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Geochemical transfer and preliminary health risk assessment of thallium in a riverine system in the Pearl River Basin, South China

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ABSTRACT

Thallium is a highly toxic element, whose geochemical dispersion, transfer and potential health risks in aquatic systems are far from understood. This study aims to investigate the distribution of Tl in the surface water from an ultra-large Tl-bearing pyrite open-mining site and its associated riverine system of Yunfu city, western of the Pearl River Basin (PRB). Concentrations of 2.75–194.4 μg/L of Tl were found in the surface water from the mining site. Compared with other trace metals measured (Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn), Tl experienced little precipitation by conventional lime-dosing treatment of mine water and readily moved through the river trace. The distribution of Tl in the river watershed during both the dry season (Tl: 0.01–9.15 μg/L) and wet season (Tl: 0.03–1.92 μg/L) generally followed a decreasing concentration pattern downstream of the pyrite mining site for the upper and middle reaches. However, some unexpected Tl elevations were observed in the lower reaches. Concentrations of Tl correlated well with concentrations of Ca, Mn, Sr, sulfate, total dissolved solids and water conductivity values for both the dry season and the wet season. Finally, health risk assessment suggests that Tl may pose non-carcinogenic health risks to local residents over a long time. This study highlights not only anthropogenically-induced but also hidden naturally-occurring Tl enrichment in the hydrosphere of the PRB, and enhances the understanding of aqueous geochemistry of Tl.

1. Introduction

Surface water contamination with trace metals has become a serious environmental concern worldwide, owing to their toxicity, persistence and bioaccumulation (Babula et al., 2008; Klavins et al., 2000; Muhammad et al., 2011). The Pearl River Basin (PRB) covers an area of roughly 461,000 km^2 with a population of 21.4 million people, including many big cities like Guangzhou, Hong Kong, and Macao (Sun et al., 2010). It bears abundant sulfide metal ores in the upper and middle reaches, and excessive metal mining and smelting has resulted in large amounts of potentially toxic trace metals since the end of the 1970s (Ouyang et al., 2006).

Thallium (Tl) is a typical trace metal of toxicity to mammals higher than that of Cd, Pb and Hg, and it is reported to have induced many therapeutic, occupational and accidental poisoning (Anagboso et al., 2013; Xiao et al., 2003; Peter and Viraraghavan, 2005). However, compared to Cd, As, Pb, Hg, Cu and Zn, the environmental behavior of Tl is much less studied, and many aspects are still unknown (Law and Turner, 2011; Peter and Viraraghavan, 2005). As a rare but widely spread element, Tl is present in natural environments usually at very low concentrations, with an average concentration of 0.49 μg/g in the continental crust and of 0.013 μg/g in the oceanic crust (Peter and Viraraghavan, 2005). Independent thallium minerals are very rare. To date, only fifty-six have been found in nature, but Tl is an abundant minor component, relatively concentrated in many sulfide minerals (e.g. pyrite, galena, sphalerite, chalcopyrite) and in minerals of potassium (Jakubowska et al., 2007; Karbowska et al., 2014; Vaněk et al., 2012). Therefore, Tl is usually recovered as a byproduct of the smelting of Pb, Zn and Cu ores and of sulfuric acid production, where pyrite (FeS_2) is used as raw material. While less than 15 t of Tl are produced worldwide annually, it is estimated that 2000–5000 tons per year are mobilized by industrial processes (Kazantzis, 2000; Peter and Viraraghavan, 2005).

There are many sulfide mineral resources enriched in Tl in China, but its recycling in the mining or smelting or related industrial activities has not ever been considered (Xiao et al., 2012; Zhou et al., 2008). Specifically, two ultra-large Tl-bearing sulfide ore deposits (the Pb–Zn bedrock and the pyrite bedrock) are located in the Pearl River Basin (PRB). As documented, minerals of the Pb–Zn bedrock and the pyrite bedrock

