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Lipid biomarkers and organic matter carbon isotopes in estuarine sediments as proxies for evaluating seawater intrusion

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ABSTRACT

Coastal wetlands and estuarine sediments are characteristics of tide-dominated environments and retain a record of seawater intrusion and possibly sea-level changes. A variety of methods including the C/N ratio and $\delta^{13}C$ of bulk organic matter in the sediment have been employed in estuarine studies, but they are generally non-specific indicators. Here we report using lipid biomarkers to evaluate the extent of seawater intrusion based on an estuary in eastern China, Xinyanggang. Along the river from the estuary mouth upstream to the freshwater head, the vegetation shifts quickly from salt-tolerant *Spartina* (C_4) to the less tolerant reed *Phragmites* (C_3), both of which have distinguished $\delta^{13}C$ values and biomarker distribution. The $\delta^{13}C$ values of particulate organic matter (POM) and surface sediment decreased from the estuary mouth upstream, indicating the reduced contributions from *Spartina* and marine phytoplankton to the POM and surface sediment and increased inputs from *Phragmites*. The C_{32}/C_{30} alkanol and cholesterol/sitosterol ratio decreased in the surface sediments, faithfully recording the variations in the contributions from *Spartina* and *Phragmites*. The combination of biomarker distribution and organic matter $\delta^{13}C$ in the sediments can be used as indicators for sea water intrusion into the estuary/river.

1. Introduction

Sea level rise and associated seawater intrusion is a threat to coastal industries, agriculture and habitation. This is especially true for 3.2 billion people in Asia who live close to a coast with a gentle topography (Hinrichsen, 1998). The annual mean sea levels of the Eastern China Sea have been rising at a speed of about 2.1–2.3 mm/yr since 1960 (Liu, 1992). Therefore, understanding the effects of sea level variations in the Holocene is essential for predicting future changes under increased anthropogenic CO_2 release and global warming (Lamb et al., 2006).

River, estuarine and coastal wetlands link continents and oceans and their sediments are characteristics of tide-dominated environments and preserve information about sea-level changes (Chmura et al., 1987; Wilson et al., 2005a, b; Lamb et al., 2006). Traditionally, microfossils have been widely used to reconstruct past sea-level changes and paleoenvironments in coastal areas (see review by Lamb et al., 2006), but they are susceptible to chemical and mechanical damages, restricting coastal sea level reconstructions (Wilson et al., 2005a). Total organic carbon (TOC) and TOC/TN in the sediment have been used as a tool to track the source of organic matter, and environmental changes in coastal and estuarine regions (Chmura et al., 1987; Choi et al., 2001; Wilson et al., 2005a, b; Lamb et al., 2006, 2007; Kemp et al., 2012). However, the loss of labile nitrogen in sediments probably complicates C/N ratios and affects its reliability as faithful recorders of organic matter sources (Sampei and Matsumoto, 2001).

Bulk organic matter $\delta^{13}C$ values are a more robust tool for tracking the material source in the marine sediments. Wilson et al. (2005a, b) studied $\delta^{13}C$ and TOC/TN in the suspended particles, surface sediments and plants in the Mersey Estuary in the UK. Their results showed the POM in river sediments originated mainly from terrestrial vegetation based on the large isotopic range between marine and terrestrial input. Fontugne and Jouanneau (1987) found a general trend of heavier $\delta^{13}C_{POM}$ values with increasing salinity seawards. Middelburg and Herman (2007) suggested that the correlation between $\delta^{13}C_{POM}$ values and salinity is more significant in river-dominated estuaries than in tidal-dominated estuaries.

Freshwater phytoplankton in the river use the dissolved CO_2 for photosynthesis and its $\delta^{13}C$ value is about −30‰, while phytoplankton in the sea water mainly use ^{13}C enriched HCO_3^- as the carbon source for photosynthesis so that it has higher $\delta^{13}C$ values,

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about −18‰ (Meyers, 1994; Middelburg and Nieuwenhuize, 1998). However, such difference in the sediment or POM could also be biased by variations in the proportion of coastal C_4 vs. C_3 plants from the mouth of estuary to the freshwater head. C_3 plants use the Calvin cycle, preferentially utilizing $^{12}CO_2$ and resulting in much more negative $\delta^{13}C$ values, while C_4 plants use Hatch–Slack cycle which has much less carbon isotope fractionation (Smith and Epstein, 1971; O'Leary, 1988).

