Basin-scale comprehensive assessment of cadmium pollution, risk, and toxicity in riverine sediments of the Haihe Basin in north China

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A B S T R A C T  
A comprehensive and detailed investigation of cadmium (Cd) pollution in surface riverine sediments of the Haihe Basin in north China was carried out. Total Cd concentrations in these sediments ranged from 0.153 to 22.1 mg/kg, exceeding the soil background value at all sampling sites. The mean Cd concentration of the bioavailable fraction was 0.557 mg/kg, accounting on average for 51.58% of the total Cd. A mean value of the Cd enrichment factor of 11.6 suggested that Cd has accumulated in most riverine sediments, resulting in a high degree of anthropogenic pollution. In fact, there were high levels of Cd pollution in the riverine sediments throughout the Haihe Basin, yielding geo-accumulation index values for Cd from 0.071 to 7.25. According to the potential ecological risk index, risk assessment code, and consensus-based sediment quality guidelines, Cd was a serious pollutant in this ecosystem. Because it occurred as a high proportion in the exchangeable/acid soluble fraction (21.21% on average), it may also have biological toxicity. Our findings indicated that it is important to consider Cd in control strategies for managing riverine sediment pollution in the Haihe Basin.

1. Introduction

Sediments may provide a record of the history of heavy metal pollution in aquatic ecosystems (Shang et al., 2012; Zhang and Shan, 2008). A number of studies have shown that metal contamination of sediments is increasing, posing a serious threat to the health of aquatic systems globally (Kucuksezgin et al., 2008; Nobi et al., 2010; Zhang et al., 2014). Specifically, there is a great deal of concern over cadmium (Cd), a highly toxic metal (Gao et al., 2013; Nemati et al., 2011), found to occur in significant quantities in the sediments of many areas, such as Bohai Bay and Zhu River in China, and the Tíbagi River in Brazil (Galunin et al., 2014; Gao and Chen, 2012; Tang et al., 2014). However, few researchers have conducted comprehensive and detailed investigations of Cd pollution, risk, and toxicity of riverine sediments on such a large scale as the Haihe Basin (with an area of 318,000 km²) of north China.

In China, heavy metal contamination of riverine sediments did not attract much attention from researchers or governments prior to the year 2000, and relatively few studies were carried out before this time (He et al., 1998; Zhao et al., 1999). Industrial and mining activities that always discharge heavy metals through atmospheric emissions or effluent into the rivers have been increasing continuously and rapidly, especially in the Haihe Basin (Tang et al., 2013). This area, located in northern China, is an important political, economic, and cultural center of China. The Haihe Basin includes nine major watersheds: Luan He (LH), Bei San He (BSH), Yong Ding He (YDH), Da Qing He (DQH), Haihe Gan-liu (HG), Zi Ya He (ZYH), Hei Long Gang (HLG), Zhang Wei He (ZWH), and Tu-hai Ma-xia He (TMH), as outlined by the Water Resources Protection Bureau of the Haihe Basin in China (WRPPHRB, 2011). To date, there have only been some studies of Cd pollution in the sediments of one or several rivers of a given watershed (Liu et al., 2009; Su et al., 2015; Tang et al., 2013). However, a comprehensive and detailed understanding of Cd concentrations, speciation, sources, pollution, risk, and toxicity across the whole basin is lacking. A study focusing on such these aspects will be very helpful in raising public awareness of Cd contamination, and in designing strategies to minimize pollution or exposure risk in the rivers of the Haihe Basin.

Using 220 sediment sampling sites within the Haihe Basin, this study was carried out to investigate: 1) Cd content and speciation in the surface sediments; 2) the Cd was of natural or anthropogenic origin, based on its enrichment factor (EF) and a Pearson correlation analysis (CA); 3) the degree of Cd pollution based on the geo-accumulation index (Igeo); 4) to assess the risk associated with Cd based on the potential ecological risk index (Er) and risk assessment code (RAC); and 5)
the potential biological toxicity of the sediments by consensus-based sediment quality guidelines (SQGs) and the mean probable effect concentration quotient \((Q_{m-PEC})\). These investigations facilitated a basin-scale analysis of the pollution status, risk and toxicity related to Cd in the riverine sediments of the Haihe Basin.