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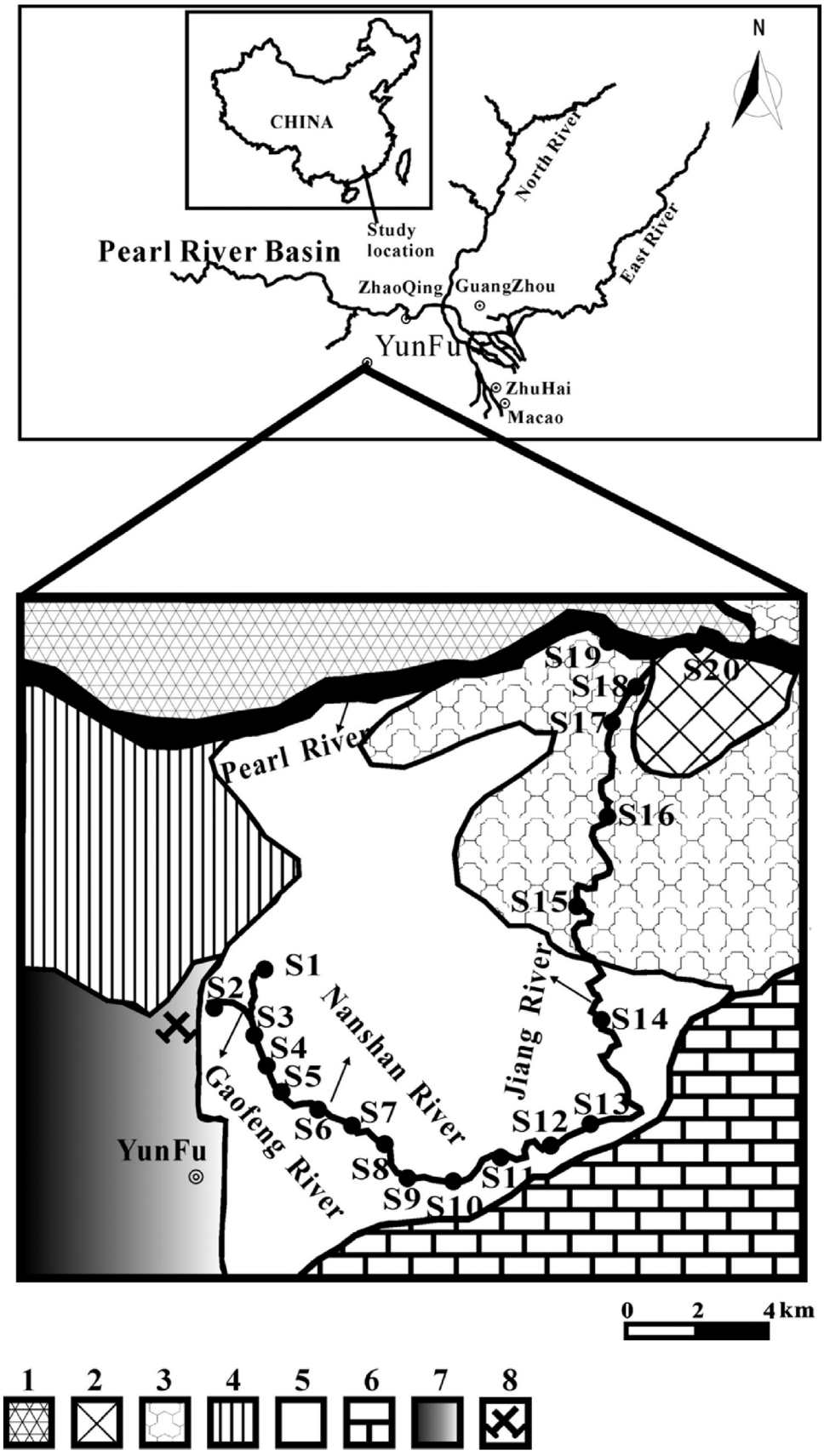
showed an average Tl content around 10 μg/g and 50 μg/g, respectively. However, Tl pollution has been often ignored in China, partly due to its relatively low abundance and associated difficulties with analysis in natural water samples (Das et al., 2007; Lukaszewski et al., 1996; Krasnodębska-Ostręga et al., 2013), though the maximum contaminant level in drinking water of China has been fixed at 0.1 μg/L since 2006 (MOH and SAC, 2006), much lower than the limiting value of 2 μg/L for drinking water in the USA (US EPA, 2006). Therefore, enormous



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