



Distribution features and controls of heavy metals in surface sediments from the riverbed of the Ningxia-Inner Mongolian reaches, Yellow River, China



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HIGHLIGHTS

- The coarse particle component in bed materials is chiefly from the bordering deserts along the Yellow River.
- The clay and silt in bed materials chiefly originate from the upper reaches of the Yellow River.
- The fine sand is identified as a hybrid sediment.
- The most contaminated reaches of the Yellow River are adjacent to the industrial cities.

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ABSTRACT

Fifty-six riverbed surface sediment (RSS) samples were collected along the Ningxia-Inner Mongolian reaches of the Yellow River (NIMYR). These samples were analyzed to determine their heavy metal concentrations (Co, Cr, Ni, Cu, V and Zn), grain sizes, sediment sources and the causes of their heavy metal contamination. The cumulative distribution functions of the heavy metals in RSS of these reaches are plotted to identify the geochemical baseline level (GBL) of each element and determine the average background concentration of each heavy metal. Principal component analysis and hierarchical cluster analysis are conducted based on the grain sizes of RSS, and the samples are classified into two groups: coarse grained samples (CGS) and fine grained samples (FGS). The degree of heavy metal contamination for each sample is identified by its enrichment factor (EF). The results reveal that the coarse particle component (medium sand and coarse sand) in the bed materials is chiefly from the bordering deserts along the Yellow River. The clay and silt in the bed materials chiefly originate from the upper reaches of the Yellow River, and the fine sand is identified as a hybrid sediment derived from the upper reaches of the Yellow River and the bordering deserts. The CGS primarily appear in the reaches bordering deserts, and the sites are near the confluence of gullies and the Yellow River. The FGS are located adjacent to cities with especially strong industrial activity such as Wuhai, Bayan Nur, Baotou and Togtoh. The Cr, Ni, Cu, V and Zn concentrations (mg kg^{-1}) are 84.34 ± 49.46 , 30.21 ± 7.90 , 25.01 ± 7.61 , 73.17 ± 18.92 and 55.62 ± 18.93 in the FGS and 65.07 ± 19.51 , 23.86 ± 6.84 , 18.04 ± 3.8 , 53.47 ± 10.57 and 34.89 ± 9.19 in the CGS respectively, and the concentrations of Co in the CGS (213.40 ± 69.71) are notably higher than in the FGS (112.02 ± 48.87) and greater than the Co GBL (210). The most contaminated samples in the NIMYR are adjacent to the cities of Wuhai ($\text{EF}_{\text{Cr}} = 5.19$; $\text{EF}_{\text{Ni}} = 1.96$), Bayan Nur ($\text{EF}_{\text{Cr}} = 5.88$; $\text{EF}_{\text{Ni}} = 2.08$) and Baotou ($\text{EF}_{\text{Cu}} = 1.55$; $\text{EF}_{\text{Zn}} = 1.68$) where the Cr, Ni, Cu, V and Zn concentrations are above the correlated GBLs (85, 34, 27, 75 and 62 mg kg^{-1} , respectively), which are mostly affected by industrial processes, and samples that are only moderately contaminated by heavy metals are found in the reaches bordering desert (Wuhai-Baotou) because contaminated sediments are diluted by uncontaminated desert sand. In contrast, all of the Cu, Cr, Ni, V and Zn concentrations in RSS of the Qingtongxia-Wuhai reach are lower than the correlated GBLs of elements.

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1. Introduction

Heavy metals in aquatic environments are a source of grave concern because of their toxicity, persistence in the environment, transport through flowing water, and subsequent accumulation in the bodies of aquatic microorganisms, flora and fauna, which may, in turn, enter the human food chain and cause a host of health problems (Abdullah and Royle, 1972; Deniseger et al., 1990; Bryan and Langston, 1992; Klavins et al., 2000; Liu et al., 2003, 2005; Loska et al., 2004; Boularbah et al., 2006; Peng et al., 2009; Yi et al., 2011; Gao and Chen, 2012; Fu et al., 2013; Zhang et al., 2014). Heavy metals in rivers undergo numerous changes during their transport due to dissolution, precipitation and sorption phenomena in natural media (Akçay et al., 2003; Mil-Homens et al., 2006), and they are chiefly transported by suspended particles (Miller, 1997; Sponza and Karaoglu, 2002). For instance, nickel contamination of bed materials appearing far from the source of pollution was attributed to the long distance transport of particles loaded in the Aliğa metal industry district, Turkey (Sponza and Karaoglu, 2002). Miller (1997) demonstrated that commonly 90–99% of the total heavy metals were transported by fluvial particles.

Heavy metals discharged into rivers during their transport were distributed between the overlying water column and the bed materials. Sediments not only play the role of the carrier of contaminants but also can potentially act as a secondary source of contaminants in aquatic systems (Swedish EPA, 2000; Sin et al., 2001; Julien, 2002; Filgueiras et al., 2004; Shipley et al., 2011). Changing environmental conditions in the system, especially the resuspension of sediments may render the remobilization of contaminants from sediments by mechanical disturbance. Di Toro et al. (1986), as well as Skei (1992), have demonstrated that heavy metals in the surface sediments would be released into the overlying water column by physicochemical process. Apparently, with the increasing heavy metal concentration in sediment, the quantity of heavy metals desorbed from the sediment would increase (Lee et al., 2003).

