



Heavy metal spatial variability and historical changes in the Yangtze River estuary and North Jiangsu tidal flat



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ABSTRACT

This research focuses on the spatial and temporal patterns of heavy metals from the Yangtze River estuary and the tidal flat of north Jiangsu. Most heavy metals in the surficial sediments after normalization to Ti decreased seaward at the Yangtze River estuary. The core records showed that the heavy metal variations in the last 50 years were primarily linked to natural weathering input of trace elements. However, significant heavy metal pollution (mainly Ni, Pb, Cd, Cu and As) were in the two study areas, with anthropogenic inventories accounting for 23–40% percent of the total pollution. Sequential extraction showed that Pb, Cu and Ni were present largely in the non-residual fraction, which indicated the potential bioavailability in the study areas. The SEM/EDS together with sequential extraction facilitated the easy tracing of the origin/sources of heavy metals in a simple way in the estuary and the tidal flat.

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1. Introduction

Heavy metal problems are still of many concerns all over the world. The number of ecological and health problems associated with environmental contamination continues to rise. Heavy metals in estuary and tidal flat may originate from various sources in the environment, including industrial pollution, atmospheric deposition, river or ocean transportation, non-point sources and natural geochemical processes. Recently, simultaneous multielement determination of trace elements in the environment samples by inductively coupled plasma emission spectrometry (ICP-OES/AES) is becoming especially important and receiving more and more attention (Diop et al., 2015; Karbasi et al., 2009; Morata et al., 2007; Schipper et al., 2008; Suzuki, 2006).

Generally speaking, comparisons of total metal concentrations have been used widely in a number of studies to determining and assessing the distribution and environmental risk of heavy metals in the coastal areas. However, it is generally recognized that the toxicity, environmental and health effects of heavy metals are basically dependent on their mobility and availability. To the best

of our knowledge, it is insufficient to estimate the environmental impact of contaminated sediments merely through the determination of total metal concentration, which critically depends on the specific chemical species and binding states, and the sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) is considered to be the most fashionable process to evaluate metal speciation in the environment (Arenas-Lago et al., 2014, 2015; Huang et al., 2013; Zhai et al., 2014).

However, the sequential extraction procedure have some problems when determining the availability and the association of heavy metals with different geochemical soil fractions (Arenas-Lago et al., 2014, 2015). The choice and order of extracts, the length of the process, the solid/liquid ratio, and the procedure of sample preparation and conservation may affect the soil, suspended particles and sediment in a different way (Filgueiras et al., 2002).

Recently, the scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS) and chemical analyses were applied in order to trace the origin of trace metals in the various environmental samples (El-Mufleh et al., 2014; El Baghdadi et al., 2011; Famera et al., 2013; Moon et al., 2012; Morata et al., 2007; Sobanska et al., 2014; Suzuki, 2006). Although the sensitivity of the scanning electron microscopy techniques was relatively low, it has been found

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to provide information about the distribution and interactions of heavy metals, the surface of the sediment components and about the mobility and availability of the metals (Arenas-Lago et al., 2014, 2015). Consequently, the BCR method combined the SEM/EDS method can provide detail information about the solid microstructure that retain heavy metals.

Temporal and spatial variations in contaminant levels can be induced by natural sediment variability and pollutant supply and also depend on environmental conditions at the water–sediment interface. Although spatially heterogeneous, well preserved tidal flats and big river estuary sediments can constitute representative media to measure the chemical composition of coastal areas and can be used to reconstruct the pollution history over a long period of time. Unfortunately, such information is very limited in coastal areas of China, especially investigations in the Yangtze River estuary and the tidal flats at the north Jiangsu province (Bai et al., 2011; Chen et al., 2007; Jing, 1999; Zeng and Wu, 2013; Zhang et al., 2009).

In previous studies, we have shown that the characteristics of the radionuclides of ^{210}Pb , ^{137}Cs , ^{239}Pu and ^{240}Pu in the Yangtze River estuary and the north Jiangsu tidal flats (Liu et al., 2010, 2013a). In the present study, we aimed to assess the historical human impact as preserved in the marine sedimentary record in the past 60 years, to estimate the relationship between radionuclides and heavy metals, and to obtain more accurate evaluations of the levels and different sources of the pollution in the areas. Furthermore, the combination of BCR and SEM/EDS provided an easy way to quickly estimate the sources, potential bioavailability and toxicity of heavy metals in the coastal estuary and the tidal flat areas.

