Hydrogeochemical processes of thallium in a rural area of Southwest Guizhou, China

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Abstract The water system in a rural area of Lanmuchar in Southwest Guizhou is facing a risk of thallium (Tl) contamination due to Tl mineralization around the area. The major trace elements and Tl in the water system are studied to understand the hydrogeochemical processes of Tl constrained by Tl mineralization. The results showed that the dispersion pattern of Tl follows a descending order in concentration from mine groundwater (deep groundwater) → stream water → shallow groundwater → background water, reflecting the impact of Tl mineralization on the hydrogeochemical composition. Tl concentrations in stream water in both regimes are remarkably higher (2–30 fold) downstream than up- and mid-streams, probably caused by the unidentified discharge of deep groundwater. Low Tl levels are detected in the current drinking water, however, the highly elevated Tl in stream water and ground water may pose a potential environmental risk through daily washing and agricultural irrigation. This study suggests that human activities, such as agricultural irrigation, could intensify the environmental risk of Tl.

Key words thallium; hydrogeochemical process; environmental impact

1 Introduction

Thallium is one of the 13 priority pollutants listed by USEPA (Keith and Tellidiard, 1979). It is rare but widely distributed nearly in all natural waters. The mean concentrations of thallium are 0.012–0.0612 μg/L in sea water (Flegal and Patterson, 1985), 0.066–0.715 μg/L in river water (Hall and Pelchat, 1996), 0.001–0.036 μg/L in lake water (Cheam et al., 1995), 0.001–1.264 μg/L in ground water (Hall and Pelchat, 1996), 0.001–0.006 μg/L in stream water (Dall’Aglio et al., 1994), and 0.0003–0.0009 μg/L in arctic snow water (Cheam et al., 1996). The hydrogeochemistry of thallium has been less documented than that of other metals (i.e., Cu, Pb, Zn, As, Hg, Cd) in spite of its high toxic potential.

A rural area in SW Guizhou Province, China, known to have been attacked by chronic Tl poisoning in the 1960’s–1970’s, has been targeted for study. The Hg-Tl mineralized area of Lanmuchar in Xingren County is the study area. Mercury ores have been mined at Lanmuchar for over 300 years, which thereafter causes Tl dispersion in the local environment. The contents of Tl in drinking water (well water) measured by previous researchers range from 3.7 to 40 μg/L (Zhou Daxing and Liu Dingnan, 1985). These values are significantly higher than those in other aquatic systems such as stream water, ground water or lake water. Thallium poisoning, which affected a large portion of the population and caused symptoms such as hair loss, body-aches, reduced vision and blindness, was thought largely to be due to Tl contamination in drinking water and vegetables (Zhou Daxing and Liu Dingnan, 1985). After 30 years, however, there are much less data available on Tl content in the local aquatic system and its current environmental impact is unknown either. In order to help fill this information gap, we conducted this hydrogeochemical investigation and tried to determine the dispersion characteristics of Tl in drinking water, stream water and ground water, and their impacts on the local ecosystem.

2 Land features and climate

The study area is located in the Lanmuchar area, Huilong Town, Xingren County, Guizhou Province, China. The Lanmuchar area is famous for a typical mineralization of Hg-Tl-As sulfides. Sulfide minerals of extensive occurrence, such as lordanite, cinnabar, realgar, orpiment and pyrite are the primary carriers of Tl, Hg and As in the rocks and ores (Chen Dalian et al., 2003; Xiao Tangfu et al., 2004a; Zhang Zhong and Zhang Baogui, 1996). The exposed rocks include the Changxing Formation (P2c: limestone), the Dalong Formation (P2d: arkosic shale), the Longtian
Formation (P2J: limestone, argillite and coal seams) and the Yelang Formation (T/y: siltstone, argillite and limestone). The Qingshui Stream is the only water source available in the Lammuchang area. It runs through the main populated area from north to south and drops into a sinkhole located about 3 km downstream.

3 Sampling and analysis

Groundwater was sampled from shallow springs, deep mine groundwater and karstic caves (Fig. 1). Stream water samples were collected throughout the Qingshui Stream. All water samples were filtered on site by using Millipore Sterivex syringe capsules containing 0.45 μm cellulose acetate filters. Two filtered sub-samples of water were sealed in pre-cleaned (previously soaked in 1% ultra-pure HCl and rinsed with deionized water) 60 mL Nalgene bottles, one for anion analysis and the other for cation measurement (preserved with 0.4% ultra-pure HNO₃ to acidify the sample pH to 2.0). All the samples were numbered when collected and then stored in coolers at 4°C. Physical parameters, such as EC and pH, were measured in the field.

Thallium was analyzed by direct inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer SCIEX-ELAN6000). The major elements Na, K, Mg, and Ca were determined by ICP emission spectrometry (ICP-ES, Perkin Elmer OPTIMA3300), the anions Cl⁻ and SO₄²⁻ by ion chromatography, and HCO₃⁻ by acid-base titration technique. The detection limit (DL) of TI is 0.005 μg/L. The analytical precision at the 95% confidence level, determined by QA/QC through the duplicates, and the reference sample OTT96 (GSC, Ottawa), is better than 15% for major ions and TI. All the blanks are below DL.

4 Results and discussion

4.1 Groundwater geochemistry

The geochemistry data for all the investigated samples are presented in Table 1. The electrical conductivity (EC) values of most of the samples are generally below 1000 μS/cm, whereas those of deep mine groundwaters are all over 1000 μS/cm; the highest and lowest measured values for all the investigated waters are 2000 μS/cm (the upper limit of the measurement range) and 181 μS/cm, respectively. The pH values for all the samples range from 7.1 to 8.3, with the exception of deep mine groundwaters, which show low pH values ranging from 2.6 to 3.6.

Major elements of groundwater and surface water (stream water in the base-flow regime) are plotted on a Piper plot (Fig. 2). The Piper plot indicates two distinct groundwater types. The first is a Ca²⁺-SO₄²⁻ type of water, which was sampled from deep mine groundwater; and the other is a Ca²⁺-HCO₃⁻ type of water, which was sampled from shallow groundwater. As can be seen in Fig. 2, Ca²⁺ is the major cation whereas SO₄²⁻ and HCO₃⁻ are dominant anion components.