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Heavy metal fractions and ecological risk assessment in sediments from urban, rural and reclamation-affected rivers of the Pearl River Estuary, China

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HIGHLIGHTS

- Higher heavy metals contents were found in urban river sediment.
- Cd posed a medium-to-high potential ecological risk to the river environment.
- Reducible and residual fractions were the major geochemical phases of heavy metals.
- Cd, Cu and Zn exhibited moderately to heavily polluted in river sediment.
- Sediment organic carbon affected the distribution of metals in organic fraction.

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ABSTRACT

Rapid urbanization and reclamation processes in coastal areas have resulted in serious pollution to the aquatic environment. Less is known on the geochemical fractions and ecological risks in river sediment under various human activities pressures, which is essential for addressing the connections between heavy metal pollution and anthropogenic influences. River sediments were collected from different landscapes (i.e., urban, rural and reclamation areas) to investigate the impacts of urbanization and reclamation on the metallic pollution levels and ecological risks in the Pear River Estuary of China. Results showed that Cd, Zn and Cu with high total contents and geoaccumulation index (I_{geo}) were the primary metals in the Peal River sediments. Generally, urban river sediments, especially the surface sediment layer (0–10 cm), exhibited higher metallic pollution levels. As for geochemical fractions, reducible and residual fractions were the dominant forms for six determined metals. And the percentage of heavy metals bound to Fe-Mn oxides decreased with increasing soil depth but the reverse tendency was observed for residual fractions. Compared with rural river sediments, heavy metals were highly associated with the exchangeable and carbonate fractions in both urban and reclamation-affected river sediments, suggesting that anthropogenic activities mainly increased the active forms of metals. Approximately 80% of Cd existed in the non-residual fraction and posed medium to high ecological risk according to the risk assessment code (RAC) values. The redundancy analysis (RDA) revealed that both urbanization and reclamation processes would cause similar metallic characteristics, and sediment organic matter (SOC) might be the prominent influencing factor.

1. Introduction

Heavy metals pollution have aroused widespread attention around the world since recent decades due to their persistence, toxicity and bioaccumulation in the water and soil/sediment environment (Ke et al., 2017; Li et al., 2016; Sungur et al., 2015; Singh et al., 2007). Several metals are essential for normal human metabolism (e.g., Cr, Mn, Ni, Cu and Zn), while overexposure to those metals will have detrimental effects to human health and cause

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chronic intoxication (Li et al., 2014c). However, arsenic, cadmium, and lead are not required for metabolic activity and can have obvious toxic effect on human body at much low levels (US EPA, 1999).

With the rapid development of industries, agriculture and urbanization of coastal zone in China, large amount of polluted water without effective purification treatment was discharged into estuarine rivers. Contaminants such as heavy metals carried by rivers would be easily absorbed by river sediments and cause enrichment, and then pose toxic effect to flora and fauna there (Vosoogh et al., 2016; Bai et al., 2012). Therefore, sediments often act as sinks for heavy metals, which can be adopted as an efficient indicator for monitoring heavy metal pollution levels and pollution sources apportionment in coastal areas (Palleiro et al., 2016; Ye et al., 2012). Meanwhile, heavy metals in river sediments may be released into water columns by physical, chemical and biological processes, which in turn can increase pollution levels of surrounding waters. However, information on the total contents of heavy metals can not efficiently reflect the physical and chemical behaviors in environment (Xiao et al., 2015), while the chemical fractions through sequential extractions can contribute to understanding geochemical processes and bioavailability of them.

In river sediments, heavy metals can exist in various chemical forms which was associated with their chemical interactions, biological availability, mobility and potential toxicity (Najamuddin et al., 2016), including exchangeable; carbonate, occluded with Fe, Al or Mn oxides (reducible), organic fractions (oxidizable), and residual fractions (Palleiro et al., 2016; Neto et al., 2016; Tessier et al., 1979). In general, the mobility and availability decrease in the order of exchangeable > carbonate > reducible > oxidizable > residual (Sungur et al., 2015). Exchangeable fractions are considered to be directly absorbed by aquatic organisms, whereas carbonate, reducible and oxidizable fractions can be able to be transformed into active forms when soil/sediment environment (e.g., pH, salinity, redox conditions) changed (Huang et al., 2017; Ma et al., 2016; Wang et al., 2016). Conversely, residual fractions which are considered to be incorporated into the crystalline lattices of soil/sediment clay appear relatively inactive (Palleiro et al., 2016). Heavy metals are derived from lithogenic sources and anthropogenic sources. Generally, anthropogenic metals are mainly presented in liable extractable fractions when they enter into the river sediments, whereas those from lithogenic sources occur as the residual fractions (Najamuddin et al., 2016; Palleiro et al., 2016). Therefore, the determination of chemical fractions in heavy metals is helpful for source identification and potential toxicity assessment.

