



Baseline

## Distribution, sources, and fluxes of heavy metals in the Pearl River Delta, South China



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## ABSTRACT

Riverine samples were collected at various locations in the Pearl River Delta (PRD) to determine the concentrations of heavy metals (Cr, Ni, Cu, Mn, Zn, Cd, and Pb) in time and space and to estimate the fluxes of heavy metals to the coastal waters off South China. Most of the elements exhibit clear temporal and spatial trends. Principal component analysis shows that surface erosion is the major factor affecting metal concentrations in particulates in the PRD. Natural geology is an important source of these heavy metals. The annual fluxes of Cr, Ni, Cu, Mn, Zn, Cd, and Pb in upstream and downstream were 445, 256, 241, 3293, 1279, 12, and 317 t/year and 1823, 1144, 1786, 15,634, 6183, 74, and 2017 t/year, respectively. A comparison indicated that the annual fluxes of Mn accounted for 1.3% of the global river fluxes, whereas other elements contribute <1%.

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With the rapid development of industrial and agricultural production, particularly coastal areas of light and heavy industries, pollution of marine environment by heavy metals has become more serious (He and Fan, 2006). Heavy metals are known to be toxic, and are persistent in the natural environment (Sun et al., 2015). Increased loadings of pollutants associated with intensified anthropogenic activities can significantly change the water quality (Yang et al., 2012), threatening both sustainable economic development and humans' quality of life. Heavy metals are one of the most persistent pollutants in aquatic ecosystems, as they may change their chemical form and do not decompose. Rivers are the major contributors of coastal pollution, as most of the heavy metal elements reach sea through rivers (He and Fan, 2006). Therefore, riverine fluxes have been the subject of much study on the hydrogeochemical cycle (Meybeck and Vörösmarty, 2005).

The Pearl River Delta (PRD) is the most important region for waterborne commerce in South China (Yang et al., 2012). PRD is one of the most economically active areas in China. Studies on pollution have shown that the rapid economic development of the upstream Pearl River has changed the pattern of contamination, significantly affecting the water quality of its downstream waters (Zhang et al., 2012). For example, studies in 2005 showed that downstream monitoring of the Beijiang River revealed a cadmium concentration of 0.05 mg/l, which is 10 times the acceptable limit set by the China National Standards GB3838-2002 (Environmental Quality Standards for Surface Water)

(Huang and Li, 2007). This caused a direct economic loss of >50 million Chinese yuan and an indirect economic loss of >100 million Chinese yuan to the enterprise (Dai and Lv, 2006). At present, numerous studies on heavy metals have mainly focused on the eight estuaries of the Pearl River (Ip et al., 2007; Wang et al., 2008; Yu et al., 2010), plus the Pearl River itself in the Guangzhou region (Min et al., 2000; Li et al., 2009; Niu et al., 2010). However, none of these studies quantified the fluxes of heavy metals, and reports on heavy metal pollution in the upstream of Pearl River are limited. The subjects of these studies have primarily been the river sediments (Liu et al., 2003; Guo et al., 2010; Yu et al., 2010), aquatic organisms (Fang et al., 2003; Zhang and Ou, 2005), organic pollutants (Zhang et al., 2012), heavy metals in soil (Wong et al., 2002; Zhang et al., 2010), and soluble trace elements (Ouyang et al., 2006a). Less attention has been paid to the distribution of pollutants between dissolved and particulate states, the concentration of heavy metals in the upstream waters, and the quantitative contribution of the upstream heavy metals to the downstream concentrations and the eventual input to the South China coastal waters.

Therefore, this study was conducted to assess water quality and heavy metal pollution in the PRD upstream areas. The purpose of this study was to quantify the amount of heavy metals at each section of the PRD and find the possible sources of contamination. In order to achieve this, a sampling campaign was conducted from June 2009 to June 2010 to collect riverine samples from nine upstream sites and four downstream sites. Heavy metals such as Cr, Ni, Cu, Mn, Zn, Cd, and Pb in the dissolved and suspended particulate phases were measured. The specific objectives of this study were to (1) evaluate the temporal and spatial distributions of heavy metals in the PRD sampling

