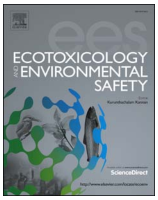
Ecotoxicology and Environmental Safety 139 (2017) 263–271

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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



Heavy metal concentrations and speciation in riverine sediments and the risks posed in three urban belts in the Haihe Basin

Chao Zhang[a,b], Baoqing Shan[a,b,*], Wenzhong Tang[a,b,*], Lixin Dong[c], Wenqiang Zhang[a], Yuansheng Pei[d]

[a] *State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China*
[b] *University of Chinese Academy of Science, Beijing 100049, PR China*
[c] *Tianjin Hydraulic Research Insititute, Tianjin 300061, PR China*
[d] *School of Environment, Beijing Normal University, Beijing 100875, PR China*

ARTICLE INFO

Keywords:
Urban belt
Heavy metal
Chemical speciation
Risk assessment
Source analysis

ABSTRACT

Heavy metal (Cr, Cu, Ni, Pb, and Zn) pollution and the risks posed by the heavy metals in riverine sediments in a mountainous urban-belt area (MB), a mountain–plain urban-belt area (MPB), and a plain urban-belt area (PB) in the Haihe Basin, China, were assessed. The enrichment factors indicated that the sediments were more polluted with Cu and Zn than with the other metals, especially in the MPB. The sediments in the MPB were strongly affected by Cu and Zn inputs from anthropogenic sources. The risk assessment codes and individual contamination factors showed that Zn was mobile and posed ecological risks, the exchangeable fractions being 21.1%, 21.2%, and 19.2% of the total Zn concentrations in the samples from the MB, MPB, and PB, respectively. Cr, Cu, and Zn in the sediments from the MPB were potentially highly bioavailable because the non-residual fractions were 56.2%, 54.9%, and 56.5%, respectively, of the total concentrations. The potential risks posed by the heavy metals (determined from the chemical fractions of the heavy metals) in the different areas generally decreased in the order MPB > MB > PB. Pictorial representation of cluster analysis results showed that urbanization development level could cause Cr and Zn pollution in the urban riverine sediments to become more severe.

1. Introduction

A great deal of attention has been paid in recent years to heavy pollution in urban riverine sediment due to rapid industrialization and urbanization (Islam et al., 2015; Martínez-Santos et al., 2015; Yu et al., 2011). The bioavailability and biological toxicity of heavy metals are affected not only by the total concentration of the heavy metals but also by the speciation of the metals (Yang et al., 2014). Different chemical forms of heavy metals in sediment have different chemical stabilities and biological availabilities and pose varying ecological risks. The European Community Bureau of Reference (BCR) standard method is a widely used sequential extraction method for determining the chemical speciation of heavy metals (Arain et al., 2008; Gao and Chen, 2012). The bioavailability of a metal is related to the concentrations of the metal in the acid-soluble, reducible, and oxidizable fractions, and the residual fraction is not bioavailable and remains stable for long periods (Rosado et al., 2016; Yin et al., 2014; Zhang et al., 2014). Heavy metals in the acid-soluble fraction of sediment are considered to be unstable because they can be released to the aqueous phase and therefore become more bioavailable (Gao and Chen, 2012). The proportion of the total concentration in the acid-soluble fraction by determining the risk assessment code (RAC), which is widely used to estimate the bioavailability of and risks posed by heavy metals in sediment (de Andrade Passos et al., 2010; Singh et al., 2005).

The Haihe Basin is one of the most developed and most densely populated regions in China. The total concentrations of heavy metals in sediments in urban rivers in the Haihe Basin have been studied (Liu et al., 2009; Tang et al., 2013). Water bodies in urban areas in the Haihe Basin receive wastewater from sewage treatment plants, pollutants from non-point sources, and untreated industrial wastewater, and the aquatic environment has been markedly degraded as rapid social and economic development and population increases have occurred (Gao and Chen, 2012). The Haihe Basin contains more than 24 cities with populations and developed areas of different sizes. There are major cities in mountainous areas, on the plain, and where the mountains and plain meet. The grain sizes, textures, mineral (e.g., Fe and Mn oxide)

---

* Corresponding authors at: State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China.
E-mail addresses: bqshan@rcees.ac.cn (B. Shan), wztang@rcees.ac.cn (W. Tang).

http://dx.doi.org/10.1016/j.ecoenv.2017.01.047
Received 2 August 2016; Received in revised form 26 January 2017; Accepted 27 January 2017

contents, and mobility of sediments are different in urban rivers in different geographic areas, and these parameters indirectly affect the bioavailability, mobility, and toxicity of heavy metals in the sediments (Huang et al., 2012; Zhang et al., 2014). The degree of urbanization and economic development of a city affect the organic matter (OM) and acid volatile sulfide deposition rates, and therefore also influence the distributions and chemical speciation of heavy metals (Hong et al., 2010; Strom et al., 2011). It is therefore necessary to assess the heavy metal contamination of sediment in urban rivers in different geographic positions within the Haihe Basin to determine the bioavailability, mobility, and toxicity of heavy metals and provide basic information for future river management.

Chemical fractions of heavy metals and statistical analysis have been widely used to study the contamination characteristics and bioavailability of heavy metals in sediment. These methods were used in the current study, which was performed with three aims. The first aim was to determine the concentrations and speciation of heavy metals in sediments in major urban rivers in three city belts of the Haihe Basin. The second aim was to use the chemical fractions of the heavy metals, determined using a modified BCR three-stage extraction procedure, to identify the risks, the bioavailability, and potential mobility of the heavy metals found in the sediments of rivers in different urban belt types. The third aim was to identify the sources of the heavy metals and the factors that influence the transportation of the metals to the sediments in the rivers using statistical methods (i.e., pictorial representation of cluster analysis [PRCA], canonical correspondence analysis [CCA], and Spearman's correlation matrices).

