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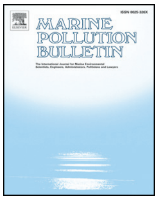

Behavior of suspended particles in the Changjiang Estuary: Size distribution and trace metal contamination

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ABSTRACT

Suspended particulate matter (SPM) samples were collected along a salinity gradient in the Changjiang Estuary in June 2011. A custom-built water elutriation apparatus was used to separate the suspended sediments into five size fractions. The results indicated that Cr and Pb originated from natural weathering processes, whereas Cu, Zn, and Cd originated from other sources. The distribution of most trace metals in different particle sizes increased with decreasing particle size. The contents of Fe/Mn and organic matter were confirmed to play an important role in increasing the level of heavy metal contents. The Cu, Pb, Zn, and Cd contents varied significantly with increasing salinity in the medium–low salinity region, thus indicating the release of Cu, Pb, Zn, and Cd particles. Thus, the transfer of polluted fine particles into the open sea is probably accompanied by release of pollutants into the dissolved compartment, thereby amplifying the potential harmful effects to marine organisms.

1. Introduction

Environmental pollution and its associated risks are of major concern due to the rapid increase in industrialization, rapid economic development, urbanization, population growth, and agricultural industry. Trace metals are among the most persistent pollutants in the ecosystem such as water, sediments, and biota because of their resistance to decomposition under natural conditions (Jain et al., 2008; Paramasivam et al., 2015). Trace metals may be generated throughout wastewater, industrial activities (Azimi et al., 2005), and agriculture (Waeles et al., 2007). Trace metals may be transported by rivers to coastal areas through continuous, diffuse inputs or during flood events, and can then accumulate in marine sediments. Their input into the water column and in the sediments may be a threat to the quality of coastal areas (Weber et al., 2009; Rocha et al., 2011).

Due to convenient traffic conditions and abundant natural resources, estuarine areas often have high population densities and intense economic activity. These regions are located in the transitional zone and are influenced by the land, river, and ocean, which results in a dynamic and vulnerable environment (Kharroubi et al., 2012; Wang et al., 2014). The physicochemical properties of the suspended particulate matter (SPM) undergo significant changes during freshwater/seawater mixing; the behavior of the suspended particles depends on their properties and concentrations and the organic matter content (Oursel et al., 2014). Metals in the water column can undergo rapid desorption or, conversely, are adsorbed onto particles. Suspended particulates settle directly, or after flocculation, and accumulate in sediments, which consequently act as a metal sink (Bay et al., 2003; Tessier et al., 2011; Oursel et al., 2014). The sediments are important components of estuarine ecosystems (Dong et al., 2012). In recent years, the sediments have been increasingly recognized as a major sink and source of contamination, and they provide an essential link between chemical and biological processes (Sheykhi and Moore, 2013; Wang et al., 2014). Particle size plays a significant role in controlling trace metal concentrations in the particulate fraction, whereby the concentrations tend to increase with decreasing particle size (Cai et al., 2002; Ljung et al., 2006; Semlali et al., 2001). The mobility and biological effectiveness of particulate trace metals have a strong correlation with the size and composition of particulate fractions (Cai et al., 2002; Ljung et al., 2006; Semlali et al., 2001). Varying size fractions have different composition and properties, which affect the behavior of trace metals in the water environment. Therefore, it is important to recognize trace metals in different fractions of particles that are used to determine their degree of mobility, availability, and persistence in the environment (Guillen et al., 2011). Thus, the impact of particulate characteristics/physicochemical properties on heavy metal concentrations in riverine suspended particle should also be analyzed.

The Yangtze River Estuary is one of the world's largest estuaries, home to over 15 million people (Z.Y. Chen et al., 2001). Due to urbanization and industrial development, metal contamination in the Yangtze River Estuary has attracted recent attention (Z. Chen et al., 2001; Zhang, 1999; Zhang et al., 2001; Feng et al., 2004). Although several studies

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have been conducted in the Yangtze River Estuary, few have focused on suspended particles and the distribution patterns of trace metals in different particle size fractions. In order to assess the future environmental risks, it is important to know the particle size scale in which the trace metals are preferentially distributed. The objectives of this study are as follows: (1) to assess the contamination levels of Cu, Pb, Cr, Zn, and Cd in suspended particulate matter; (2) to investigate the distribution patterns of trace metals in different particle size fractions; and (3) to discuss the mixing behavior of trace metals in the Changjiang Estuary.

2. Materials and methods

2.1. Study area

With a water discharge of 928.2 × 10^9 m^3/year, the Changjiang is the fourth largest aquatic system, following the Amazon, Zaire, and Orinoco, and drains into the ocean. The annual sediment load of the river is 0.5 × 10^9 t/year with an average suspended sediment level of 544 mg/L (Z.Y. Chen et al., 2001). The highest monthly water discharge occurs from June to August and the lowest from December to February (Zhao et al., 2015). The monthly sediment load also exhibits a seasonal pattern in the Changjiang River. The sediment peak occurs in July, and the lowest value occurs during winter months. Furthermore, the Changjiang River transports 88.7% of the annual sediment load between May and October, whereas only 11.3% of the annual sediment load is transported during other months (Zhao et al., 2015). The Changjiang Estuary is the pathway through which the Changjiang River discharges into the East Sea. In the estuary, the sediment regimes are affected by a strong tidal amplitude (average: 4.5–5.0 m) and current (up to 2.0–2.5 m/s) (Zhang, 1999). The tide may affect a region of ca. 300–350 km in the lower reaches of the river and the brackish waters reach 100 km inland from the mouth. Previous work has reported that 50% of the riverine sediments are deposited in the region close to the river mouth and shallow water areas (water depth < 50 m), and the rest is transported eastward and southward on the shelf region (Milliman et al., 1985).

