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

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ABSTRACT

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 Tibagi 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 $km^2$) 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 (WRPBHRB, 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 ($I_{geo}$); 4) to assess the risk associated with Cd based on the potential ecological risk index ($E_r^i$) and risk assessment code (RAC); and 5)

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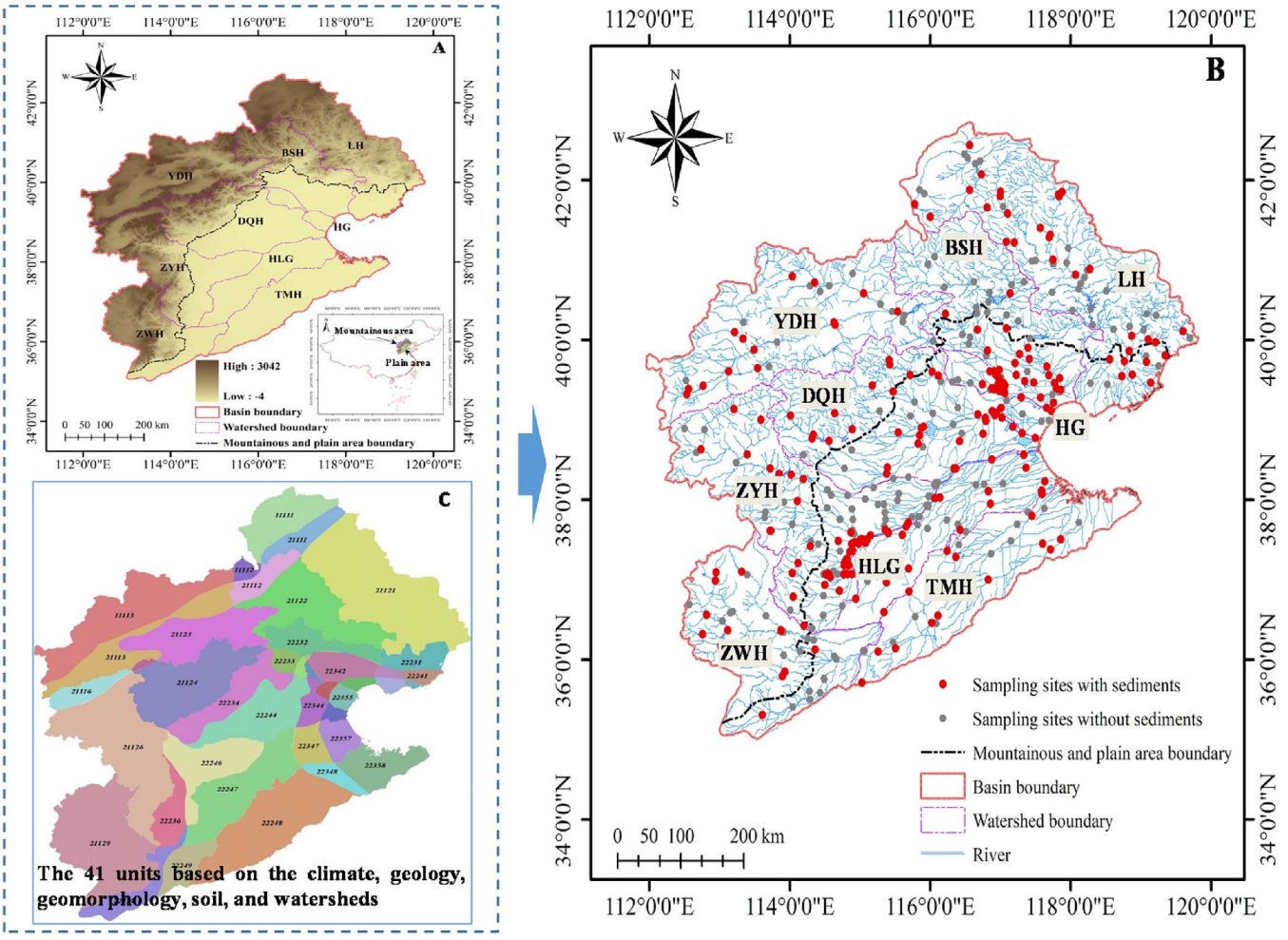


**Fig. 1.** Altitude in meters (A), sampling sites in the rivers (B), and the 41 framework units (C) of the Haihe Basin of north China. Luan He (LH), Bei San He (BSH), Yong Ding He (YDH), Da Qing He (DQH), Hai-he Gan-liu (HG), Zi Ya He (ZYH), Hei Long Gang (HLG), Zhang Wei He (ZWH), and Tu-hai Ma-xia He (TMH).

the potential biological toxicity of the sediments by consensus-based sediment quality guidelines (SQGs) and the mean probable effect concentration quotient ($Q_{m\text{-}PEC}$). 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 $km^2$, 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