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Lipid biomarkers in suspended particulate matter and surface sediments in the Pearl River Estuary, a subtropical estuary in southern China

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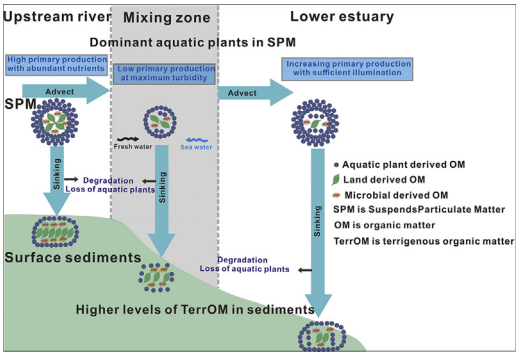
HIGHLIGHTS

- N-alkyl lipids and sterols in SPM and sediments along salinity gradient were studied.
- Aquatic lipids were dominant in SPM, but terrestrial lipids increased in sediments.
- Substantial input of terrestrial *n*-alkanes occurred in May when rainfall was highest.

GRAPHICAL ABSTRACT



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ABSTRACT

Lipid biomarkers in sediments in the Pearl River Estuary (PRE) have been studied in several previous studies, but little is known about their occurrence in the overlying water. Here, we determined the concentrations of lipids (*n*-alkanes, *n*-alkanols, sterols and fatty acids) in suspended particulate matter (SPM) in surface water and in sediments from the PRE. The data will improve our understanding of the sources, transport and sedimentation of lipids in estuarine environments. Our results showed that short-chain ($C_{14–20}$) *n*-alkyl lipids contributed more than long-chain ($C_{21–34}$) *n*-alkyl lipids to the total lipid concentrations in both SPM and sediments, suggesting aquatic plants and bacteria were the main contributors, whereas terrestrial organic matter (OM) were the minor contributors of *n*-alkyl lipids. It suggested that phytoplankton and bacteria contributing >65% to the *n*-alkyl lipids of SPM based on the three end-member mixing models. The concentrations of most lipids, except *n*-alkanes, decreased quickly in the low-salinity mixing zone and slowly decreased thereafter, with a transient slight increased when the salinity was 20–25, which would have been caused by variations of primary production in the aquatic system. In May, when rainfall was highest, lipids were characterized by a substantial contribution of terrestrial *n*-alkanes in the upstream SPM. Microbial activity and lipid degradation were found to occur in the water, and were most intense in the low–salinity mixing zone. Terrigenous lipids contributed more to the total lipid concentrations in sediments than in SPM, which demonstrated that terrigenous OM is relatively recalcitrant, and aquatic phytoplankton-derived OM is labile.

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1. Introduction

Organic matter (OM) is present in estuarine environments and along adjacent coasts as particulate OM (POM), dissolved OM (DOM) and sedimented OM (SOM). These types of OM are complex mixtures of biological molecules from different sources, e.g., from terrestrial plants and soil (Gordon and Goni, 2003; Wang et al., 2004), autochthonous and exogenous phytoplankton (Raymond and Hopkinson, 2003; Canuel et al., 2007), and bacteria (Heidelberg et al., 2002). Dynamic physical and biogeochemical processes can affect the distribution, nature and fate of OM at the land–sea interface (Moran et al., 2000; Canuel, 2001; Arzayus and Canuel, 2005). OM is often characterized by analyzing its bulk properties, such as the total organic carbon (TOC) and total nitrogen (TN) contents, the C/N ratio, and the stable carbon and nitrogen isotope compositions (using $\delta^{13}C$ and $\delta^{15}N$ values) (Hedges et al., 1988; Canuel et al., 1997; Raymond and Bauer, 2001; Sarma et al., 2014; Ye et al., 2017). These bulk parameters are useful for identifying sources of OM, especially in simple two-end-member systems (reviewed by Bauer and Bianchi (2011)). However, the OM sources are in fact multiples, and the C/N ratios and $\delta^{13}C$ and $\delta^{15}N$ values for different sources often overlap, giving ambiguous results (Canuel et al., 1997; Cloern et al. 2002; Hu et al., 2006a). In addition, OM degradation can also alter these bulk properties, confounding the source appointment (Meybeck, 1982; Chen et al., 2008; Canuel and Hardison, 2016). In comparison, the relative concentrations of different biological molecules such as *n*-alkanes, fatty alcohols, and fatty acids can allow OM sources to be identified in detail and allow the processes affecting OM to be studied in molecular level (Hu et al., 2006b). For example, it is difficult to distinguish between OM from vascular plants and freshwater phytoplankton using $\delta^{13}C$ and $\delta^{15}N$ values, but these types of OM can be distinguished by their *n*-alkyl lipid molecular weight distributions (Hu et al., 2009; Strong et al., 2012). Other sources of OM can be identified using certain lipid biomarkers. For example, odd-carbon-numbered low molecular weight (LMW, nC_{12-20}) and branched-chain fatty acids (iso- and anteiso- fatty acids) can indicate OM supplied by bacteria (Volkman et al., 1998; Hu et al., 2006b), and nC_{16} and nC_{18} alkanes, the odd–even predominance (OEP) index for *n*-alkanes, and the pristane (Pr): Phytane (Ph) ratio can indicate human influences on OM, such as the presence of petroleum pollution (Adi et al., 2006; Rushdi et al., 2006; Aloulou et al., 2010).

