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Contamination trends of trace metals and coupling with algal productivity in sediment cores in Pearl River Delta, South China

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HIGHLIGHTS

- Sediment cores were collected from reservoir sediments of the Pearl River Delta.
- Cu, Zn, Ag, Cd, and As were significantly accumulated during last three decades.
- Heavy metals were strongly associated with algal organic matter in the sediments.
- Principal component analysis was used to assess the enrichment of heavy metals.
- Sedimentary process of heavy metals was affected by primary productivity.

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ABSTRACT

Several sediment cores from the Pearl River Delta were collected to investigate the relationship of trace metal contamination with algae-derived organic matter in the last 50 years. Trace metals were analyzed with ICP-MS, and algal organic matter (AOM) was measured with Rock-Eval pyrolysis. It was found that Cu, Zn, Ag, Cd, and As were elevated in the last three decades from three reservoirs, while all of the target metals showed no significant enrichment in estuarine sediment cores. Cu, Cr, Co, Cd, Zn, Ag, Ni, As, and Mn normalized to Ti were strongly associated with AOM in the sediments of eutrophic reservoirs, suggesting that AOM played an important role in controlling the accumulation of trace metals. Principal component analysis (PCA) and enrichment factor (EF) were also used to assess the enrichment of trace metals. The above result indicated that the sedimentary process of As, Cd, Cu, Zn, Ni, Cr, Co, Ag, and Mn was significantly affected or/and controlled by primary productivity in eutrophic, non-point polluted reservoirs.

1. Introduction

Heavy metals in fast industrialization areas are one of the environmental problems. When they enter the aquatic system, they are mainly bound to particulate matter and eventually settled into sediments. Numerous investigators have investigated the contamination of heavy metals in the aquatic ecosystem (Fernandes, 1997; Vicente-Martorell et al., 2009).

During the recent years, significant impacts of natural organic matter (NOM) on distribution of mercury in sediments have been observed (Kainz et al., 2003; Kainz and Lucotte, 2006). Algal organic matter (AOM) as a biological pump effect in Arctic and sub-Arctic lakes may significantly affect the concentrations of mercury in sediments during the past decades (Sanei and Goodarzi, 2006; Outridge et al., 2007; Carrie et al., 2009; Stern et al., 2009). Although one investigation (Kirk et al., 2011) on fourteen Canadian Arctic and sub Arctic lakes suggested that phytoplankton was not an important factor in controlling mercury concentrations of sediments, recent studies on some Chinese lakes indicated important impacts of AOM not only on activity of ^{210}Pb but also on contents of polycyclic aromatic hydrocarbons in sediments (Xu et al., 2011; Wu et al., 2012). Therefore, the accumulation mechanism of contaminants by AOM in sediments and its affecting factors need further investigations.

Pearl River Delta (PRD) covers an area of 461,000 km^2 with subtropical monsoon climate and has become one of the most developed regions in China in recent years (Wong et al., 2003). Nonpoint source pollution of heavy metals in the PRD has not been well investigated, especially in suburb and rural aquatic environments. Reservoirs in these areas, which are mainly fed by the precipitation, are suitable to the investigation on non-point source pollution of heavy metals. Atmospheric deposition is the major pathway of heavy metals in this aquatic system. Moreover, the

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accumulation and deposition of heavy metals in different trophic aquatic systems may experience different processes (Sanei and Goodarzi, 2006). Therefore, it is essential to assess their contamination levels and biogeochemical cycling.

This study investigated the accumulation of heavy metals during sedimentary process in a period of 50 years in subtropical reservoirs far from industrial centers. Deposition history of heavy metals was analyzed by using ^{210}Pb and ^{137}Cs radiometric dating. The relationship between heavy metals and algae-derived organic matter was also studied. Other processes such as physical and biological disturbation, sedimentation mechanism, hydrologic effect, diagenesis and remobilization were also taken into consideration. This study would help to assess the actual anthropogenic impacts and to improve the environmental management and abatement policy in the PRD.

2. Methodology

2.1. Study areas

Three reservoirs (Zengtang, Lian'an, and Xingfengjiang) in the PRD were chosen to collect the sediment cores. Some basic properties of these three reservoirs are shown in Table S1 in Supporting data.

Zengtang reservoir (ZT) (23.22°N, 113.76°W) is a shallow, meso-eutrophic lake located in the east of Zengcheng city, and covers a surface area of 2.53 km^2 with a catchment area of 34.4 km^2. It has a mean depth of 2.5 m and maximum depth of 5 m. It is about 35 km away from the southern industrial center in Guangzhou. It is mainly fed by rainfall and heavily influenced by the atmospheric input. ZT reservoir had been an oligo-mesotropic lake before 2003, and then has been becoming an eutrophication lake due to increasing nitrogen and phosphorus by fry misuse (Liu et al., 2011).