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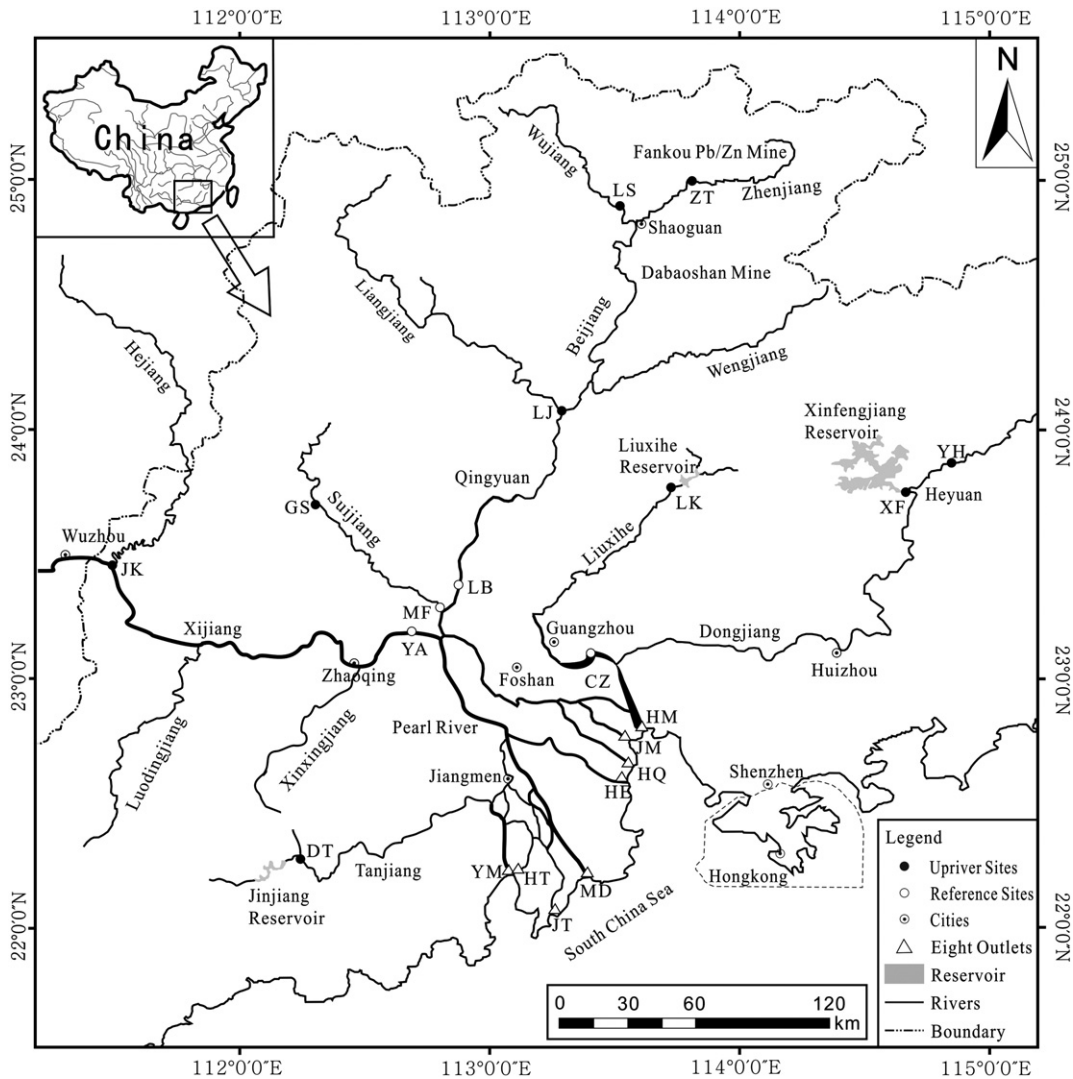
areas; (2) examine potential sources of the target metals; and (3) quantify the total annual inputs of the target heavy metals from upstream to downstream areas of the Pearl River and the output fluxes to the global rivers.

The PRD is located in 102°14'–115°53'E, 21°31'–26°49'N (Fig. 1), and the average annual rainfall is 1200–2200 mm. The riverine runoff amounts to approximately 336 billion m<sup>3</sup> annually, but seasonally variable, that is, the runoff during the high-flow period (April–September) normally accounts for 80% of the total annual amount.

In general, the Pearl River is the collection of all rivers/streams in the PRD, including three main tributaries: the Xijiang River, Beijiang River, and Dongjiang River (Fig. 1). These three rivers account for 89.6% of the total flow of the Pearl River. The Xijiang River is the main stream of Pearl River, with annual runoff accounting for 70.8% of its total flow. The Dongjiang River basin majorly contains granite and clay rocks, whereas limestone and shale are the main rock types of the Xijiang River basin. The upper reaches of the Xijiang River drain the famous karst landforms in South China. The Beijiang River basin is composed of different rock types, including granite, limestone, and clay rocks, and runs across the city of Shaoguan, which is well known for its high production of nonferrous metals. The Dongjiang River is the major source of drinking water for >40 million residents of Hong Kong, Shenzhen, Guangzhou, and other cities. The Pearl River drains

into the sea through the following eight outlets: Humen, Jiaomen, Hongqili, Hengmen, Modaomen, Jitimen, Hutiaomen, and Yamen (Fig. 1).

The water samples were collected manually in acid-rinsed polyethylene bottles from September 2009 to June 2010. The Guangdong Meteorological Yearbook reported that the average annual rainfall in Guangdong province was 1530 mm, which is 15% less than that in 2009. Regional distribution was much in the southwest than in the northeast. In 2010, the average annual rainfall was 1867.7 mm (Meteorological Bureau of Guangdong Province, 2010 and 2011). In 2009, the total amount of water that flows into the sea in the Guangdong province was 315.21 billion m<sup>3</sup>, and the water from the eight aforementioned outlets of the PRD into the sea was 255.22 billion m<sup>3</sup>. The amount of the water flowing into the sea was 32.6% less than the previous year and 24.6% less than the average value. In 2010, the total amount of water flowing into the sea was 376.64 billion m<sup>3</sup>, and the water from the eight outlets of the PRD into the sea was 295.9 billion m<sup>3</sup>. The amount of the water flowing into the sea was 19.5% less than the previous year and 6.3% less than the average value (Water Resources Department of Guangdong Province, 2009 and 2010). The samples were collected at 50 cm below the surface of the river. The sample bottles were capped immediately, sealed between two polyethylene bags, and transported to the laboratory.



**Fig. 1.** Location of the sampling sites. (Zhoutian (ZT); Lishi (LS); Gushui (GS); Mafang (MF); Yihe (YH); Xinfeng (XF); Lianjiang (LJ); Lubao (LB); Jiangkou (JK); Yongan (YA); Liangkou (LK); Changzhou (CZ); and Datian (DT)) in upstream of the Pearl River Delta (dotted lines indicate its draining boundary) and the eight major riverine runoff outlets (Yamen (YM); Hutiaomen (HT); Jitimen (JT); Modaomen (MD); Hengmen (HE); Hongqimen (HQ); Jiaomen (JM); and Humen (HM)).

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