2. Material and methods

2.1. Study area

The Haihe Basin (35°–43° N, 112°–120° E), located mainly within the province of Hebei, includes Beijing, Tianjin, parts of Inner Mongolia, and parts of the provinces of Shanxi, Henan, and Shandong (Fig. 1). This region has the highest population density in China, particularly in the plain region. The total population of the Haihe Basin is 130 million (11% of the total Chinese population), and the GDP is USD \(2.3 \times 10^{12}\) (12% of the total Chinese GDP). The annual average temperature in the basin ranges from 0 to 14 °C. The annual average precipitation is 547 mm, of which 75%–85% occurs from June to August (Ding et al., 2015).

Heavy industrial development and rapid urbanization have caused a great deal of pollution of surface waters in the Haihe Basin. As a result, this region has attracted much attention from the Chinese government and has been identified as one of the most important basins in the National 11th, 12th, and 13th Five-Year Plans for Water Pollution Control. The Haihe Basin contains approximately 113 rivers with a catchment area greater than 500 km², comprising the nine major watersheds of the Water Resources Protection Bureau of the Haihe Basin in China (WRPBHRB, 2011).

2.2. Sample collection and analysis

Before selecting sampling sites, we divided the Haihe Basin into 41 units, reflecting climate, geology, geomorphology, soil, and watersheds. Using this framework of units, we selected sites to reflect the diversity of the river systems. In our study, 220 sampling sites with sediments were selected to investigate Cd pollution in the rivers of the Haihe Basin (Fig. 1). Thus, surface sediments (0–10 cm; triplicate samples at each site) were collected in the middle of the rivers from May to August of 2013 within the LH, BSH, YDH, DQH, HG, ZYH, HLG, ZWH and TMH watersheds, using a Peterson grab sampler. Of the original 410 sampling sites, sampling at approximately 190 sites was not pursued, because they had a hard riverbed composed almost completely of sand and gravel, had been dried up for many years, or had signs of environmental dredging carried out as sediment contaminant remediation (including sediment removal).

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. These dried samples were stored at \(-80\) °C until they were analyzed. Concentrations of Cd, Fe, and Mn in the surface riverine sediments from all 220 sampling sites were determined (Fig. 1). Organic matter (OM) content was measured by residual titration with...
K$_2$Cr$_2$O$_7$ (Bao, 2000), while the grain size of the sediments was measured with a laser particle size analyzer (Mastersizer 2000, Malvern, UK) over the range of 0.020–2000 μm. For total heavy metal analysis, sediment samples (0.100 g) were treated in a 5:1 mixture of hydrofluoric: perchloric acid (Tessier et al., 1979) by microwave digestion (MARS Xpress; CEM, Matthews, NC, USA); and the digestion conditions are listed in Table S1. The metal speciation in the sediments was determined using the modified European Community Bureau of Reference (BCR) three-step sequential extraction procedure; more detailed information is given in Table S2 (Arain et al., 2008; Nemati et al., 2011). This method provides the proportion of Cd present as B1 (exchangeable/acid soluble), B2 (reducible), B3 (oxidizable), and B4 (residual) fractions in the sediments. All of the above solutions were stored at 4 °C prior to analysis. Cd was measured by inductively coupled plasma-mass spectrometry (ICP-MS) (7500a; Agilent Technologies, Santa Clara, CA, USA), while Fe and Mn were measured by inductively coupled plasma–optical emission spectrometry (ICP-OES) (Optima 2000DV; PerkinElmer, Waltham, MA, USA). To ensure laboratory quality control, sediment reference materials (GBW07303a and GBW07436; National Institute of Metrology, Beijing, China) and triplicate samples were analyzed. Accepted recovery varied from 93% to 116%, while precision was within 6% of the relative standard deviation (RSD).

