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Characterization of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China

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Sediment in Wuli River, Cishan River, and Lianshan River has been contaminated by heavy metals and adverse effects would be expected frequently in Wuli River and Cishan River.

Abstract

Wuli River, Cishan River, and Lianshan River are three freshwater rivers flowing through Huludao City, in a region of northeast China strongly affected by industrialization. Contamination assessment has never been conducted in a comprehensive way. For the first time, the contamination of three rivers impacted by different sources in the same city was compared. This work investigated the distribution and sources of Hg, Pb, Cd, Zn and Cu in the surface sediments of Wuli River, Cishan River, and Lianshan River, and assessed heavy metal toxicity risk with the application of two different sets of Sediment Quality Guideline (SQG) indices (effect range low/effect range median values, ERL/ERM; and threshold effect level/probable effect level, TEL/PEL). Furthermore, this study used a toxic unit approach to compare and gauge the individual and combined metal contamination for Hg, Pb, Cd, Zn and Cu. Results showed that Hg contamination in the sediments of Wuli River originated from previous sediment contamination of the chlor-alkali producing industry, and Pb, Cd, Zn and Cu contamination was mainly derived from atmospheric deposition and unknown small pollution sources. Heavy metal contamination to Cishan River sediments was mainly derived from Huludao Zinc Plant, while atmospheric deposition, sewage wastewater and unknown small pollution were the primary sources for Lianshan River. The potential acute toxicity in sediment of Wuli River may be primarily due to Hg contamination. Hg is the major toxicity contributor, accounting for 53.3–93.2%, 7.9–54.9% to total toxicity in Wuli River and Lianshan River, respectively, followed by Cd. In Cishan River, Cd is the major sediment toxicity contributor, however, accounting for 63.2–66.9% of total toxicity.

Keywords: Sediment; Sediment quality guidelines; Huludao City; Freshwater

1. Introduction

Sediments represent the largest pool of metals in aquatic environments (Daskalakis and O'Connor, 1995). More than 90% of the heavy metal load in aquatic systems is bound to suspended particulate matter and sediments (Calmano et al., 1993). Sediments polluted with various kinds of hazardous and toxic substances have been found, including trace elements which accumulate in sediments via several pathways: disposal of liquid effluents, terrestrial runoff, and leachate carrying chemicals originating from numerous urban, industrial, and agricultural activities, as well as atmospheric deposition (Rivail Da Silva et al., 1996; Karageorgis et al., 2002; Mucha et al., 2003). The distribution of heavy metals in sediments adjacent to populated areas can provide researchers with evidence of the anthropogenic impact on ecosystems and aid in assessing the risks associated with discharged human waste. The build-up of metals in sediments has significant

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environmental implications for local communities, as well as for river water quality (Demirak et al., 2006).

Sediment quality guidelines (SQGs) are very useful to screen sediment contamination by comparing sediment contaminant concentration with the corresponding quality guideline (Caeiro et al., 2005). These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist the interpretation of sediment quality (Wenning and Ingersoll, 2002). SQGs, including sediment quality criteria, sediment quality objectives and sediment quality standards, have been developed by various federal and provincial agencies in North America for both freshwater and marine ecosystems (Pekey et al., 2004; Caeiro et al., 2005). Such SQGs have been used in numerous applications, including designing monitoring programs, interpreting historical data, evaluating the need for detailed sediment quality assessments, assessing the quality of prospective dredged materials, conducting remedial investigations and ecological risk assessments, and developing sediment quality remediation objectives (Long et al., 1995; Smith et al., 1996; Long and MacDonald, 1998).

Huludao City is an industrial base in Liaoning Province. Wuli River, Cishan River, and Lianshan River are three freshwater rivers which flow through Huludao City, and reach the sea at Jinzhou Gulf. The ecosystems of the three rivers are impacted significantly by historic and current anthropogenic loadings of a variety of pollutants (Na Zheng et al., 2007), including heavy metals. Mercury (Hg) is a contaminant of primary concern in the three rivers (Na Zheng et al., 2007). This is due in part to continued inputs of metals from point sources and atmospheric deposition to the watershed, as well as its ability to be transformed to monomethylmercury (MMHg) via natural processes (Gilmour and Henry, 1991; Benoit et al., 2003). In this study, in order to compare the characterization of heavy metal contamination in sediments in the three rivers, the distribution of Hg, Pb, Cd, Zn and Cu were investigated in the surface sediments and typical sediment profiles of Wuli River, Cishan River and Lianshan River. The ecological risk of sediment was assessed with the application of two different sets of SQG indices. The characteristics of combined contamination were also studied using the toxic unit approach.

