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Pore water nutrient characteristics and the fluxes across the sediment in the Pearl River estuary and adjacent waters, China

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A B S T R A C T

Spatio-temporal distribution of pore water nutrients and the fluxes at the sediment-water interface (SWI) were investigated to probe into the geochemical behavior of nutrients associated with early diagenesis of organic matter (OM), and to study the accumulation and transformation processes of nutrients at the SWI, as well as to discuss the impact of riverine inputs on nutrients in the Pearl River estuary (PRE) and adjacent offshore areas. Nutrient concentrations decreased from the upper to the lower reaches of the estuary, suggesting that there was a high input of anthropogenic nutrients and the estuary was acting as a nutrient sink. Dissolved inorganic nitrogen (DIN: the sum of NH_4–N, NO_3–N and NO_2–N) concentrations in the water column and the pore water were higher in the estuary than at offshore areas due to the riverine discharge and the high accumulation rate in the estuary. NO_3–N concentration was the highest of the three forms of DIN in the overlying water and showed a sharp decrease from the surficial sediment with increasing sediment depth, indicating that there was strong denitrification at the SWI. NH_4–N, mainly deriving from the anaerobic degradation of OM, was the main form of DIN in the pore water and increased with depth. Negative NO_3–N fluxes (into the sediment) and positive NH_4–N fluxes (from the sediment) were commonly observed from incubation experiments, indicating the denitrification occurred at the SWI. DIN flux suggested that the sediment was a sink of DIN in spring, however, the sediment was the source of DIN in summer and winter. Nutrients dominantly diffused out of the sediment, suggesting that the sediment was the source of nutrients in spring at adjacent offshore areas. The fluxes directed that PO_4–P mainly diffused into the sediment while SiO_4–Si mainly diffused out of the sediment.

1. Introduction

Coastal and estuarine areas are characterized by high accumulation rates and high productivities in the surface waters. These areas are sinks for organic matter (OM) and nutrients entering both from their catchments and also from the adjacent lands and urban areas, and in turn they are sources of such materials to the adjacent coast (Kennish and Fertig, 2012). Sediment is a large reservoir of nutrients and plays an essential environmental role due to its capacity to store or release different compounds from or to the water column (Southwell et al., 2010, 2011). OM produced by phytoplankton from inorganic nutrients in the euphotic zone through photosynthesis sinks to the sediment. Most of OM decomposes and the remaining material is buried in the sediment, which is called OM diagenesis controlled by physical, chemical and biological processes and it significantly affects the element cycling (Reed et al., 2011). OM degradation is the main driver to the early diagenesis, together with OM remineralization in the sediment, to release inorganic nutrients to the pore water, and then the inorganic nutrients can flux into the overlying water and return to the euphotic zone. The regeneration of dissolved inorganic nitrogen

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(DIN), PO_4 and SiO_4 in sediment is significant to the nutrients equilibrium mechanisms and to sustaining the primary production in water, so it is very important in the global biogeochemical cycle (Glé et al., 2008; Llebot et al., 2010).

This study focused on the Pearl River estuary (PRE), which is located between Guangdong Province and Hong Kong being an important region for waterborne commerce in southern China. The Pearl River delta is the region of the fastest development in China. With the rapid development of economy and urbanization in recent years, the Pearl River delta region has experienced increasing human influences and a growing pressure on the local environment. Increasing amounts of wastewater and other pollutants have discharged into the PRE without proper treatment, which has had a significant impact on the aquatic environment. It was reported that the Pearl River carried on average an amount of 35×10^{10} m^3 yr^{-1} of freshwater and a sediment load of 8.5×10^7 tons yr^{-1} into the South China Sea (Yin et al., 2001). Dramatic increases of the delivery of the river-borne nutrients and changes in nutrient ratios have known to result in eutrophication and unusual phytoplankton blooms (Yin et al., 2011; Shen et al., 2012). The nutrient fluxes at the surface–water interface (SWI) were not only influenced by the nutrient concentration gradient between the overlying water and the pore water, but the content and composition of OM, the percentage fines, bottom water oxygen concentration and penetration depth, activity of benthic organisms and bacteria etc. (Vopel et al., 2012; Kaiser et al., 2013). Studies of pore water nutrient distribution/exchange and the fluxes at the SWI significantly help to probe into the transfer and transformation of nutrients in this estuarine environment with complex chemical, biological and physical conditions, which will provide an important reference for the environmental research in this area and others. However, there was still limited information about the early diagenesis of OM and nutrient cycling in this complex and important subtropical estuary system. The main objectives of this study were (1) to investigate the temporal and spatial distributions of nutrients in sediment pore water, (2) to discuss the influences of riverine inputs and early diagenesis on nutrient materials, (3) to assess the nutrient fluxes at the SWI and to discuss the nutrient accumulation and transport.

