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Geochemical dispersal of thallium and accompanying metals in sediment profiles from a smelter-impacted area in South China

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Thallium is a trace metal with a toxicity greater than that of Pb, Cd and Hg. This study complements the authors' previous research, with main focus on contamination by Tl and accompanying metals (Pb, Zn, Cd, and Cu) in sediments from an area historically affected by Pb-Zn smelting in Shaoguan city (northern Guangdong Province, South China). In order to provide complex data on the geochemistry of anthropogenic Tl in sediments, total contents and geochemical fractionation of Tl and the other metals were comparatively studied for two different sediment profiles, core A from the Pb-Zn smelter outlet (a major Tl pollution point-source) and core B from the inlet of the North River (natural water courses near the smelter). Surprisingly high enrichment of Tl was observed across both depth profiles, with varying distribution patterns versus depth. Further comparison of Tl contents and its geochemical fractions in the upper, middle and bottom horizons of core A and core B, in combination with mineralogical phases of the sediments, clearly demonstrated both lateral and vertical mobility of Tl, due to complex processes such as mechanical disturbance/mixing, long-term alteration/dissolution of smelter-derived particles, and vertical migration of Tl through colloidal (or microparticle) transport with alumino-phyllosilicates and Fe/Mn (hydr)oxides. Relatively high abundance of Tl in the labile fractions of all selected sediments from both locations highlights a potentially significant environmental risk to the local ecological system in the near future.

1. Introduction

Thallium is one of the most toxic metals in terrestrial environmental systems (Nriagu, 1998; Peter and Viraraghavan, 2005; Xiao et al., 2012; Álvarez-Ayuso et al., 2013), due to its acute and chronic effect on health for most organisms (Vaněk et al., 2013). As compared to other toxic metals like Pb, Cd, and Hg, Tl pollution occurs to a much lesser extent worldwide. However, since Tl is an accompanying element in various metal sulfide ores and coals, Tl contamination can result from emissions and solid wastes from various smelting and mining activities (Peter and Viraraghavan, 2005; Anagboso et al., 2013; Jakubowska et al., 2007a, b; Lis et al., 2003; Liu et al., 2010; Lukaszewski et al., 2012; Turner et al., 2010; Vaněk et al., 2010a, 2010b, 2013; Yang et al., 2009; Karbowska et al., 2014; Gomez-Gonzalez et al., 2015). Naturally occurring Tl enrichment due to weathering of Tl-Hg-As sulfides has also been found in the Lanmuchang area, southwestern Guizhou Province, China (Xiao et al., 2004). High-temperature smelting processing of Tl-bearing ores (PbS, FeS_2, ZnS, etc.) is usually regarded as the dominant source of significant Tl contamination in the environment (Nriagu, 1998; Peter and Viraraghavan, 2005; Vaněk et al., 2013 and references therein), as most Tl compounds are easily volatilized at high temperatures (Vaněk et al., 2013; Liu et al., 2016a,b; Yan et al., 2001; Antón et al., 2013). Average Tl contents often surpass 10 mg kg^{-1} in soils and sediments from such smelter-impacted areas (Lis et al., 2003; Vaněk et al., 2013;

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Boughriet et al., 2007).

Since Tl pollution was found to occur successively in the Pearl River branches (such as the North River, the He River), this issue has raised public concerns all over China. Specially for the North River, waste discharge from a large Pb-Zn smelter using Pb-Zn ores enriched with Tl was mainly blamed for the Tl pollution (Xiao et al., 2012; Liu et al., 2016a,b). The smelter has processed such ores ever since the 1970s. During the last several decades, substantial amounts of Tl-rich wastes have been discharged into the nearby water courses (Liu et al., 2016a,b). When Tl is present in waters, it may be easily taken up by aquatic organisms, both in its monovalent and trivalent state (Zitko and Carson, 1975; Casiot et al., 2009; Lin et al., 2005; Borgmann et al., 1998; Lan and Lin, 2005; Pickard et al., 2001; Lapointe and Couture, 2010). Substitution of K^+ by Tl^+ is assumed to be the main mechanism in biogeochemical reactions/cycling (Madejón et al., 2007).

As one of the main branches of the Pearl River, the North River flows through Shaoguan, Qingyuan and other administrative regions of the Guangdong Province. It acts as the primary water supply for the urban agglomeration area in the province. Intensive industrial activities along the riverside have seriously degraded the water quality and eventually endangered human health. After the outbreak of Tl pollution in the North River in late 2010, the Pb-Zn smelting activities were considerably reduced. Subsequently, Tl levels in the river water showed an obvious decline to less than 0.1 μg L^{-1} (the drinking water limit in China). Sediments developed in the watershed near a smelter are susceptible to serious metal contamination, due to the long-term deposition of smelting wastes. It has been widely recognized that river sediments act both as a sink and as a potential source of metal contaminants (Krasnodębska-Ostręga et al., 2005; 2006; Bird, 2011). However, contents and distribution of Tl in the sediments are largely unknown for the North River.

