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Reconstruction of anthropogenic eutrophication in the region off the Changjiang Estuary and central Yellow Sea: From decades to centuries

Zhuo-Yi Zhu*, Ying Wu, Jing Zhang, Jin-Zhou Du, Guo-Sen Zhang

State Key Laboratory of Estuarine and Coastal Research, East China Normal University, No. 3663, Zhongshan Road North, Shanghai 200062, PR China

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ABSTRACT

Anthropogenic activities are known to induce estuarine and coastal eutrophication. However, the eutrophication history over a longer time scale (e.g., over hundreds of years) is often missing, and this perspective is important for an objective assessment of recent-decades anthropogenic activities. To reconstruct eutrophication history in this region, two sediment cores were taken, core E4 in the region off the Changjiang Estuary in the coast of East China Sea, and core E2 in the central Yellow Sea. High sedimentation rate (3.8 cm/yr) of core E4 enabled us to reconstruct a detailed anthropogenic eutrophication history for the past 70 years, while the history at least back to 1855 was further revealed via core E2. Sedimentary nitrogen isotopes ($\delta^{15}N$) in core E4 showed a gradually depleting trend from 5‰ (1930s) to 3.8‰ in the top, which is consistent with the increasing riverine nitrogen flux over the past few decades. A negative relationship was found between total sedimentary Chla (=preserved chlorophyll *a*+its degradation products) and $\delta^{15}N$ ($r^2=0.68$), suggesting the promotion of estuarine productivity by chemical fertilizer-N. Preserved diagnostic pigments ratio (peridinin/fucoxanthin) further suggests that after 1995, the influence of dinoflagellates has been increasing compared to diatoms. At a longer time scale (i.e., core E2), sedimentary $\delta^{15}N$ also decreased from 5.1‰ (before 1855) to 4.4‰ (at top layer). As normalized fossil cyanobacterial pigment (zeaxanthin) showed a decreasing trend from before 1855 to the top of the core, we propose that the decreasing sedimentary $\delta^{15}N$ after 1855 was not due to assimilation of atmospheric nitrogen, but due to excess nutrients input to the central Yellow Sea, which promoted primary production. This is further proved by preserved pheopigments, which continuously increased from 41.7 nmol g OC^{-1} (before 1855) to 251 nmol g OC^{-1} (at top layer) in core E2. Besides revealing the eutrophication history, big history events were also recorded, including the 1998 flood of the Changjiang River (core E4) and the shift of the Yellow River mouth in 1855 (core E2).

1. Introduction

In the past few decades, eutrophication has become a problem worldwide. It causes a series of problems such as blooms and hypoxia in estuaries and the adjacent coastal zone. In spite of studies of the consequences of eutrophication, our understanding of eutrophication history is still often limited. This is, however, important for an objective assessment of the recent decades of anthropogenic activities. Due to the lack of an instrumental record of historical data, identifying biomarkers/proxies of eutrophication in the sediment is a promising technique to help reveal the history of eutrophication (Bianchi et al., 2000).

As bulk parameters, carbon and nitrogen isotopes are reliable tools for reconstructing the paleoproductivity of aquatic systems (Schelske and Hodell, 1991). In a closed aquatic system, phytoplankton preferentially assimilate light carbon ($^{12}CO_2$) and nitrogen ($DI^{14}N$), and the phytoplankton carbon and nitrogen become heavier. When primary production is continuous and occurring at a high rate, nitrogen becomes depleted. Under this conditions, phytoplankton have to access to a heavier nitrogen part. As a result, the sinking organic matter becomes progressively enriched in ^{15}N (Hodell and Schelske, 1998). Raleigh fractionation decides that ^{13}C and ^{15}N fractionation decreasing with increasing CO_2 and nitrogen uptake such that little or no isotopic fractionation occurs under CO_2 or nitrogen-limited conditions (Goericke et al., 1994). Increased or decreased productivity in a closed system should be reflected by an increase or decrease, respectively, in the $\delta^{13}C_{org}$ and $\delta^{15}N$ of organic matter that was produced in surface waters (Hodell and Schelske, 1998). Besides productivity, other factors such as pH, temperature, and growth rate can affect the $\delta^{13}C_{org}$ of phytoplankton (Hinga et al., 1994; Laws et al., 1995). Changes in trophic structure may also influence the $\delta^{15}N$ of organic matter. In an open system, in which allochthonous inputs are important (e.g., estuaries and coasts), carbon and nitrogen

