Chemistry in Daya Bay. In: Han, W.Y. (Ed.), Marine Chemistry of the Nansha Islands and South China Sea. China Ocean Press, Beijing, China, pp. 60–103.

Hedges, J.I., Stern, J.H., 1984. Carbon and nitrogen determinations of carbonate-containing solids. Limnology and Oceanography 29, 657–663.

Hostettler, F.D., Pereira, W.E., Kvenvolden, K.A., van Green, A., Luoma, S.N., Fuller, C.C., Anima, R., 1999. A record of hydrocarbon input to San Francisco Bay as traced by biomarker profiles in surface sediment and sediment core. Marine Chemistry 64, 115–127.

Hwang, R.J., Heidrick, T., Mertani, B., Qivayanti, Li, M., 2002. Correlation and migration studies of North Central Sumatra oils. Organic Geochemistry 33, 1361–1379.

ten Haven, H.L., Rohmer, M., Rullkötter, J., Bisseret, P., 1989. Tetrahymanol, the most likely precursor of gammacerane occurs ubiquitously in marine sediments. Geochimica et Cosmochimica Acta 53, 3073–3079.

Jacquot, F., Le Dreau, Y., Doumenq, P., Munoz, D., 1999. The origins of hydrocarbons trapped in the lake of Berre sediments. Chemosphere 39, 1407–1419.

Li, B., 2000. The distribution of *n*-alkanes and PAHs in sediments of Bohai and Yellow Sea. Ms. D. thesis, p. 89.

Lü, X., Zhai, S., 2006. Distributions and sources of organic biomarkers in surface sediments from the Changjiang (Yangtze River) Estuary, China. Continental Shelf Research 26, 1–14.

Lü, X., Zhai, S., Niu, L., 2006. Sources and preservation of organic matter in recent sediment from the Yangtze River Estuary, China. Scientia Marina 70, 47–58.

Medeiros, P.M., Bícego, M.C., Castelao, R.M., Rosso, C.D., Fillmann, G., Zamboni, A.J., 2005. Natural and anthropogenic hydrocarbon inputs to sediments of Patos Lagoon Estuary, Brazil. Environment International 31, 77–87.

Mille, G., Guiliano, M., Asia, L., Malleret, L., Jalaluddin, N., 2006. Sources of hydrocarbons in sediments of the Bay of Fort de France (Martinique). Chemosphere 64, 1062–1073.

Moldowan, J.M., Seifert, W.K., Gallegos, E.J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. AAPG Bulletin 69, 1255–1268.

Muniz, P., Danulat, E., Yannicelli, B., García-Alonso, J., Medina, G., Bícego, M.C., 2004. Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo Harbour (Uruguay). Environment International 29, 1019–1028.

Page, D.S., Boehm, P.D., Douglas, G.S., Bence, A.E., Burns, W.A., Mankiewicz, P.J., 1996. The natural petroleum hydrocarbon background in subtidal sediments of Prince William Sound, Alaska, USA. Environmental Toxicology and Chemistry 15, 1266–1281.

Pan, J.P., Cai, G.X., 1996. Annual Research Reports of Marine Biology Research Station at Daya Bay, Chinese Academy of Sciences, I. Science Press, Beijing, China, p. 183.

Pan, J.P., Wang, Z.D., 1998. Annual Research Reports of Marine Biology Research Station at Daya Bay, Chinese Academy of Sciences, II. Science Press, Beijing, China, p. 190.

Peters, K.E., Moldowan, J.M., 1991. Effects of source, thermal maturity and biodegradation on the distribution and isomerization of homohopanes in petroleum. Organic Geochemistry 17, 47–61.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide, Vol. 2, Biomarkers and Isotopes in Petroleum Exploration and Earth History, second ed. Cambridge University Press, UK, 700 pp.

Peters, K.E., Moldowan, J.M., 1993. The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall, Englewood Cliffs, New Jersey, 363 pp.

Readman, J.W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J.-P., Cattini, C., Mee, L.D., 2002. Petroleum and PAH contamination of the Black Sea. Marine Pollution Bulletin 44, 48–62.

