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Risk Assessment of Heavy Metal Pollution in Sediments of the Fenghe River by the Fuzzy Synthetic Evaluation Model and Multivariate Statistical Methods

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ABSTRACT

Concentrations of heavy metals in 74 sediment samples from the Fenghe River, which originates from the north of the Qinling Mountains and flows through Xi'an, Shaanxi Province, China, were characterized by employing geographic information system (GIS) mapping, fuzzy synthetic assessment, and multivariate statistical analysis to determine the enrichment characteristics of heavy metals as well as their potential risks of pollution to sediments. Al, Cd, and Co were the major pollutants, with a high enrichment factor (EF) value. Heavy metal concentrations from samples near the paper plant were maintained at a high level. Significant enrichment of Al, Ba, Cr, Ni, Pb, and Co was found in the midstream and downstream, while high concentration of Cu occurred in the headwater stream. Based on the cluster and principal component analyses, sediment metals mainly came from the paper plants, agronomic practices, natural sources, and tourism, with a contribution of 51.59%, 23.01%, 14.21%, and 9.88%, respectively. Sediment pollution assessment explored using fuzzy theory based on the entropy method and toxicity coefficient showed that 26, 32, and 11 sites fell into Class III (slightly polluted), Class IV (moderately polluted), and Class V (heavily polluted), respectively, and their scores of membership degree in the polluted level were on the rise, suggesting a relatively high degree of sediment metal pollution in the study area. Closely related to the excessive industrial and agricultural applications, metal pollution in sediment is necessary to be addressed in the Fenghe River.

Key Words: fuzzy theory, risk analysis, river ecosystem, sediment pollution, spatial analysis

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INTRODUCTION

As an important component of river systems, sediment is one of the largest containers and resources of harmful substances and acts as a major role in maintaining the normal aquatic habitats (Amorosi *et al.*, 2013; Zhao and Li, 2013). In fluvial environments, sediments from the river function as a medium for aquatic flora and fauna to grow or as a pool to dispose of hazardous metals, as well as a pollutant reservoir for the surface water, groundwater and plants (Varol, 2011; Grygar *et al.*, 2013). Metal pollution is of great concern due to their abundance, persistence, and toxicity in the aquatic environment (Tan *et al.*, 2006; Zhang *et al.*, 2014). High levels of sediment metals may impose a persistent burden on the natural growth of aquatic flora and fauna, cause the deterioration of water quality, and impair human health through the food chains (Yang *et al.*, 2009; Zeng and Wu, 2009). Heavy metals are continuously introduced into fluvial environments through mining, combustion residues, vehicle emissions, transportation, and some other human activities with rapid urbanization and industrialization all over the world (Subida *et al.*, 2013; Wang *et al.*, 2013; Zhang *et al.*, 2014). Based on the enrichment factor (EF) (Lourenço *et al.*, 2010), Viers (2009) revealed that the majority of the world river systems are seriously suffering from metal pollution, particularly in Asia (China and India), Europe, and North America. In the case of metals such as Pb and Cd, the EF can be higher than 60 and 100, respectively (Viers, 2009; Varol, 2011). The study of Walling (2006) suggested that the climate change and biogeochemical cycle were closely related to the high level of sediment metals. Using the global sediment flux of 15 $\times$ 10^9 t year^{-1} (Walling, 2006), the global metal flux transported by

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the river sediment from the continents to the oceans is approximately 23 × 10^3 t $year^{-1}$ for Cd, 916 × 10^3 t $year^{-1}$ for Pb, 1 140 × 10^3 t $year^{-1}$ for Cu, 1 118 × 10^3 t $year^{-1}$ for Ni, 338 × 10^3 t $year^{-1}$ for Co, and 3 123 × 10^3 t $year^{-1}$ for Zn, respectively, and the values are on the rise (Viers, 2009).

