phytoplankton and bacteria assessed in in-situ mesocosms. Ecotoxicol. Environ. Safe 59, 349–369.

Ng, P.K.L., Sivasothi, N., 1999. A guide to the mangroves of Singapore. Singapore Science Center, Singapore.

Ong Che, R.G., 1999. Concentration of 7 heavy metals in sediment and mangrove root samples from Mai Po, Hong Kong. Mar. Pollut. Bull. 39, 269–279.

Páez-Osuna, F., Ruiz-Fernández, A.C., Botello, A.V., Ponce-Vélez, G., Osuna-López, J.I., Frías-Espericueta, M.G., López-López, G., Zazueta-Padilla, H.M., 2002. Concentrations of selected trace metals (Cu, Pb, Zn), organochlorines (PCBs, HCB) and total PAHs in mangrove oysters from the Pacific Coast of Mexico: an overview. Mar. Pollut. Bull. 44, 1296–1313.

Peerzada, N., Eastbrook, C., Guinea, M., 1990. Heavy metal concentration in *Telescopium* from Darwin Harbour, N.T., Australia. Mar. Pollut. Bull. 6, 307–308.

Soto-Jimenez, M.F., Paez-Osuna, F., 2001. Distribution and normalization of heavy metal concentrations in Mangrove and Lagoonal sediments from Mazatlan Harbor (SE Gulf California). Estuarine, Coastal Shelf Sci. 53, 259–274.

Tam, N.F.Y., Wong, Y.S., 1995a. Mangrove soils as *sinks* for wastewater-borne pollutants. Hydrobiologia 296, 231–242.

Tam, N.F.Y., Wong, Y.S., 1995b. Spatial and temporal variations of heavy metals contamination in sediments of a mangrove swamp in Hong Kong. Mar. Pollut. Bull. 31, 254–261.

Tam, N.F.Y., Wong, Y.S., 1996. Retention and distribution of heavy metals in mangrove soils receiving wastewater. Environ. Pollut. 94, 283–291.

Tam, N.F.Y., Wong, Y.S., 2000. Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. Environ. Pollut. 110, 195–205.

US EPA Method 3052, 1996. Microwave assisted acid digestion of siliceous and organically based matrices.

Wood, A., Khalik, H.J., Zaharudin, Ahmad, Noor, Azhar, Shazili, M.D., Rosnan, Yaakob, Roy, Carpenter, 1997. Geochemistry of sediments in Johor Strait between Malaysia and Singapore. Continental Shelf Res. 17, 1207–1228.

Wurl, O., Obbard, J.P., 2004. A review of pollutants in the sea-surface microlayer (SML): a unique habitat for marine organisms. Mar. Pollut. Bull. 48, 1016–1030.

Zhang, Z., Liu, L., Liu, C., Cai, W., 2003. Studies on the sea surface microlayer II. The layer of sudden change of physical and chemical properties. J. Colloid Interface Sci. 264, 148–159.

Zhang, Z., Liu, L., Zhao, H., Fu, Y., Wu, Z., 1996. Studies of Ternary Complexes at Liquid–Solid Interfaces in sea water by the *E*(%)–pH curve method. J. Colloid Interface Sci. 182, 158–165.

Zhang, Z., Wang, W., Liu, L., Fu, Y., Wu, Z., 1997. Studies of ternary surface complexes at liquid–solid interfaces in seawater: III. Comparative studies of the *E*(%)–pH curves and the diffuse reflectance IR spectra of the α-FeOOH–Cu(II)–Tryptophan system. J. Colloid Interface Sci. 190, 1–8.

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Sources and transport of hydrocarbons in sediments from the Changjiang River Estuary, China

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Estuarine areas serve as final receptors of organic matter from natural and anthropogenic sources. The former includes autochthonous input of planktonic and benthic primary production together with allochthonous inputs, such as terrigenous run-off and marine tidally advected material (Gagosian and Peltzer, 1986; Bouloubassi and Saliot, 1993; Thornton and McManus, 1994). Hydrocarbons are important components of organic inputs and are commonly found in the environment as complex mixtures from multiple sources: biogenic, diagenetic, petrogenic and pyrogenic (Yunker et al., 1993; Hostettler et al., 1999). Discrimination between biogenic and anthropogenic origins, as well as the further recognition of inputs from petrogenic, pyrogenic and domestic waste sources, requires the use of organic compounds that maintain the "signature" of their origins and structural modifications which occurred during transport (Bouloubassi and Saliot, 1993; Medeiros et al., 2004).

The Changjiang River is one of the largest rivers in the world in terms of suspended sediment load, water discharge, length, and drainage area (Eisma, 1998). The river has formed a broad tide-dominated delta at its mouth since 6000–7000 years BP (Li and Li, 1983; Chen and Stanley, 1995). The Changjiang River delta plays a key role in the Chinese economy. Shanghai, the most important industrial and economic city of China, is located near the river mouth. Two thirds of Shanghai's administrative area (including the suburban district) is located in the Changjiang River delta. One of the four largest fishing grounds in China, the Zhoushan Fishing Ground, is situated in the outer reaches of the zone influenced by river fresh water. The Changjiang River runs into the transitional area between the East China Sea and the Yellow Sea. The continental shelf of the Yellow Sea and East China Sea is one of the largest and most productive shelves in the world (Yang et al., 2002; Jeng and Huh, 2004). Therefore, human

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activities (anthropogenic effects and both industrial (oil refineries and terminals, fertilizer-producing plants, fishery industries) and urban areas) and marine productivity undoubtedly influence the natural environment of the estuary and adjacent continental shelf.