Rieley, G., Collier, R.J., Jones, D.M., Eglinton, G., 1991. The biogeochemistry of Ellesmere Lake, UK, I: source correlation of leaf wax inputs to the sedimentary record. Organic Geochemistry 17, 901–912.

Riva, A., Caccialanza, P., Quagliaroli, F., 1988. Recognition of 18α(*H*)-oleanane in several crudes and Tertiary-Upper Cretaceous sediments. Organic Geochemistry 13, 671–675.

Schwark, L., Zink, K., Lechterbeck, J., 2002. Reconstruction of postglacial to early Holocene vegetation history in terrestrial Central Europe via cuticular lipid biomarkers and pollen records from lake sediments. Geology 30, 463–466.

Seifert, W.K., Moldowan, J.M., 1986. Use of biological markers in petroleum exploration. In: Johns, R.B. (Ed.), Biological Markers in the Sedimentary Record. Elsevier, Amsterdam, pp. 261–290.

Seki, O., Yoshikawa, C., Nakatsuka, T., Kawamura, K., Wakatsuchi, M., 2006. Fluxes, source and transport of organic matter in the western Sea of Okhotsk: stable carbon isotopic ratios of *n*-alkanes and total organic carbon. Deep-Sea Research I 53, 253–270.

Simoneit, B.R.T., 1984. Application of molecular marks analysis to reconcile sources of carbonaceous particulates in tropospheric aerosols. Science of the Total Environment 36, 61–72.

Simoneit, B.R.T., 1986. Characterization of organic constituents in aerosols in relation to their origin and transport: a review. International Journal of Environmental Analytical Chemistry 23, 207–237.

Simoneit, B.R.T., Cardoso, J.N., Robinson, N., 1990. An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. Chemosphere 21, 1285–1301.

Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Köster, J., Schouten, S., Hayes, J.M., de Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column stratification. Geochimica et Cosmochimica Acta 59, 1895–1900.

Song, X., Huang, L., Zhang, J., Huang, X., Zhang, J., Yin, J., Tan, Y., Liu, S., 2004. Variation of phytoplankton biomass and primary production in Daya Bay during spring and summer. Marine Pollution Bulletin 49, 1036–1044.

Steinhauer, M.S., Boehm, P.D., 1992. The composition and distribution of saturated and aromatic hydrocarbons in nearshore sediments, river sediments, and coastal peat of Alaskan Beaufort Sea: implications for detecting anthropogenic hydrocarbon inputs. Marine Environmental Research 33, 223–253.

Stout, S.A., Uhler, A.D., McCarthy, K.J., Emsbo-Mattingly, S., 2002. Chemical fingerprinting of hydrocarbons. In: Murphy, B.L., Morrison, R. (Eds.), Introduction to Environmental Forensics. Academic Press, Boston, pp. 137–260.

Tang, D.L., Kester, D.R., Wang, Z., Lian, J., Kawamura, H., 2003. AVHRR satellite remote sensing and shipboard measurements of the thermal plume from the Daya Bay, nuclear power station, China. Remote Sensing of Environment 84, 506–515.

Tulloch, A.P., 1976. Chemistry of waxes of higher plants. In: Kolattukudy, P.E. (Ed.), Chemistry and Biochemistry of Natural Waxes. Elsevier, Amsterdam, pp. 236–252.

UNEP (United Nations Environment Programme), 1995. Determination of Petroleum Hydrocarbons in Selected Marine Organisms. Reference Method for Marine Pollution Studies No. 72. UNEP/IOC/IAEA/FAO.

Venkatesan, M.I., 1989. Tetrahymanol: its widespread occurrence and geochemical significance. Geochimica et Cosmochimica Acta 53, 3095–3101.

Venkatesan, M.I., Brenner, S., Ruth, E., Bonilla, J., Kaplan, I.R., 1980. Hydrocarbons in age-dated sediment cores from two basins in the Southern California Bight. Geochimica et Cosmochimica Acta 44, 789–802.