As one of the earliest regions of implementing China's open-door and reform policies since the 1980s, the Pearl River Estuary (PRE) has become one of the most developed areas in China. Rapid economic development and population growth in the PRE has led to rapid urbanization and heavy reclamation to meet the requirements of people, which has caused a series of environmental problems including metallic contamination, e.g., higher heavy metal pollution levels in the aquatic systems (Li et al., 2007; Bai et al., 2011; Gu et al., 2014; Zhao et al., 2016). Urbanization would aggravate the heavy metals pollution in both urbanized and peri-urban areas (Bai et al., 2016; Coxon et al., 2016). The timing of urbanization, population density, traffic volume and industrialized land area are positively correlated with metal contents in surrounding soils (Argyraki and Kelepertzis, 2014; Qiao et al., 2013). Meanwhile, coastal reclamation has brought heavy metal pollution due to heavy agrochemical applications (Bai et al., 2011). Bai et al. (2011) presented that Cd, Pb, Zn and Cu in wetland soils increased with reclamation time. Xiao et al. (2015) also found the elevated heavy metal contents in soil after wetland reclamation. Moreover, long-term agricultural inputs and increased human activities had greatly influenced the contents of heavy metals (Ma et al., 2015). In the PRE, most studies have focused on the total contents of heavy metals and their pollution levels in agricultural soils (Gu et al., 2014; Wong et al., 2002), wetland soils or sediments (Bai et al., 2011; Li et al., 2007), aquatic systems (Wang et al., 2016; Geng et al., 2015), and marine sediments (Zhao et al., 2016; Yang et al., 2012; Li et al., 2000). These studies mainly focus on the total contents of heavy metals and their pollution levels. However, little information is available on the geochemical fractionation of heavy metals and its depth-distribution patterns in river system sediments affected by urbanization and reclamation, especially in this developing zone with various landscapes.

Due to intensive human activities (e.g., industrialization, urbanization, reclamation projects and others) (Bai and Liu, 2014; Nilsson et al., 2005), The Pearl River has become one of the most highly impacted rivers in the world. Various river systems are suffering from different anthropogenic disturbances, metallic pollution levels and geochemical fractions in river sediments would vary largely depending on the upstream discharges, circumjacent disturbances and hydrographic environment characteristics (Wang et al., 2016). The objectives of this study were: (1) to investigate the distribution and geochemical fractionation of heavy metals in urban river sediments (URS), rural river sediments (RRS) and reclamation-affected river sediments (RARS) at surface (0–10 cm), middle (10–20 cm) and bottom (20–30 cm) layers of sediment cores; (2) to assess the pollution levels and ecological risks of these river sediments using geoaccumulation index (I_{geo}, for total contents) and risk assessment code (RAC, for chemical fractions); and (3) to reveal the relationships between heavy metals and sediment physicochemical properties according to correlation analysis and redundancy analysis (RDA).

2. Materials and methods

2.1. Study area

The Pearl River Estuary (PRE) is located in Guangdong province of China (102°14′–115°53′ E, 21°31′–26°49′ N, Fig. 1), facing to the South China Sea and is adjacent to Hong Kong and Macao. The annual mean temperature is 14–22 °C and the annual average precipitation is 1200–2200 mm (Wu et al., 2016; Geng et al., 2015). As the second largest river in China in terms of water discharge, the Pearl River is considered to be one of the world's most complicated fluvial networks (Wu et al., 2016).

The Pearl River is mainly composed of three tributaries such as the Dongjiang River, Beijiang River, and Xijiang River (Fig. 1), in which Xijiang River is the main stream and its annual runoff accounts for approximately 70% of the total flow (Geng et al., 2015) and nearly four fifths of its total flow occurs from April to September (Ye et al., 2012). The Pearl River Estuary is mostly covered by late Quaternary sediments, and the bedrock is formed during Cambrian to Tertiary outcrops (Wang et al., 2016; Long, 1997). The soils are rich in iron and aluminum oxides, but lack of soluble salt, alkali metal and alkali-earth metal due to the intensive eluviation under complex and varied hydrothermal conditions of this area (Zhang et al., 2015).

The urbanization-affected Panyu district and the reclamation-affected Nansha district were chosen as our study area. In selected urban rivers, the road networks, domestic sewage and industrial plants might be the main sources of heavy metals. These rivers flow through the whole Panyu District of Guangzhou City, residential buildings, producing department and roads are on the both sides of these rivers. Wanqingsha district was a region of shallow sea one hundred years ago until it began to be reclaimed