Lipid biomarkers are specific to particular organisms. If they are found in the sediment intervals, the existence of their precursors and the environment favorable for them could be established. In addition, most biomarkers can well survive in the sediment for hundreds of thousands of years (Meyers, 1994). As a result they have not only been widely used to track vegetation and phytoplankton from different sources in marine/lake sediments and loess deposits (e.g. Eglinton et al., 1962; Cranwell et al., 1987; Volkman et al., 1998; Zhang et al., 2003, 2004, 2006, 2014), but also used in estuarine sediment to investigate the source of organic matter (e.g. Volkman, 1986; Prahl et al., 1994; Ohkouchi et al., 1997; Xu et al., 2006; Pisani et al., 2013). For example, Prahl et al. (1994) applied long-chain *n*-alkanes derived from the surface waxes of higher plants and phenolic and hydroxyalkanoic compounds from vascular plant as indicators of terrestrial input to the Washington margin. Ohkouchi et al. (1997) used C_{25}–C_{35} *n*-alkanes, C_{24}–C_{28} *n*-fatty alcohols and C_{23}–C_{34} fatty acids to indicate the terrestrial input, and C_{17}–C_{20} alkane, pristane, cholesterol and dinosterol to represent the marine organisms in the sediments of west tropical Pacific Caroline Basin.

Particular biomarkers for certain types of plants in the estuary region can be established and thus provide a more definitive tool to track the source material. For example, Xu et al. (2006) used taraxerol, a biomarker for mangroves to indicate the influence of seawater from the Florida Bay. In the coastal and estuarine areas, organic matter can be supplied both from autochthonous sources (such as plants growing on the sediment surface/river bank) and allochthonous sources (organic material transported predominantly by the tide or a river). In addition, plants adapted to the estuarine mouth and to the fresh water dominated upstream areas are different due to the salinity gradient, which might be characterized by different biomarkers and thereby, if well preserved, could be a new indicator for seawater intrusion and possibly paleo-sea level fluctuations.

Here we report a comprehensive study in an estuary in eastern China (Fig. 1). We collected water, suspended particles, surface sediments and vegetation from the estuarine mouth to the up-stream head. In addition to traditional TOC/$\delta^{13}C$ values of bulk organic matter in the sediments, we also analyzed water δD and $\delta^{18}O$ values, TOC/$\delta^{13}C$ values of plants and particulate organic matter (POM). We analyzed the distribution of lipid biomarkers in the plants living in and adapted to the estuarine mouth and freshwater dominated head, and in the surface sediment, which enable us to evaluate the potential of biomarkers to indicate the distance (extent) of seawater intrusion, which might be related with sea level change.

2. Methods

2.1. Study region

The Xinyanggang River is located inside the Yancheng National Nature Reserve (YNNR) at the Yellow Sea coastal region of Jiangsu Province, China, with longitude/latitude of 32°200′ to 34°370′N and 119°290′ to 121°160′E (Fig. 1a, b). The YNNR is the largest tidal flat wetland nature reserve in the world, with a total area of approximately 4530 km^2 and the coastline of approximately 528 km

Fig. 1. Study area and sampling sites: a) Location of Xinyanggang River; b) Sampling sites in Xinyanggang River.

(Zhang et al., 2011). The weather in YNNR is transitional from warm temperate to subtropical, and is characteristic of a monsoon climate. The annual average temperature is 14–15 °C with an average temperature of 0–2.5 °C in January and of 26.5–27.5 °C in July. Annual precipitation ranges from 900 mm to 1050 mm. Xinyanggang River is 69.8 km long, 140–180 m wide, and has a watershed area 2478 km^2. The annual discharge is about 2.1×10^8 m^3.

An estuary usually refers to a partly enclosed coastal body of brackish water with one or more rivers or streams flowing into it, and with a free connection to the open sea. YNNR estuaries also form a transition zone between river environments and maritime environments and are subject to both marine influences, such as