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# Spatial variation, environmental assessment and source identification of heavy metals in sediments of the Yangtze River Estuary

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ABSTRACT

In order to analyze the spatial distribution patterns, pollution sources and ecological risks of heavy metals (As, Cd, Cr, Cu, Mn, Ni, Pb and Zn), 30 sediment samples were taken from in the Yangtze River Estuary (YRE). The results indicated that the contamination ranking of heavy metals was As > Cr > Cd > Ni > Mn > Pb > Zn > Cu. In the various areas, the pollution magnitude decreased as follows: adjacent sea > river mouth > inner-region. Compared to data published for other regions, the YRE data indicated that the sediment was not severely contaminated by heavy metals. In the YRE, natural and anthropogenic inputs dominated the distribution patterns of the heavy metals. Beyond that, the hydrodynamic conditions, such as the Taiwan warm current, coastal current and Yangtze diluted water, also caused distribution variations in the study areas.



Due to convenient traffic conditions and unsurpassed natural resources, estuarine areas are often regions with high population densities and intense economic activity (Oursel et al., 2013). These regions are located in the transitional zone and are controlled by the land, river and ocean, which results in dynamic and vulnerable environments (Kharroubi et al., 2012). Sediments are important components of the estuarine ecosystems (Dong et al., 2012). Due to their physical and chemical properties, estuarine sediments are highly susceptible to pollution (Cheng et al., 2013; Hu et al., 2013). In recent years, sediments were increasingly recognized as a major sink and source of contamination; they provide an essential link between chemical and biological processes (Sheykhi and Moore, 2013). Thus, the proper assessment of sediment contamination in estuaries is crucial.

It is well known that heavy metal pollution records in sediments reveal significant impacts on the environment in estuarine areas (Selvam et al., 2012). Heavy metals enter into aquatic environments through atmospheric deposition, sewage outfalls, urban storm water and agricultural and industrial runoff. Then, the metals are absorbed and preserved in sediment, which enriches organisms through the food chain (Cheng et al., 2013). Heavy metals in the sediment may recycle into the water column via sediment resuspension, adsorption and changing chemical conditions (Dong et al., 2012). Some researchers have proven that heavy metal concentrations in the sediment are more sensitive than those in other materials (Mutia et al., 2012). Thus, it is essential to analyze heavy metal concentrations and distributions in sediment.

The distribution and accumulation of heavy metals are influenced by complex factors, such as sediment composition and structure, grain-size, and the hydrodynamic conditions (Christophoridis et al., 2009; Qiao et al., 2013). Due to these multiple factors, heavy metal concentrations in sediment change spatially and temporally (Liu et al., 2011). Sediments are important carriers of heavy metals in estuarine regions, and they can reflect the quality of an aquatic system (Qiao et al., 2013). The spatial distribution of heavy metals in sediments are also very important when clarifying the pollution history of aquatic systems, and it has proved very useful for distinguishing the heavy metals in sediments that are impacted by natural or anthropogenic factors (Rubio et al., 2001; Morillo et al., 2004; Kharroubi et al., 2012). Furthermore, the spatial distribution of heavy metals at global/local scales can provide a hydro-geochemical framework for assessing the sources and mechanisms of metal input and enrichment (Arakel and Hongjun, 1992). Therefore, it is meaningful to study the spatial and temporal variations of heavy metals in sediment throughout the entire estuarine region. Geostatistics, geographic information systems (GIS) and statistical analysis provide useful tools for the study of spatial uncertainty and hazard assessment (Ho et al., 2013; Simasuwannarong et al., 2012; Delgado et al., 2011). In recent decades, many researchers used sample site data to model the spatial distribution of heavy metals in sediment (Delgado et al., 2010; Forsythe et al., 2013; Maanan et al., 2013).

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Distinguishing between the different sources of heavy metals in sediment helps to control and reduce sediment pollution. Related research indicated that heavy metals in the environment mostly originate from lithogenic and anthropogenic sources (Zhou et al., 2008). The common methods for distinguishing the pollution sources include element speciation, profile distribution, and spatial distribution (Boruvka et al., 2005). In the last decade, studies on the sources of pollution using GIS were primarily limited to the mapping of pollutants/pollution indices; however, this method is not sufficiently reliable to distinguish the sources of pollutants. Additional methods should be incorporated, such as multivariable statistics and chemometrics, to identify the sources of pollutants, apportion natural versus anthropogenic contributions, and provide information on transport processes and environmental conditions (Facchinelli et al., 2001; Han et al., 2006; Lee et al., 2006; Parizanganeh et al., 2007; Zhang et al., 2012; Wani et al., 2013). Multivariate statistical, geostatistical and GIS-based approaches to identify heavy metal sources in sediment have been widely used in sediment pollution studies at the regional scale (Chabukdhara and Nema, 2012).