2.3. Relevant assessment and statistical analysis

EF values were calculated to obtain information regarding the degree of enrichment of Cd in the sediments (Bhuiyan et al., 2010; Zhang et al., 2009). The pollution status and risks associated with Cd in surface sediments were assessed using the $I_{geo}$ (Cheng and Yap, 2015; Christophoridis et al., 2009), and $E_{f}$ (Guo et al., 2010; Hakanson, 1980; Yi et al., 2011). Additionally, RAC, SQGs, and Q$_{geo-P}$ values were used to evaluate sediment ecological toxicity by determining whether surface sediments were nontoxic or toxic to benthic organisms based on their Cd concentrations (Cheng and Yap, 2015; MacDonald et al., 2000; Perin et al., 1985). Details of these assessment methods are outlined in the Supplementary Materials (Table S3). Furthermore, Cd data were analyzed using SPSS Statistics 18.0 for Windows (IBM, Armonk, NY, USA), and a CA was used to assess relationships between Cd, and Fe, Mn, OM, and Mz. ArcGIS 10.1 (Esri, Redlands, CA, USA) was also used to process our experimental data.

3. Results and discussion

3.1. Cadmium concentrations and speciation in the surface riverine sediments

The spatial distribution of total Cd concentrations in the surface riverine sediments of the Haihe Basin is shown in Fig. 2. Total Cd concentrations ranged from 0.153 to 22.1 mg/kg, with an average of 1.08 mg/kg. Compared with data reported from other rivers in China and elsewhere globally (Table S4), the sediments of this study had high Cd concentrations. Spatially, the five regions with the highest Cd concentrations in the surface riverine sediments of the Haihe Basin were the northern region of the YDH watershed, the central region of the BSH watershed, the eastern region of the ZWH watershed, the southern region of the ZWH watershed, and the junction region of HLG, TMH, and ZWH watersheds. The highest values were 3.90, 13.3, 9.86, 11.9, and 22.1 mg/kg, respectively. Overall, Cd concentrations in the plain and coastal regions with heavy industrial development and rapid urbanization, especially near the cities were higher than those in the mountainous region of the Haihe Basin (Fig. S1).

The speciation of Cd in the sediments, determined by BCR sequential extraction, is shown in Fig. 3; while the percentage of total Cd occurring in the different fractions is shown in Fig. S2. Clearly, the majority of Cd occurred in the B1 and B4 fractions. In the surface riverine sediments of the Haihe Basin, the mean concentrations of Cd in the B1, B2, B3, and B4 fractions were 0.229, 0.217, 0.111, and 0.523 mg/kg, respectively, representing an average of 21.21%, 20.12%, 10.25%, and 48.42% of the total Cd concentrations, respectively. Spatially, concentrations of Cd in the B1 fraction were highest in the junction region of HLG, TMH, and ZWH watersheds (maximum value = 16.0 mg/kg). The distribution of concentrations in the B2 fraction (maximum value = 3.52 mg/kg) was similar to the B1 fraction. Interestingly, in the junction region of YDH, BSH, and DQH watersheds, and the junction region of HLG, TMH, and ZWH watersheds, the highest concentrations of Cd occurred in the B3 fraction.

3.2. Cadmium sources and pollution in the surface riverine sediments

The EF values of Cd were calculated to determine the potential sources of Cd in the surface riverine sediments of the Haihe Basin. (Fig. 4). The Cd EF values ranged from 0.249 to 211, with an average value of 11.6. The distribution of the EF values was similar to the total Cd concentrations within this basin. An EF value greater than 1.5 suggests that a significant portion of the metals originated from noncrustal or anthropogenic sources in the sediments (Li et al., 2010). Clearly, Cd was anthropogenically enriched in most sediments of the Haihe Basin (having EF values > 1.5), indicating a high degree of anthropogenic pollution in this basin. Therefore, EF may be a useful indicator of the role of anthropogenic processes in generating the Cd distribution in surface riverine sediments of the Haihe Basin. In addition, Cd in an ironic form, bound to carbonates, and in the exchangeable fraction, is released to the B1 fraction. This represents the fraction most easily enriched in sediments; it is also the fraction most easily re-mobilized, when environmental conditions change (Nemati et al., 2011). Therefore, Cd in the B1 fraction should receive more attention during development of effective control strategies for Cd pollution in riverine sediments.