Lian'an reservoir (LA) (23.4°N, 113.66°W) covers a catchment area of 43 km^2 and is the largest drinking-water reservoir in Zengcheng city. It is situated in the northwest of ZT reservoir and is far away from the southern industrial center in Guangzhou. A dam was constructed in 1960, which raised the water level to its maximum depth of 60 m. According to the aquatic data we collected, this reservoir can be classified as a mesotrophic lake and is mainly fed by precipitation.

Xinfengjiang reservoir (XFJ) (23.77°N, 114.57°W) is the largest reservoir in Guangdong province, which covers a surface area of 370 km^2 and a catchment area of 5730 km^2. It has supplied drinkable water to several cities since the construction in 1958. The average depth of XFJ is 28.7 m and the maximum depth is more than 93 m. In order to prevent the water pollution, industry activity is prohibited. Especially after 1990, a lot of efforts were taken for the management and protection of this valuable reservoir. Therefore, the reservoir maintains low nutrient level and low aquatic biomass, and has been classified as an oligotrophic lake by many investigators (Lin et al., 2003). XFJ reservoir is 200 km away from the southern industrial center. PRE and its upstream river network form the largest river system in South China. This river network covers a watershed area of more than 8000 km^2. Pearl River Estuary (PRE) is a bell-shaped area, with the distance from north to south averaging about 49 km, and from east to west varying from 4 km to 58 km. The southern part of PRE is far away from the southern industrial center and is not affected by point source contaminants. Two sediment cores in PRE were collected. All the five sampling sites were shown in Fig. 1.

2.2. Sample collection

In 2010 and 2011, undisturbed sediment cores were collected from three reservoirs and the southern PRE using a 6 cm diameter gravity corer with a Plexiglass liner. The water depths for the sampling sites at ZT, LA and XFJ reservoir are 1 m, 17 m, and 36 m, and those at estuarine No. 1 and No. 2 are 17 and 20 m, respectively. The core liners were cleaned before each sampling with native water. The sediments were collected in the center of the three reservoirs. The sediment cores were sliced at 2 cm thick intervals with

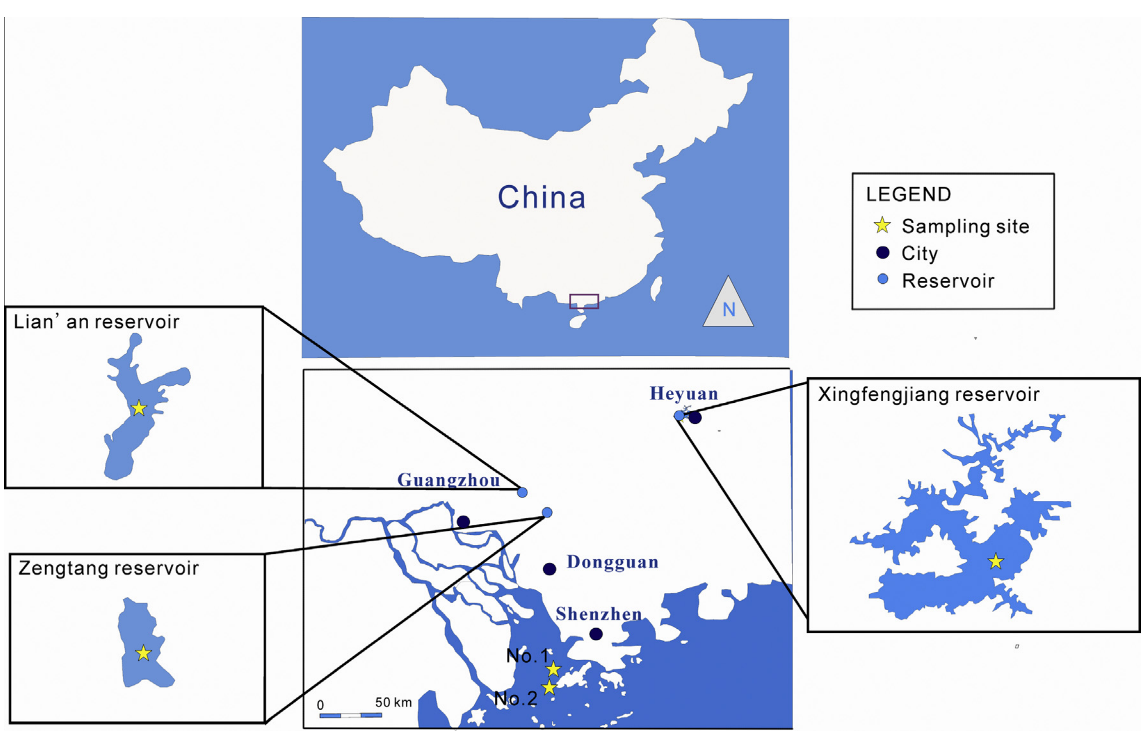

Fig. 1. The location of sampling sites in Pearl River Delta and Estuary.