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Sources and fate of organic carbon and nitrogen from land to ocean: Identified by coupling stable isotopes with C/N ratio

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A B S T R A C T

The transport of organic matter in coastal areas plays an important role in global biogeochemical cycles. The present study used stable isotopes including carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) and C/N ratio to assess the sources and fate of organic carbon and nitrogen in soils and sediments of a coastal plain-river plume-bay system. Changes of the $\delta^{13}C$ and $\delta^{15}N$ values from natural to agricultural soils in the Yellow River coastal plain reflected the contribution of C_4 carbon, decomposition of organic matter and application of nitrogen fertilizer. The organic carbon in the marine sediments adjacent to the coastal plain mainly originated from C_3-dominated terrestrial systems. The spatial heterogeneity of both $\delta^{13}C$ and $\delta^{15}N$ values indicated that Yellow River sediment transport and anthropogenic wastewater discharge were two driving forces for the sedimentary organic carbon and nitrogen dynamics in large river plume and inner bay areas. Meanwhile, the marine primary production and denitrification process as affected by excessive nutrient input also contributed to the cycling of organic matter. Wetland soils, cropland soils, vegetable soils, coastal and deep-sea sediments were the five systems controlling the cycle of organic carbon and nitrogen in the study area. A significant positive correlation between $\delta^{13}C$ and $\delta^{15}N$ in the Yellow River coastal plain-plume-bay region was observed, which implied the flux of organic matter from a labile pool in source regions into a more recalcitrant pool in sink regions. These findings would provide a better understanding of carbon sequestration in the coastal soil and sediment.

1. Introduction

The coastal zone and river mouth systems are important interfaces between the continent and ocean, and the exchange and sequestration of the carbon and nitrogen among land, river and ocean have an impact on the biogeochemistry of these elements at a global scale (Hedges and Keil, 1995; de Haas et al., 2002; Bianchi and Allison, 2009). The carbon and nitrogen accumulated in the coastal sediments are heterogeneous and complex mixture of organic materials with different characteristics and from different sources (marine and freshwater phytoplankton, soil, leaf debris, wastewater, kerogen etc.) (Cloern et al., 2002; Lamb et al., 2006; Schreiner et al., 2013; Cai et al., 2015). Soils from different land types are the main source of riverine organic matter, contributing >90% of the buried organic carbon in the marine sediments occurring in "terrigenous-deltaic" regions near river mouths (Berner, 1989; Raymond and Bauer, 2001; Tao et al., 2015). Land-use change including reclamation and managed agro-ecosystem development can increase export of soil-derived organic carbon stored in aquatic sediments (Bianchi, 2011). The delivery, reaction, and burial of organic carbon and nitrogen are dependent on transport-reaction cycles within both the terrestrial sources and oceanic sedimentary sinks (Blair and Aller, 2012). Understanding the sources, characteristics and environmental fate of the organic matter in the coastal soils and sediments is key to understanding the importance of the coastal system on the mitigation of climate change (Bauer et al., 2013; Regnier et al., 2013).

Due to the complex nature of carbon and nitrogen in the coastal zone, stable isotope ($\delta^{13}C$ and $\delta^{15}N$) techniques and C/N ratio are robust tools that have been frequently used to elucidate sources, mixing and transformations of carbon and nitrogen in the terrestrial, estuarine and coastal regions, based on the different

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signatures of the sources (Zhang et al., 2007; Ramaswamy et al., 2008; Cai et al., 2015). In general, terrestrial organic matter has depleted $\delta^{13}C$ and $\delta^{15}N$ values when compared to marine organic matter (Lamb et al., 2006). However, a single stable isotope is insufficient to identify the sources of organic matter because of the complicated contributions in the coastal areas. Hence, dual isotopes (both $\delta^{13}C$ and $\delta^{15}N$) along with the carbon and nitrogen ratios can be applied to improve the accuracy of source identification (Middelburg and Herman, 2007; Cai et al., 2015). Moreover, geographical mapping of isotope ratios over a large area can also contribute to identifying the specific sources in different regions by using the spatial variability of the isotopic signatures (Hu et al., 2006; Liu et al., 2015). Furthermore, $\delta^{13}C$ and $\delta^{15}N$ are also useful in understanding the fate of organic matter in the coastal environment based on the isotopic fractionations caused by physical, chemical, and biological processes. For example, the organic matter degradation driven by bacterial and/or fungal activities results in the enrichment of isotopic values due to the preferential decomposition of $^{13}C/^{15}N$ depleted compounds (Lehmann et al., 2002). Middelburg and Herman (2007) observed an increase in $\delta^{15}N$ values up to 20% driven by heterotrophic activities in the Scheldt estuary.

