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Spatial distributions of $\delta^{13}C$, $\delta^{15}N$ and C/N ratios in suspended particulate organic matter of a bay under serious anthropogenic influences: Daya Bay, China

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ABSTRACT

Stable isotopic signatures ($\delta^{13}C$ and $\delta^{15}N$) and C/N ratios of suspended particulate organic matter (POM) were investigated from the surface water of Daya Bay during summer and winter of 2015. The relatively high $\delta^{13}C_{POM}$ values suggested the input of ^{13}C-depleted terrigenous organic matter was low in Daya Bay. There were significant correlations between $\delta^{13}C_{POM}$ values and chlorophyll *a* concentrations both during summer and winter, suggesting the $\delta^{13}C_{POM}$ values were mainly controlled by the phytoplankton biomass in the surface water. The distribution of $\delta^{15}N_{POM}$ values was more complicated than that of $\delta^{13}C_{POM}$ and displayed low values in the outer bay and the Dan'ao River estuary. ^{15}N-depleted ammonia originating from industrial wastewater might have strongly influenced the water quality and stable isotopic signatures of POM near the Dan'ao River estuary. The $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$ values strongly reflect the influences of anthropogenic activity and eutrophication in Daya Bay.

1. Introduction

Eutrophication and environmental pollution have caused serious problems in estuarine and coastal waters worldwide (Lotze et al., 2006). Suspended particulate organic matter (POM) found in coastal waters consists of a complex mixture of organic compounds originating from marine and terrigenous sources and is sensitive to human activity and eutrophication (Tesi et al., 2007; Harmelin-Vivien et al., 2008). Anthropogenic activity significantly influences the POM distribution, especially in the bay areas and estuarine zones (Gao et al., 2012). Many studies have focused on the POM content because it provides much information on material sources, energy transport pathways and anthropogenic disturbances in aquatic ecosystems (Sato et al., 2006; Zhang et al., 2014).

Stable carbon and nitrogen isotopes ($\delta^{13}C$ and $\delta^{15}N$), and C/N ratios are widely used to distinguish the source of organic matter and the influence of anthropogenic activity in an aquatic environment (Zhang et al., 2007; Gao et al., 2012; Kanaya et al., 2013). Because terrigenous and marine primary producers use different photosynthetic pathways, terrigenous and marine organic matter present different carbon and nitrogen isotopic ratios (Peterson and Fry, 1987). Terrigenous organic matter generally exhibits more depleted $\delta^{13}C$ values (generally < −28‰) relative to marine organic matter (~ −22‰) (Cifuentes and Eldridge, 1998; Harmelin-Vivien et al., 2008; Ramaswamy et al., 2008). The organic matter $\delta^{13}C$ values usually increase from the internal part to the seaward side of an estuary, suggesting an increasing contribution of marine photosynthetic organic matter towards the seaward side (Gireeshkumar et al., 2013; Zhang et al., 2014). Furthermore, the $\delta^{13}C_{POM}$ values of eutrophic waters are commonly elevated and can increase significantly during periods of algal blooms (Nakatsuka et al., 1992; Canuel and Cloern, 1995; Savoye et al., 2003). The $\delta^{15}N$ values are more sensitive relative to $\delta^{13}C$ to environmental pollution and variations in biogeochemical processing in POM. The N isotopes are commonly used to track anthropogenic nitrogen in estuarine food webs and detect the causes of eutrophication (McClelland et al., 1997; Constanzo et al., 2001). The $\delta^{15}N$ values vary significantly in different contaminants, ranging from −2‰ to 4‰ in nitrogen from artificial fertilizers and from 10‰ to 20‰ in human and animal excreta (Ruiz-Fernandez et al., 2002; Cole et al., 2004). Organic matter derived from sewage usually has higher $\delta^{15}N$ values, and the $\delta^{15}N_{POM}$ content is an indicator of anthropogenic pollution (Fogg et al., 1998; Constanzo et al., 2001; Cole et al., 2004). Several studies suggested anthropogenic activity exerts a significant influence on spatial variations in $\delta^{13}C$ and $\delta^{15}N$ signatures of eutrophic coastal waters relative to that of natural processes (Sato et al., 2006; Gao et al., 2012). In general, the $\delta^{13}C$ signatures and C/N ratios of POM are used to assess the source of organic matter in an ecosystem, whereas the $\delta^{15}N$ signatures are used to evaluate the anthropogenic discharge and trophic structure of aquatic organisms.

Daya Bay is one of the largest and most important bays along the coast of southern China. The region recently underwent massive

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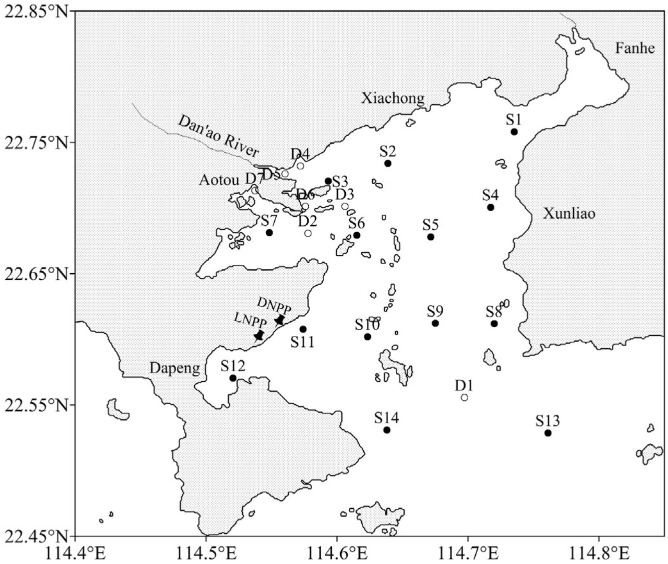