This study complements the authors' previous research, which was focused on Tl distribution and its geochemical fractionation in the raw Pb-Zn ores and in their solid smelting wastes discharged from the large Pb-Zn smelter (Liu et al., 2016a). There is a lack of systematic data concerning the fate of anthropogenic Tl in sediments of the North River. Consequently, the main objectives of this study are (i) to investigate the contents and dispersal characteristics of Tl and accompanying metals in two representative sediment profiles from smelting-affected catchments, (ii) to identify the main mineral scavengers of Tl in the sediments, and (iii) to uncover dominant Tl dispersion processes.

2. Materials and methods

2.1. Study area and sampling

The North River has a catchment area of approximately 56,456 km^2 with 12.6 million inhabitants. It is the second largest branch of the Pearl River, with a main stream of 468 km in length and a runoff volume of 4.82×10^{10} m^3 $year^{-1}$. As shown in Fig. 1, the Pb-Zn smelter, notorious for triggering Tl pollution, is located on the bank of the North River. It was constructed in 1966 and uses the Imperial Smelt Process (ISP) technology for the production of Pb and Zn. Since its construction, the annual production has increased from several tons to dozens of tons until October 2010, when Tl pollution in the North River water was disclosed by local media. Thereafter, release of Tl into the environment has been strongly reduced, and strict pollution control for Tl was established. However, the legacy of Tl pollution is still present in the sediments of the North River, for the smelter has used Tl-rich ores without pollution control over decades.

Sampling was performed during July 2012 in the North River Basin. Two sediment cores were extracted using a gravity corer. As displayed in Fig. 1, one core was sampled from the smelter outlet (core A), which represents a major Tl pollution point-source. The other core was taken from the inlet of the North River (core B), which is located approximately 2 km downstream of the smelter outlet. In total, thirteen sub-sediment samples were obtained from core A and fifteen from core B. There was no significant distortion of the top sediment layer nor any loss of surface sediments during the gravity coring. The core was cut into 2-cm thick slices along its length using a stainless-steel cutter, and stored in pre-cleaned plastic bags at 4 °C prior to laboratory analysis. Sub-samples were dried to constant weight at 50 °C and were then hand-ground in an agate mortar to obtain fine particles (<100 μm).

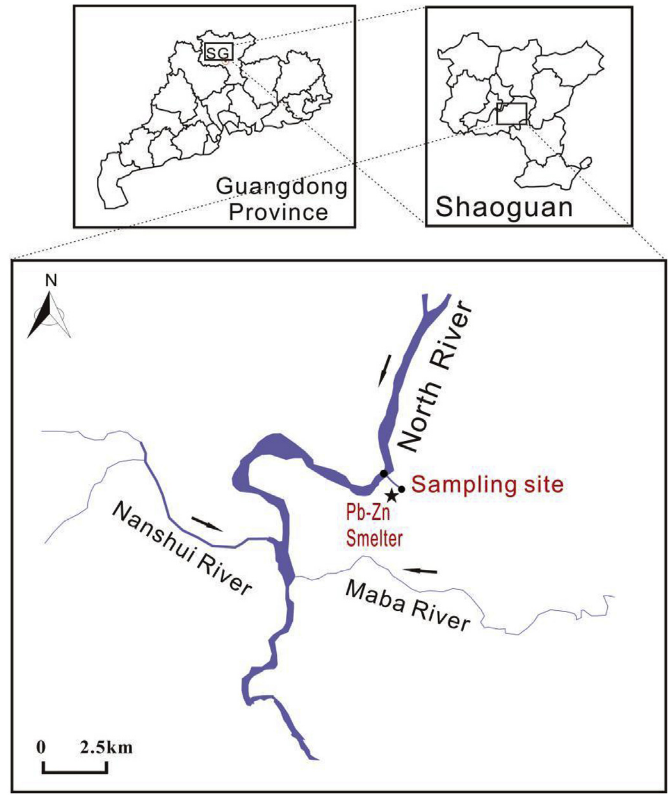

Fig. 1. Sampling site in the studied riverine system of the Pb-Zn smelting area in Shaoguan city (SG), Northern Guangdong Province, China. The topmost insertions depict the location of SG in the Guangdong Province (on the left) and the location of the river system in SG (on the right). The main map shows the sampling locations of the sediment cores (●) and the location of the Pb-Zn smelter (★). The arrows indicate the flow direction.

2.2. Sediment characterization

For the determination of 'total' contents of Tl, Pb, Zn, Cd, and Cu, the sediment samples were digested using a mixture of concentrated HNO_3, HF, and $HClO_4$ on a hotplate at 150 °C, as described in previous studies (Liu et al., 2016a, 2016b). The geochemical fractionations of Tl and other metals in selected sediments from different depths of each core were determined using the standard sequential extraction procedure recommended by IRMM (Institute for Reference Materials and Measurement, Europe) (Rauret et al., 2000; Cuong and Obbard, 2006). According to the IRMM protocol, the fractions are referred to as follows: (i) exchangeable/acid-extractable fraction (0.11 mol L^{-1} CH_3COOH-extractable, F1), (ii) reducible fraction (0.5 mol L^{-1} $NH_2OH \cdot HCl$-extractable, F2), (iii)