ARTICLE IN PRESS

MPB-07740; No of Pages 8

Marine Pollution Bulletin xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Spatial distribution and pollution evaluation of heavy metals in Yangtze estuary sediment

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ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form 19 May 2016
Accepted 23 May 2016
Available online xxxx

Keywords:
Heavy metals
Yangtze River estuary
Spatial distribution
Ecological risk assessment
Geographic information system

ABSTRACT

To analyze the spatial distribution patterns and ecological risks of heavy metals, 30 sediment samples were taken in the Yangtze River Estuary (YRE) in May 2011. The content of Al, As, Cr, Cu, Fe, Mn, Ni and Pb increased as follows: inner-region < river mouth < adjacent sea. According to I_{geo} and *RI*, As, Cr and Cd were the main pollutants. What is more, the greatest contaminated area appeared at the river mouth of the south branch of YRE. In Tucker 3, considering the fractions of metals, Mn turned to be the severest pollutant and As did not contribute too much to the contamination of the YRE. That was most probably because that Mn was closely related to the carbonate-associated (CARB) and As was related to organic-associated (OM) which is more stable than CARB. The fractions played an important role in the contamination assessment of heavy metals.

The estuary which is the confluence area of surface runoff and seawater is not only the main watercourse to transport the terrestrial matter into the sea but also the primary settling area (Ralston and Geyer 2009). However, anthropogenic activities have released large amounts of toxic substances into estuaries, causing many problems such as the increasing amount of endangered species and ecological deterioration (Curtosi et al. 2010; Mathivanan and Rajaram 2014; Chassaing et al. 2015; Islam et al. 2015). Sediments are important components of the estuarine ecosystems and they are the major sources and sinks of the toxic substances in water environment (Monikh et al. 2013). Therefore, it is crucial to assess the sediment contamination in estuarine areas.

Among toxic substances, heavy metals are priority environmental pollutants in estuaries (Alves et al. 2014). Most of heavy metals in water are adsorbed and keep accumulating in the sediment (Fisher-Power et al. 2016). As long as there are some changes with environmental condition, heavy metals adsorbed in the sediment will dissolve in the water, causing secondary contamination (Aleksander-Kwaterczak and Helios-Rybicka 2009; Kim et al. 2010; Gillan et al. 2012). The heavy metals have also shown obvious cytotoxicity and lasting harmfulness, probably causing serious harm to organisms including human beings (Järup 2003; Oyewale and Musa 2006). Because of their bioaccumulation capacity and environmental persistence, special attention should be paid on sedimentary heavy metals (Venkatesha Raju et al. 2012; Sayadi et al. 2015).

To assess the contamination degree of heavy metals, many methods have been used. Among those methods, the index of geo-accumulation (I_{geo}) was widely used since it takes the effects of the human activities into consideration. However, it ignores the toxicity differences among different heavy metals (Ali et al. 2013; Yan et al., 2015). Additional methods should be incorporated to assess the contamination of heavy metals. The potential ecological risk index (*RI*) proposed by Hakanson comprehensively considered issues such as the toxicity of heavy metals and comprehensive effect of multiple contaminants (Zhang et al. 2012). It is widely used in quality evaluation of sediments (Li C. et al., 2015; Zhang et al. 2015; Chen et al. 2016).

The content of heavy metal is a useful indicator of contamination assessment (Mânzatu et al. 2015; Janadeleh et al. 2016; Karbassi et al. 2016). However, it does not provide enough information about toxicity of heavy metals (Vaezi et al. 2015). The mobility of heavy metals, as well as their toxicities, greatly depends on their fractions (Lin et al. 2003; Singh and Kalamdhad 2013). Tessier divided element into five fractions (Tessier et al. 1979). Exchangeable, carbonate-associated fractions are more unstable and bioavailable than other fractions (Singh and Kalamdhad 2012; Singh et al. 2015). Therefore, evaluation of the fractions of elements qualitatively and quantitatively is an important basis in assessing the toxicity of the elements and research on their migration and transformation (Elkhatib and Moharem 2015). Many scholars have considered the difference of fractions in their researches using methods such as the *N*-way principal component analysis (Wang et al. 2013; Shin and Kim 2015).

In this study, based on the heavy metal sample data in the sediments of Yangtze River estuary in May 2011, the main objectives of the present study were to (1) estimating heavy metal concentrations and to evaluate their contamination level in sediments; (2) describing the distribution pattern of heavy metals in sediments; (3) evaluating heavy metal

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http://dx.doi.org/10.1016/j.marpolbul.2016.05.060
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Please cite this article as: Liu, R., et al., Spatial distribution and pollution evaluation of heavy metals in Yangtze estuary sediment, Marine Pollution Bulletin (2016), http://dx.doi.org/10.1016/j.marpolbul.2016.05.060

