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Use of aliphatic hydrocarbons to infer terrestrial organic matter in coastal marine sediments off China

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ABSTRACT

Sediment samples from the marine systems along the coast of China, covering Yellow Sea, inner shelf of the East China Sea (ECS) and the South China Sea (SCS), were analyzed for *n*-alkanes and organic carbon. The concentrations of $\Sigma n\text{–}C_{15-35}$ were 120–1680 ng g^{-1} dry weight with an average of 560 ng g^{-1}. Short-chain *n*-alkanes ($<C_{21}$) in Yellow Sea and the SCS were derived from mixed bacteria and planktonic sources, while those in the ECS inner shelf were mainly of planktonic sources. Long-chain *n*-alkanes ($>C_{21}$) were mainly derived from terrestrial higher plants. Organic carbon deposited into Yellow Sea and Southeast Hainan within the SCS was mainly of terrestrial (13–110%; mean: 58%) and marine (48–110%; mean: 86%) sources, respectively. On the other hand, organic carbon accumulated in the SCS adjacent to the Pearl River Estuary was derived from both terrestrial and marine sources.

Approximately 70% of the Earth's surface is covered by oceans, whereas ~80% of the global organic carbon in oceans is buried in coastal marine systems adjacent to rivers (Goni et al., 2006; Hedges and Keil, 1995). Therefore, nearshore coastal areas, especially estuaries and continental shelves, play an important role in global cycling of organic matter (Goni et al., 2006). In this regard, examining the potential sources and transport mechanisms of organic matter in continental shelf sediments is of great significance in understanding the environmental fate of terrestrial organic materials.

The coast of China is largely surrounded by marginal seas, from north to south including Bohai Sea, Yellow Sea, the East China Sea (ECS) and the South China Sea (SCS). Both terrestrially and aquatically produced organic materials could deposit and be preserved in coastal marine sediments. Terrestrial organic materials can be transported to coastal areas via hydrodynamic and/or atmospheric flows. On one hand, the abundant water systems of China (Fig. S1, Supplementary material), e.g., from north to south the Yellow River, Yangtze River, Min River and Pearl River, play an important role in transporting terrestrial materials into the coastal marine environment. For example, a previous study estimated that 9.2×10^5 tons of total organic carbon (TOC) were annually discharged from the Pearl River Delta of South China to the coastal ocean through riverine runoff (Ni et al., 2008). Furthermore, estuarine organic materials may be redistributed under the effect of ocean current systems (Fig. 1) (Hu, 1984; Wu et al., 2001). On the other hand, long-range atmospheric transport can introduce terrestrial organic materials to areas distant from the points of discharge.

One approach to understanding the sources and transport mechanisms of organic materials accumulated in continental shelf sediments is to utilize molecular organic geochemical methods, among which aliphatic hydrocarbons (*n*-alkanes) have been widely utilized (Colombo et al., 2005; Doskey, 2001; Tolosa et al., 1996). There are allochthonous and autochthonous sources for *n*-alkanes preserved in sediments (Doskey, 2001). Allochthonous *n*-alkanes largely stem from terrestrial higher plant waxes and petroleum residues, whereas autochthonous ones mainly originate from aquatic organisms, such as planktons and bacteria. Therefore, *n*-alkanes can be used as molecular tracers to diagnose potential sources and transport mechanisms, as well as to assess the relative importance of terrestrial and aquatic origins, for organic materials (Doskey, 2001).

Comprehensive studies of aliphatic hydrocarbons in surface sediments have been conducted in the entire Bohai Sea (Hu et al., 2009b), the ECS and southern Okinawa Trough (Jeng and Huh, 2008), and the northern SCS (Hu et al., 2009a). To our knowledge, there has been only one study concerning the historical records of aliphatic hydrocarbons in Yellow Sea (Wu et al., 2001), and no study has been conducted to examine the spatial divergence of sediment aliphatic hydrocarbons within the coastal marine systems (Yellow Sea, the ECS and the SCS) of China. The present study was conducted to investigate the spatial divergence of *n*-alkanes and TOC in coastal marine sediments off China, with