Venkatesan, M.I., Kaplan, I.R., 1982. Distribution and transport of hydrocarbons in surface sediments of the Alaskan outer continental shelf. Geochimica et Cosmochimica Acta 46, 2135–2149.

Volkman, J.K., Holdworth, D.C., Neil, G.P., Bavor, H.J.J., 1992. Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments. Science of the Total Environment 112, 203–219.

Wang, X.-C., Sun, S., Ma, H.-Q., Liu, Y., 2006. Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. Marine Pollution Bulletin 52, 129–138.

Wang, Z.D., Fingas, M., 2005. Oil and petroleum product fingerprinting analysis by gas chromatographic techniques. In: Nollet, L. (Ed.), Chromatographic Analysis of the Environment, third ed. CRC Press, New York, pp. 1027–1101.

Wang, Z.D., Fingas, M., Blenkinsopp, S., Sergy, G., Landriault, M., Sigouin, L., Lambert, P., 1998. Study of the 25-year-old Nipisi oil spill: persistence of oil residues and comparisons between surface and subsurface sediments. Environmental Science and Technology 32, 2222–2232.

Wang, Z.D., Fingas, M., Sigouin, L., 2001. Characterization and identification of a "mystery" oil spill from Quebec (1999. Journal of Chromatography A 909, 155–169.

Wang, Z.D., Fingas, M., Yang, C., Christensen, J.H., 2006a. Crude oil and refined product fingerprinting: principles. In: Morrison, R.D., Murphy, B.L. (Eds.), Environmental Forensics – Contaminant Specific Guide. Academic Press, Elsevier, pp. 339–407.

Wang, Z.D., Stout, S.A., Fingas, M., 2006b. Forensic fingerprinting of biomarkers for oil spill characterization and source identification. Environmental Forensics 7, 105–146.

Wang, Z.H., Qi, Y.Z., Chen, J.F., Xu, N., Yang, Y.F., 2006c. Phytoplankton abundance, community structure and nutrients in cultural areas of Daya Bay, South China Sea. Journal of Marine Systems 62, 85–94.

Wu, Y., Zhang, J., Mi, T.-Z., Li, B., 2001. Occurrence of *n*-alkanes and polycyclic aromatic hydrocarbons in the core sediments of the Yellow Sea. Marine Chemistry 76, 1–15.

Xie, S., Wang, Z., Wang, H., Chen, F., An, C., 2002. The occurrence of a grassy vegetation over the Chinese loess Plateau since the last interglacier: the molecular fossil record. Science in China (Series D) 45, 53–62.

Xu, G.Z., 1989. Environments and Resources of Daya Bay. Anhui Science and Technology Publishing House, Hefei, China, pp. 10–16.

Yamamoto, K., Kurata, Y., Takayanagi, Y., Nishimura, A., Mimura, K., 2003. Latitudinal change of normal paraffin composition in the northwest Pacific sediments. Marine Geology 196, 157–170.

Yunker, M.B., Macdonald, R.W., Cretney, W.J., Fowler, B.R., McLaughlin, F.A., 1993. Alkane, terpene and polycyclic aromatic hydrocarbon geochemistry of the Mackenzie River and Mackenzie Shelf: riverine contributions to Beaufort Sea coastal sediment. Geochimica et Cosmochimica Acta 57, 3041–3061.

Zaghden, H., Kallel, M., Louati, A., Elleuch, B., Oudot, J., Saliot, A., 2005. Hydrocarbons in surface sediments from the Sfax coastal zone, (Tunisia) Mediterranean Sea. Marine Pollution Bulletin 50, 1287–1294.

Zheng, G.J., Richardson, B.J., 1999. Petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in Hong Kong marine sediments. Chemosphere 38, 2625–2632.

Zhou, J.L., Maskaoui, K., Qiu, Y.W., Hong, H.S., Wang, Z.D., 2001. Polychlorinated biphenyl congeners and organochlorine insecticides in the water column and sediments of Daya Bay, China. Environmental Pollution 113, 373–384.

Zhou, J.L., Maskaoui, K., 2003. Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. Environmental Pollution 121, 269–281.