2. Materials and methods

2.1. Study area

The study was focused on urban rivers in economically important large and medium cities in the Haihe Basin. These urban rivers receive domestic raw sewage, household waste, and industrial waste from the cities they pass through (Pernet-Coudrier et al., 2012). Urban expansion and human activities have caused river ecosystem, including sediment, in the Haihe Basin to deteriorate rapidly in recent decades (Guo and Shen, 2015). The Haihe Basin is in North China, between 112°E and 120°E and 35°N and 43°N. There are 24 medium and large cities in the Haihe Basin. The total population of the Haihe Basin is 130 million (11.2% of the total Chinese population), and the GDP is USD 2.3×10^{12} (12% of the total Chinese GDP). The Haihe Basin is the largest water system in North China.

The Haihe Basin is divided into a mountainous region and a plain, as is shown in Fig. 1. The major cities in the Haihe Basin were divided into three urban belts, a mountainous urban belt (MB), a mountain–plain urban belt (MPB), and a plain urban belt (PB), as shown in Fig. 1. There were seven cities in the MB, ten in the MPB, and seven in the PB, as shown Fig. S1 in the Supporting Information (SI).

2.2. Sediment sample collection

A total of 159 sampling stations were selected, but surface sediment samples (0–10 cm deep) were collected from only 116 sampling stations because the surface sediment was almost entirely sand and gravel at 43 of the stations. Three parallel samples were collected at each sampling station. Each sample was collected using a plastic grab. The samples were collected in July and August 2014. The urban belts were defined as the areas up to between 40 km and 80 km from the centers of cities and within the boundary of the Haihe Basin.

The results presented for each sampling site are the means of the results for the three parallel samples that were collected at the site. There were 32, 49, and 35 sampling sites on urban rivers in the MB, MPB, and PB, respectively. Each sediment sample was placed in a labeled acid-rinsed polyethylene plastic bag, and the samples were stored in an icebox to transport them to the laboratory. Each sample was then freeze-dried, ground, homogenized, passed through a 100-mesh sieve, and stored in a polypropylene bottle. The dried samples were then stored at −80 °C until they were analyzed.

2.3. Analytical methods

A modified three-stage BCR sequential extraction procedure was used to determine the Cr, Cu, Fe, Ni, Pb, and Zn distributions in different chemical fractions in the samples (Arain et al., 2008). The four fractions that were determined were operationally defined as a water- and acid-soluble fraction (F1), a reducible fraction (F2), an oxidizable fraction (F3), and a residual fraction (F4). Detailed information on the modified BCR sequential extraction method is given in Table S1 in SI. Duplicate samples, standard reference samples, and blanks were analyzed to provide quality assurance and quality control information. The sequential extraction procedure was assessed by comparing the sums of the metal concentrations in the BCR sequential extraction fractions with the metal concentrations in total digests, as described in the SI. A sediment standard reference material GBW07436 (National Institute of Metrology, Beijing, China) was analyzed to assess the accuracy of the optimized BCR procedure. The recoveries of the chemical fractions of heavy metals ranged from 92% to 105%, and the relative standard deviation (used to indicate the precision of the method) was less than 5%.

For total heavy metal analysis, sediment samples (0.1000 g) were digested with 5 ml HF: $HClO_4$ (5:1) mixture in a microwave digestion equipment (MARS Xpress; CEM, Matthews, NC, USA) under the conditions described in Table S2. The heavy metal concentrations in the sediment extracts were determined using an Optima 2000DV inductively coupled plasma optical emission spectrometer (Perkin Elmer, Waltham, MA, USA), which gave detection limits of 0.003–0.050 mg/L, and an Agilent 7500a inductively coupled plasma mass spectrometer (Agilent Technologies, Santa Clara, CA, USA), which gave detection limits of 0.025–0.200 μg/L. The precision and accuracy of the Cr, Cu, Ni, Pb, and Zn results were assessed by analyzing the sediment standard reference material GBW07304 (National Institute of Metrology, Beijing, China). The recoveries for Cr, Cu, Ni, Pb, and Zn were 94–101%, 95–107%, 91–105%, 94–109%, 93–108%, respectively. The results were acceptable, and within ± 10% of each other were found when replicate samples were analyzed. The OM contents of the samples and the sizes of the particles in the samples were determined using the methods described in the SI.

2.4. Assessment of heavy metal contamination of the sediment samples and the risks posed

Heavy metal pollution in sediment is often assessed using the RAC, which is achieved by comparing the proportion of the total metal concentration in the F1 extract to a scale, as described in the SI (Sundaray et al., 2011; Zhai et al., 2014). The relative stabilities of the heavy metal concentrations in the sediment samples were assessed using individual contamination factors (ICFs) (Zhao et al., 2012). The ICF for a metal was determined by dividing the sum of the metal concentrations in the non-residue phases (F1, F2, and F3) by the concentration in the residual phase (F4), as described in the SI. The risks posed by heavy metals in sediment in the study area are categorized using the RACs and ICFs in Tables S3 and S4 in the SI. Enrichment factors (EF) of heavy metals in river sediments were calculated using following formula (Selvaraj et al., 2004):

$$EF=(C_x/C_{Fe})_S/(C_x/C_{Fe})_B$$

where C_x and C_{Fe} denote the concentrations of metals element x and Fe in the samples of sediment (S) and background concentration of metals (B). In addition, the concentration of Fe was analyzed to calculate the enrichment factor for each element. In this study, the soil background