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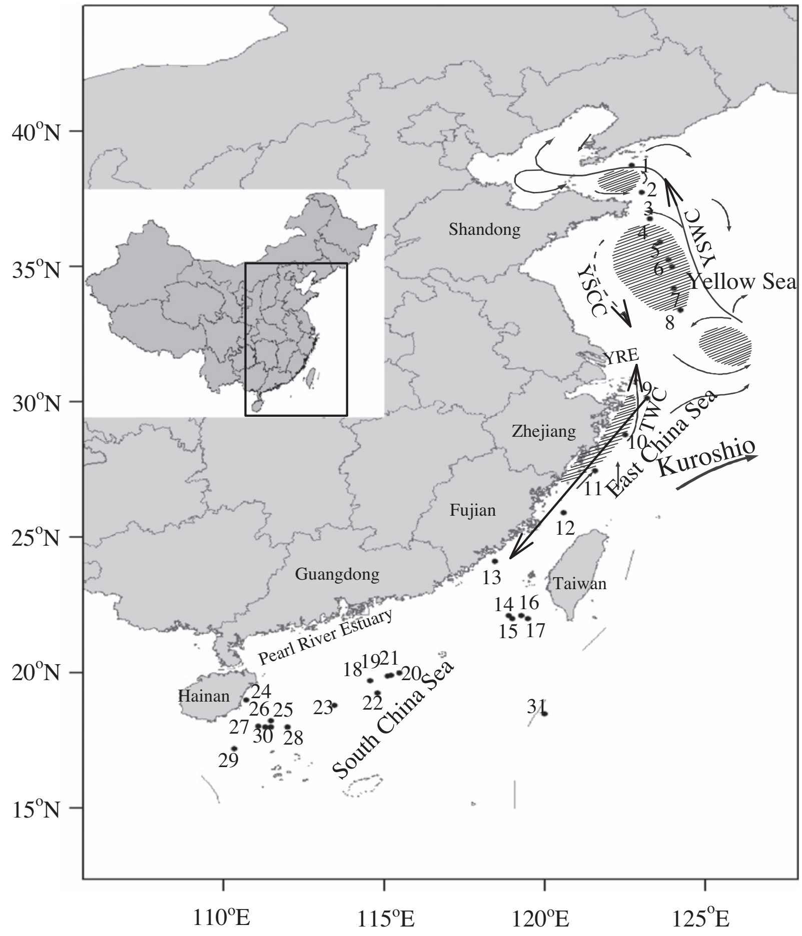

Fig. 1. Map showing the sampling sites on the continental shelf of China. The straight arrow along the ECS inner shelf indicates the southward decreasing trend of sedimentation rate (Huh and Su, 1999) and the direction of coastal current (Liu et al., 2007). The fingerprints in Yellow Sea and along the shelf of the East China Sea represent the mud area, while the curve arrows point to the direction of ocean currents. YSCC and YSWC refers to Yellow Sea coastal current and Yellow Sea warm current, respectively. This schematic diagram of mud areas and ocean currents is adopted from Refs. (Hu, 1984; Wu et al., 2001).

the aims of examining the potential input sources and transport mechanisms of terrestrial organic materials.

A set of surface sediment samples from the continental shelf of China, from north to south covering Yellow Sea, the ECS inner shelf and the SCS (Fig. 1), were collected on board the South China Sea Open Cruise (R/V SHIYAN III) and the Open Research Cruise Offshore China (R/V KEXUE I) from August to September in 2007 using a stainless steel grab sampler. For ease of comparison, samples are grouped on a geographical basis as follows: (a) Yellow Sea (sites 1–8); (b) the ECS inner shelf (sites 9–13); (c) Southwest Taiwan within the SCS (sites 14–17); (d) the SCS adjacent to the Pearl River Estuary (PRE) (sites 18–23); (e) Southeast Hainan within the SCS (sites 24–30), and (f) Northwest Philippines within the SCS (site 31; Philippines is not shown). On a large scale, sites 14–31 are also considered being located within the SCS.

The procedures for sample extraction and extract purification/fractionation of n-alkanes used in the present study were detailed in a previous study (Wang et al., 2008) with slight modifications. Upon addition of a surrogate standard n–C_{24}–d_{50} (n–C_i–d_j, where 'n' designates normal alkane and subscripts 'i' and 'j' indicate carbon number and deuterium number, respectively), freeze-dried and homogenized sediment samples were Soxhlet-extracted with 200 mL of a mixture of hexane:acetone (1:1 in volume) for 48 h. Prior to extraction, copper sheets were added to each sample for removal of elemental sulfur. Each extract after Soxhlet extraction was concentrated to approximately 1 mL with a Zymark TurboVap 500 (Hopkinton, MA, USA) and purified/fractionated with a glass column packed with silica/alumina. Five milliliters of hexane were used to wash the column and the eluent was discarded. The fraction containing n-alkanes was eluted with an additional 20 mL of hexane; the eluent was concentrated to 0.5 mL and spiked with a known amount of the internal standard (n–C_{30}–d_{62}) for subsequent instrumental analysis.

The concentrations of n-alkanes were determined with a Shimadzu Model 2010 gas chromatograph–mass spectrometer equipped with an AOC-20i auto injector (Shimadzu, Japan). The chromatographic separation of the target analytes was achieved with a 30 m × 0.25 mm-i.d. (0.25-μm film thickness) DB-5 column (J&W Scientific, Folsom, CA, USA). Extract injection was performed in the splitless/split mode with a splitless injection time of 1 min. Column temperature was programmed from 80 °C (held for 1 min) to 290 °C at a rate of 5 °C/min, and held for 30 min at the final temperature. The interface and ion source temperatures were maintained at 250 °C. Peak confirmation of n-alkane congeners was achieved with mass spectra acquired in the full scan mode, while quantification was based on characteristic ion at m/z 85 and 71.

The contents of TOC in the sediment samples (Table S1, Supplementary material) were measured with an elemental analyzer (Vario EL III Elementar, Germany) after inorganic carbon was removed with 10% HCl.

Standards of pristane (Pri) and phytane (Phy) obtained from the Laboratories of Dr. Ehrenstorfer (Augsburg, Germany), and a standard mixture containing n–C_{14}, n–C_{15}, n–C_{16}, n–C_{17}, n–C_{18}, n–C_{19},