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Baseline

The porewater nutrient and heavy metal characteristics in sediment cores and their benthic fluxes in Daya Bay, South China

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ABSTRACT

Nutrient and heavy metal (Fe, Mn, Ni, Cu, Pb, Zn, Cr, Cd and As) concentrations in porewater in sediment cores and their diffusive benthic fluxes were investigated in Daya Bay, South China, to study the accumulation and transfer of nutrients/metals at the sediment-water interface, and to discuss the impact of human activities on nutrients/metals. Nutrients and heavy metals displayed different profiles in porewater, which was mainly attributed to the distinct biogeochemical conditions in sediments. Total mean fluxes of nutrients (except NO_3 and NO_2) and metals in study area were positive, indicating nutrients and metals diffused from the sediment to overlying water, and sediment was generally the source of nutrients/metals. Human activities and the weak hydrodynamic force made nutrients/metals accumulate in sediment, so the sediment should be paid more attention to as the endogenesis of contamination in Daya Bay waters.

Estuarine and coastal bays, which are regions of active land-ocean interaction, respond sensitively to natural processes and anthropogenic activities. In recent decades, economic development and the increase in population poured plenty of pollutants such as nutrients and heavy metals into these areas (Li et al., 2013; Wetzel et al., 2013). These pollutants entered both from catchments and also from the adjacent lands and urban areas, and ultimately most of them deposited in the sediments. Sediment is a large reservoir of pollutants and plays an essential environmental role due to its capacity to store or release pollutants from or to the water column (Ip et al., 2007; Wang et al., 2016). For example, in many marine systems, the release from sediments was an important source of nutrients (Berelson et al., 1998). The element characteristics in porewater reflect the material geochemical cycling in sediments, and porewater is also the vital medium connecting the sediment and the overlying water. When the dissolved pollutants in sediments move from porewater to overlying water, they significantly influence the material cycling in overlying water through the diffusion and further transformation occurred at the sediment-water interface (Santos-Echeandia et al., 2009; Zhang et al., 2013; Kalnejais et al., 2015). So sediment-water interface plays a vital role in the cycling, transfer and preservation of materials in ecosystem, and the fluxes of nutrients/metals at the surface-water interface are not only influenced by the nutrient/metal concentration gradient between overlying water and porewater, but the content and composition of organic matter, bottom water oxygen concentration and penetration depth, activities of benthic organisms and bacteria etc. (Vopel et al., 2012; Kaiser et al., 2013). In this sense, the estimation of fluxes of pollutants across the sediment-water interface is significant to assess the biogeochemical cycling of materials, sedimentary environment and the quality of ecosystem.

Daya Bay, a subtropical drowned valley bay with an area of about 700 km^2, composed of a series of sub-basins, is situated in the northern part of the South China Sea (Fig. 1). No major rivers discharge into Daya Bay, and most of the water there originates from the South China Sea. Since the 1980s, marine aquaculture industry and petroleum chemical industry have been rapidly developed in Daya Bay, with the construction of two nuclear power plants and the simultaneous development of tourism and urbanization. These anthropogenic activities have had a significant impact on the aquatic environment of Daya Bay, especially on the west and north parts of the bay (Song et al., 2009; Qiu, 2015; Gu et al., 2016). The main objectives of this study were (1) to investigate the concentrations and distribution of nutrients and heavy metals (Fe, Mn, Ni, Cu, Pb, Zn, Cr, Cd and As) mainly in sediment porewater; (2) to assess the nutrient and heavy metal diffusive benthic

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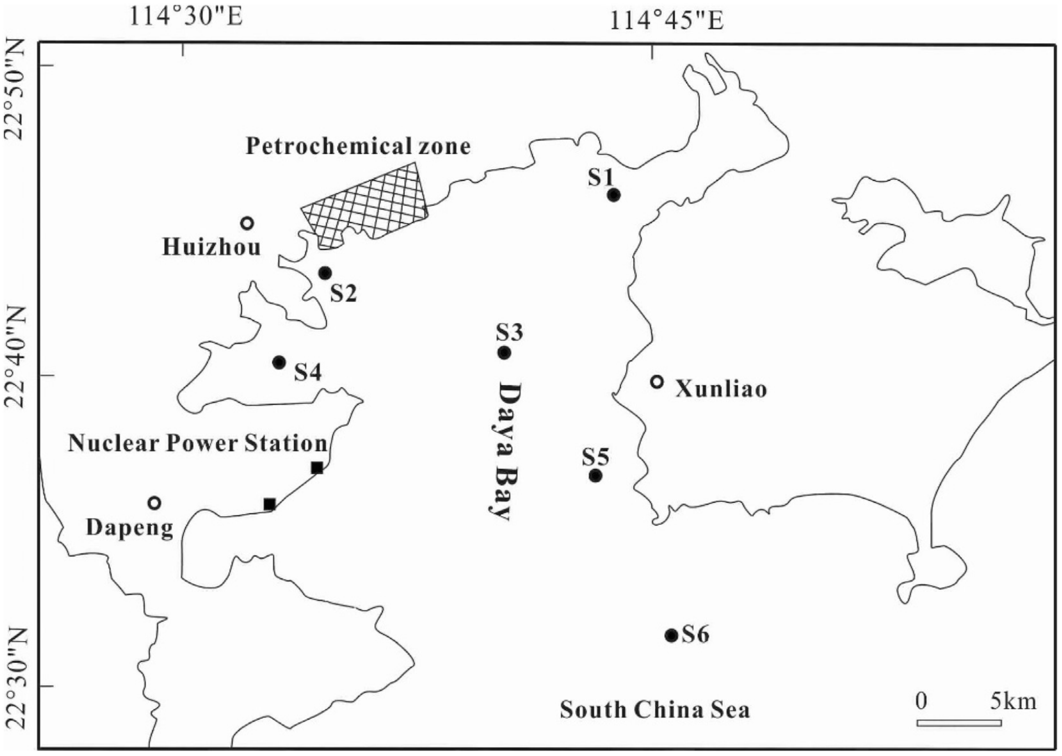