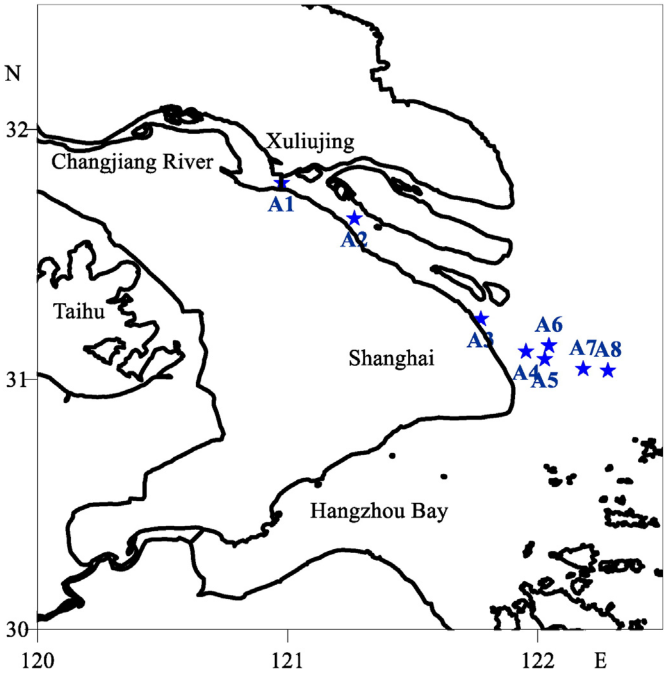

Fig. 1. The locations of sampling stations in the Changjiang Estuary.

2.2. Sample collection

Sampling was conducted onboard the RV Runjiang 1 in June 2011 (Fig. 1). Surface water and SPM samples collected at eight stations along a salinity gradient starting near Xuliujing and extended seaward to an area with a salinity of ca. 25. (Fig. 1). A custom-built water elutriation apparatus, built according to Walling and Woodward (1993) as illustrated in Fig. 2, was used to separate the suspended sediments into clay—very fine silt (<8 μm), fine silt (8–16 μm), medium silt (16–32 μm), coarse silt (32–63 μm), and sand (>63 μm) (He et al. 2009). The apparatus consisted of four organic glass sedimentation chambers linked by organic glass tubes, a peristaltic pump with variable speed control and a 50-L capacity outflow container (V). The SPM samples were imported to the system through an organic glass tube, which then flowed through the sedimentation chambers and peristaltic pump, and were finally collected in the 50-L container (V). In each chamber, the samples entered the bottom via a “long” organic glass tube and flowed to the next chamber at the top. The peristaltic pump is positioned after the 200-mm sedimentation chamber to maintain a constant flow in the system (He et al., 2009).

An approximately 100–150 L of water sample was collected in June 2011 from each station. After allowing the particulates to settle for approximately 24 h, the clear water was decanted and stored for use as carrier water in the elutriation process, and the SPM that remained in the container was used for elutriation. When a sampling run was initiated, the water elutriator was filled with clear water drawn from the container. After enough slurry was drawn into the apparatus, the clear water was drawn through the system until the sedimentation chambers were completely flushed (He et al., 2009). The suspended particulate samples collected from each sedimentation chamber were filtered through 0.45-μm-pore-size acid-washed Millipore filters and were frozen. The slurry collected in the outflow containers was left to settle for approximately 72 h and was then decanted. The suspended particles were collected on filters and frozen. The distribution of each particle size fraction was calculated by determining the weight of each size fraction.

2.3. Analytical methods

For each particle size fraction and bulk SPM, approximately 0.100 g of well-ground sample was digested with 5.00 mL HNO_3, 2.00 mL $HClO_4$, and 1.50 mL HF in a PTFE (polytetrafluoroethylene) reactor at 160 °C for 6 h following the methods adopted by Li et al. (2008). The total amounts of Cu, Pb, Zn, Cr, Fe, and Mn were determined using inductively coupled plasma-atomic emission spectrometry (ICP–AES, Thermo-6300). The amount of Cd was determined by graphite furnace atomic absorption spectrometry (GFAAS, Thermo-SOLLARM6). The detection limits were 0.016, 0.034, 0.005, 0.004, 0.0002, 0.014, and 0.002 mg/L for Cu, Pb, Zn, Cr, Cd, Fe, and Mn, respectively. The reference standard for offshore marine sediment (GBW07314, The Second Institute of Oceanography, SOA, P.R. China) and reagent blanks were used as the quality control sample during the analysis. The values obtained for all the studied elements fall in the required range of certified contents. The relative standard deviations ($n = 3$) of the duplicate samples and blank samples were <10% and 5%, respectively. The concentration of the samples was verified by the blank in this study.

The concentrations of TOC (total organic carbon; relative precision ± 5%) were determined using a CHNOS Elemental Analyzer (Model: Vario EL III). The weight percentages of TOC were analyzed after removing the carbonate fraction with vapor-phase acidification.

3. Results and discussion

3.1. SPM and particle size distribution

The salinity and SPM values are shown in Fig. 3. The results indicate that the estuary is dominated by freshwater inside the river mouth and

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