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A magnetic record of heavy metal pollution in the Yangtze River subaqueous delta

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HIGHLIGHTS

- Magnetic parameters can be used as heavy metal pollution proxy.
- Heavy metal contents in the Yangtze River estuary increase since the 1960s.
- Heavy metal pollution is largely driven by population growth in the catchment.

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ABSTRACT

The rapid industrial development in the Yangtze River watershed over the last several decades has drawn great attention with respect to heavy metal pollution to the Yangtze River estuary and nearby coastal areas. In this study, a 236 cm long sediment core was retrieved from the Yangtze River subaqueous delta (122°36′ E, 31°00′ N) in 2008 and analyzed for magnetic properties and geochemical compositions to investigate heavy metal pollution history. The activity of ^{137}Cs peaked at depth 140 cm, with a broad plateau between 120 cm and 140 cm, suggesting an average sedimentation rate of 3.11 cm yr^{-1} for the upper 140 cm layer. Magnetic susceptibility (χ), saturation isothermal remanent magnetization (SIRM), anhysteretic remanent magnetization (χ_{ARM}) and heavy metal enrichment factors (EF) all showed an upward increase trend above depth 140 cm, suggesting that increased ferrimagnetic mineral concentration was accompanied by heavy metal enrichment in the sediment. Geochemical and granolumetric analyses showed that sediment sources and particle sizes played minor roles in the variations of magnetic properties. The effect of diagenesis, which can lead to the selective removal of magnetic minerals, was noticeable in the lower part of the core (140–236 cm). Co-variation between magnetic properties (χ, SIRM and χ_{ARM}) and EF of Cu and Pb suggests that the elevated ferrimagnetic mineral concentration can be used as an indicator of heavy metal pollution in the reconstruction of environmental changes in estuarine and coastal settings.

1. Introduction

Delta deposit is formed by accumulation of river-derived sediment in a coastal water body. Materials transferred at the interface between riverine and marine environment provides information related to environmental changes in the drainage basin caused by either natural process and/or anthropogenic activities at time scale from decades to centuries or even longer. Influence of human activities on the catchment area and estuary such as heavy metal pollution, coastal water eutrophication and hypoxia is noticeable with the industrialization (Li et al., 2002; Chen et al., 2004; Guo et al., 2007; Liu et al., 2008; Brush, 2009; Zhu et al., 2011; Irabien et al., 2012). A number of studies have shown the success in using subaqueous delta deposits to reconstruct environmental changes in the catchment–estuary system over the last several centuries (Benninger et al., 1979; Valette-Silver, 1993; Yang et al., 1999; Syvitski et al., 2005; Swarzenski et al., 2008; Zong et al., 2009; Harding et al., 2010; Xia et al., 2011; Birch et al., 2013).

The Yangtze River is the third largest river in the world (~6300 km in length). It delivers a huge amount of sediment to the estuary annually (ca. 4.8×10^8 tons, 1951–1979), of which approximately half deposits near the river mouth (Milliman and Meade, 1983). Sedimentation rate at the deposition center of the subaqueous delta was reported as high as 6.3 cm yr^{-1} (Chen et al., 2004). Due to the large population of more than 0.4 billion people and economic growth in this catchment area (1.8×10^6 km^2), the environmental impact (e.g., deforestation, soil erosion, damming and sewage discharge) in the watershed have drawn great attentions (Yang et al., 2003, 2007, 2011; Liu et al., 2007;

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Xu and Milliman, 2009). Several studies have reported heavy metal and organic compound pollution based on sediment cores taken from Yangtze River subaqueous delta (Liu et al., 2000; Chen et al., 2004; Hao et al., 2008; Yang et al., 2012).

Magnetic minerals (mainly iron oxides and sulfides) are ubiquitous in sediments. Their concentrations, grain sizes and mineralogy assemblages provide information on sediment sources, transport, deposition, post-depositional diagenesis, and even anthropogenic input (Thompson and Oldfield, 1986). Magnetic properties such as magnetic susceptibility (χ), saturation isothermal remanent magnetization (SIRM) of loess, lacustrine, coastal and marine deposits have been widely used for environmental reconstruction (Zhou et al., 1990; Oldfield, 1994; Maher, 1998; Zhang et al., 2007; Zheng et al., 2010). Previous studies have confirmed that magnetic measurements can be used to characterize heavy metal pollution which is due to the associated emission of magnetic particles from industrial discharge, vehicle exhausts and abrasion products (Thompson and Oldfield, 1986; Maher and Thompson, 1999; Evans and Heller, 2003). Therefore elevated SIRM or χ values can be used to indicate heavy metal pollution (Lu and Bai, 2006; Horng et al., 2009; Zhang et al., 2011, 2013; Wang et al., 2012; Zhu et al., 2012, 2013).

Our previous work reveals that magnetic properties (e.g., anhysteretic remanent magnetization χ_{ARM}) of surface intertidal sediments in the Yangtze Estuary displayed good correlations with heavy metal concentrations (Zhang et al., 2007). It is well documented that post-depositional diagenesis has an influence on magnetic properties (Thompson and Oldfield, 1986). This study aims to find out whether such relationships can still be held true. A 236 cm sediment core (CX32) collected from the Yangtze River subaqueous delta was analyzed for magnetic and geochemical properties, with the purpose to explore potential application of magnetic approach to heavy metal pollution history reconstruction in estuarine and coastal environment.

2. Samples and methods

A 236 cm sediment core (CX32) was collected from a site with water depth of 19.0 m in the Yangtze River subaqueous delta (122°36′ E, 31°00′ N) in 2008 using a gravity core sampler (Fig. 1). The core was then sectioned at 4 cm interval throughout the core. The samples were dried at 40 °C and ground with a mortar and a pestle except for the grain size analysis.