Fig. 1. Map showing the study area and the sampling sites in Daya Bay.

fluxes; (3) to discuss the influence of human activities on the transport and accumulation of nutrients and heavy metals, and to provide significant dataset for sustainable development of marine ecosystems in Daya Bay.

In this paper, six sediment cores (S1–S6) were sampled in August 2015 using a gravity sampler. The overlying water was siphoned off and then the sediment cores were sliced at 1 cm interval. We selected the subsamples densely at the upper layers but sparsely at the lower layers, then the subsamples were centrifuged to separate the porewater. The porewater and overlying water were filtered immediately through 0.7 μm pore glass fiber filter (GF/F, Whatman). The filters used for metal analyses were soaked in 20% HNO_3 for 24 h, then were washed 3 times with ultrapure water to remove the adsorbed heavy metals. The filtrate for metal analyses was acidified to $pH < 2.0$ by MERCK extra pure HNO_3 and then was kept under 4 °C till analyses. The filters for nutrient and dissolved organic carbon analyses were burned at 450 °C for 1 h, and the filtrate was frozen under − 20 °C until analyses.

Concentrations of NO_3, NO_2, NH_4, SiO_3 and PO_4 were determined ultraviolet-visible spectro-photometrically according to the methods described by Grasshoff et al. (1983). The precisions of duplications for NO_3, NO_2, NH_4, SiO_3 and PO_4 were 3%, 1%, 1%, 4% and 4%, respectively. The concentrations of As, Cu, Pb, Zn, Cr, Cd, Ni, Fe and Mn were determined using ICP-MS. The limit of detection was 0.001–0.02 μg/L (0.001 μg/L for Cd, 0.02 μg/L for Zn, and 0.01 μg/L for the rest metals). The recovery of elements was 85–115%. In additional, pH values of overlying water were determined with a pH meter and dissolved oxygen concentrations were determined using the Winkler titration method according to Gao and Song (2008) just after sampling. Dissolved organic carbon concentrations in overlying water were measured with a liquiTOC II analyzer.

The nutrient and metal diffusive fluxes were estimated by the gradients in the porewater profiles according to Fick's 1st law (Berner, 1980) and calculated by the following equation,

$$F_d = \Phi D_s (\partial C/\partial Z)_{Z=0} \tag{1}$$

where C was the concentration of nutrient/metal, and Z was the sediment sampling depth from the sediment-seawater interface. F_d was the nutrient/metal flux, and Φ was the water content (porosity) in surface sediment samples determined by weight difference after baking in an oven at 105 °C for 24 h. D_s was the whole sediment diffusive coefficient expressed by Krom and Berner (1980) as,

$$D_s = \Phi D_0 (\Phi \le 0.7) \text{ or } D_s = \Phi^2 D_0 (\Phi > 0.7) \tag{2}$$

Φ values ranged between 0.48 and 0.60 (according to the data analyzed in this study), so we used the equation $D_s = \Phi\ D_0$ in this paper.

Where D_0 was the diffusive coefficient in infinite dilution, the values for NO_2, NO_3, NH_4, PO_4 and SiO_3 were 19.8, 19.1, 19.0, 10.0 and 7.34 ($\times 10^{-6}$ cm^2/s), and the values for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were 7.17, 5.49, 7.33, 7.19, 6.88, 6.79, 9.45 and 7.15 ($\times 10^{-6}$ cm^2/s) at 25 °C. Therein, 25 °C represented the bottom water temperature in summer.

Cluster analyses (CA) were used to the samples and the sampling sites based on the heavy metal concentrations to discover the metal accumulation patterns in porewater, and also to observe the correlations between sites. For example, metals clustered into one group mean they probably share similar pollution sources, or analogous transformation/migration processes in the certain circumstances. Additionally, Pearson correlation analyses were applied to overlying water data in order to explore the correlations between the chemical parameters and nutrient/metal levels.

Nutrient concentrations in overlying water and porewater were plotted in Fig. 2. NH_4, NO_2 and NO_3 concentrations in overlying water were 15.70 ± 8.11, 1.03 ± 0.41 and 4.87 ± 3.25 μmol/L, respectively. Concentrations of DIN ($NH_4 + NO_2 + NO_3$) in overlying water showed obvious variations between sites, with the highest value occurred at S6 and the lowest value at S5. The proportions of NH_4, NO_2 and NO_3 in DIN were 72 ± 14%, 5 ± 2% and 23 ± 12%, respectively, and NH_4 was dominant in DIN in overlying water, indicating a reductive environment in the bottom water in Daya Bay, with the general dissolved oxygen concentrations of 5.21–5.72 mg/L at S1–S6. Concentrations of PO_4 and SiO_3 in overlying water were 1.00 ± 0.44