The Yellow River coastal plain is a newly formed coastal fluvial plain since 1855. In total, 12 major shifts of the river course occurred between 1855 and 1976 due to rapid channel siltation (Pang and Si, 1979). In 1996, the main channel was artificially diverted northeast forming the Qing 8 course. Due to the large sediment load (1×10^9 t year^{-1} in history) of the Yellow River, the river mouth area expanded rapidly at a mean speed of 42 km^2 year^{-1} before 1970s (Zhang et al., 1990), while it decreased to 20–25 km^2 year^{-1} from 1976 to 1999 (Wang and Liang, 2000). Although the sediment load continued to decline, partly due to dam constructions and soil and water conversion measures, the coastal area nevertheless increased from 2003 to 2011 (Kong et al., 2015). Meanwhile, the coastal erosion of promontory occurred when the water and sediment supply became cut off (Kong et al., 2015). The Yellow River coastal plain is thus an active land-ocean interaction area, and the river mouth region is heavily impacted by sediment input from a substantial amount of terrestrial materials, including particulate organic matter from the Yellow River sediment discharge (Qiao et al., 2010; Tao et al., 2015). Since the discovery of the Shengli oilfield in 1960s, the Yellow River Delta region has undergone rapid industrialization. In 1983, Dongying City as the core area of the delta was founded to meet the economic and social development. Recently, the Yellow River coastal plain has become as an ecological agricultural and industrial production area at the national level promoted by China's state council since 2009. The rapid urbanization and economic growth could result in the inputs of agricultural wastes, industrial discharge and city sewage wastewater into the ocean through the Yellow River and other large rivers around the Bohai Bay and Laizhou Bay (Zhang et al., 2006). All these discharges eventually contribute to the organic matter in the sediments of the Bohai Sea.

Although some studies have been carried out to assess the contribution of terrigenous organic matter to the Yellow River plume and its immediate surrounding areas (Bigot et al., 1989; Cai, 1994), a detailed understanding of the sources and fate of carbon and nitrogen from the coastal plain and rivers to the bulk sediment in offshore marine areas remains poorly documented. Data on organic carbon, total nitrogen and their elemental ratios and isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) covering both soil and sediment across the coastal plain, river plume and bay area were collected. The objectives of the study based on these data include (1) seeking the patterns of organic matter in the soils from nature to cropping systems, (2) elucidating the sources of carbon and nitrogen deposited in the marine sediment, and (3) examining the fate of the terrigenous organic matter in the coastal zone.

2. Materials and methods

2.1. Study area

The study area is on the north coast of China, covering the Yellow River coastal plain, the Yellow River plume, Laizhou Bay and south of Bohai Bay from the land to the sea (Fig. 1). The area is characterized of a huge amount of sediment loading in the coastal zone. Approximately 1×10^9 t year^{-1} sediment form Yellow River is discharged into the Bohai Sea, which is the second largest sediment input from a single river worldwide (Milliman and Syvitski, 1992), with 85% of the annual total sediment input during the flood season (Li et al., 1998).

The suspended sediments in the Yellow River plume are transported southward and southeastward to Laizhou Bay, and northward to Bohai Bay (Qiao et al., 2010). The transportation of the suspended sediments along the coast is dominated by isobath-parallel tidal current with a velocity of <1.0 m/s, which flows

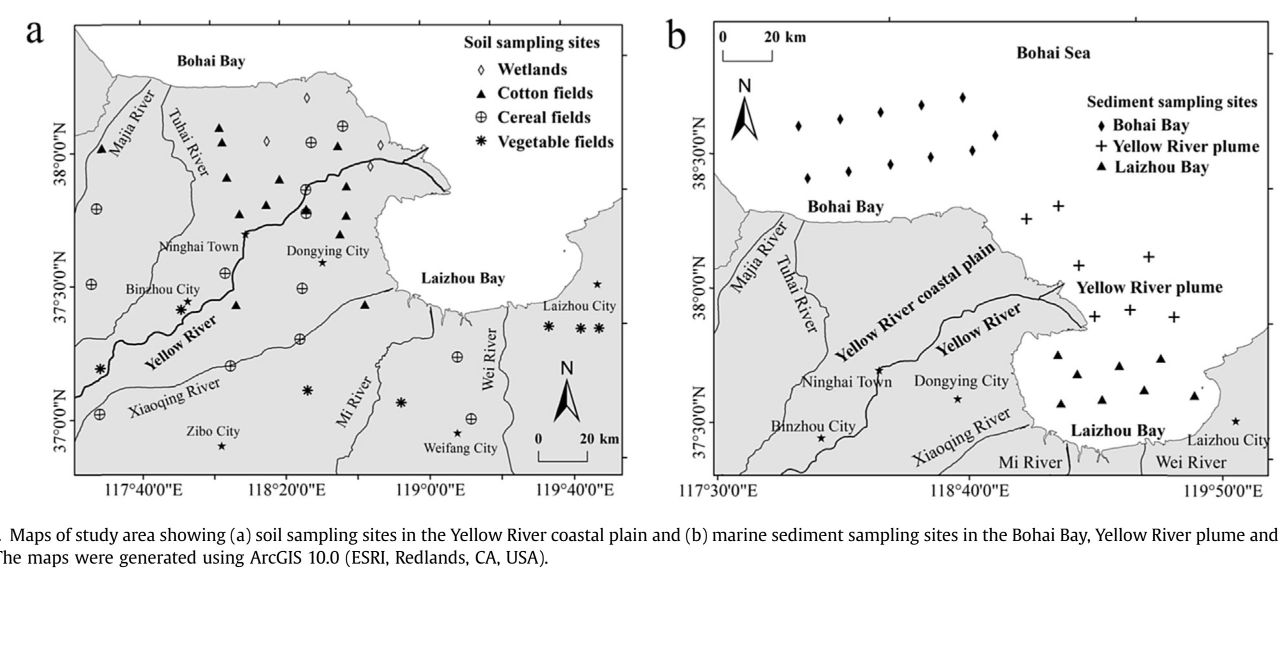

Fig. 1. Maps of study area showing (a) soil sampling sites in the Yellow River coastal plain and (b) marine sediment sampling sites in the Bohai Bay, Yellow River plume and Laizhou Bay. The maps were generated using ArcGIS 10.0 (ESRI, Redlands, CA, USA).