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Baseline

Biogeochemistry of bulk organic matter and biogenic elements in surface sediments of the Yangtze River Estuary and adjacent sea

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ABSTRACT

This study investigated the distribution and roles of total organic carbon (TOC), biogenic silicon (BSi), various forms of nitrogen (N) and phosphorus (P), and the stable carbon isotope ($\delta^{13}\text{C}$) in surface sediments of the Yangtze River Estuary (YRE) and adjacent sea. Terrestrial input accounted for 12–63% of total organic matter in the study area. The distribution of biogenic elements was affected by the Changjiang Diluted Water, the Jiangsu Coastal Current, human activities, marine biological processes, and the sediment grain size. Potentially bioavailable N and P accounted for an average 79.6% of the total N (TN) and 31.8% of the total P (TP), respectively. The burial fluxes for TOC, BSi, TN and TP were 39.74–2194.32, 17.34–517.48, 5.02–188.85 and 3.10–62.72 $\mu\text{mol cm}^{-2} \text{yr}^{-1}$, respectively. The molar ratios of total N/P (1.2–5.0), Si/P (5.0–14.8) and Fe/P (21–61) indicated that much of the P was sequestered in sediments.

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Larger river-dominated coastal margins are active interfaces between terrestrial and oceanic environments, and are subject to large discharges of riverine materials, anthropogenic inputs and complex biogeochemical processes (Bianchi and Allison, 2009). As >80% of global burial of organic carbon happens in these shallow marine systems, the sedimentary organic matter in estuarine–shelf regions plays a significant role in the context of the global carbon cycle (Hedges and Keil, 1995; Tesi et al., 2007). Nitrogen (N), phosphorus (P) and silicon (Si) are primary nutrients, and play important roles in the biogeochemical cycling of biogenic elements in estuaries and continental shelves (Liu et al., 2005a; Falco et al., 2010; Slomp, 2011). Thus, an investigation of total organic carbon (TOC), biogenic silicon (BSi), and various N and P forms in marine sediments is essential for evaluating the response of aquatic ecosystems to global climate and environmental changes, and the impacts of human activities (De Lange, 1992; Schenau and De Lange, 2001; Krom et al., 2004; Liu et al., 2004; Yu et al., 2012b).

The Yangtze River (Changjiang) Estuary (YRE) and the adjacent inner shelf of the East China Sea (ECS) form one of the largest estuarine–shelf systems in the world, and annually receive huge quantities of particulate matter transported by the Yangtze River

(Milliman et al., 1985). The rapid economy development in the Yangtze River catchment has resulted in excessive nutrient discharge and changes in relative nutrient concentrations. This has had many detrimental impacts on aquatic ecosystems of the YRE and adjacent sea (Chai et al., 2006; Zhou et al., 2008; Zhu et al., 2011b), including eutrophication, harmful algal blooms, and seasonal hypoxia in bottom waters.

Most previous studies of the sedimentary organic matter and biogenic elements of the YRE and adjacent shelf have focused on the concentration and distribution of TOC, total N (TN) and P species, and their relationships to sediment grain size (Kao et al., 2003; Deng et al., 2006; Fang et al., 2007; Zhu et al., 2011a; Meng et al., 2014); several studies have also considered BSi (Liu et al., 2005a; Wang et al., 2014). However, studies on the biogeochemical cycling of TOC, BSi, and various N and P forms in the YRE and adjacent sea, have been largely ignored. To help elucidate the biogeochemical cycling of organic matter and other biogenic elements cycling in the YRE and adjacent sea, we undertook measurements of grain size, TOC, BSi, various N and P fractions, the stable carbon isotope ($\delta^{13}\text{C}$) and heavy metals in surface sediments. We also investigated factors influencing their distribution, determined the potential bioavailability of N and P, estimated burial fluxes of the biogenic elements, and assessed potential nutrient limitations in these aquatic ecosystems.