The Yangtze River Estuary (YRE) is one of the world's largest estuaries (Chen et al., 2012). Located within an area with one of the highest population densities and fastest developing economies in China, the YRE has suffered heavy metal contamination (Feng et al., 2004). The heavy metal pollution status of the YRE has attracted considerable attention. Recent studies mainly focused on assessing the contamination and ecological risks of heavy metals. Researchers discovered that the distributions of heavy metals in sediment exhibit a typical banded diffusion pattern in the YRE, with high concentrations near the river mouth that follow a decreasing trend in the offshore direction (Dong et al., 2012; Li et al., 2013). Other studies indicated that the highest potential ecological risk index appeared in the south branch of the YRE, which is mainly due to terrestrial pollution in Shanghai (Sheng et al., 2008; An et al., 2009; Zhang et al., 2009). Although heavy metal pollution has been investigated in the YRE, only sparse systemic research on the spatial distribution of heavy metals has been performed (Li et al., 2013). Hence, assessing the contamination and ecological risks of heavy metals in sediment using multiple approaches that are based on the various metal assessment indices and spatial analysis tools is meaningful. The assessment would help characterize the contamination sources in surface sediments and provide a tool for effectively protecting the estuary environment.

In this study, based on the heavy metal sample data in the YRE sediment, the geo-accumulation index ($I_{geo}$), enrichment factors (EFs), degree of contamination (DC), ecological risk index (RI) and principal components (PCs) were applied to determine the degree of contamination. The contributing sources of heavy metals were identified using geostatistics and multivariate statistics. The aims of this paper were to (1) examine the spatial variation of the heavy metals in the surface sediments of the YRE; (2) define the pollution levels of the heavy metals; and (3) identify the sources of the heavy metals. The results of this study can be used by managers to evaluate the sediment environment and take effective measures to control pollution.

The YRE is located on the boundary between the Yellow Sea and the East China Sea (Fig. 1). The estuary is divided into 4 branches by 3 islands: Chongming Island, Changxing Island and Hengsha Island. Shanghai, located in the YRE, is one of the largest cities in China; the city has a significant level of industrial activity, which has a direct impact on the Yangtze delta. More than 30 $km^3\ a^{-1}$ of sewage that is discharged from its drainage basin was delivered to the YRE. The sewage consists of 32% domestic wastewater and 68% industrial wastewater by volume (Chen et al., 2012).

In August 2010, 30 typical sampling sites were established (121E–122.75E, 31.75N–32N) (Fig. 1). At each station, we collected three surface sediments and mixed the samples to form a composite sample. The surface sediments were sampled to a depth of 2–5 cm. A total of 30 composite samples were obtained, one from each station. Then the samples were air-dried and homogenized. The sediment samples were brought to the Institute of Geophysical and Geochemical Exploration of the Chinese Academy of Geological Sciences, which is certificated by the China National Accreditation Board for Laboratories (CNAL). The concentrations of heavy metals (As, Cd, Cr, Cu, Mn, Ni, Pb and Zn) were measured using the inductively coupled plasma-mass spectrometry method (ICP-MS, Thermo), which has been applied by many other researchers (Zhao et al., 2013).

Quality assurance and quality control were assessed using duplicates, method blanks, and standard reference materials. The accuracy of the determination method was systematically and routinely examined with standard reference materials (GSF). Three replicates were conducted to determine the total contents of the metals. The metal contents of the standard reference materials were found to be within 86–102% of the certified values.

The spatial variations of heavy metal contamination and all of the indices were analyzed with the geostatistical method and ArcGIS9.3. Geostatistics is a branch of statistics that focuses on spatial or spatio-temporal datasets, and it is widely used in geology, hydrology, meteorology, geography, environmental science, soil science and agriculture (Forsythe et al., 2013; Heise et al., 2013; Joseph et al., 2013; Lark and Lapworth, 2013; Liu et al., 2013; Toal and Keane, 2013).

Geostatistics involves describing spatial patterns (semivariograms) and predicting the values of attributes at unsampled locations (kriging). Ordinary kriging is the most widely used geostatistical technique; it takes into account the direction of variations and incorporates trends into the interpolation to create better predictions (Wani et al., 2013; Ward et al., 2013). Ordinary kriging is estimated by a linear combination of the observed values with weights:

$$Z^*(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i) \quad (1)$$

where $Z^*(x_0)$ is the estimated value of $Z$ at the point $x_0$, $Z(x_i)$ is the sampled value at the point $x_i$ and $\lambda_i$ is the weight placed on $Z(x_i)$.

To assess metal contamination, the geo-accumulation index ($I_{geo}$), enrichment factors (EF), degree of contamination (DC), and ecological risk index (RI) are calculated. $I_{geo}$ and EF are the most popular methods used to evaluate the ecological risk posed by a single metal; DC and RI provide comprehensive information on the environmental risks posed by the presence of multiple metal elements (Caeiro et al., 2005; Li et al., 2012; Zhao et al., 2012; Cheng et al., 2013; Hou et al., 2013).

$I_{geo}$ is used to define and determine metal contamination in sediments by comparing current concentrations with pre-industrial levels (Zhao et al., 2012). The index is calculated using the following equation:

$$I_{geo} = Log_2\left(\frac{C_n}{1.5B_n}\right) \quad (2)$$

where $C_n$ is the measured concentration of metal $n$ in the sediment, 1.5 is used as a factor to minimize possible variations in the background values due to geogenic effects, and $B_n$ is the geochemical background value of metal $n$.

$I_{geo}$ is divided into seven classes, from Class 0 to Class 6 (Table 1); each class represents a unique contamination level. The background values are from other literature (Muller, 1969).

EF is used to assess the level of contamination and the possible anthropogenic impact on sediments (Martin et al., 2012). The background concentrations of Al, Fe, or Si in the Earth's crust were used