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Sedimentary organic and inorganic records of eutrophication and hypoxia in and off the Changjiang Estuary over the last century

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Organic and inorganic sedimentary parameters in and off the Changjiang Estuary have been analyzed to reconstruct historical trends in eutrophication and hypoxia over the last century. The lipid biomarker concentrations in the Changjiang Estuary mud area (CEMA) indicated eutrophication accelerated after the 1970s. Meanwhile, Mo/Al indicated hypoxia has increased since 1960s. Eutrophication and hypoxia in the CEMA are primarily a result of the dramatically increased load of terrestrial nutrients from the Changjiang to the East China Sea. The lipid biomarker concentrations in the southwest Cheju Island mud area (SCIMA) showed primary production is controlled mainly by changes in regional climate and marine current. No significant hypoxia occurred in the SCIMA over the past century as indicated by Mo/Al. Therefore, geochemical indicators of eutrophication and hypoxia revealed different patterns between the CEMA and SCIMA, suggesting the role of river-derived nutrients in sustaining eutrophication and hypoxia in the CEMA since the 1960s.

1. Introduction

Eutrophication and hypoxia are two of the most intractable ecological and environmental issues in estuaries and coasts worldwide, including the Changjiang Estuary (Diaz, 2001; Fulweiler et al., 2012; Zhang et al., 2010). Over the past century these phenomena have increased in severity, greatly impacting marine ecosystems (Bianchi et al., 2010; Diaz and Rosenberg, 2008; Rabalais et al., 2004). The Changjiang Estuary is now suffering from harmful algal blooms and hypoxia due to anthropogenic influences such as urbanization, increased fertilizer use, industrial sewage discharge, deforestation and the construction of large hydraulic projects (Hu et al., 2012; Li et al., 2011; Wang, 2006, 2009; Zhao et al., 2012; Zhu et al., 2011, 2014). Numerous studies focus on either eutrophication or hypoxia in the Changjiang Estuary, including field status and characteristics, annual cycle, mechanisms of formation and maintenance, sedimentary records of historical trend, or regional differences between this estuary and other large estuaries (Chai et al., 2006; Chen et al., 2007; Li et al., 2002, 2011; Rabouille et al., 2008; Wang, 2006, 2009; Wang et al., 2012; Wei et al., 2007; Zhao et al., 2012). However, little is known about the relationship between eutrophication and hypoxia and their coupled effects on the marine ecosystem of the Changjiang Estuary. Understanding this topic is crucial to expand our knowledge of anthropogenic-induced consequences to marine ecology, the environment and biogeochemical cycles in large estuaries (Howarth et al., 2011; Zhang et al., 2010).

The marine environment of estuaries and their adjacent areas are impacted by both natural changes and human activities, with significant regional characteristics (Zhang et al., 2010). In the Changjiang Estuary/East China Sea region, previous studies mainly focused on estuarine and coastal eutrophication or hypoxia issues (see citations above). Few have conducted a regional comparison of these issues between inshore and offshore in the Chinese marginal seas (Zhu et al., 2014). The regional comparison study allows the identification of similarities and differences in historical trends of eutrophication and hypoxia as well as their controlling factors, and can provide new insights into a long-term ecosystem shift and its mechanisms under the influence of varied natural and anthropogenic factors.

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Until now, historical changes in ecosystem health resulting from eutrophication and hypoxia in the Changjiang Estuary have not been thoroughly evaluated due to the absence of long-term environmental monitoring data. Fortunately, the elemental, molecular, and isotopic signatures of organic matter preserved in sediments can be used to reconstruct historical changes in transport processes of carbon and nutrients in estuarine regions, and the interactions between terrestrial activities and coastal environment (Chen et al., 2001; Eadie et al., 1994; Rabalais et al., 2007; Swarzenski et al., 2008). Many techniques used to trace environmental change employ biogenic elements (e.g., C, N and their isotopes) to explain material sources (Struck et al., 2000; Wu et al., 2007; Yang et al., 2009). For example, the molar ratio of C:N and $\delta^{13}C_{org}$ can provide information on organic matter sources in estuaries (Hu et al., 2008; Li et al., 2011; Perdue and Koprivnjak, 2007). However, proxies may be differentially affected post-depositionally based on the strength of hypoxic conditions (e.g., the minimum value of dissolved oxygen concentration, duration of hypoxia) (Burdige, 2007; Swarzenski et al., 2008). Consequently, it is necessary to select multiple biological and geochemical indicators in a multi-proxy approach to reconstruct eutrophication and hypoxia in estuaries (Dell'Anno et al., 2002; Gooday et al., 2009; Swarzenski et al., 2008; Zhao et al., 2012; Zimmerman and Canuel, 2000).

In this study, we present a historical record of total organic carbon (TOC), its stable isotope ratio ($\delta^{13}C_{org}$), biomarkers (brassicasterol, dinosterol, alkenones and *n*-alkanols) and the redox sensitive element molybdenum (Mo) in sediment core samples collected from the Changjiang Estuary mud area (CEMA), which experiences eutrophication and seasonal hypoxia, and the southwest Cheju Island mud area (SCIMA), where eutrophication and hypoxia are absent. We then compare these sedimentary proxies with historical nutrient data of the Changjiang drainage basin and Changjiang Estuary, sedimentary redox sensitive indicators in the Changjiang Estuary, and the East Asian summer and winter monsoon indices. The primary goals of this study are to use these geochemical parameters in down-core sediments where radiochemical age models have been developed to: (1) compare and discuss the relationship between eutrophication and hypoxia by using organic and inorganic proxies as indicators in the CEMA for the first time; and (2) identify the differences in historical trends of eutrophication and hypoxia and their controlling factors in and around the Changjiang Estuary.