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The YRE is of particular interest to research on organic geochemistry and biogeochemistry because of its global importance (Fig. 1). The Yangtze River is the world's third longest river (6300 km) and the largest river in China. It has a drainage area of $1.8 \times 10^6 \text{ km}^2$ (Li et al., 2007), annually discharges $9.0 \times 10^{11} \text{ m}^3$ of fresh water, and transports 5.0×10^8 tons of sediments and 1.2×10^7 tons of particulate organic matter to the YRE and adjacent sea (Milliman et al., 1985; Chen and Zong, 1998). The hydrodynamic conditions in the study area are very complex, with the main factors including the Changjiang Diluted Water (CDW), the Taiwan Warm Current (TWC), the Kuroshio Current (KC), the Jiangsu Coastal Current (JCC) and the Zhejiang–Fujian Coastal Current (ZFCC) (Fig. 1) (Liu et al., 2007). Generally, a strong northeast winter monsoon prevails from late September to early April, and a weaker southwest summer monsoon occurs from May to August. Most of the Yangtze River-derived sediments are temporarily deposited in the YRE subaqueous delta in the wet season (Liu et al., 2006). During the dry season the stronger northeast monsoon intensifies the coastal currents, the southeastward JCC transports the sediments originally deposited in the old Huanghe delta into the ECS (which may be an important source of sediment to the northern ECS shelf; Hu and Yang, 2001), and the sediments initially deposited in the YRE subaqueous delta are resuspended and transported primarily southward by the ZFCC (Liu et al., 2006). Thus, the largest muddy patch is found in the ECS inner shelf (to approximately 60 m depth), within a narrow band extending from the subaqueous delta southward to the Taiwan Strait. In contrast, because of the absence of a contemporary sediment supply, strong winnowing and resuspension, most of the outer continental shelves of the ECS (water depth 60–200 m) are characterized by relict sand (Wu et al., 2013) that retains the sedimentary characteristics and morphological features of the last stage of the Late Pleistocene (Hu and Yang, 2001).

Three field studies were conducted in the YRE and adjacent sea on board the *R/V Beidou*, in October 2006, and in February and May 2007. The sampling stations are shown in Fig. 1. Surface sediment samples (0–2 cm) from 63 stations were collected using a stainless steel box sampler, and immediately frozen at -20°C for return to

the laboratory. Prior to analysis the sediment samples were lyophilized, and homogenized by grinding using an agate mortar and pestle. Subsamples were analyzed for biogenic elements, $\delta^{13}\text{C}$, and heavy metals. Sediment samples taken prior to grinding were used to determine the sediment grain size.

Grain size (D , μm) was analyzed using a laser particle size analyzer (Mastersizer 2000; Malvern Instruments Ltd., Malvern, Worcestershire, UK) capable of analyzing particle sizes from 0.02 to 2000 μm . Three sediment size categories were distinguished: (1) clay: $D < 4 \mu\text{m}$; (2) silt: $4 < D < 63 \mu\text{m}$; and (3) sand: $D > 63 \mu\text{m}$. The samples were analyzed in duplicate, and the analytical relative error was $< 2\%$. The mean grain size is reported as Φ , where $\Phi = -\log_2 D$ (D unit: mm) (Krumbein, 1934).

The TOC and TN concentrations were determined using a CHNOS Elemental Analyzer (Vario EL-III; Elementar Analysensysteme GmbH, Germany). The subsamples were directly measured for the TN content, while for measurement of the TOC content the sediments were acid-treated (Zhang et al., 1997). Based on duplicate measurements, the precision for TOC and TN was $< 6\%$ and 1.2% , respectively (Liu et al., 2010). The $\delta^{13}\text{C}$ was analyzed using a thermal DELTA^{plus}/XL mass spectrometer at the State Key Laboratory of Estuarine and Coastal Research (SKLEC), China, as described by Zhang et al. (2007). Duplicate determinations were made for each of the samples. The final isotope ratio is reported in δ notation. The isotopic composition is expressed by Eq. (1):

$$\delta(\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad (1)$$

where $\delta(\text{‰})$ stands for $\delta^{13}\text{C}(\text{‰})$, and R_{sample} and R_{standard} are the isotopic $^{13}\text{C}/^{12}\text{C}$ ratios of the samples and standards, respectively. The international carbon standard was Pee Dee Belemnite (PDB). The analytical precision was $\pm 0.2\text{‰}$ ($n = 6$), based on replicate analyses of the same sample.