CA is also a convenient way to identify the factors controlling heavy metal concentrations and their possible sources (Chai et al., 2015; Dragovic et al., 2008). Therefore, correlations between Cd and other sediment properties are presented in Table S5. As shown in Figs. S3–S6, the ranges and mean values of Fe, Mn, and OM contents in the surface riverine sediments are as follows: Fe, 0.350%–16.2% (3.69%); Mn, 11.9–4500 (685) mg/kg; and OM, 0.285%–31.37% (5.01%). Additionally, mean grain size (Mz) of the riverine sediments ranged from 7.98 to 426 μm, with an average diameter of 68.4 μm. The correlations between different fractions of Cd in the sediments were complex. The total Cd content was significantly positively correlated with the percentage of Cd occurring in each different fraction (p < 0.01), except for the B3 fraction. Moreover, positive correlations among the B1 fraction Cd, B2 fraction Cd, and B3 fraction Cd indicated they all had the same anthropogenic sources, possibly including mining activities, battery production, and agricultural fertilizers. OM content was significantly positively correlated with the concentration of Cd in the B3 fraction (p < 0.01), indicating a strong association of oxidizable Cd with OM (Queena et al., 2009). No correlations were observed between Cd and Fe, Cd and Mn, or Cd and Mz.

Here, the $I_{geo}$ value was used to verify the degree of Cd pollution in the sediments (Fig. 4). According to this measure, there were high levels of Cd pollution in most of the riverine sediments; the $I_{geo}$ values for Cd ranged from 0.071 to 7.25, with an average of 2.25. These values indicate moderately to strongly polluted sediments in these rivers. The percentages of the $I_{geo}$ values occurring within the intervals 0–1, 1–2, 2–3, 3–4, 4–5, and > 5 were 13.63%, 23.64%, 45.91%, 12.27%, 1.82%, and 2.73%, respectively. These findings showed that the riverine surface sediments of the Haihe Basin had been heavily contaminated with Cd, because of anthropogenic inputs, consistent with the EF results.

3.3. Cadmium risk and toxicity in the surface riverine sediments

The risk associated with Cd in the surface riverine sediments of the
study area was assessed using \( E_i \) and the RAC. Potential ecological risk (PER) represents the sensitivity of the biological community to a given substance and indicates the risk posed by heavy metals (Fu et al., 2014; Ma et al., 2013). Calculated PER indices of Cd \( (E_i) \) for this study are presented in Fig. 5. In the Haihe Basin, the \( E_i \) values of Cd in the sediments ranged from 47.3 to 6869, with an average of 334, indicating very high PER related to Cd in the riverine sediments. These findings were consistent with the EF and \( I_{geo} \) results. Cd in these sediments was associated with a very high PER in 16.81% of the sampling sites; while high PER values were recorded for 48.64%, considerable PER for 22.73%, and a moderate PER for 11.82% of sites.

Heavy metals are bound to/on carriers (e.g., carbonate, organic matter, sulfides, and Fe/Mn oxides) in the sediments; these are defined as different fractions, whereby their binding strength determines their bioavailability and the risk associated with their presence in aquatic ecosystems (Nemati et al., 2011). Here, the RAC was determined using the percentage of Cd occurring in the B1 fraction. This is because Cd weakly bound to the solid phase usually poses a greater risk to the aquatic environment (Jain, 2004). In this study, 18.11% (mean value) of the total Cd occurred in the B1 fraction (Fig. S2). The high proportion of metals in this fraction is indicative of anthropogenic pollution (Weng et al., 2014; Yang et al., 2009). According to the RAC classification shown in Table S3, Cd in the surface riverine sediments is associated with a very high or high risk in 10.45% of sampling sites; while a medium risk occurred in 50.91%, low risk in 36.36%; and no risk in only 2.20% of sampling sites. Therefore, significant Cd remediation measures should be carried out as soon as possible on the riverine sediments of the Haihe Basin, especially in the junction region of HLG, TMH, and ZWH watersheds, according to the results of both \( E_i \) and the RAC.