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* Corresponding author. Tel.: +86 2162233890.
E-mail addresses: zyzhu@sklec.ecnu.edu.cn, zhu.zhuoyi@163.com (Z.-Y. Zhu).

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isotopes should be viewed with care, as their isotopes may vary due to the allochthonous sources. This can be especially true for nitrogen, as eutrophication usually results in an increasing output of nitrogen (e.g., chemical fertilizer) into aquatic systems, the isotope of which is at atmospheric N_2 ratios (~0‰).

In addition to carbon and nitrogen isotopes, phytoplankton pigments in the sediment are direct evidence of ecosystem changes in the past in terms of both total phytoplankton biomass and community structure (Bianchi et al., 2002; Fulton et al., 2012; Furlong and Carpenter, 1988). However, care must be taken when using sedimentary pigments as historical indicators of phytoplankton, as degradation of pigments occurs both in the water column and sediment (Chen et al., 2001; Leavitt, 1993 and references therein). In the sediment, factors that favor preservation of pigments quality and concentrations include high productivity, a reducing environment, and elevated sedimentation rate (Chen et al., 2005), whereas disturbance (e.g., bioturbation and/or resuspension) of the sediment can change the redox conditions, or even resuspend the deposited pigments back into the water column (Hong et al., 2002). The micro-environment of the compounds is also important for its apparent stability (e.g., encapsulation effect, Ogawa and Tanoue, 2003). With respect for pigments, if the chloroplast membrane wrapped the pigments up during algae cell senescence, apparent stability of the pigments is then expected to be high due to the protection from the membrane outside. Although direct evidence is lacking, chlorophylls (and pheopigments) have been found to be composed of both labile and refractory parts in some studies (Stephens et al., 1997).

The Changjiang (Yangtze River) is among the largest rivers worldwide (Milliman and Meade, 1983). China followed an open policy to develop its economy after the late 1970s, and agriculture and industry were developed rapidly. With the rapid development of the economy, the Changjiang River has been affected by strong anthropogenic activities (e.g., damming, fertilizer uses) and is experiencing eutrophication (Zhang et al., 1999). This is very clear for the past few decades. Not only did the application of fertilizer-N increase 106%, but the fertilizer-use efficiency decreased 36% (Bao et al., 2006). As a consequence, the annual nitrogen flux at the Datong Station (one of the hydrographic monitoring stations in the Changjiang) changed from 100×10^6 kg in 1968 to 300×10^6 kg in 1978, and then exceeded 1200×10^6 kg in 1997 (Yan and Zhang, 2003). Accordingly, algal blooms in the estuary increased greatly after the 1980s (Ye et al., 2004), and there is an increase in bottom hypoxia in recent decades (Zhu et al., 2011). Tang et al. (2006) also reported a potential trend of a shift from diatom blooms to dinoflagellates blooms in the estuary and adjacent coastal zone. Besides eutrophication, the big flood in 1998 is another important historical event for the Changjiang River. Another large flood also affected the Yellow River, the second largest river in China. The historical flood in 1855 caused the shift of the mouth of the Yellow River. Today, the Yellow River enters into the Bohai, whereas it previously entered into the Yellow Sea (YS) before 1855 (Fig. 1). Due to the slow exchange between the Bohai and the YS, the impact of the Yellow River to the central YS was greatly reduced after 1855.