Numerous studies have been conducted to assess and establish the extent of metal contamination in rivers (Olive, 1973; Zhang et al., 2001; Akçay et al., 2003; Sakan et al., 2007; Vicente-Martorell et al., 2009; Yang et al., 2009; Mohiuddin et al., 2010; Wang et al., 2012; Dong et al., 2014). These studies, which investigated fluvial sediments, mostly examined cobalt (Co), chromium (Cr), nickel (Ni), copper (Cu), vanadium (V) and zinc (Zn) (Akçay et al., 2003; Sakan et al., 2007; Mohiuddin et al., 2010; Hayzoun et al., 2014). Akçay et al. (2003) reported that pollution levels were significant, especially for Cr and Zn, in the Gediz River and for Co and Zn in the Buyuk Menderes River. The sediments sampled in the Sebou River, the largest river in Morocco, were also heavily contaminated with Cr and moderately to heavily contaminated with Ni, Cu and Zn (Hayzoun et al., 2014). The mean concentrations of Cr, Cu, V and Zn in the sediments of the downstream portion of the Tsurumi River in Japan greatly exceed the average worldwide shale concentrations and average Japanese river sediment concentrations (Mohiuddin et al., 2010). The Yellow River is China's second longest river and is well-known due to its high suspended sediment concentration, rapid sedimentation rate in its lower reach, frequent floods and overused water resources (Yu, 2002; Fu et al., 2004; Sato et al., 2008; Wang and Li, 2011). The Ningxia-Inner Mongolian reaches of the Yellow River (NIMYR) are centers of residence for ethnic minorities, such as the Hui (Muslim) and Mongols, and are also important energy bases and major grain producing areas in northwest China. Therefore, this area plays an important role in Chinese industry and agriculture. However, the industry in the Yellow River basin follows long-held patterns of low

investment, high consumption, large water usage and severe pollution. In the mid-1980s to early 1990s, small-scale production of paper, fertilizer, leather and dyes in the Yellow River basin rose sharply, which gave rise to contaminant sources and continuous discharge of sewage in the area. Meanwhile, a disproportionate amount of wastewater from point sources that did not meet disposal standards was discharged directly into the Yellow River (Yellow River Conservancy Commission of China (YRCC), 2002). The sewage discharged into the main channel of the Yellow River reached 4.2 billion cubic meters per year in the early 1990s, which was more than double that from the early 1980s, and which was the chief culprit of degrading water quality (YRCC, 2002). Currently, the sewage from the basin of the Yellow River is 3.376 billion cubic meters per year, and only 48.6% of the main channel and main tributaries of the Yellow River meet the water quality standard (YRCC, 2013). Thus, studying the sediments in the Yellow River is urgent.

The geochemical baseline level (GBL) was used to describe the contemporaneous variation in concentration of an element in the surficial environment since it was first introduced by the international geochemical mapping programs (Salminen and Tarvainen, 1997; Darnley, 1997; Reimann and Garrett, 2005; Meklit et al., 2009; Jiang et al., 2013; Liu et al., 2013; Lin et al., 2013). The cumulative distribution function (CDF), plotted as a function of elemental concentrations, can be used to identify the GBL of trace elements in sediments (Matschullat et al., 2000; Jiang et al., 2013; Lin et al., 2013; Liu et al., 2013). The CDFs of Co, Cr, Ni, Cu, V and Zn in bed materials from the NIMYR have been calculated to ascertain the GBL and average background values of those elements. The GBLs have been used to provide reasonable assessments of the distribution of contaminated features. The patterns of storage and transfer and the GBLs of heavy metals in the sediments investigated in this study will not only provide valuable baseline data for contaminants related to the environmental impact assessment of heavy metals in arid systems but can also serve as a resource for local and regional environmental management and water resource planning authorities.

2. Study area

The focus area of this study is the NIMYR, which loops north from the city of Qingtongxia located in the Ningxia Hui Autonomous Region, bends south near the city of Bayan Nur, flows east to the city of Togtoh and stays in the Inner Mongolia Autonomous Region for 730 km (a drainage area of 164,746 km²) (Fig. 1). This area belongs to the middle to lower reaches of the upper Yellow River in terms of its geology. The Qingtongxia-Dengkou reach of the Yellow River flows in a tectonic depression basin. The river course of Qingtongxia-Shizuishan reach emerges onto a flat alluvial plain (Length: 199.0 km, Width: 0.2–5 km, Gradient: 0.24‰) and the river course of Shizuishan-Dengkou reach of the Yellow River is relatively narrow, similar to a canyon (Length: 106 km, Width: 0.3–0.7 km, Gradient: 0.29‰) (Yao et al., 2011). After traversing the above reaches, the channel emerges onto a flat alluvial plain again (Length: 425 km, Width: 0.5–2.5 km, Gradient: 0.13‰) (Yang, 2002; Yao et al., 2011). These reaches are located along the fringe of the East Asian monsoon belt and clearly bear features of a continental climate. The westerly and northwesterly winds (Mean Annual Wind Speed: 2.7–4.5 ms⁻¹) prevalently appear this areas with a low and unevenly distributed annual precipitation (150–363 mm). According to statistical data by YRCC, average annual runoff at the Qingtongxia gauging station (1952–2007) is 238.12×10^8 m³ and the annual sediment load is 1.18×10^8 t (Yao et al., 2011). The values of sunshine duration (almost 2600–3400 h y⁻¹), evaporation, and solar irradiance (≥ 10 °C

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