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Sedimentary records of metal speciation in the Yangtze Estuary: Role of hydrological events

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HIGHLIGHTS

- Chronological records of metal deposition at different estuarine sites were studied.
- Sedimentary metal speciation reveal responses to upstream hydrological events.
- The transformation of metal speciation can explain the intercepting role of dams.
- Sediment particles and organic carbon are the proxies for the metals deposition.

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ABSTRACT

Chemical speciation of Al, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb and Zn in two typical ^{210}Pb-dated sediment cores (i.e., the CJ03 site and CJ06 site) in the Yangtze Estuary was investigated to reveal their different responses to upstream hydrological events. Cluster analysis and correlation analysis (CA) demonstrated that the CJ03 site, which is located in the main river channel, experienced significant influences from river hydrology. Specifically, metals in liable fractions (exchangeable, carbonate, reducible and organic fractions) were sensitive to water fluxes, while conservative fractions (residual fractions) have higher affinity with sediment inputs. By comparison, the CJ06 site in shoal correlated better with total organic carbon (TOC), and was influenced more by the surrounding cities. Evidently decreased sediment discharge and their fluctuated size composition and varied metal concentrations accorded well with the time when the impoundment of dams and disastrous flood occurred. The transformation of metals in liable speciation into conservative phases reflected the intercepting role of dams. Metals in the reducible and organic fractions were significantly affected by the varied redox conditions caused by hydrological events.

1. Introduction

Hydrological events in the upstream river often have potential to change the physiochemical and redox conditions in the estuarine areas (Rudek et al., 1991), and these alterations have a tendency to affect the fate and transport of toxic contaminants like heavy metals (Masresha et al., 2011; Lenoble et al., 2013). As an important sink for metals in marine and coastal environments, sediment can record the environmental behaviors of metals under hydrological extremes (Baborowski et al., 2012). With the assistance of dating techniques, chronological records of metal deposition preserved in sediments may help reveal the historical accumulation of sedimentary metals (Thapalia et al., 2010). By far, chronological records from sediments have been employed to investigate the relationship between metal accumulations with economic growth (Hosono et al., 2010), agricultural intensification (Zhang and Shan, 2008) and atmospheric emission (Katahira et al., 2009), etc. However, relatively little attention has been paid to explore the relation between hydrological events and metal accumulation.

The construction of dam is a kind of hydrological event that can cause significant impacts on downstream areas (Chai et al., 2009; Wang et al., 2012). The most evident impact may be the change of sediment grain size, because it is known that dams capture all but the finest sediments (Luo et al., 2012). The fining sediment grain has greater capacity for metal scavenging, and ultimately varies the metal accumulation behaviors of sediments (Karlsson et al., 2010). Meanwhile, the impoundment and drainage of dams would definitely change the salinity and redox conditions in the estuary (Soltero et al., 1973), which may affect the immobilization and release of sediment-associated metals (Acosta et al., 2011;

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Zhao et al., 2013). Besides the construction of dam, flood is another important hydrological event. Variation in flood water characteristics and flood frequency may have profound influence on the topography, sedimentation rates, redox conditions and plant growth for particular areas in the downstream areas, affecting the fate and transport of sedimentary metals (Du Laing et al., 2009; Claff et al., 2011).

Generally, the sediment-associated metals are investigated based on total metal concentrations (Allen et al., 1980). However, this approach often fails to offer accurate information on the processes and dynamics of the mobility of metals. Metal speciation obtained from the sequential extraction procedure is now recognized to be an effective tool to achieve this information (Wu et al., 2006). In the sequential extraction procedure, sediment samples are subjected to chemicals of decreasing pH and increasing oxidizing strength to eliminate the operationally-defined host speciation (Ngiam and Lim, 2001). According to Tessier et al. (1979), particulate metals in sediments could be partitioned into five speciation: exchangeable, carbonate, reducible, organic and residual. The exchangeable metals are likely to be affected if water ionic composition changes, while the metals bound to carbonates are susceptible to changes of pH. Metals bound to reducible and organic speciation are susceptible to the redox conditions, while the residual metals are not expected to be released in solution under natural conditions.

As one of the world's largest estuaries, the Yangtze Estuary is characterized by large water and sediment discharge, large interseasonal water-level changes, and continuous seaward progradation (Saito et al., 2001). In this study, two typical core sediments were taken in the estuary to investigate the historical accumulation of Al, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb and Zn. Special attention was paid to the relationship between hydrological events and metal accumulation behaviors. The roles of sediment grain size, water flux, sediment discharge, and redox conditions caused by the hydrological events (e.g., the construction of dams and flood) in affecting metal variation were fully discussed through the study of metal speciation.

