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The distribution and seasonal variations of sedimentary organic matter in the East China Sea shelf

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ABSTRACT

We sampled the surface sediments of the East China Sea shelf (ECSS) in spring and autumn, 2014, and analyzed the biogenic element concentrations and stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopic compositions to study the distribution and seasonal variations of sedimentary organic matter (OM). The average concentrations of TOC, TN and OP in autumn decreased obviously compared with those in spring. The increase of $\delta^{15}N$ values in autumn indicated the priority utilization of ^{14}N by bacterial decomposition activity. The values of $\delta^{13}C$ were used to trace organic matter sources. The estimated percentages for terrestrial OM were in the range of 0–34.6%. They generally decreased seaward in nearshore areas, indicating the decrease of terrigenous influence. There was an obvious tongue-shaped region with relatively low percentages of terrestrial OM (< 12%) in the northern part of the ECSS, which may be a reflection of the intrusion pathway of the outer seawater.

1. Introduction

Coastal sediments receive organic matter from different sources, including autochthonous inputs of phytoplankton primary productivity, and allochthonous inputs such as terrigenous, river runoff, and anthropogenic sources (Graham et al., 2001; Lamb et al., 2006). Since organic carbon and nitrogen stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) and C/N elemental ratios of surface sediments from different sources generally have different values, data can be used to identify the organic matter provenance in coastal marine environments (Voβ and Struck, 1997; Ruiz-Fuiz-Fernández et al., 2002; Kubo and Kanda, 2017; Sanil Kumar et al., 2017; Yu and Zhang, 2017). For instance, high $\delta^{15}N$ values of 10–14‰ may characterize recent river borne particulates (Voβ and Struck, 1997), low $\delta^{13}C$ values of −27.94 to −26.05‰ may indicate terrestrial inputs from higher plants (Sanil Kumar et al., 2017) and C/N ratios of 15.13–29.69 may signal a combined input of both autochthonous and terrestrial organic matter sources (Sanil Kumar et al., 2017).

However, values of $\delta^{13}C$, $\delta^{15}N$ and C/N ratios in surface sediments may have seasonal variations due to the influence of primary production or organic matter degradation (Voβ and Struck, 1997; Kubo and Kanda, 2017). For example, high winter nutrient concentrations, together with short residence time of water masses in spring, could result in a large fractionation of nitrate during uptake and hence low ^{15}N in the phytoplankton (Mariotti et al., 1984; Montoya et al., 1990). The settlement of the phytoplankton may then result in seasonal variations of $\delta^{15}N$ in the surface sediments. It was reported that seasonal changes in the isotope signal are evident in the surface sediments of the Pomeranian Bight, southern Baltic Sea (Voβ and Struck, 1997). Microbial processes can additionally increase ^{15}N in particles through degradation (Owens, 1985; Cifuentes et al., 1988). For C/N ratios, post-depositional changes could occur, which would result in the inaccuracy of source identification (Meyers, 1994). The $\delta^{13}C$ values usually increased with increasing productivity (Hodell and Schelske, 1998; Kang et al., 2017). These characteristics of $\delta^{13}C$, $\delta^{15}N$ and C/N may limit their use in the identification of the organic matter provenance (Thornton and MacManus, 1994; Voβ and Struck, 1997).

The dispersal of the Changjiang (Yangtze River)-derived and

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marine-derived sediments in the East China Sea shelf (ECSS), China, is largely affected by the seasonal hydrodynamics (Li et al., 2014a). The discharge of the Changjiang is highly seasonal with its peak in summer and 75% of the river runoff occurring during the flood/rainy season between May and October (Rabouille et al., 2008). The Kuroshio Current, which has profound effect on the eco-environment of the East China Sea shelf, generally moves away from the shelf in summer and moves close to and sometimes onto the northern shelf of Taiwan (Tang et al., 2000). Previous studies have shown that terrestrial organic matter (OM) is a critical component of sedimentary OM with its percentages ranging from 5% to 57% in the mud regions of the Changjiang Estuary and the adjacent ECSS (Zhang et al., 2007; Xing et al., 2011; Hu et al., 2012; X. Li et al., 2012; Li et al., 2014a). Furthermore, these studies also provide valuable insights regarding the spatial variations, abundance, age as well as burial of sedimentary OM in this dynamic environment. In summary, the valuable insights mainly included the following contents: terrestrial organic matter accounted for an increasing fraction of sedimentary OM seaward in the Changjiang Estuary (Zhang et al., 2007; Xing et al., 2011; Hu et al., 2012; X. Li et al., 2012; Li et al., 2014a); winter wind/wave energy and hydrodynamic sorting had a substantial effect on sediment OM redistribution in the inner shelf of the East China Sea (X. Li et al., 2012); the increasing input of freshwater plankton and eutrophication were important driving forces for carbon cycling in the Changjiang Estuary and its adjacent regions (Li et al., 2014a). However, the sources, distribution and seasonal variations of sedimentary OM in the ECSS remain poorly explored. This paper presented data on $\delta^{13}C$, $\delta^{15}N$, total organic carbon (TOC), total nitrogen (TN) and related parameters for the surface sediments in the ECSS in spring and autumn and the sources and decay of sedimentary organic matter in this area were also discussed.

