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Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China

Xin Ke [a,*], Shaofeng Gui [a], Hao Huang [b], Haijun Zhang [a], Chunyong Wang [a], Wei Guo [b]

[a] *College of Energy and Environment, Shenyang Aerospace University, Shenyang 110136, China*
[b] *College of Agronomy, Shenyang Agriculture University, Shenyang 110161, China*

HIGHLIGHTS

- Speciation analysis showed that Cd, Pb and Zn have high bioavailability.
- PCA revealed that Cd and Zn were mainly from agriculture sources.
- Cd posed higher potential ecological risk in this studied area.

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ABSTRACT

Surface sediment samples collected from 19 sites in the Liaohe River protected area were analysed for heavy metals to evaluate their potential ecological risk. The results demonstrated that the degree of pollution from seven heavy metals decreases in the following sequence: cadmium(Cd)>arsenic(As)>copper(Cu)>nickel(Ni)>lead(Pb)>chromium(Cr)>zinc(Zn). The metal speciation analysis indicated that Cd, Pb and Zn were dominated by non-residual fractions and have high mobility and bioavailability, indicating significant anthropogenic sources. Based on the potential ecological risk index (PERI), geo-accumulation index (I_{geo}) and risk assessment code (RAC), Cd made the most dominant contribution, with a high to very high potential ecological risk being determined in this studied area. Moreover, in reference to the results of multivariate statistical analyses, we deduced that Cd and Zn originated from agriculture sources within the Liaohe River protected area, whereas Cu, Cr and Ni primarily originated from natural sources.

1. Introduction

Because of industrial growth and development, water environments are increasingly exposed to heavy metal pollutants (HMs), which are serious pollutants of aquatic ecosystems because of their environmental persistence, bioaccumulation and ability to be incorporated into the food chain (Xiao et al., 2015; Bastami et al., 2014; Bodin et al., 2013). Heavy metals are deposited in sediment by adsorption, hydrolysis and co-precipitation processes, causing a potential threat to aquatic biota and human health (Singh et al., 2005; Suresh et al., 2015). However, the mobility of heavy metals in aquatic systems depends on various conditions, such as chemical and biological factors that involve their desorption from sediment and release into overlying water (Hill et al., 2013). Hence, sediment is the ultimate receptor of pollutants and a potential secondary source of contamination in overlying waters (Santos et al., 2003).

With the rise in chemical, metallurgy, mining, petrochemical and agriculture industries, the Liaohe River has been affected by pollution and ecological environment threats (Zhuang and Gao, 2015; Ke et al., 2015a,b). During that period, municipal domestic sewage and industrial waste were discharged directly into the river, having a detrimental impact on the ecological environment and human health (Lu and Li, 2006).

Based on the content, distribution and speciation of heavy metals, numerous analytical techniques have been applied for the assessment of potential ecological risks in surface sediment from aquatic ecosystems (Tssier et al., 1979; Yang et al., 2009; Yu et al., 2011).

Zahra et al. (2014) used environmental factors, the geo-accumulation index (I_{geo}), sediment quality guidelines (SQG_S) and

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[*] Corresponding author.
E-mail address: kex@iae.ac.cn (X. Ke).

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the metal pollution index to quantify the degree of total metal pollution and assess the ecological risk of heavy metals in sediment (Zahra et al., 2014). In terms of I_{geo}, the chemical speciation and geographical spatial heterogeneity factors for different heavy metals are ignored. Although the potential ecological risk index (PERI) considers both the toxicities and total concentration of heavy metals, chemical speciation is neglected and it involves a high level of subjectivity (Singh et al., 2005; Li et al., 2007; Zhu et al., 2012; Maanan et al., 2014b). In fact, the toxicity and mobility of heavy metals in the environment depends on their chemical forms (Perin et al., 1997). Risk assessment code (RAC) was introduced based on its advantage of comprehensive analysis of heavy metals and other components in sediment; thus, it provides a better interpretation of the relationship between the bioavailable fraction and mineral mobility, as well as the environmental risk of heavy metals (Yang et al., 2014). Up until now, no systematic or integrated research has focused on the ecological risk assessment of heavy metal contamination in the Liaohe River protected area. Li et al. (2016) examined sediment from the Liaohe Estuary to determine the spatial distribution and potential ecological risk of heavy metals and found that heavy metal pollution in the Liaohe Estuary was dominated by cadmium (Cd) and mercury (Hg). However, the source of their identification has not been determined, and the chemical fraction in heavy metals and their bioavailability remains unclear. Although the distribution of several heavy metals in sediment from the Shuangtaizi estuary, located downstream of the Liaohe River, has been previously studied, there is limited information concerning heavy metal pollution in the Liaohe River protected area (Mora et al., 2004; Fu et al., 2014).