Li et al. (2011) studied the eutrophication history of the region off the Changjiang Estuary over the past few decades using preserved pigments. Fucoxanthin and zeaxanthin are diagnostic pigments for diatoms and cyanobacteria respectively, and their data suggested an increase of diatoms and cyanobacteria abundance after 1979, attributed to anthropogenic activities. Although the variation of phytoplankton abundance over the past few decades are now well described by Li et al. (2011), a more detailed annual reconstruction is missing. More importantly, the eutrophication history over longer time scale (e.g., hundreds of years) remains unclear. This is important for a longer perspective and an objective assessment of the recent decades of anthropogenic activities.

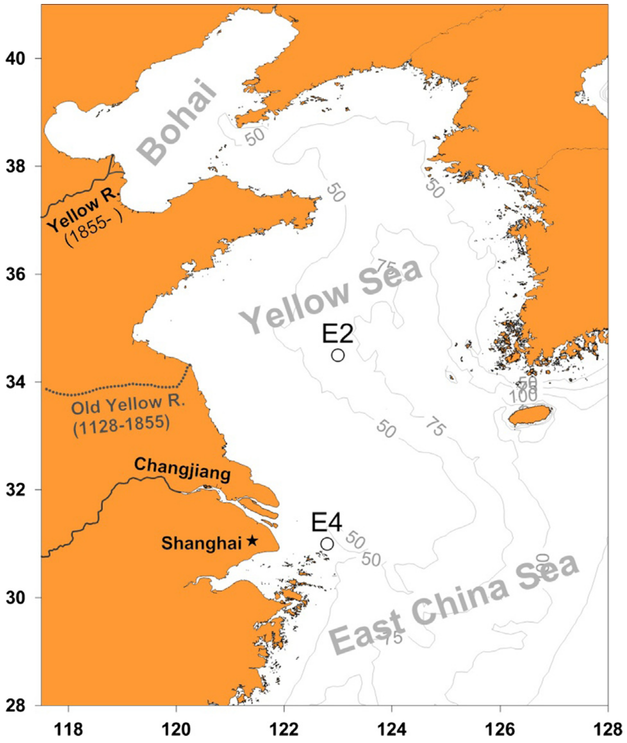

Fig. 1. Study area and sampling stations (core E2 and core E4).

In the present work, two sediment cores were taken from region off the Changjiang Estuary and the central YS, respectively. The YS and the Changjiang Estuary are closely adjacent (i.e., open connected) and topographically there is not barrier between the estuarine region and the YS (Fig. 1). These two regions are both under East Asian monsoon climate and they are both under strong north wind in winter whereas in summer the south wind prevails. Also, the Changjiang diluted water can greatly affect the YS in summer (Lie et al., 2003), which often flows northeast wards in the surface. On the other aspect, Subei Coastal current flows southwards from the Yellow Sea to the Changjiang estuary (Su, 1998). So the Changjiang Estuary and the YS are coupled and interacting in both materials and energy (Su, 1998), making these two system comparable. The difference is that central YS is less influenced by terrestrial impact, whereas the terrestrial impact should be greatly considered in the Changjiang Estuary. Therefore, the Changjiang Estuary can be considered as a region under typical anthropogenic activities impact, whereas the central YS provides us background trend information.

Because of the high sedimentation rate (on the order of cm/year), we are able to present a more detailed description of preserved sedimentary pigments than previous work in the Changjiang Estuary. With the detailed profiles, an exponential decay model was applied to chlorophyll concentration. After apply the effect of the early diagenesis, anthropogenic activities over the past few decades was evaluated in the context of the former study. Further, based on the core from the YS, the eutrophication background is addressed over a longer time scale of over hundreds of years.

2. Materials and methods

2.1. *Sediment cores sampling*

Two sediment cores, E2 (143 cm length; water depth: 77 m; 122.8°E, 31°N) and E4 (270 cm length; water depth: 22 m; 123°E, 34.5°N), were collected by gravity corer with minimal disturbance