Sedimentary forms of N usually include inorganic nitrogen (IN) and organic nitrogen (ON). The former is composed of exchangeable nitrate ($\text{NO}_3^-_{\text{ex}}$), ammonium ($\text{NH}_4^+_{\text{ex}}$) and fixed ammonium (N_{fix}) (Silva and Bremner, 1966). Sedimentary $\text{NH}_4^+_{\text{ex}}$ and $\text{NO}_3^-_{\text{ex}}$ forms were leached for 5 min using 0.5 M KCl. The extracted NH_4^+ and NO_3^- were

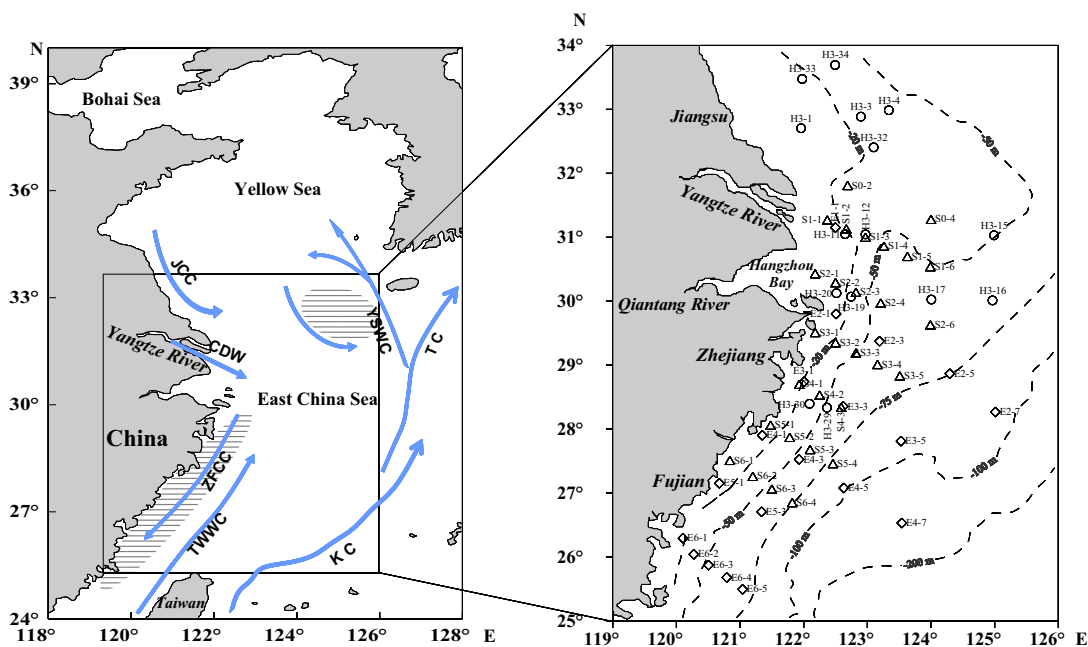


Fig. 1. Sampling stations and sampling periods. “○”: October 2006; “◇”: February 2007; “△”: May 2007. The localized upwelling areas are shadowed (based on Hu, 1984), and the arrows indicate the direction of currents in the YRE and adjacent sea (from Liu et al., 2007). JCC: Jiangsu Coastal Current; CDW: Changjiang Dilute Water; ZFCC: Zhejiang–Fujian Coastal Current; TWWC: Taiwan Warm Current; KC: Kuroshio Current; TC: Tsushima Current; YSWC: Yellow Sea Warm Current.

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