This paper aims to determine the composition, levels and sources of hydrocarbons based on an examination of the following geochemical markers: aliphatic hydrocarbons (normal and isoprenoid alkanes), petroleum biomarkers (terpanes, hopanes and steranes) and polycyclic aromatic hydrocarbons (PAHs), as well as determining the statistical correlation between different geochemical marker concentrations and between the geochemical marker concentrations and sediment grain sizes, which help to distinguish the origins of different biomarkers and assess the transportation of these compounds.

Sediment samples were collected from four sites (site 8, 11, 17 and 26) of the Changjiang River Estuary using by a grab sampler in June 2003 (Fig. 1). Only the top 2 cm of undisturbed surface sediments were sampled, and were placed in precleaned glass boxes, and stored in a freezer at −20 °C until further analysis.

Sediment samples were freeze-dried, finely ground and homogenized in an agate mill. Dry sediment samples were extracted with a mixture of dichloromethane–methanol (2:1, v/v) in a Soxhlet extractor for 72 h. The dissolved part was fractionated by column chromatography on alumina over silica gel with different solvents sequentially. The different components of the dissolved fraction, including aliphatic hydrocarbons, aromatic hydrocarbons, ketones, alcohols and non-hydrocarbons (fatty acids and asphaltenes), were obtained by successively eluting with petroleum-ether, benzene, 10% ethyl acetate in hexane, 20% ethyl acetate in hexane and methanol.

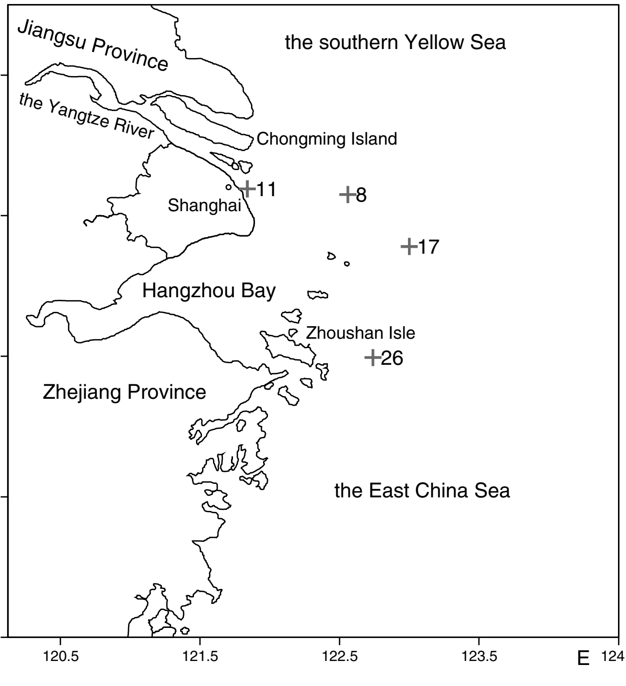

Fig. 1. Sampling sites from the Changjiang River Estuary, China.

The aliphatic and aromatic hydrocarbons were analyzed by gas chromatography–mass spectrometry (GC–MS), using a HP 6890N GC interfaced to a HP 5973N MS. The GC column used was an elastic silica capillary column (HP-5 30 m × 0.25 mm × 0.25 μm). The temperature was programmed from 80 to 290 °C at 4 °C min^{-1}, then kept for 30 min. Nitrogen was used as carrier gas. MS operating conditions were: EI ionization, ion source 230 °C, electron energy 70 eV, interface temperature 280 °C. Compound identification was based on standard spectrogram stocks (NISTO2L) and the individual mass spectra retention times in comparison to published MS data (e.g. Volkman et al., 1992; Logan and Eglinton, 1994; Mangelsdorf and Rullkötter, 2003).

The composition of aliphatic and aromatic hydrocarbons was quantified by the "peak area normalization method". The contents of *n*-alkanes, pristane (Pr), phytane (Ph), hopanes and steranes were calculated from total ionization chromatography (TIC) of the saturated hydrocarbons fraction by the "peak area normalization method". The composition of hopanes and steranes was calculated from the GC–MS chromatography of m/z 191 and m/z 217, respectively. The content of different aromatic hydrocarbons was calculated from total ionization chromatography (TIC) of the aromatic hydrocarbons fraction. The values of different compositions were revised according to their different responsive data. Anthracene was added as a surrogate internal standard to blank and real sample solution (Manoli and Samara, 1999). Recovery efficiency for fortified sample ranged between 85% and 113%. The precision of the analytical method, evaluated in terms of repeatability of the experimental results ($n = 9$) for the analysis of a real sample (the site 8) and expressed in terms of the relative standard deviation, was usually below ±15%. All solvents were glass distilled. Procedural blanks showed no interfering contribution of hydrocarbons from the freeze drying step, reagents and solvents.

The grain sizes of the sediment samples were determined with a Malvern laser sedimentometer, model Mastersizer 2000, with an analysis capacity of particle sizes ranging from 0.02 to 2000 μm.

Table 1 shows the total concentrations of *n*-alkanes ranging from C_{14} to C_{37}, as well as the isoprenoid hydrocarbon individual concentrations, and diagnostic criteria useful for the identification of natural or anthropogenic origins within the sediments.

The total *n*-alkane concentrations varied from 23.38 to 38.47 μg g^{-1} (dry weight). The highest concentrations occurred at site 26, and the lowest at site 11. The *n*-alkanes showed a bimodal distribution with the major peak at C_{18} or C_{19} and C_{29} or C_{31}, except at site 17 (Fig. 2 and Table 1). The distribution pattern is indicative of a mixture of marine autogenic and terrigenous organic matters input (Duan, 2000; Mangelsdorf and Rullkötter, 2003). The major peaks (C_{26} and C_{28}) of long chain *n*-alkanes at site 17 show that