The bioavailability and ecotoxicity of heavy metals are directly dependent on their speciation in sediments (Dong et al., 2013). Thus, the bioavailability and ecotoxicity of heavy metals can be described in terms of various fractions: metals occurring in the B1 and B2 fractions.
are directly bioavailable and are the most toxic; metals in the B3 fraction are potentially bioavailable and toxic, with the likelihood of their bioavailability increasing over time; while metals in the B4 fraction appear to be nontoxic (Yuan et al., 2011). In this study, the percentage of Cd occurring in the bioavailable fractions (B1 + B2 + B3) was 51.58% in the surface riverine sediments, with mean concentrations of these fractions reaching 0.557 mg/kg (Fig. S7). The high Cd content of these bioavailable fractions demonstrates that Cd poses an ecological risk to the environment in the study area.

SQGs and $Q_{bio-PEC}$ values were used to further examine the ecotoxicity of Cd in the sediments of the Haihe Basin (Fig. S8 and Fig. 5). Cd concentrations exceeded the background values in 100% of the sampling sites, indicating that Cd had varying accumulation degrees in all the riverine sediments of the Haihe Basin. In particular, 33.64% of sediments had concentrations that exceeded the threshold effect concentration (TEC), while 2.73% had concentrations exceeding the probable effect concentration (PEC) (Fig. S7). Based on these results, adverse effect of Cd was expected in this environment. The $Q_{bio-PEC}$ can
be used as an index of sediment toxicity associated with heavy metals. A $Q_{m\text{-PEC}}$ value below 0.5 indicates that the surface sediment is not toxic to benthic organisms, while a $Q_{m\text{-PEC}} > 1.5$ indicates that adverse effects on benthic organisms are likely to occur. In this study, $Q_{m\text{-PEC}}$ values ranged from 0.031 to 4.46, with an average value of 0.217 (Fig. 5). Specifically, there were five regions with high $Q_{m\text{-PEC}}$ values, yielding a similar spatial distribution to total Cd concentrations in the Haihe Basin.

In the riverine sediments of the Haihe Basin, Cd has reached very high levels (maximum value = 22.1 mg/kg), indicating a high degree of anthropogenically-derived Cd accumulation (maximum EF value = 211), especially in the plain and coastal regions (Fig. 3). These sources may include mining and industrial activities, as well as agricultural ones. Especially in the plain and coastal regions of the Haihe Basin, Cd pollution, risk, and toxicity of surface riverine sediments are all high, as indicated by the high percentage of Cd occurring in the bioavailable fraction (average value = 51.58%). Such high bioavailability may lead to adverse impacts on human and ecosystem health (Lambert et al., 2007; Zhao et al., 2007).

4. Conclusions

Cd concentrations, speciation, sources, pollution, risk, and toxicity were assessed in surface riverine sediments of the Haihe Basin of north China. Total Cd concentrations (from 0.153 to 22.1 mg/kg) in the sediments all exceeded the soil background value. The five regions with the highest Cd concentrations were the northern region of the YDH watershed, the central region of the BSH watershed, the eastern region...
of the ZYH watershed, the eastern region of the ZWH watershed, and the junction region of the HLG, TMH, and ZWH watersheds. According to EF and Igeo values, Cd appeared to have been derived from anthropogenic sources in most of the riverine sediments of the Haise Basin, especially in the plain and coastal regions, where sediments were polluted with Cd to a high degree. Additionally, based on both total concentrations and speciation, Cd posed a risk in all sediments sampled in this study, and was highly bioavailable, which may result in adverse effects on the benthic organisms in the rivers. The results of this study will be useful in the development of effective control strategies for Cd pollution in riverine sediments of the Haise Basin.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecolind.2017.06.011.

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