2. Materials and methods

2.1. Site description and sampling

There are two main mud areas in the East China Sea: one is in the Changjiang Estuary (i.e., the CEMA) and along the Zhejiang-Fujian coast southward, and another is off the southwest coast of Cheju Island (i.e., the SCIMA) (Qin et al., 1987) (Fig. 1). The nutrient concentrations in the CEMA are controlled predominantly by inputs from the Changjiang, while sediments are mainly sourced from allochthonous terrestrial inputs from the Changjiang, which are carried and deposited along the inner shelf of East China Sea by the southward-flowing Subei Coastal Current and Zhejiang Coastal Current (Liu et al., 2006), and also from autochthonous marine biological residue deposition (Wang et al., 2008; Yan et al., 2010; Zhou et al., 2008). In the Changjiang Estuary, phytoplankton and harmful algae bloom in spring and summer, and large density stratification occurs due to the significant salinity difference between the fresh diluted water from the Changjiang and salty water from the Taiwan Warm Current (Wei et al., 2007). As a result, hypoxia occurs and maintains mainly in the core area of 122°30′–123°00′E, 30°50′–31°30′N (Li et al., 2002; Wang, 2006). The SCIMA is off the estuarine hypoxia zone and without modern riverine material input. It might be formed by the East China Sea cold eddies and/or northward-flowing Huanghai Warm Current with upwelling (Hu, 1984; Yanagi and Inoue, 1995). Sediments in the SCIMA are sourced mainly from old Huanghe estuarine sediments delivered by the north Jiangsu coastal current in winter, and less from Changjiang diluted water in summer (Guo et al., 2003) (Fig. 1).

Two sediment cores were collected with a gravity corer in May and June 2006 and stored frozen (−2 °C). Core CJ43 (122°51′E, 31°03′N, 43 m water depth, 205 cm core length) was collected from the CEMA; core CJ56 (124°49′E, 31°06′N, 56 m water depth, 102 cm core length) was collected from the SCIMA (Fig. 1). Samples were sectioned in 1 cm intervals from 0 to 30 cm for core CJ43; and in 1 cm intervals from 0 to 10 cm and in 2 cm intervals from 10 to 30 cm for core CJ56. Sediment chronology was determined by excess ^{210}Pb activity, and resulting linear sedimentation rates are 0.22 cm/a ($r = 0.98$) for core CJ43, and 0.20 cm/a ($r = 0.97$) for core CJ56 (Feng et al., 2009). The upper 30 cm (ca. 150 a) of each core sample were employed to reconstruct historical changes in eutrophication and hypoxia over the last century by analyzing multiple geochemical proxies.

2.2. Analyses of particle size

Sediment particle size was analyzed according to *Specifications for oceanographic survey: Marine geology and geophysics survey* (GB/T 12763.8-2007) by an MAM 5005 laser particle analyzer (Malvern, UK).

2.3. Analyses of sedimentary organic carbon (TOC) and stable isotope ratio ($\delta^{13}C_{org}$)

Freeze-dried sediment samples were homogenized and acidified with 1 M HCl to remove carbonates. TOC content was measured using an EA1110 elemental analyzer (Carlo Erba, Italy). Precision was <3% and accuracy was <1.5% for the TOC standard samples.

An additional 200 mg of homogenized, carbonate-free dry sediments were analyzed for carbon stable isotopic signatures ($\delta^{13}C_{org}$) using a DELTA plus AD continuous flow stable isotope ratio mass spectrometer (IRMS, Thermo, Germany). $\delta^{13}C_{org}$ values were calibrated against international standards (Vienna PeeDee Belemnite [VPDB]) (Precision was ±0.2‰), and were reported as:

$$\delta(‰) = [(R_{sample} - R_{standard})/R_{standard}] \times 1000 \quad (1)$$

where R is the ratio ^{13}C:^{12}C.

The contribution of terrestrial source TOC in a sediment core ($\%OC_{terr}$) can be estimated by the following two end-member mixing model formula:

$$\%OC_{terr} = (R_{sam} - R_{mar})/(R_{terr} - R_{mar}) \times 100 \quad (2)$$

where R_{sam} is the measured $\delta^{13}C$ value of a given sample, R_{mar} and R_{terr} are the marine and terrestrial end-member $\delta^{13}C$ values, respectively.

2.4. Determination of the redox sensitive element Mo

Dry sediment samples were analyzed for the redox sensitive element Mo via ICP–MS at the Institute of Geophysical and Geochemical Exploration, CAGS. Standard reference materials (GSD-09 and GSD-10 GBW) and parallel samples were analyzed to monitor analytical precision and accuracy. The relative standard deviation was 0.8% for standard samples, and was 4.1% for duplicate samples.