2. Materials and methods

2.1. Study area

Huludao City (40°56′ N, 120°28′ E) is in Liaoning Province in northeast China, near Liaodong Gulf (Fig. 1). The production of petrochemicals and nonferrous metal smelting are the primary industries of Huludao City. Jinxi Chemical Factory and Huludao Zinc Plant (the largest zinc smelting plant in Asia) are the main industrial enterprises in Huludao City. Wuli River has a long history of chlor-alkali producing impacts from Jinxi Chemical Factory, while a large amount of waste from Huludao Zinc Plant was discharged into Cishan River, resulting in serious contamination in the two rivers (Zhao and Yan, 1997; Zheng et al., 2007). By contrast, there is no obvious pollution source found along Lianshang River. According to historical data, wastes from Jinxi Chemical Factory and Jinxi Petroleum Chemical Factory were discharged into Wuli River near site W2. However, the use of mercury cathodes in Jinxi Chemical Factor ceased after 1998, and wastewater discharged to Wuli River has been greatly reduced since then. Large amounts of waste from Huludao Zinc Plant were discharged into the Cishan River estuary. There was no large pollution source along Lianshan River, except waste from villagers who lived along it.

2.2. Sediment sampling

Grain size plays a significant role in determining elemental concentrations in sediments (Szefer et al., 1996). It is recommended that a particle size fraction of <63μm should be applied for analysis because this is most nearly equivalent to materials carried in suspension, the most important system for transport of sediments (Salomons and Förstner, 1984; Chen et al., 1994). In this study, the contamination of sediments with particle size fractions <63μm were investigated.

Surface sediment samples were collected from 10 sites in Wuli River, 6 sites in Cishan River and 4 sites in Lianshan River in May 2005 (Fig. 1). Typical sediment profiles from the W7 (Wuli River) and C4 (Cishan River) sites are shown in Fig. 2. These sites were selected because sediment samples at different depths could be easily collected and are not affected by estuary and pollution sources. Sediment samples at depth intervals of 0–5, 5–10, 10–15, 15–20, 20–25, 25–30 and 30–35 cm were collected at these sites. Samples were placed in dark-colored polyethylene bags, refrigerated and returned to the laboratory immediately. Samples were air dried at 4 °C, crushed, passed through 0.063-mm mesh sieve and stored at 4 °C in the dark before analysis of properties and concentrations of heavy metals.

2.3. Heavy metal analysis and quality control

Samples were digested using the method of H_2SO_4–HNO_3–V_2O_5 (GB/T 17136-1997) and $HClO_4$–HNO_3–HF (GB/T 17138, 17141-1997), respectively. The cold atomic absorption technique was used to determine the concentration of total Hg in samples and blanks using F732-V Hg detector. Concentrations of Pb, Cd, Zn, Cu and Fe were analyzed by inductively coupled plasma atomic emission spectrometry, ICP/AES (ICPS-7500, Shimadzu, Japan). For those samples to which ICP/AES was insufficiently sensitive, total metals were determined by a graphite furnace AAS (GFAAS, GBC932AA, Australia). Analytical reagent blanks were prepared with each batch of digestion set and then analyzed for the same element of the samples. The accuracy and precision of the analytical method was estimated by analyzing a sediment Standard Reference Material (GBW 07304(GSD-4)). Accuracy of the analytical method was given as percent recoveries for each of the elements. Results are reported in Table 1.

2.4. Sediment quality guidelines

Two sets of SQGs developed for freshwater ecosystems (MacDonald et al., 2000) were applied in this study to assess the ecotoxicology of trace element concentrations in sediments: (a) the effect range low (ERL)/effect range median (ERM) and (b) the threshold effect level (TEL)/probable effect level (PEL) values. Low range values (i.e., ERLs or TELs) are concentrations below which adverse effects upon sediment dwelling fauna would be infrequently expected. In contrast, the ERMs and PELs represent chemical concentrations above which adverse effects are likely to occur (MacDonald et al., 2000). Furthermore, toxic units were used to normalize the toxicity of the various metals to allow comparison of their relative effects, defined as the ratio of the determined concentration to PEL value (Pedersen et al., 1998).

3. Results and discussion

3.1. Pattern of heavy metal contamination along rivers

3.1.1. Heavy metal distribution in surface sediment

The distributions of Hg, Pb, Cd, Zn and Cu in surface sediments of Wuli River, Cishan River, and Lianshan River are