Fig. 1. Location of sampling stations in Daya Bay. Stations S1–S14 were sampled during the summer and winter cruises, whereas the D1–D7 stations were only sampled during the winter cruise. LNPP and DNPP represent “Daya Bay nuclear power plant” and “Ling'ao nuclear power plant”, respectively.

economic growth and urban development around Daya Bay and human activity accompanied by the discharge of anthropogenic nutrients have substantially modified the bay's ecosystem (Wang et al., 2008; Wu et al., 2009). The water quality in Daya Bay was good in the 1980's with low nutrient concentrations and a high biodiversity and productivity (Xu, 1989; Qing et al., 1996). During the few decades, the water quality degraded, especially in the west and north coastal areas of the bay (Qiu, 2001; Wang et al., 2008). Long term data reveal Daya Bay did undergo a shift from oligotrophic to mesotrophic status from the 1980's to recent years (Wang et al., 2008). The bay's ecological environment has been extensively studied, including the nutrient status (Qiu, 2001; Wu et al., 2009), red tides (Li et al., 1993; Song et al., 2009), plankton community (Wang et al., 2006; Ma et al., 2014), food web structure (Chen et al., 2015), persistent organic pollutants (Zhou et al., 2001; Yan et al., 2009), and level of trace metals (Yu et al., 2010). The impact and source of anthropogenic nutrients on ecosystems are a major environmental concern in coastal regions. The POM stable isotopic signatures and C/N elemental ratios can precisely reflect the environmental variations in aquatic ecosystems. However, carbon and nitrogen stable isotopic data are scarce for Daya Bay and there is no study concerning the distribution of $\delta^{13}C$ and $\delta^{15}N$ in POM.

Thus, the $\delta^{13}C$, $\delta^{15}N$ and C/N ratio in POM were investigated from the surface waters of Daya Bay during summer and winter. The isotopic correlations with environmental factors and eutrophic status were also discussed. We hope the findings of this study will contribute to a better understanding of the environmental change in Daya Bay under anthropogenic influences.

2. Materials and methods

Daya Bay is a subtropical drowned valley bay covering an area of 600 km^2 in South China. The bay water depth ranges from 6 to 16 m with the western part being deeper than the eastern part (Xu, 1989). Seasonal variations are obvious. The minimal sea surface temperature occurs during winter (averaging 17.3 °C) and the maximum occurs in summer (averaging 29.3 °C). Daya Bay contains diverse ecological habitats, including coral communities, mangroves, rock reefs, sandy shores and mudflats (Wang et al., 2008). Two nuclear power plants (NPP), Daya Bay NPP and Ling'ao NPP, are situated on the western coast of Daya Bay and came into operation in 1994 and 2002, respectively. No large river discharges into the bay, however, there are more than ten seasonal streams flowing into the bay from a short distance along the coast (Han, 1995). The river discharges exert a small influence on the Daya Bay water, and most of the water originates from the South China Sea. Fish, shrimp and shellfish aquaculture are well developed, with cage culture industry widespread in the inner waters. The

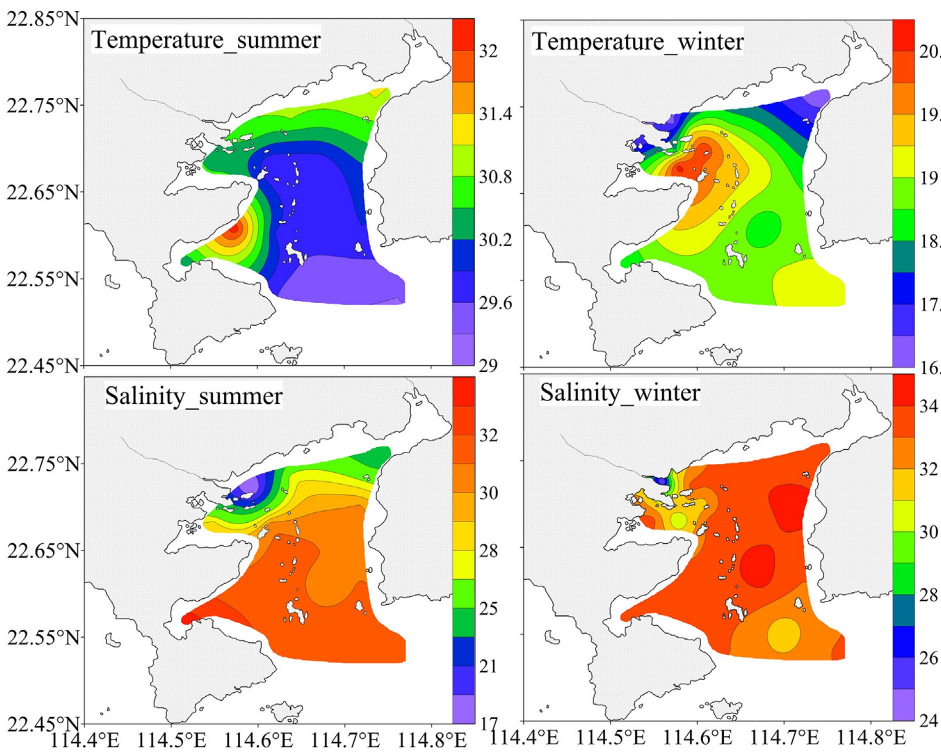

Fig. 2. Distribution of temperature and salinity in the surface waters of Daya Bay.