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Reconstructing the historical pollution levels and ecological risks over the past sixty years in sediments of the Beijiang River, South China

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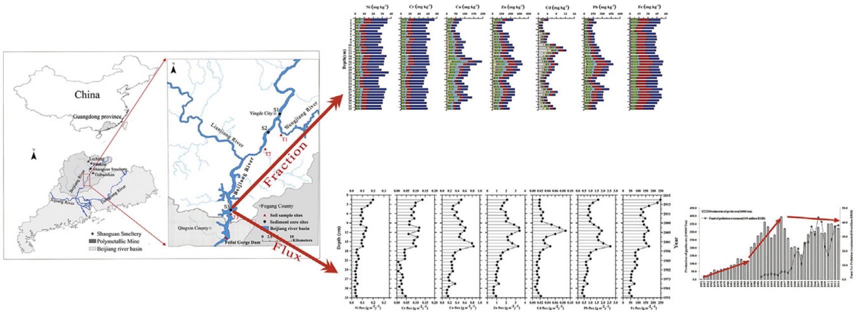
HIGHLIGHTS

- Historical pollution levels and ecological risk of metals were reconstructed in the Beijiang River.
- Integrated sediment quality assessment methods were used.
- Flood events resulted in higher residual fraction of metals.
- Sedimentation rate increased significantly after the Dam was constructed.
- Human activities increased metals bioavailability and biotoxicity.

GRAPHICAL ABSTRACT



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ABSTRACT

Three sediment cores were collected from the Beijiang River to investigate the effects of human activities on the geochemical fractions of trace metals (Ni, Cr, Cu, Zn, Cd, Pb and Fe) and to reconstruct the ecological risks for the period 1951–2015. Cd had the highest concentration in exchangeable and carbonate fractions and was probably contributed by smelting wastewater. High Cu, Zn and Pb contents were observed in the iron oxide fraction (mean values of 32.2%, 38.2% and 43.9%, respectively), reflecting the influence of mining activities. Flood events led to coarser sediment grain sizes and higher trace metal residual fractions at upstream sites (S1 and S2). Similar to the mining history of the basin, the excess metal fluxes of Cu, Zn, Pb, and Fe in the ^{210}Pb-dating core (S3) increased slowly from 1951 to 1987, increased rapidly from 1988 to 1998 and decreased gradually after 1999 because of government intervention. However, the excess Cd flux decreased continuously from 1951 to 1961, increased from 1961 to 2005, and declined by approximately 78.2% from 2005 to 2014. The excess Ni and Cr fluxes increased noticeably after 1996 because of the increasing sedimentation rate after the construction of the Feilai Gorge Dam. The enrichment factor (EF) and ratio of secondary and primary phases (RSP) indicated that sediments (S3) were moderately to strongly polluted by Cu, Zn and Pb from 1961 to 2007 and extremely polluted by Cd from 1951 to 2011. Human activities increased the bioavailable metal concentrations and resulted in a high risk of toxicity to benthic organisms, especially during intense mining activity (1990s) and Cd pollution incidents (2005). Cd and Pb were primarily responsible for the sediment toxicity in the Beijiang River. The integrated pollution and risk assessment methods provided a clearer understanding of the aquatic environmental quality.

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1. Introduction

Trace metal contamination can seriously impact aquatic organisms and threaten human health via the food chain due to the toxicity, persistence and bioaccumulation problems associated with these metals (Horai et al., 2007; McCormick et al., 1994; Roman et al., 2007). Metals enter a river system via natural inputs (e.g., rock weathering) and anthropogenic inputs. Anthropogenic sources include mining activities, smelting industries, and waste incineration as well as biomass and fossil fuel combustion. Among these sources, smelting wastewater and/or acid mine drainage (AMD) have been the most concerning due to the serious damage they cause to the aquatic ecosystem (Sakan et al., 2015; Audry et al., 2004; Axtmann and Luoma, 1991; Equeenuddin et al., 2013; Galán et al., 2003; Rybicka et al., 2005; Schaider et al., 2007). As an important part of river ecosystems, sediment often acts as a major sink for trace metals (Kronvang et al., 2003; Liu et al., 2016; Ntekim et al., 1993; Sadeghi et al., 2012; Singh et al., 2003) and accounts for 30–98% of the total metal loads in the river (Gibbs, 1973). Therefore, sediment has become a valuable environmental archive for the investigation of anthropogenic contamination (Gao et al., 2017; Alves et al., 2014; Xiao et al., 2014; Swarzenski et al., 2008).

The impacts of anthropogenic activities on river ecosystems vary considerably over time. However, for most rivers globally, the historical impacts of anthropogenic activities on river ecosystems are hard to evaluate because of the lack of long-term monitoring and historical archives. Some studies have used core sediment profiles to reconstruct the historical impacts of anthropogenic activities in aquatic environments with stable depositional conditions, such as estuaries, lakes and reservoirs (Dhivert et al., 2015; Córdoba et al., 2016; Fernández et al., 2003; Müller et al., 2000; G. Zhang et al., 2016; Y. Zhang et al., 2016). However, there are still not enough well-documented studies using lead-210 (^{210}Pb) dating technique to rebuild the historical ecological risk of trace metals in the rivers affected by mining and industrial activities (Conrad et al., 2007; Grousset et al., 1999; Wang et al., 2015).

