Marine Pollution Bulletin xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Spatial distribution, risk assessment and source identification of heavy metals in sediments of the Yangtze River Estuary, China

Deming Han [a], Jinping Cheng [a,*], Xianfeng Hu [b], Zhenyi Jiang [b], Lei Mo [b], Hao Xu [a], Yuning Ma [a], Xiaojia Chen [a], Heling Wang [a]

[a] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[b] Water (Ocean) Administrative Service Center, Shanghai Municipal Oceanic Bureau, Shanghai 200050, China

ARTICLE INFO

Article history:
Received 19 July 2016
Received in revised form 25 November 2016
Accepted 25 November 2016
Available online xxxx

Keywords:
Heavy metal
Sediment
Source identification
Positive factor matrix (PMF)
Yangtze River Estuary (YRE)

ABSTRACT

The aim of this study was to determine the spatial distribution, potential risks and sources of seven heavy metals in sediments of the Yangtze River Estuary. Analyses of 55 sediment samples revealed that the distributions of metals within the YRE were determined by the combined effects of their sources, hydrodynamic conditions, pH and Eh. According to the geoaccumulation index (I_{geo}) and sediment quality guidelines, Pb, Cd and Cr were present at low levels of pollution, with Cd posing the largest ecological risk. Positive Factor Matrix (PMF) results indicated that Hg, Zn, As, Pb and Cr mainly originated from natural geological background sources, while Cu originated from anthropogenic activities and atmospheric deposition was the source of Cd. These three sources contributed to 53.0%, 32.8% and 14.2%, respectively of total heavy metal concentrations. These results suggest that reducing the emission of Cd would promote a reduction of potential risks in sediments of the YRE.

1. Introduction

Heavy metals are toxic substances, which persist in the environment. Heavy metals originate from various sources, including natural processes, anthropogenic activities and atmospheric deposition (Xu et al., 2014; Zhang et al., 2016). Heavy metals tend to be adsorbed and accumulated in sediments as opposed to water or suspended solids. Sediments can act as a final sink for heavy metals in the aquatic environment (Guo and Yang, 2016) and have previously been used as a medium to evaluate heavy metal contamination (Vicente-Martorell et al., 2009). When environmental conditions such as pH, oxidation-reduction potential (Eh), salinity and organic matter change, heavy metals fixed in sediments can be dissolved into the water again, causing secondary contamination (Esslemont, 2000; Xu et al., 2016). Heavy metals can also bioaccumulate through the food chain (Guédron et al., 2014), posing potential biological and ecological risks.

Estuaries are the meeting point of rivers and the sea, and also act as a buffer between land and sea (Chen et al., 2013; Vicente-Martorell et al., 2009). Estuaries represent the main passage for terrestrial materials entering the sea and receive large amounts of fluvial materials including anthropogenic metals. The interaction of surface runoff and tidal currents (Wan et al., 2014; Zheng et al., 2012), results in variations in physical and chemical properties in estuaries, such as grain size, water flow velocity, salinity, pH, Eh and organic matter (Yuan et al., 2014). These variations play a key role in the transportation, deposition and resuspension of suspended solids in water (Pourabadehei and Mulligan, 2016; Wang et al., 2016), ultimately influencing the spatial distribution, transformation and bioaccumulation of heavy metals in an estuary.

The Yangtze River Estuary (YRE) is one of the largest estuaries in China and is subject to heavy metal contamination due to the rapid economic and industrial development of the city of Shanghai, located on the coast (Guo and Yang, 2016; Liu et al., 2015). The presence of harbors, petrochemical industries, industries and shipyards within the YRE, results in large amounts of industrial effluent and municipal sewage being discharged into the YRE. Previous studies have investigated heavy metals in the YRE (Dong et al., 2014; Gu et al., 2013; Guo and Yang, 2016), mainly focusing on the inner river or estuary area. However, metal contamination varies both temporally and spatially (Hu et al., 2013; Liu et al., 2015) and information regarding the sources of heavy metals is often lacking. Identifying these sources is essential to developing a scientific pollution control strategy. Therefore, carrying out sustained and in-depth investigations of heavy metals in the sediment of the YRE remains important. The objectives of the present study were: (1) to assess contamination levels of the heavy metals copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and zinc (Zn) in the YRE; (2) to evaluate the biological and ecological risks of these heavy metals using sediment quality guidelines (SQGs) and the potential ecological risk index (RI) method; and (3) to identify their origins and contributions using a positive matrix factorization (PMF) model.

* Corresponding author at: 800 Dongchuan Road, Minhang District, Shanghai, China.
E-mail address: jpcheng@sjtu.edu.cn (J. Cheng).