2. Sampling and methods

2.1. Studied areas and sediment sampling

A detail description of the studied areas and sample collection is given by Liu et al. In brief, the Yangtze River is one of the world's most important rivers. With a water discharge of 905 billion cubic meters per year and mean annual sediment discharge of 432 million tons, its water discharge and sediment load are respectively the fifth and fourth largest in the world. The large volumes of sediment supplied by the Yangtze River are intensively deposited at the estuary with a maximum deposition rate of 5.4 cm/a, making the study area the depocenter of a sub-aqueous delta.

Shanghai metropolis, located along the Yangtze River estuary, is the largest city with the most active industrial activities in China. It discharges more than 6.0 million tons of industrial and domestic sewage water into the Yangtze River estuary daily (Chen et al., 2004).

The tidal flat in north Jiangsu is the largest continuously distributed coastal wetland (5100 km²) in China. It extended 884 km long from north to south, with an average width from 10 km to 13 km. Sediments from the old Yellow River and the Yangtze River estuaries are two dominating sources. The tidal flat is affected by the marine monsoon climate with prevailing south-eastern wind in summer and prevailing northwestern wind controlled by tropical depression in winter.

Sheyang tidal flat is an intact tidal flat in Jiangsu, which has global ecological and bio-diversity protection significance. Sheyang River and Sheyang River flow in the north and south part of the tidal flat, respectively.

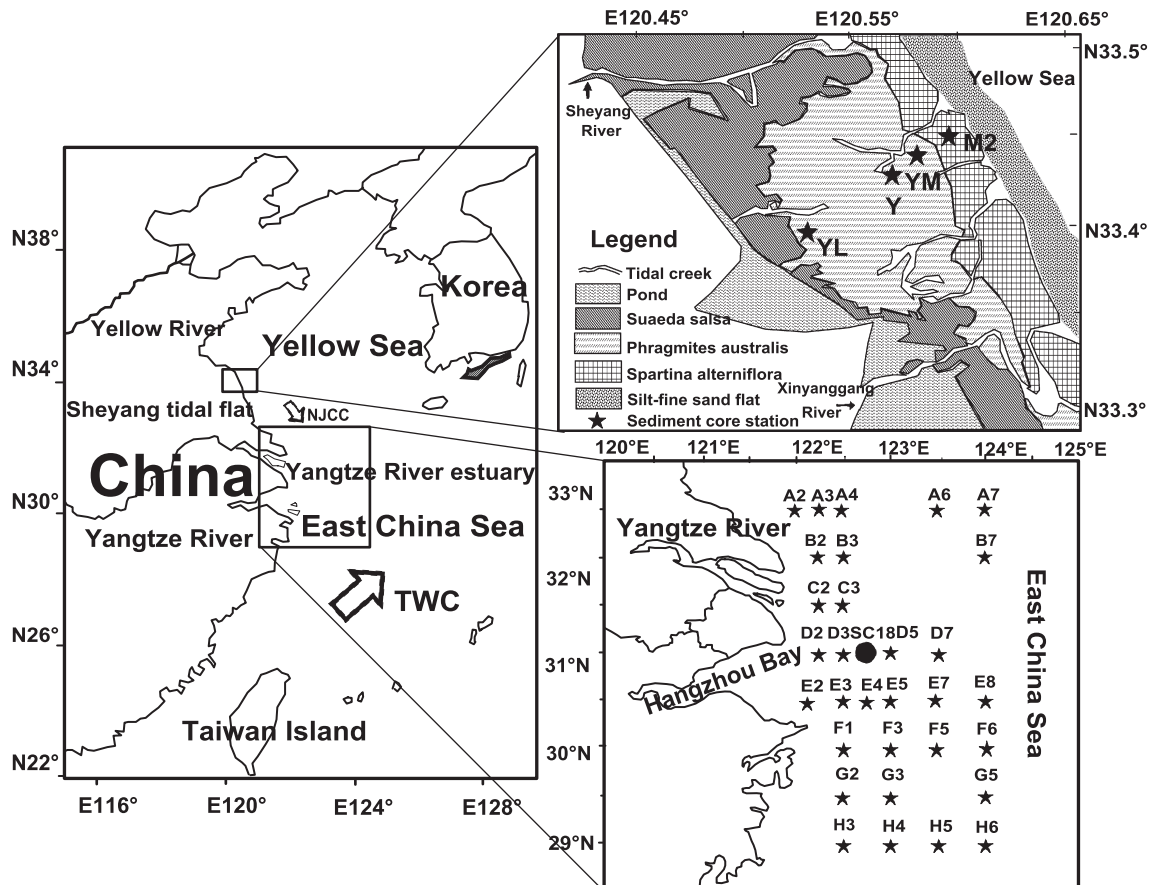


Fig. 1. Map of the sampling sites. The Sheyang tidal flat map was redrawn from Liu et al. (2010), and the Yangtze River estuary map was redrawn from Liu et al. (2011).

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