The ^{210}Pb dating technique is widely used to identify sedimentary chronologies on time scales of 100–150 years (Córdoba et al., 2016; Appleby, 2008). A high-precision dating result is dependent on reliable age models (Jones et al., 2009). Generally, the constant ^{210}Pb flux and constant sedimentation rate model (CF-CS) describes a situation in which ^{210}Pb activity decreases exponentially with depth (Guo and Yang, 2016). However, ^{210}Pb activity profiles exhibit significant deviations from the simple exponential decline in most cases for river sediment, which limits the application of the CF-CS model (Mulsow et al., 2009; Chapron et al., 2007). On the other hand, the constant rate of excess ^{210} Pb supply (CRS) model can provide better calculated results for a situation with variable sedimentation rates, especially when the results are validated by other discrete sedimentary markers (such as pollution incidents) (Grousset et al., 1999; Delbono et al., 2016).

In terms of basin management, understanding the pollution and ecological risk of trace metals in both the past and present is a prerequisite for pollution remediation. Many methods (such as enrichment factor, anthropogenic metal flux, ratio of secondary and primary phases, bioavailable metal index and toxic risk index, etc.) have been developed to assess the anthropogenic inputs, pollution levels, bioavailability and toxicity of trace metals in sediment (Wang et al., 2014; Gómez-Álvarez et al., 2011; Rosado et al., 2016; Spencer et al., 2003). However, each of these methods is insufficient for obtaining a clear idea of the general status of an aquatic ecosystem. Instead, the integrated pollution and risk assessment methods, including a group of simple methods that complement each other, can improve the understanding of the overall environmental quality of the water body (Rosado et al., 2016).

Analyzing geochemical fractions of trace metals is very useful for pollution and ecological risk assessment, because only a specific fraction of a metal may have adverse effects on the environment (Sundaray et al., 2011). Generally, a high concentration of metals in the exchangeable and carbonate fractions will lead to more bioavailable metals in the sediment, thereby resulting in more severe toxic effects on aquatic organisms (Rosado et al., 2016), whereas metal in the residual fraction is not bioavailable and presents a low ecological risk. Chemical speciation of trace metals in sediment can be significantly affected by anthropogenic activities. For example, anthropogenic activities noticeably affected the non-residual fraction of trace metals in the Shima River (Gao et al., 2018). Xie et al. (2018) reported that approximately 82.1–91.2% of trace metals in sediment were associated with the amorphous (e.g., Schwertmannite and ferrihydrite) and crystalline iron oxides (e.g., Goethite and hematite) in a mining-impacted stream, indicating the impact of the mining activities. A similar study was conducted by Schaider et al. (2014), who confirmed that iron oxides were responsible for the transportation of >70% of the Pb and 40% of the Zn in the Tar Creek stream.

In recent decades, mining and smelting activities were rapidly developed in the upper stream of the Beijiang River, including the polymetallic mines in Fankou, Lechang and Dabaoshan, which produce iron, copper, lead, zinc and molybdenum (Gao et al., 2012), and the smelter in Shaoguan, which is the third largest metal producer in China. The excessive wastewater discharge brought large amount of trace metals to the river and caused aquatic environments to deteriorate (Song et al., 2011). Specially, a serious Cd pollution incident occurred in 2005 when untreated smelting wastewater was discharged into the river (Zhang and Chao, 2009). To evaluate the impact of anthropogenic activities on the Beijiang River in recent decades, undisturbed sediment core samples were collected to 1) analyze the contents of trace metals and their geochemical fractions; 2) reconstruct the pollution history of trace metals in the Beijiang River; 3) evaluate the anthropogenic inputs, bioavailability, pollution degree and ecological risk of trace metals based on the excess flux (EM_{ex}), enrichment factor (EF), ratio of secondary and primary phases (RSP), bioavailable metal index (BMI), and toxic risk index (TRI); and 4) identify the sources of trace metals.

2. Materials and methods

2.1. Study area and sampling

The Beijiang River presents 1528.4 $m^3 s^{-1}$ of runoff and is the second large tributary of the Pearl River in southern China (Chen et al., 2009). This river is also an important source of drinking water and a navigation channel for Guangdong Province (He et al., 2014; Gao et al., 2012). However, due to the intense mining and industrial activities, the drinking water safety of the local residents has been seriously threatened (Song et al., 2011). In addition, flood disasters often occur in the catchment, with two huge flood events occurring in 1982 and 1994 with peak flows of 18,000 $m^3 s^{-1}$ and 17,500 $m^3 s^{-1}$, respectively (Luo, 2006). To control floods and produce electric power, the Feilai Gorge Dam was constructed in the lower reach of the study area in 1999 (Fig. 1).

Three background soil samples (T1–T3) and three sediment cores (S1–S3) were collected along the river in June 2015 (Fig. 1). In areas located far from human activities, which were believed to have negligible anthropogenic metal inputs, representative forest soil samples at the top 0–10 cm surface layer were collected with a stainless steel auger. Three sediment cores were collected from the river using a gravity sampler and sectioned at 1 cm intervals. The lengths of cores S1, S2 and S3 were 21, 13 and 33 cm, respectively. After sampling, all soil and sediment subsamples were packed in a clean plastic bag, stored in a cool box, returned to the laboratory and freeze-dried at −80 °C for 72 h. The dried soil and sediment samples were then ground in an agate grinder and sieved through a 0.149 mm mesh for further analysis.

2.2. Analytical methods

2.2.1. Physicochemical properties

The pH of the sediment was measured by a pH meter in a solution with a sediment/water (CO_2-free) ratio of 1:2.5. Organic matter (OM)