http://dx.doi.org/10.1016/j.marpolbul.2016.11.062
0025-326X/

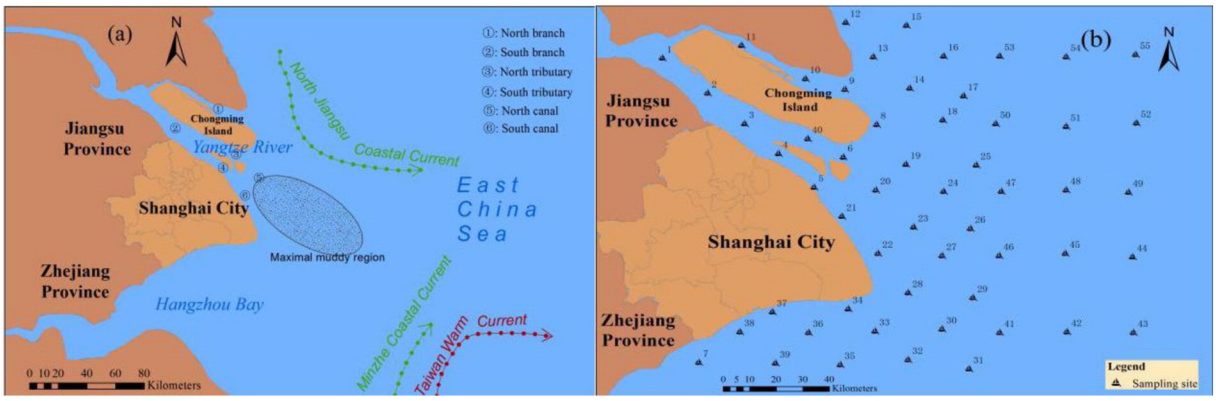

Fig. 1. Sampling sites in YRE (a for geographic location of YRE; b for sampling sites).

2. Materials and methods

2.1. Sampling sites and method

The YRE is the coastal outfall of the Yangtze River, the longest river in Asia, which discharges approximately 360 million tonnes of sediments annually (Wang et al., 2015). Chongming Island divides the YRE into a northern and southern channel, with the southern channel further separated into two tributaries (Fig. 1a). Outside of river mouth, there is a maximal muddy region (MMR) which is a tidal area where fresh water and seawater mix. The hydrodynamic conditions in the MMR promotes suspended solid retention and resuspension (Wan et al., 2014; Zheng et al., 2012), resulting in higher concentrations of suspended solids in comparison with other areas in this estuary (Gu et al., 2013).

A total of 55 surface sediment samples (0–2 cm) were collected in August 2014 (Fig. 1b). Samples were collected following a spatial grid of approximately 20 km × 20 km in the YRE. At each sampling site, three replicate samples were collected and mixed to form a representative sample. Sediment samples were collected using a Van-Veen grab sampler, then frozen, dried and turned into a powder using an agate mortar and pestle. The powdered samples were sieved through a 2-mm polyethylene sieve to remove any large stones, roots or debris and then stored at 4 °C until required.

2.2. Analysis method

Sediment samples were microwave-digested in teflon vessels to determine the concentrations of Cu, Hg, Zn, As, Pb, Cd and Cr. Samples were then treated with 2 mL HF, 5 mL $HClO_4$-HNO_3 (1:1) for approximately 30 min. After the mineralization and evaporation of the acids, 5 mL HCl was added and the samples were digested for another 30 min. Subsequently, the residue was transferred into a 25-mL flask, which was filled to volume. The concentrations of Cu, Zn, Pb, Cd and Cr were assayed using an inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer, Norwalk, CT, USA), while concentrations of Hg and As were tested using atomic fluorescence spectrometry (AFS-920). The organic matter content of the sediment was determined using the potassium dichromate oxidation-colorimetric method, while pH was determined using the glass electrode method. Eh was measured using an oxidation-reduction potential meter (PHSJ-3C, Shanghai Ceyu).

For quality assurance and quality control, China Stream Sediment Reference Materials (GB07345, GSD4/9) were also analysed and the results were within the range of certified values for the reference materials (<10%): Cu (109%), Hg (93%), Zn (91%), As (96%), Pb (105%), Cd (93%) and Cr (103%). All reagents were of analytical grade and all solutions were prepared with Milli-Q water.

2.3. Statistical analysis

2.3.1. Spatial analysis method

Geographic information system based approaches have been widely applied in environmental investigations and pollution mapping (Navoni et al., 2014; Viana and Bode, 2013; Xu et al., 2016). ArcGIS 10.2 was used in this study due to its capacity to visualize the spatial relationship of heavy metal concentrations, interpret their spatial variability and assess contamination levels. Kriging interpolation was also employed as a predictive method

2.3.2. Geo-accumulation index (I_{geo}) method

The geo-accumulation index (I_{geo}) method was first proposed by Muller (1969) and has been widely adopted to evaluate the contamination levels of heavy metals in sediments, in terms of their corresponding background values. I_{geo} can be calculated by Eq. (1):

$$I_{geo} = \log_2 \frac{C^i}{1.5 \times C^i_b} \quad (1)$$

C^i is the measured concentration of heavy metal i, while C^i_b is the geochemical background value of metal i. The background values of

Table 1
The classification of I_{geo}, ERL, ERM and m-ERM-Q.

Category	Description	Category	Description
$I_{geo} \le 0$	No pollution	≤ERL	Minimal effects range
$0 < I_{geo} \le 1$	Low pollution	>ERL, ≤ERM	Effects occasionally occur
$1 < I_{geo} \le 2$	Partial median pollution	>ERM	Effects frequently occur
$2 < I_{geo} \le 3$	Median pollution	m-ERM-Q ≤ 0.1	9% probability of toxicity
$3 < I_{geo} \le 4$	Partial serious pollution	0.1 < m-ERM-Q ≤ 0.5	21% probability of toxicity
$4 < I_{geo} \le 5$	Serious pollution	0.5 < m-ERM-Q ≤ 1.5	49% probability of toxicity
$5 < I_{geo}$	Extreme pollution	1.5 < m-ERM-Q	76% probability of toxicity

Please cite this article as: Han, D., et al., Spatial distribution, risk assessment and source identification of heavy metals in sediments of the Yangtze River Estuary, China, Marine Pollution Bulletin (2016), http://dx.doi.org/10.1016/j.marpolbul.2016.11.062