The Pearl River Estuary (PRE) is the largest estuary in South China. Many studies of SOM in the PRE have been performed in recent years using both bulk property analyses and molecular lipid analyses (Hu et al., 2006b; Hu et al., 2009; Yu et al., 2010; Strong et al., 2012; Guo et al., 2015; Ye et al., 2016, 2017). Most of these studies were focused only on SOM, and few studies have been focused on suspended particulate matter (SPM). It remains unclear how concentrations of lipids in SPM change in response to seasonal changes caused by the monsoon climate of the PRE and how the lipid concentrations in SPM and the underlying sediments are related. In this study, we investigated the distributions of lipid biomarkers, including *n*-alkanes, *n*-alkanols, sterols and fatty acids in SPM and SOM to attempt to elucidate the source, transport and the biogeochemical processing of OM in the PRE and its adjacent coast.

2. Materials and methods

2.1. Study area

The PRE (21° 00′ N to 23° 30′ N, 112° 40′ E to 114° 50′ E) consists of three sub-estuaries called Modaomen, Huangmaohai, and Lingdingyang (Fig. 1). This study was focused on Lingdingyang, the largest sub-estuary and traditionally regarded as the PRE (Fig. 1). The mean water depth is 4.8 m, and increases from north to south and from west to east (Hu et al., 2009).

The Pearl River is the second largest river in China in terms of water discharge (~330×10^9 m^3 yr^{-1}) (Wai et al., 2004). The Pearl River is a compound river system with three main tributaries, the East River, West River, and North River (Fig. 1). The PRE and the river catchments lie in a subtropical monsoon climate region, with warm temperatures and a high annual rainfall of about 2200 mm (Zhang et al., 2008). There is a warm rainy season from April to September, when ~80% of the annual precipitation falls, and a cool dry season from October to March (Wai et al., 2004). The sedimentation rates varies in the PRE and coastal shelf system, with 1.13–2.34 cm yr^{-1} in the PRE and coast, and 0.2–1.0 cm yr^{-1} on the shelf (Jia and Peng, 2003; Hu et al., 2006a).

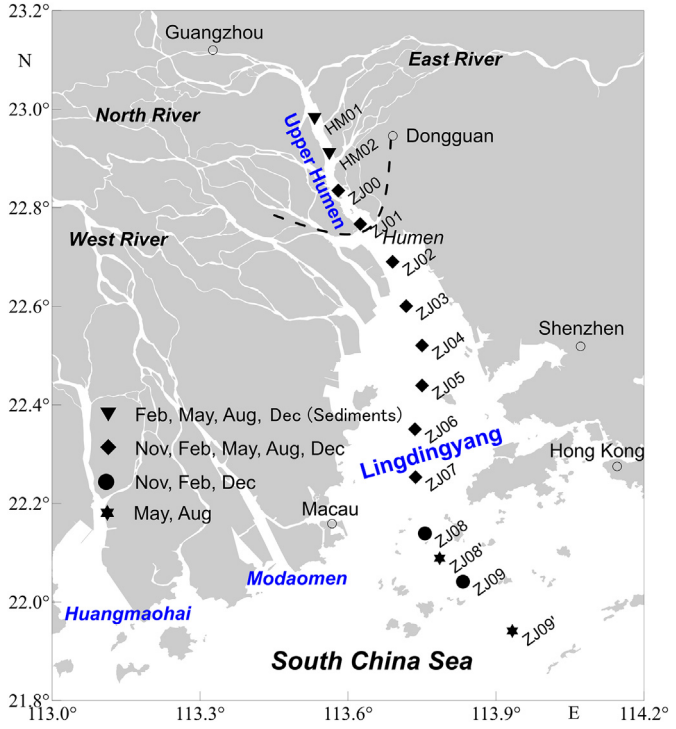

Fig. 1. Map of the Pearl River Estuary with the sampling sites marked. Surface sediments samples were collected in December 2014.

2.2. Sampling and measurements

A surface water sample of about 50 L was collected, using a submersible pump, from 0.5 m deep at each sampling site in the PRE on each of four cruises. The cruises were in November 2013, February 2014, May 2014, and August 2014. The sampling sites were along a salinity gradient, from freshwater upstream of the Humen outlet to seawater outside the PRE (see Fig. 1). The water depths at the sampling sites ranged from 5 to 28 m. A total SPM sample from each site was collected by passing a surface water sample through a pre-weighed 142 mm diameter Whatman GF/F glass-fiber filter (with 0.7 μm pores size) that had been baked at 450 °C before use. A surface sediments sample was collected from each site using a grab sampler in December 2014. The SPM and sediments samples were stored at −20 °C until being transported to the laboratory. The water temperature and salinity at each site were measured in situ using a mini conductivity temperature depth system (Valeport, Totnes, UK).

2.3. Lipid extraction and separation

Each filter with SPM attached was freeze-dried and then cut into small pieces using sterilized scissors, and each sediments sample was freeze-dried and homogenized. Each sample was then placed in a 50 mL tube to lipids extracted. The lipid extraction procedure was referred to Hu et al. (2006b, 2009). Briefly, a sample was sequentially ultrasonically extracted twice with methanol, twice with a 1:1 v/v