2. Materials and methods

2.1. Study area description

The PRE is located in southern Guangdong Province of China (represented mainly by the Lingdingyang subestuary), created by the inflows of freshwater from the Pearl River to the South China Sea through four major discharge outlets named Humen, Jiaomen, Hongqimen and Hengmen (Fig. 1). The PRE is a north-south bell-shaped area, with the distance from north to south averaging about 49 km, and from east to west varying from 4 to 58 km. The Lingdingyang subestuary was severely affected by tides and runoff, where the current and material transport varied temporally and spatially. The sampling stations in the PRE (Sites 1–6) were within the sub-tidal zone with strong freshwater and marine water interactions (Pan et al., 2002), and the estuarine plume of the freshwater-seawater mixture flowed along the west part of the estuary due to the Coriolis effect deflection. Sites 7 and 8 were located at the adjacent offshore areas beyond the PRE. Site 7 was to the south of the bay and influenced to some extent by the Pearl River plume, while Site 8 was almost free of the impact of the river discharge.

2.2. Sampling and analysis

The sediment cores at Sites 1–6 were collected in three seasons (spring, summer and winter) while Sites 7 and 8 were only sampled in spring 2003. Samples were collected using a multiple corer with the plastic core tubes being 10 cm in diameter and 61 cm in height, and the length of sampled sediment core was 25–48 cm with a volume of overlying water. The overlying water was siphoned off and then the sediment cores were sliced at 1 cm intervals in a nitrogen-filled glove bag. The sediments were centrifuged to separate the pore water on board and then filtered (0.45 μm acetate fiber membrane) and immediately frozen (−20 °C) under the protection of $HgCl_2$ until analysis. Concentrations of NH_4–N, NO_3–N, NO_2–N, PO_4–P and SiO_4–Si in water were determined spectrophotometrically with a Skalar Nutrient Analyzer according to the methods described by Grasshoff et al. (1983). In detail, nitrate was analyzed by the copper-cadmium reduction method, nitrite using the diazo-azo method and NH_4–N using the sodium hypobromite oxidation method. SiO_4–Si was analyzed by the silico-molybdenum yellow method and PO_4–P by the molybdenum blue method. The precisions of duplication for NH_4–N, NO_3–N, NO_2–N, PO_4–P and SiO_4–Si were 3.2%, 1.4%, 2.5%, 2.2% and 1.4% respectively.

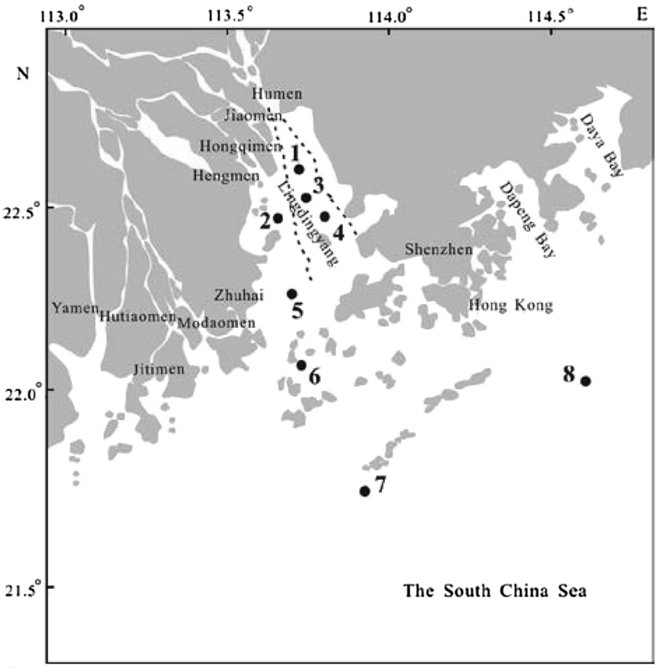

Fig. 1. Map showing the location of the Pearl River estuary (PRE) and the sampling sites of sediment cores.

2.3. Nutrient diffusive fluxes

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

$$F_d = \Phi D_s (\partial C/\partial Z)_{Z=0} \quad \left(\text{mmol m}^{-2}\text{d}^{-1}\right) \tag{1}$$

Where F_d was the nutrient flux, and Φ was the water content (porosity) in surface sediment samples determined by weight differences 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, so we used the equation $D_s = \Phi D_0$ in this study.Where D_0 was the diffusive coefficient in