2. Materials and methods

2.1. Sediment core collection

Sediment cores were collected in June 2011 in the Yangtze Estuary. Fig. 1 exhibits the two sampling sites, i.e. the CJ03 site (31°09′167″N, 122°26′333″E) located within the main river channel and the CJ06 site (30°46′128″N, 122°15′153″E) at the shoal (about −5 to −7 m depth) around the Shanghai city. At each site, three sediment cores were collected using a gravity corer. The sediment cores collected in CJ03 were around 90 cm, while the CJ06 cores were about 80 cm in depth. The sediment cores were sectioned to approximately 1 cm intervals immediately after collection. All the subsamples were preserved at −20 °C prior to analysis.

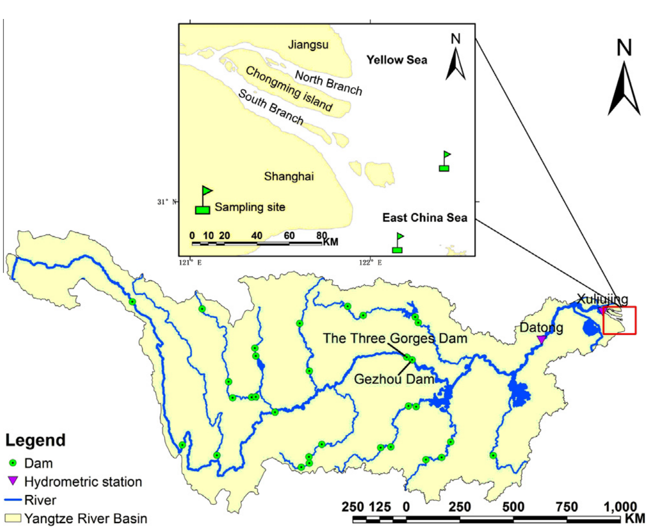

Fig. 1. Distribution of the two sampling sites in the Yangtze Estuary and the Datong hydroelectric stations and hydrometric stations in the river catchments.

2.2. Sediment dating

The sediment cores were dated at Nanjing University, Institute of Geography and Marine Science, with ^{210}Pb analysis. The ^{210}Pb was determined with the Po-α method described by Flynn (1968), after 3 weeks of storage in sealed containers to allow radioactive equilibration. The instrument used for ^{210}Pb analysis was α-spectrometer with low background (576AAlpha Spectrometer, EG&G, USA). IAEA2327 standard sample was also used for the calibration. The average depositional rates of the cores were determined to be about 4.16 cm year^{-1} for the CJ03 site and about 2.97 cm year^{-1} for the CJ06 site. Thus, based on the dating results, the general annual changes of metals in both cores were probed.

2.3. Sequential extractions procedure

The treatment and measurement of metals in the subsamples in CJ03 and CJ06 cores were conducted by the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences, which is certificated by the China National Accreditation Board for Laboratories (CNAL). The metal sequential extractions procedure was the classical five-step method proposed by Tessier et al. (1979). Total metal contents were calculated through the sums of metal content in each extraction procedure.

2.4. Analysis and quality control of the data

The concentrations of Cu, Ni, Pb, Sb and Zn in filtrates of the sequential extractions procedure were measured by an inductively coupled plasma mass spectrometer (ICP-MS, Thermo), while the concentrations of Cr, Al and Fe were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES). The accuracy of the methods was systematically and routinely examined with standard reference materials (GSF). Overall, metal contents were found to be within 87–105% of the certified values. Sediment particle sizes were analyzed by a laser particle size analyzer (Microtrac S3500, USA). Sediment proportion, i.e. clay (<4 μm), silt (4–63 μm) and sand (63–2000 μm) was worked out in this study (Zhao et al., 2012). Total organic carbons in the sediments were measured with the total organic carbon analyzer (Elementar, Germany). The annual variations of sediment discharges and water fluxes data were obtained from the Bulletin of Yangtze Sediment, by Press of Ministry of Water Resources of the People's Republic of China.

Aluminum is used for normalization in order to minimize grain-size effect while analyzing the variations of metal concentrations (Green-Ruiz and Páez-Osuna, 2001). The data used for the under-mentioned multivariate analyses included contents of metals in bulk and in different fractions, sediment size distribution, TOC contents, and the annual data of sediment discharges and water fluxes. The constrained incremental sum of squares cluster-analysis (CONISS) was conducted using PAST software version 2.16 to characterize the vertical changes in metal concentrations. Analysis was carried out with constrained method and Euclidian distance method was used for similarity measurement. Correlation analysis (CA) was assessed by the PASW 18.0 (SPSS Inc., Chicago, IL, USA).

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