



Original Articles

The use of sterols combined with isotope analyses as a tool to identify the origin of organic matter in the East China Sea



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ABSTRACT

To evaluate the sources and budgets of sedimentary organic matter in the East China Sea (ECS), bulk organic matter properties (total organic carbon (TOC), C/N ratio, carbon and nitrogen isotopic composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$)) and sterols in surface sediments were analyzed. The distributions of bulk organic matter properties and sterols showed a strong regionality with higher contents in the southern inner shelf as well as the offshore upwelling area. It was consistent with the increasing mud and chlorophyll *a* (*Chl a*) contents southwards. These distribution patterns were attributed to the terrestrial inputs by shelf circulations and phytoplankton contribution. Both of bulk organic matter properties and sterols indicated a mixture of terrestrial and marine derived organic matter inputs with marine source as a dominant input. Budgets suggested that organic carbon (OC) and sterol influxes from terrestrial source were 5.15×10^6 and 3.32×10^3 t/yr, with the Changjiang River input as the primary contributor; and while their influxes from marine source were 26.3×10^6 and 2.19×10^3 t/yr, respectively. The burial fluxes of OC and sterol were 3.99×10^6 t C/yr and 0.21×10^3 t/yr, with the inner shelf as main accumulation area. Although there was a huge amount of OC influx from terrestrial and marine sources, but only 24.6% and 10% of them could be preserved in sediments. Consequently, the combined effect of riverine input, marine primary productivity and deposition decided the organic matter behaviors in the ECS.

1. Introduction

Cycling and burial of organic matter (OM) in marine coastal sediments is important to the global cycles of C, N and other bio-elements as well as to ocean productivity and climate. Marine coastal areas, as an important sink, play a significant role in the global carbon cycle. It is reported that more than 80% of organic carbon ($\sim 130 \times 10^{12}$ g) in the sea is buried on the continental shelf and slope annually (Bernier, 1982). Marine coastal areas as an active interface between terrestrial and oceanic environments, have a large discharge of fluvial material, complex biogeochemical processes and anthropogenic inputs (Bianchi and Allison, 2009; Hu et al., 2012). Besides, marine coastal areas are usually the most active region for marine primary productivity, owing to a large amount of nutrient input from rivers and coastal upwelling. Thus, the knowledge of behaviors, sources and fates of OM, in addition to factors controlling its distribution in estuarine, coastal and shelf sediments are critical for understanding global biogeochemical cycles (Baldock et al., 2004; Blair and Aller, 2012; O'Reilly et al., 2014).

Due to the combined effect of sea-continent interaction, a fast sedimentary accumulation and high biological production, the OM source in the coastal areas is relatively complicated (Zhang et al., 2014). The OM preserved in sediments of the coastal areas is typically derived from both allochthonous terrestrial sources and autochthonous marine sources (Carreira et al., 2016; O'Reilly et al., 2014). The former mainly originates from terrestrial vascular plants, and while the latter from aquatic phytoplankton, zooplankton and aquatic macrophytes. Most of terrestrial OM (TOM) is transported from continent to ocean by fluvial input, but only a few by aeolian transport. Rivers transport about 1% of terrestrial productivity (~ 60 Gt C/yr) to the marine environment, however aeolian input is about two orders of magnitude lower than rivers (~ 0.1 Gt C/yr) (Hedges et al., 1997). Thus, the riverine input is the major source of TOM in marine environments, in particular in coastal and shelf seas. Marine OM (MOM) is primarily derived from particulate sinking detritus from the photic zone and its flux is typically proportional to the amount of primary production. The relative proportion of these various contributions and the absolute amount of OM

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deposited and ultimately preserved depend on the sources and sedimentary settings (Belicka et al., 2002; O'Reilly et al., 2014).

Bulk organic matter properties, such as TOC, C/N ratio, and carbon and nitrogen isotopic composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) have frequently been used as effective proxies for ascertaining biogeochemical processes and evaluating the OM sources in estuarine and coastal sediments (Costa et al., 2016; Li et al., 2012; Walinsky et al., 2009). Generally, TOM tends to have a more ^{13}C -depleted content and a higher C/N ratio than MOM. However, MOM tends to have enriched ^{13}C values due to it contains an important fraction of C_4 -plants. Furthermore, early diagenesis can significantly alter C/N ratios by selective loss of amino acids (Hopmans et al., 2004). Hence, this approach can easily lead to an erroneous interpretation of the relative amount of TOM in marine sediments. Therefore, it is necessary to comprehensively consider the environmental factors before using these indicators and to find a more reliable method for ensuring the accuracy and reliability in OM source identification.

An alternative approach is the use of specific molecular tracers for terrestrial and marine contributions to total sedimentary OM (Hedges et al., 1997). Lipid biomarker compounds have been widely used as tracers in characterization of OM sources and distributions in aquatic ecosystems because of their source specificity and higher resistance to bacterial degradation in comparison to other classes of organic compounds (Carreira et al., 2011; Méjanelle and Laureillard, 2008; O'Reilly et al., 2014; Xing et al., 2011). According to the selected specific lipids that represent distinct sources of OM (i.e., plankton, land plants, bacteria, soil erosion and anthropogenic activities), it is possible to identify the relative contributions and transports of autochthonous and allochthonous inputs to sediments (Biache and Philp, 2013; Kaiser et al., 2014; Ortiz et al., 2016; Tolosa et al., 2014; Xing et al., 2011; Zhu et al., 2011a). Among lipids, sterols are some of the best biomarkers, due to their resistance to degradation and their wide variety of structures (Hudson et al., 2001; McCallister et al., 2006). Sterols with various biological origins can differentiate allochthonous, autochthonous, and anthropogenic lipid carbon sources in the aquatic environments. For example, the terrestrial ecosystem contains mainly C_{29} sterols, such as ergosterol, stigmaterol, sitosterol, lanosterol and stigmastanol that form the main elements of terrestrial vascular plants and fungi, thus they are commonly used as indicators of TOM (Kim et al., 2016; Martins et al., 2011; Poerschmann et al., 2017). Sterols excreted by marine phytoplankton and zooplankton are mostly C_{28} type, such as desmosterol, brassicasterol and cholesterol, thus they can be used as tracers of MOM (Belicka et al., 2004; Kim et al., 2016; Volkman, 2003). Therefore, the combination of lipid biomarkers with bulk organic matter properties will be useful for studying the sources, transports and fates of OM. Multiple indicators (e.g., lipid biomarkers, isotopic composition and C/N ratio) have been used to clarify the OM biogeochemistry in a range of riverine, estuarine and oceanic aquatic systems (Muri et al., 2004; Villinski et al., 2008; Volkman et al., 2007; Walinsky et al., 2009; Xing et al., 2011, 2016).

