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Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques

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HIGHLIGHTS

- The Inner Mongolia section of the Yellow River contains higher pollution degree of heavy metals in sediment samples.
- Cr and Cd are two non-negligible metals which may pose higher threat to aquatic biota.
- PCA reveals that the excess Cr and Cd in study regions mostly reflect the anthropogenic sources.
- The pollution of Co and Cd may be related to the socio-economic development according to DHCA.

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ABSTRACT

Metal chemical fractions obtained by optimized BCR three-stage extraction procedure and multivariate analysis techniques were exploited for assessing 7 heavy metals (Cr, Pb, Cd, Co, Cu, Zn and Ni) in sediments from Gansu province, Ningxia and Inner Mongolia Autonomous Regions of the Yellow River in Northern China. The results indicated that higher susceptibility and bioavailability of Cr and Cd with a strong anthropogenic source were due to their higher availability in the exchangeable fraction. A portion of Pb, Cd, Co, Zn, and Ni in reducible fraction may be due to the fact that they can form stable complexes with Fe and Mn oxides. Substantial amount of Pb, Co, Ni and Cu was observed as oxidizable fraction because of their strong affinity to the organic matters so that they can complex with humic substances in sediments. The high geo-accumulation indexes (I_{geo}) for Cr and Cd showed their higher environmental risk to the aquatic biota. Principal component analysis (PCA) revealed that high toxic Cr and Cd in polluted sites (Cd in S10, S11 and Cr in S13) may be contributed to anthropogenic sources, it was consistent with the results of dual hierarchical clustering analysis (DHCA), which could give more details about contributing sources.

1. Introduction

In sediments, heavy metals are in existence in a number of chemical forms, and generally exhibit different physical and chemical behaviors in terms of chemical interaction, mobility, biological availability and potential toxicity (Sundaray et al., 2011). These chemical fractions can be obtained using the optimized BCR three-stage extraction procedure proposed by the European Community Bureau of Reference (BCR): exchangeable (soluble species, cation exchange sites and bound to carbonates), reducible (bound to Fe and Mn oxides), oxidizable (bound to organic matter and sulphides) and residual (bound to the mineral matrix), respectively (Ma and Rao, 1997). There is abundant evidence showing that the translocation ability is indicated by the total content of exchangeable heavy metals, and the bioavailability of the heavy metals is the sum of the concentrations of the exchangeable, reducible, and oxidizable heavy metals fractions, while the residual metals are mainly not available (Varol, 2011). Most of the previous studies have been limited only to the determination of the total concentrations of metals in sediments, which is a poor indicator and reflects only the maximum amount of contamination when the metal properties basically depend on their binding state, sediment

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properties like pH, total organic carbon (TOC), redox conditions and their chemical speciation (Nyamangara, 1998). In current study, principal component analysis (PCA) and dual hierarchical clustering analysis (DHCA) analysis are applied as effective methods to identify contribution sources of heavy metals among the most common multivariate statistical methods such as PCA, DHCA, factor analysis (FA) and cluster analysis (CA) and so on in environmental studies (Huang et al., 2013).

Being the extremely important water source for northern China, the Yellow River has its water quality decreased significantly with the rapid development of social-economic and population in surrounding areas since 1960s (Huang et al., 2013), and it has still suffered the continually increasing environmental pressure from large amounts of pollutants especially for heavy metals since it receives billions of tons of particulate materials annually from anthropogenic activities and surrounding rivers (Yuan et al., 2012). Gansu province, Ningxia and Inner Mongolia Autonomous Regions are the three adjacent and typically developing rural regions of the Yellow River, and they have their pillar industries with agriculture, mining and animal husbandry, which are strongly dependent on the water resources from the Yellow River (Huang et al., 2015). River sediments are important sources for the assessment of man-made contamination, it not only acts as the carrier of contaminants, but also the potential secondary sources of contaminants in aquatic system (Varol, 2011). Therefore, the assessment of heavy metals contamination in sediments from these three adjacent regions of the Yellow River is urgently needed to interpret the bioavailability, mobility and toxicity of heavy metals and provide basic information for utilization and supervision (Li et al., 2013).

