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TEMPORAL TRENDS OF THALLIUM POLLUTION IN FLUVIAL SEDIMENTS OF THE NORTH RIVER, SOUTH CHINA

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Introduction

The increasing worldwide contamination of freshwater systems with heavy metals, due to anthropogenic activities, is one of the key environmental problems facing humanity. Thallium (Tl) is a typical toxic metal, which has a toxicity to mammals comparable to Hg, Pb, and Cd. Considering its high toxicity, Tl is listed as one of the metal pollutants of priority by many countries, such as US, Germany, Canada, and China (Xiao et al., 2012). As a rare element, it usually dispersed in the natural environment with very low content. The average abundance of Tl in the continental crust is 0.49 mg kg^{-1} (Peter and Viraraghavan, 2005). However, it may be concentrated in some particular sulfide minerals and silicates, owing to its dual elemental properties of chalcophile and lithophile (Karbowska et al., 2014). Therefore, as a minor constituent of numerous metal sulfide minerals, mining and smelting of such minerals and industrial activities likewise have emitted large quantities of Tl into the environment.

Specifically the North River Basin of South China, well-known by nonferrous metal productions, bears abundant resources of sulfide minerals enriched in Tl, with content by several dozens of milligram per kilogram. With unplanned and unscientific exploitation of such resources for decades, a great environmental risk arising from Tl pollution has been formed. Knowledge of Tl pollution and its environmental behavior is prerequisite for proper environmental regulation and treatment. However, Tl pollution has been ignored for long due to its absence under supervision by government's environmental protection bureau. Fluvial sediments, as a carrier of contaminants, have been used as valuable geochemical records for studying the sources, history and changes of trace metal pollution.

In this contribution, we report a first systematic measurement of Tl and some other relevant heavy metal contents in a representative fluvial sediment profile from the North River in the vicinity of various mining, smelting and related factories. The aims are to quantify the level of Tl recorded in the vertical profile, to enhance the understanding of Tl transport behaviors, and to assess Tl pollution history in this area.

Methods

In December, 2014, a fluvial sediment core with a length of 117 cm was collected at intervals of 3-cm distances from the North River, near the convergence of effluents discharged from various industrial activities, such as Pb-Zn smelting and mining. The core was cut into sub-samples of 3-cm length in the field, and packed in plastic bags immediately to avoid oxidation. Sub-samples were then dried at room temperature and sieved prior to further analysis. For total digestion, the samples were digested on hot-plate by HNO_3 and HF mixtures. Contents of Tl, Cr, Ni, Cu, Zn, Cd, and Pb were determined by means of

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Elan 6100 DRCII, PerkinElmer, USA). The geochemical fractions of heavy metals (Tl, Cr, Ni, Cu, Zn, Cd, and Pb) in samples from selected depths of the sediment core were obtained by using an IRMM (Institute for Reference Materials and Measurement, Europe) sequential extraction procedure combined with ICP-MS.

Results

As compared with the reference soil from the South China, all these metals are generally enriched in the sediments, and the average contents of Cu, Zn, Cd, and Pb even by a factor of about 10 to 600. Obvious fluctuations of Tl and other analyzed heavy metals occurred along the sediment profile, with neither an increasing nor a decreasing trend. But several sharp peaks can be observed in some parts of the core. Metals like Cr, Ni, Cu and Zn follow similar variations with Tl along the depth profile. For example, obviously higher levels of Tl, Cr, Ni, Cu and Zn can be found rather in the topmost layers. A significant positive correlation is observed between Tl, Ni, Cd, Zn and Cu.

The geochemical fractions of Tl, Cr, Ni, Cu, Zn, Cd, and Pb were analyzed in selected sediments to study their transfer along the profile. The results showed that Tl was mostly resided in the residual fraction, with the percentage ranging from 46.4 % to 76.6 %, with a mean value of 65.2 %. Lower proportions of Tl were found in the reducible and oxidizable fractions, with the lowest present in the weak-acid-exchangeable fraction. The relatively high associations of Tl in the residual fraction could be ascribed for easy substitution of Tl over K in the silicate lattice of the sediments. Variations of Tl in the reducible percentage may indicate that Fe-Mn (hydr)oxides play a significant role in Tl transfer across the depth profile. In addition, the average enrichment factors (EFs) categorized the sediment by a very high enrichment of Cd (Level IV), a significant enrichment of Zn, Cu and Pb (Level III), a moderate enrichment of Tl (Level II) and a deficiency to minimal enrichment of Cr and Ni (Level I).

Conclusion

The knowledge of Tl in the fluvial sediment profile of the watershed nearby the industrial mining and smelting site is essential for unveiling the pollution history, predicting element migration and developing emission control and remediation strategies. Significantly positive relationship between Tl and Cu, Cd and Zn indicated that they may share common pollution sources. Overall medium enrichment of Tl and extremely high enrichment of Cd were found in all the sediments across the depth profile. About 20% to 50% of Tl present in the mobile fractions may be released under alterations of environmental conditions. All these results may suggest that the river has been polluted by Tl for a long-term. The highly toxic metal Tl may have potentials to pose a great threat to the local ecosystem. It is high time to take effective measures for the remediation of the pollution.

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