In this study, we chose some representative sites as the study area and conducted a novel, systematical risk assessment of heavy metals in the Liaohe River protected area. Hence, this study aimed to (1)investigate the concentration distribution characteristics of heavy metals (arsenic(As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)) in the surface sediment of the Liaohe River protected area; (2) assess the ecological risk of heavy metals in sediment and (3) identify the natural or anthropogenic sources of metals using statistical techniques.

2. Materials and methods

2.1. Description of the study area

The Liaohe River, a natural cradle of Chinese civilization, is one of the most important aquatic ecosystems in China because it serves the economic and social development in northeast China and is an important economy and community activity centre (Li, 2013; Zhang et al., 2013). The protected area (123°55′E to 121°41′E and 43°02′N to 40°47′N) is located in the Liaoning province, with an area of ~1869 km^2 and annual flow of 302 $km^3 \cdot r^{-1}$, beginning at the confluence of east and west Liaohe River, meandering through the Tieling, Shenyang, Anshan and Panjin cities and emptying into the Bohai Sea (Ren et al., 2015). The main land-use types of the Liaohe River protected area are farmland and residential areas. Particularly, the largest proportion of land-use type is farmland, which accounts for 41.22% of the total area (Li and Song, 2013). Because of the extent of coastal city and chemical industry enterprise, pollution is becoming a more serious problem. Additionally, social-economic activities in this region, such as machinery, paper, pharmaceutical, copper, printing, food and other major industrial projects increase the pollution risk (Ke et al., 2015b).

2.2. Sample collection

Nineteen superficial sediment samples (0–10 cm) were collected along the Liaohe River protected area (Fig. 1) in October 2013. A superficial 10 cm layer was collected because it is more chemically and biologically active than the deep layers and because more benthic organisms occupy this layer (Simpson et al., 2005; Salem et al., 2014). The sampling locations were selected based on the historical chemical analyses of sediment from the entire river basin. At each site, three surface sediments were collected and placed into polyethylene bags and sealed. After sampling, the sediment samples were transported to the laboratory and stored at 4 °C until further analysis.

2.3. Sample pretreatment and basic parameters analysis

The heavy metal concentration in sediment reflects the status of aquatic systems (Zhu et al., 2012). The concentration of heavy metals was accessed according to the methods of Jiang et al. (2014) and Gao et al. (2010) with some modifications. Briefly, the sediment samples (0.5 g) were digested in 20 mL of a 1:1:2 guaranteed reagent $HNO_3 + HClO_4 + HF$ for 10 h. Inductively coupled plasma-optical emission spectrometry(ICP-OES, Thermo) was applied for the determination of heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn). The total organic matter content (TOC) and pH were measured to show the general characteristics of sediment samples. In this study, the TOC was determined by the weight-loss-on-ignition method, at a temperature of 550 °C for 24 h (Ramasamy et al., 2014).

2.4. Quality assurance and quality control (QA/QC)

Quality assurance and quality control were assessed in duplicates, with method blanks and standard reference materials. Three replicates were conducted for the determination of the total content of the metals. The relative standard deviation (RSD) was greater than 5% for all tests. All of the analyses were carried out in duplicate, and the results were expressed as the mean concentration. The quality of the analytical procedures was tested by the recovery measurements on the Chinese national geo-standard (GBW-07333 and GBW-07314). The results were consistent with the reference values, and the differences were within ±10%. All of the reagents were guaranteed analytical grade or higher. The lab glassware (bottles, tubes, etc.) were pre-cleaned by soaking in 10% HNO_3(w/w) for at least 2 days, followed by soaking and rinsing with de-ionized water prior to use (Zhuang and Gao, 2015).

2.5. Assessment of sediment contamination

2.5.1. Sediment quality guidelines (SQGs)

The sediment quality guidelines (SQGs) provided a simple, comparative mean for assessing the risk of contamination in an aquatic ecosystem (Macdonald et al., 2000). In this study, two types of limit values were applied to evaluate the potential risk of the ecosystem, based on the concentration of pollutants, threshold effect concentration (TEC) and probable effect concentration (PEC) (Feng et al., 2011). The concentrations below the TEC represent a minimal-effect range, which is intended to estimate the conditions where biological effects are rarely observed (Suresh et al., 2015). Concentrations equal to or greater than the TEC, but less than the PEC represent a range where biological effects occasionally occur. Concentrations at or above the PEC represent a probable effect range where adverse biological effects frequently occur (Zhang et al., 2013).