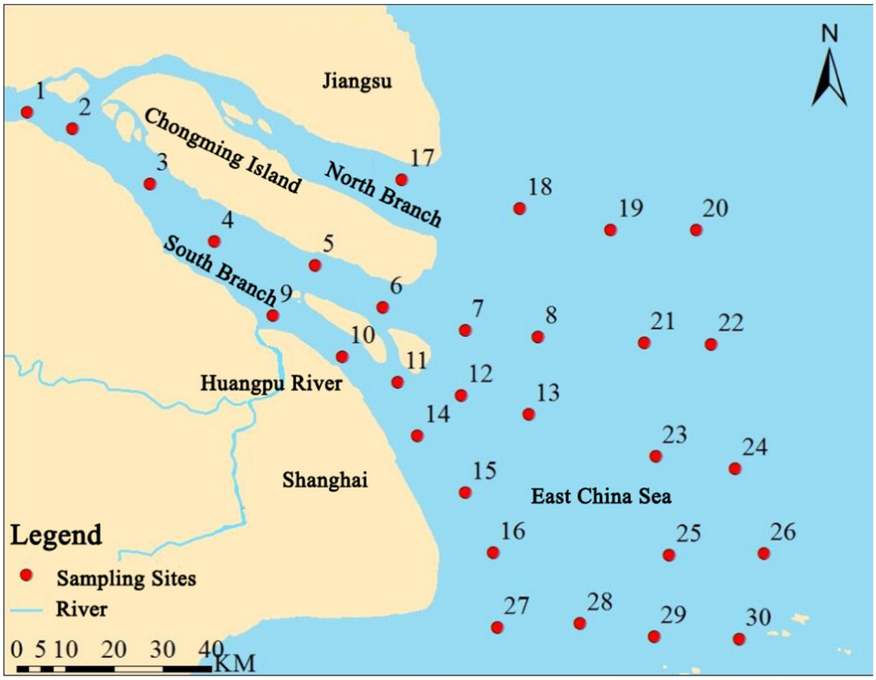

Fig. 1. Locations of the Yangtze River Estuary and 30 sampling sites.

pollution status and its potential ecological risk; and (4) exploring relationship among distribution, species and fraction of heavy metals.

The Yangtze River Estuary (YRE), the boundary between the Yellow Sea and the East China Sea, is divided into two main branches by Chongming Island (Fig. 1). YRE is the coastal outfall of Yangtze River which ranks third in length (6300 km), and it is on the most important strategic position of economic and social development in Yangtze River Basin (Chen et al. 2013; Adeleye et al. 2015). The land-based runoff and the highly polluted Huangpu River are two main sources of the contamination of the YRE (Guo et al. 2014). A considerable degree of contamination exists in the YRE and its adjacent sea (Zhang et al. 2009; Yin et al. 2015).

Table 1
The classification of *Igeo* and *RI*.

Index	Category	Description
Geoaccumulation index (*Igeo*)	*Igeo* ≤ 0	Practically uncontaminated
	0 < *Igeo* ≤ 1	Uncontaminated to moderately contaminated
	1 < *Igeo* ≤ 2	Moderately contaminated
	2 < *Igeo* ≤ 3	Moderately to heavily contaminated
	3 < *Igeo* ≤ 4	Heavily contaminated
	4 < *Igeo* ≤ 5	Heavily to extremely contaminated
	5 < *Igeo*	Extremely contaminated
Ecological risk (*RI*)	*RI* ≤ 150	Low risk
	150 < *RI* ≤ 300	Moderate risk
	300 < *RI* ≤ 600	Considerable risk
	600 < *RI*	High risk

In May 2011, 30 typical sampling sites were established covering practically the whole Yangtze estuary. For each site, sample was obtained by mixing three subsamples collected at that site. Then the samples were immediately cryopreserved in bags made of PTFE. After the removal of litter, stone particles and organisms, the refrigerated samples were dried, ground and shaken through nylon membrane sieve (0.284 mm) to obtain a fine homogeneous powder and stored at 4 °C for further analysis. The Tessier sequential extraction procedure was used to analyze the contents of different fractions (exchangeable (EXC), carbonate-associated (CARB), Fe–Mn oxides-associated (Fe/Mn), organic-associated (OM) and residual fractions (RES)) of metals (Shao et al. 2013; Rosado et al. 2016). And 12 metals were estimated: aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), ferrum (Fe), hydrargyrum (Hg), manganese (Mn), nickel (Ni), plumbum (Pb), stibonium (Sb) and zinc (Zn). The content of each metal is the sum of five corresponding fraction contents.

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. Three replicates were conducted to determine the total contents of the metals and errors were controlled within allowed scope.

The geo-accumulation index (I_{geo}), ecological risk index (*RI*) and *N*-way principal component analysis were used to assess metal contamination. Because of the shortage of geochemical background values of Al, Fe, Hg and Sb, only eight metals: As, Cd, Cr, Cu, Mn, Ni, Pb and Zn were assessed through I_{geo} and *RI*. The classification of each index was listed in Table 1.

I_{geo} is the most popular method used to evaluate the pollution of single element which considers the background value (Yao 2008; Wang

Table 2
Concentrations of heavy metals (μg/g).

Element	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Zn
May 2011	65557.22	9.96	0.15	87.17	25.51	36254.97	0.05	680.49	32.24	24.18	0.66	84.91
December 2007	69670.59	13.54	2.82	98.32	48.61	43644.83	0.16	–	41.49	50.77	–	129.73
August 2010	–	9.10	0.19	79.10	24.70	–	–	772.70	31.90	23.80	–	82.90
February 2011	–	9.00	0.20	80.90	23.90	–	–	715.50	32.00	23.40	–	78.10
Background value	–	1.50	0.10	35.00	25.00	–	–	600.00	20.00	20.00	–	71.00

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