Basing on chemical fractions and statistical methods have been widely applied in studies of element source recognition in soil and sediment, the primary objectives of the present work are (i) to investigate the concentrations and spatial distribution of heavy metals (Cr, Pb, Cd, Co, Cu, Zn and Ni) in sediments in Gansu, Ningxia and Inner Mongolia sections of the Yellow River by the high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS), (ii) to assess the bioavailability, potential mobility, transferability and contamination level of heavy metals in different chemical fractions in sediments by using of the optimized BCR three-stage extraction procedure and the geo-accumulation index (I_{geo}), and (iii) to identify the contributing sources of heavy metals in sediment samples with the multivariate statistical methods including PCA and DHCA.

2. Materials and methods

2.1. Study area

As the second largest river in China and sixth largest river in the world, the Yellow River (Fig. 1) is famous for its high sand content, frequent floods and currently overused water resources (Yao et al., 2011). It is supporting a population of 107 million, irrigating 15% of the agricultural land, and contributing to 9% of China's GDP (Hu et al., 2015). Gansu, Ningxia and Inner Mongolia, the developing arid or semi-arid regions are located in the northern part of China (Liu et al., 2015), the study area is starting at Linxia (Gansu) and ending at Qingshuihe (Inner Mongolia) with a total length of 1249.2 km (Fig. 1). Gansu, Ningxia and Inner Mongolia are regarded as the upper, middle and lower reach of the Yellow River, respectively.

2.2. Sediment samples collection

Surface sediments (top 10 cm) are collected by using plastic grabs in May 2014. Fig. 1 shows the locations of the sampling sites. S1–S3 sediment samples are collected from Gansu area of the Yellow River, ten samples of S4–S9 and S10–S13 are taken from Ningxia and Inner Mongolia areas of the Yellow River, respectively.

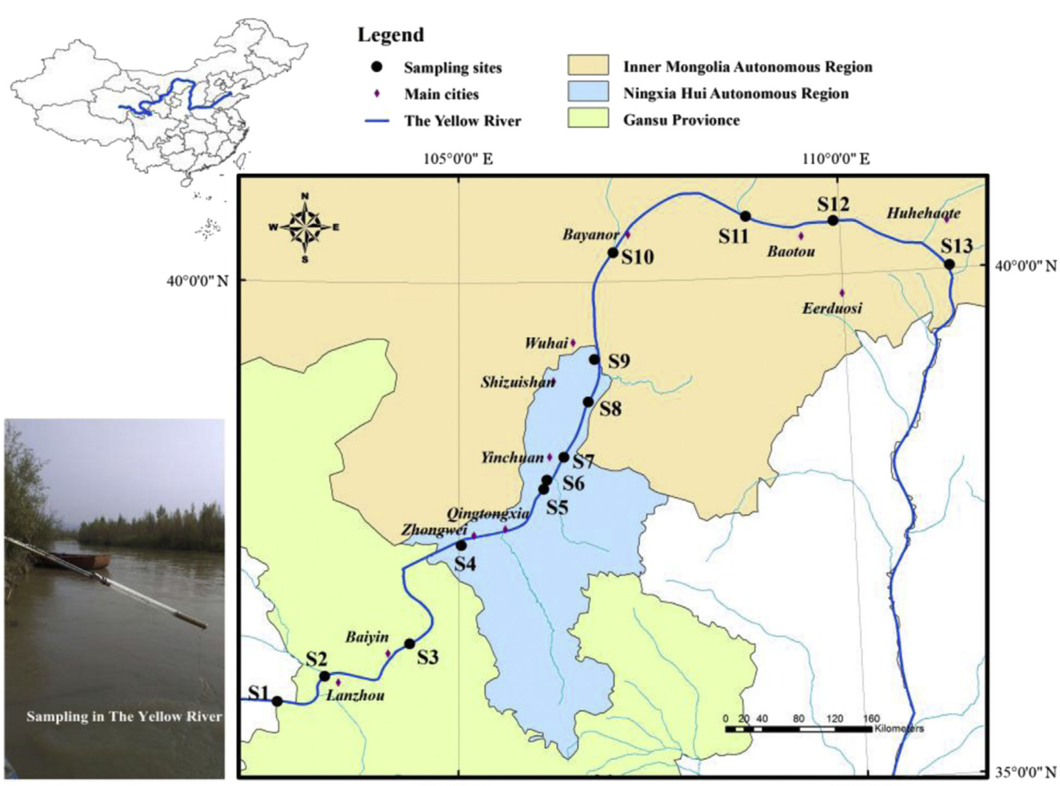

Fig. 1. Map showing station locations.