The assessment of the pollution degree of sediment metals is important for risk management (Grygar *et al.*, 2013; Zhang *et al.*, 2014). Many methods have been established, yet some defects of these models simultaneously accompany. For instance, single factor index (P_i), geo-accumulation index (I_{geo}), and EF are suitable only for risk assessment of a single metal (Zeng and Wu, 2009; Varol, 2011; Amorosi *et al.*, 2013), Nemerow index (NI) may overestimate the metal pollution degree (Zhao and Li, 2013), and pollution load index (PLI) emphasizes the spatial distribution of metals but ignores some metals with low concentration but highly toxicity (Yang *et al.*, 2009). Potential risk index (RI) and back-propagation neural network (BPNN) model have widely been applied in the recent decades; however, weighting set may limit their applicability due to variation of the geochemical background values and classification criteria (Varol, 2011; Subida *et al.*, 2013). To address this problem, fuzzy theory is introduced to assess and classify pollution degree of heavy metals (Lourenço *et al.*, 2010). Based on membership functions, it is proved to be useful to settle the fuzzy characteristics of metal pollution degree with a gradual change from light to heavy (Tan *et al.*, 2006).

Previous researches have largely focused on the metal pollution in sediments of many rivers and lakes in the economically developed areas of China, and revealed that anthropogenic activities contribute to the sediment pollution of Cd, Co, Cu, Ni, Pb, and Zn (Viers, 2009; Yang *et al.*, 2009; Zeng and Wu, 2009). The Fenghe River is one of the major sources of water supply in Xi'an, the largest city in Northwest China, and has undergone serious metal pollution in the river ecosystem owing to the rapid socioeconomic growth in the past few decades (Wang *et al.*, 2013). However, little information is available about metal pollution in sediments of this area. Therefore, a systematic investigation and an objective assessment are necessary to properly manage the ecological risk in the sediments caused by hazardous metal pollution.

The aim of this study was to determine the enrichment characteristics of heavy metals as well as their potential risks of pollution in sediments, by employing geographic information system (GIS) mapping, fuzzy synthetic assessment, and multivariate statistical analysis.

MATERIALS AND METHODS

Description of study area and sample analysis

With a length of 81 km, the Fenghe River (108°35′–109°09′ E, 33°50′–34°20′ N) originates from the north of the Qinling Mountains and flows through Xi'an, Shaanxi Province of China. The annual mean discharge is 2.58 × 10^{10} m^3 $year^{-1}$ with significant seasonal variations. As the largest tributary in the southern part of the Weihe River in the Yellow River basin (Fig. 1), the Fenghe River consists of 56 valleys and drains with an area of 1 460 km^2, transitioning between semi-arid and sub-humid zones in the northwest of China (Wang *et al.*, 2013). Two sampling campaigns were conducted in late spring–summer (from May to August), including 32 sites in 2011 and 42 sites in 2012 (Fig. 1). All the sites were located using a global positioning system.

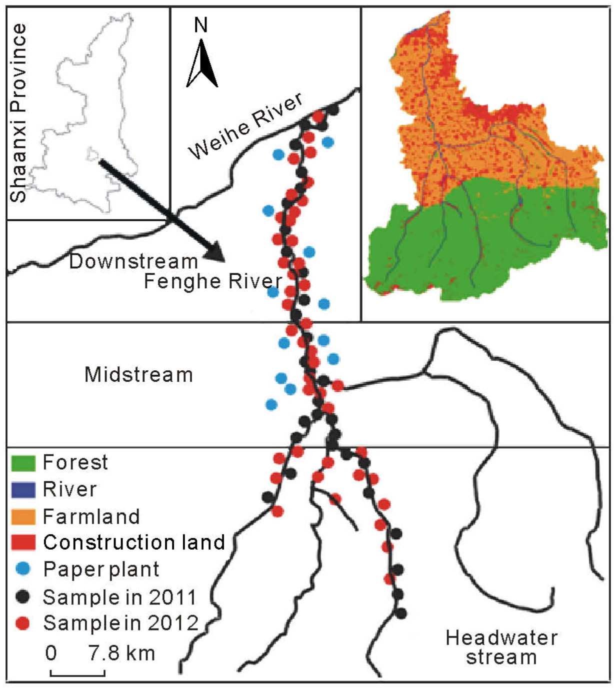

Fig. 1 Location of the study area and the distribution of sampling sites in the Fenghe River, flowing through Xi'an, Shaanxi Province of China, with land-use types shown in the top right corner.

At each site, five surface sediment (2 cm) samples were collected within an area of 2.5 m^2 (Zeng and Wu, 2009), using a gravity corer of 60 cm long and 6 cm internal diameter. The five samples were then mixed to form a composite sample (2 000 g) for this site. Each sample was sealed in the polyethylene bags and stored in a cooled box (4 °C). The samples were air-dried, sieved through a 2-mm nylon mesh and then divided into four parts using a quartering method. One part of