2. Materials and methods

2.1. Study area and sample collection

The ECSS, with moderately high primary production (Gong et al., 2003), is bordered by Chinese mainland on the western side (Fig. 1). It is a dynamic area with tremendous riverine inputs and intense current activities (Fig. 1). The Changjiang is the third largest river in the world in the length and runoff. It is also a major source of materials to the ECSS (Fig. 1; Wu et al., 2004; X. Li et al., 2012). The substantial freshwater input from the Changjiang forms the strong Changjiang Diluted Water (CDW) (Fig. 1). The Zhejiang-Fujian Coastal Current (ZFCC) flows northward in summer and southward in winter (Su, 2005; Fig. 1). The Taiwan Warm Current (TWC) perennially flows northward (Su, 2005; Fig. 1). The main stream of the KC flows northeastward along the ECSS break (Fig. 1).

The sampling of this research was carried out in May 22–June 11 (spring) and October 18–November 30 (autumn), 2014 on board R/V Science I. The study area extends approximately from the east of Zhoushan Archipelago to the north of the Taiwan Strait with water depths generally < 100 m (Fig. 1). The top ~2 cm sediments were gathered with a plastic spatula from the center part of the sampler and were kept in pre-cleaned polyethylene bags. One sample was collected from each station (30 stations in spring and 29 stations in autumn) for the analysis of grain size, TOC, TN and stable carbon and nitrogen isotopic compositions. All the collected samples were immediately frozen until further analysis.

2.2. Analytical methods

Grain size analysis was carried out by means of a Malvern Mastersizer 2000 laser diffractometer after the removal of the inorganic carbonates using 10% (v/v) HCl and the organic matter using 30% (v/v) H_2O_2 (Folk, 1974). The percentages of the following 3 groups of grain sizes were determined: < 4 μm (clay), 4–63 μm (silt), and > 63 μm (sand). 20% of the collected samples were analyzed in replicate and the relative error was < 3%.

A total of 71 freeze-dried samples (20% of the collected samples were analyzed in duplicate) were homogenized, thoroughly ground and sieved through a 200 mesh screen. About 200 and 50 mg of each freeze-dried, homogenized and ground sample were analyzed for TN and $\delta^{15}N$, respectively. About 2 g of each freeze-dried, homogenized and ground sample was weighed and loaded into a 15 ml tube, treated with 1 M HCl to remove carbonates, and freeze-dried, thoroughly ground again for the analysis of TOC and $\delta^{13}C$. Concentrations of TN and TOC were determined with an Elementar vario MACRO cube CHNS analyzer. Sulphanilamide was used as the standard reference material and the precision was 0.02% for TOC and 0.005% for TN. $\delta^{13}C$ and $\delta^{15}N$ values were obtained using the isotope ratio mass spectrometer (Thermo, MAT 253). $\delta^{13}C$ was given as ‰-deviation from the isotope composition of the PDB (Pee Dee Belemnite) standard. $\delta^{15}N$ was given as ‰-deviation from the nitrogen isotope composition of atmospheric air. The precision was ± 0.2‰ for $\delta^{13}C$ and ± 0.4‰ for $\delta^{15}N$. All the laboratory

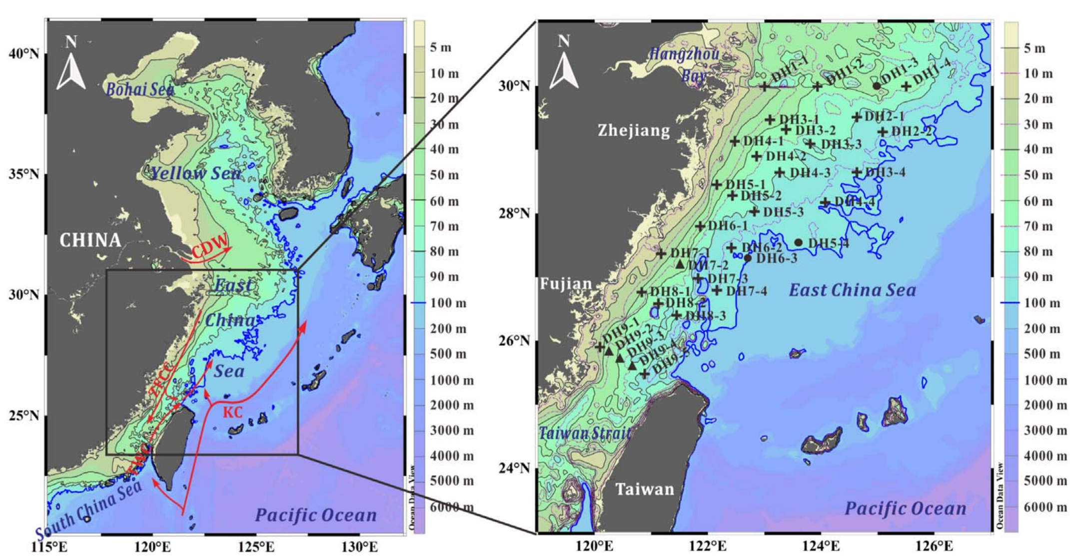

Fig. 1. Locations of sampling sites in the East China Sea shelf. + indicates the locations of sediment samples collected in both spring and autumn; ▲ indicates the locations of sediment samples collected only in spring; ● indicates the locations of sediments samples collected only in autumn. CDW, ZFCC, TWC and KC represent the Changjiang Diluted Water, the Zhejiang-Fujian Coastal Current, the Taiwan Warm Current and the Kuroshio Current, respectively.