The sediment samples were analyzed for ^{210}Pb and ^{137}Cs activities using HPGe γ spectrometer (GWL-120210S) to establish the core chronology (Appleby and Oldfield, 1978). The samples were packed in the plastic holders, sealed for three weeks and counted for approximately 24 h. Total ^{210}Pb and ^{214}Pb were determined from the gamma emissions at 46.5 keV and 351.9 keV, respectively, with the latter as the supported ^{210}Pb. Excess ^{210}Pb was calculated as the difference between total ^{210}Pb and ^{214}Pb. ^{137}Cs was determined from the gamma emissions at 661 keV.

Particle size distribution was analyzed using a laser size analyzer (Coulter LS-100Q) after treatment with 0.2 M HCl and 5% H_2O_2 to dissolve biogenic carbonate and organic matter. Sodium hexamtaphosphate (0.5 M $(NaPO_3)_6$) was added to ensure complete disaggregation before the analysis (Ru, 2000).

For sediment magnetic property analysis, low- (0.47 kHz) and high- (4.7 kHz) frequency susceptibilities (χ_{lf} and χ_{hf}, respectively) were measured using a Bartington MS2B magnetic susceptibility meter. Frequency dependent susceptibility (χ_{fd}) was calculated as $\chi_{fd} = (\chi_{lf} - \chi_{hf})$. Anhysteretic remnant magnetization (ARM) was acquired in a 0.04 mT direct current field superimposed on a peak AF demagnetization field of 100 mT, and expressed as susceptibility of ARM (χ_{ARM}). Isothermal remnant magnetization (IRM) was first imparted at 1 T and then backfields at −100 mT and −300 mT. These magnetizations are referred to as SIRM, $IRM_{-100\ mT}$ and $IRM_{-300\ mT}$, respectively, and they were mass normalized. S_{-100} and S_{-300} were calculated as $S_{-100\ mT} = 0.5 \times (SIRM\text{-}IRM_{-100\ mT}) / SIRM \times 100$ and $S_{-300\ mT} = 0.5 \times (SIRM\text{-}IRM_{-300\ mT}) / SIRM \times 100$, respectively (Bloemendal et al., 1992).

Total digestion of the sediment samples for metal concentrations was performed using a mixture of concentrated HF–HNO_3–$HClO_4$ acids. Concentrations of Fe, Mn, Al, Cr, Ni and Zn were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES, IPIS intrepid IIXSP), and Cu and Pb by atomic absorption spectrometry equipped with a graphite furnace (AANALYST800). Selected 30 samples were subjected to analysis for rare earth elements (REEs) using a VGX7 inductively coupled plasma mass spectrometry (ICP-MS). The method for REE analysis followed the procedures described in Shao et al. (2001). The China National Reference Material GSD-9 was also analyzed with measured concentrations within 10% of reference values determined.

The vertical variation of heavy metals was divided into two layers (0–140 cm and 140–236 cm). Student t-test was performed on these two sets of data to examine whether or not there is a significant difference in metal concentrations between the two layers.

Metal enrichment factor (EF) and pollution loading index (PLI) are commonly used to discern metal contamination and evaluate the extent of environmental pollution (Sinex and Wright, 1988; Tomlinson et al., 1980). Mathematically, EF is expressed as (Sinex and Wright, 1988):

$$EF = \frac{\left(\frac{Me}{Al}\right)_{sample}}{\left(\frac{Me}{Al}\right)_{background}}, \quad (1)$$

where $(Me/Al)_{sample}$ is the metal to Al ratio in the samples; $(Me/Al)_{background}$ is the ratio in background. In this study, the upper continental crust values (Taylor and McLennan, 1995) were used as the metal background values. For Cr, the updated value of 73 mg/kg by Hu and Gao (2008) was used here. Generally, an EF > 1.5 suggests that a significant portion of the element is delivered from non-crustal materials, while EF values between 0.5 and 1.5 suggest that the trace metals may be entirely from crustal material or natural weathering process (Zhang and Liu, 2002).

PLI is mathematically defined as (Angulo, 1996):

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)}, \quad (2)$$

where CF_i ($i = 1$ to n) is the ratio of $metal_i$ in sample to that in the background (Me_{sample} / $Me_{backgroud}$). In this study, PLI was calculated using Cu, Zn, Ni, Cr and Pb concentration data and the background values were the same as those used before.

To identify the origin of magnetic particles, selected samples were subjected to magnetic mineral extraction. A scanning electron microscope (SEM, JSM-5610) equipped with energy dispersive X-ray spectroscopy (EDS) was used to study the morphology and elemental composition of the extracted magnetic particles.

3. Results

3.1. Chronology

The distributions of ^{210}Pb and ^{137}Cs in the sediment were shown in Fig. 2. Excess ^{210}Pb profile showed a mixing layer at surface (0–60 cm) followed by a relatively steady state exponential decease from 60 to 140 cm. Below depth of 140 cm, excess ^{210}Pb showed a peak around 170 cm, after which it declined with depth (Fig. 2a). Based on the steady state sedimentation profile between 60 cm and 140 cm, a mean sedimentation rate of 3.14 cm yr^{-1} was obtained using the constant initial concentration (CIC) model (Appleby and Oldfield, 1978) (Fig. 2a).

Activity of ^{137}Cs peaked at depth 140 cm, with a broad plateau between 120 cm and 140 cm (Fig. 2b). The broad peaks of ^{137}Cs were also observed in other cores collected from this study area (Chen et al., 2004; Dong et al., 2009; Pan et al., 2011). Further upward, it showed a