The East China Sea (ECS) is one of the main marginal seas in China and also is a typical large river-influenced estuarine-coastal region. It is an important carbon sink, especially for terrestrial organic carbon (Fan et al., 2014). In recent years, intensified human activities and climate changes in the ECS, not only have an important impact on the TOM inputs, but also cause eutrophication and red tides in the coastal waters, which further affect the marine autochthonous input and OM distribution, thus affecting the carbon cycle in the ECS. Previous studies on OM sources and sterols in the ECS have been limited to their qualitative identification and marine sterols (Hu et al., 2012, 2014; Xing et al., 2011; Zhu et al., 2011b). However, the researches on quantitative allocation between MOM and TOM and terrestrial sterols are absent. Besides, the comprehensive study of sources and budgets of OM in the ECS based on the combination of bulk organic matter properties with sterols is scarce. Therefore, in order to characterize terrestrial and marine sources and fluxes of sedimentary OM, bulk organic matter

properties (TOC, C/N ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and sterols were determined in surface sediments of the ECS in the study. The aims were to (1) analyze the distributions and behaviors of bulk organic matter properties and sterols in the ECS; (2) discuss the potential influencing factors on bulk organic matter properties and sterols; (3) characterize the sources and fates of OM in the ECS; and (4) build preliminary budgets for OM and sterols in the ECS.

2. Materials and methods

2.1. Study area

The ECS is one of the largest shelf seas in the world and is an important sink for terrestrial matter in China. The Changjiang River is the dominant runoff and terrestrial sediment source to the ECS, with the discharge fluxes of terrestrial particulate matter and OM of $\sim 5 \times 10^8$ t and 12×10^6 t/yr annually, respectively (Wang et al., 2008; Fan et al., 2014). The main currents affecting the sediment dispersal in the ECS include the Zhejiang-Fujian Coastal Current (ZFCC), Taiwan Warm Current (TWC), Jiangsu Coastal Current (JCC), Changjiang Diluted water (CDW), Yellow Sea Warm Current (YSWC) and Kuroshio Current (KC). Most of sediment derived from the Changjiang River transports southwards along the coast by the ZFCC and deposits in the inner shelf as blocked by the TWC, forming an elongated Zhejiang-Fujian mud band from the Changjiang Estuary to the Taiwan Strait (Liu et al., 2007). The JCC has a key role in transporting sediment from the old Huanghe Estuary to the northeast mud area of the ECS (Yu et al., 2012).

2.2. Sampling

A total of 43 surface sediment samples were sampled in the ECS in May 2014 as shown in Fig. 1. Sediment samples were collected using a box sampler and the top 2 cm layers were carefully subsampled and transferred to aluminum boxes. Immediately after collection, samples were frozen and stored at -20°C until analysis. All boxes and materials used for collection were pre-combusted, solvent rinsed and stored in aluminum foil inside zip-lock bags before use.

2.3. Sterol analyses

Sterol measurement included sample processing and instrumental analyses. Sediment samples for sterol analysis were freeze-dried and then ground. About 10 g of freeze-dried samples were extracted by ultrasonication 4 times with a mixture of dichloromethane (CH_2Cl_2) and methanol (MeOH) (v/v = 3:1), after adding C_{19} *n*-alkanol (19-OH) and 5α -androstane- 3β -ol as internal standards. Activated copper was added to remove sulfur. Extracts were then reduced to 1 ml by rotary evaporation and then extracts were hydrolyzed using 6% KOH-MeOH solution. The neutral lipids were extracted with hexane and then separated into two fractions using silica gel column chromatography. Using hexane and a mixture of dichloromethane and methanol (v/v = 95:5), the non-polar fraction and polar fraction were obtained respectively. The polar fraction was dried under a gentle N_2 stream and derivatized using *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) at 70°C for 1 h before instrumental measurement.

Instrumental analyses were performed using a gas chromatography-mass spectrometry system (GC/MS; Agilent Technologies 5975C). A DB-5 type column (5% methyl-phenyl siloxane, $30\text{ m} \times 0.32\text{ mm}$ i.d. $\times 0.25\text{ }\mu\text{m}$ film) was operated with helium as the carrier gas (maintained at a constant flow rate of 1.4 ml/min) and in temperature programmed mode (starting at 80°C for 1 min, up to 200°C at $25^\circ\text{C}/\text{min}$, then to 250°C at $3^\circ\text{C}/\text{min}$ and finally to 300°C at $20^\circ\text{C}/\text{min}$, with an isothermal hold of 5 min). The GC/MS system was operated in the electron ionization (70 eV) and full scan (m/z 50–650) modes. GC/MS quantification was performed using a calibration curve (1–10 $\mu\text{g}/\text{ml}$) with commercial standards (campesterol, stigmaterol, sitosterol,

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