RESEARCH ARTICLE

Quantification of Tl (I) and Tl (III) based on microcolumn separation through ICP-MS in river sediment pore water

Atta Rasool [1,2,3] · Tangfu Xiao [4] · Salar Ali [5] · Waqar Ali [1,2] · Wajid Nasim [6]

Abstract

Thallium (Tl) is a typical toxic element, whose biological effects and geochemical behavior are closely related with its chemical speciation in the environment. In this context, the objective of the present study was to develop an effective method for separation of Tl (I) and Tl (III) based on solid-phase extraction (SPE) using anion exchange resin AG1-X8 as a sorbent and ICP-MS measurement. In this proposed method, Tl (I) and Tl (III) could be separated by selective adsorption of Tl (III)-DTPA in the resin, while Tl (III) was eluted by the solution mixed with HCl and SO_2. The validity of this method was confirmed by assays of standard solutions of Tl (I) and Tl (III), as well as with spike of contaminated samples. The present study results revealed that higher concentration of Tl (I) (245.48 μg/l) and Tl (III) (20.92 μg/l) had been found near the acid mine drainage (AMD) sample of sediment pore water. The results revealed that Tl (I) of 61.47 μg/l and Tl (III) of 9.73 μg/l were present in the river water contaminated by acid mine drainage. This thallium speciation analysis implied that the dominant Tl (I) species in the river water studied might be due to the weathering of sulfide mineral–bearing rocks, mining, and smelting activities in the studied area.

Keywords Thallium speciation · Stability · Acid mine drainages · ICP-MS · Chemical separation · Solid-phase extraction

Introduction

Thallium (Tl) is an extremely toxic heavy metal that can causes severe damage to all organisms in both the Tl (I) and

✉ Tangfu Xiao
  tfxiao@gzhu.edu.cn

1   State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences, Institute of Geochemistry, Guiyang 550081, China

2   University of Chinese Academy of Sciences, Beijing 100049, China

3   Department of Environmental Sciences, COMSATS University , Islamabad (CUI), Vehari 61100, Pakistan, Vehari, Pakistan

4   Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education; School of Environmental Science and Engineering, Guangzhou University, Guangzhou 510006, China

5   Department of Biological Sciences, University of Baltistan, Skardu 16100, Pakistan

6   Department of Agronomy, University College of Agriculture and Environmental Sciences, The Islamia University of Bahawalpur (IUB), Bahawalpur, Pakistan

Tl (III) oxidation states (Das et al. 2007; Jia et al. 2018). Despite its high toxicity, Tl is much less studied than the widely studied heavy metals such as mercury, cadmium, and lead (Ospina-Alvarez et al. 2015; Li et al. 2019). The more stable Tl (I) species tends to create stable toxic complexes with sulfur-containing compounds, while the Tl (III) is prone to form oganic complexes of greater stability with DTPA (Li et al. 2019) or EDTA (Pavlickova et al. 2006; Meeravali and Jiang 2008). Therefore, each redox state of the Tl exhibits different bioavailability and toxicity property (Lan and Lin 2005; Couture et al. 2011). However, in contrast to many other elements, little is known about the chemical speciation of Tl in the environment with related ecological effect and potential human health hazards (Cobelo-García et al. 2015). In the past years, the increasing attension has been paid to the Tl speciation in different environmental media due to its toxic effect on human, aquatic life and its distribution in the food chain (Campanella et al. 2017). Recently, a couple of river of waters and sediment contaminations by Tl have been recorded (Casiot et al. 2011; Vanek et al. 2010a, b; Campanella et al. 2016), which suggests an urgent need to systematically study the Tl-related environmental chemistry (Xu et al. 2019).

Tl is released into the environment from natural and anthropogenic processes, such as from the oxidation of Tl-

containing pyrite, and from industrial procedures in which Tl-bearing ores were used in the steel industry, coal combustion, metal mining, ferrous and non-ferrous metal smelting processes, and cement manufacture (Stafilov et al. 2013; Karbowska et al. 2014). The acid mine drainage (AMD) is a typical activity of past mining exploitation responsible for discharging the toxic heavy metals including Tl to the environment (Xu et al. 2019). In aquatic environment, Tl is present at low concentrations and Tl (I) tends to dominate over Tl (III), mostly in the form of hydrated Tl^+ due to limited complexation (Casiot et al. 2011). Although microbial processes may lead to Tl (I) oxidation (Twining et al. 2003; Karlsson et al. 2006), Tl (III) might be stabilized by hydrolysis and colloid formation or sorption to Fe (III) colloids (Karlsson et al. 2006; Peacock and Moon 2012) and Mn (IV) oxides (Lis et al. 2003). In the previously reported study, the separation of Tl (I) and Tl (III) using soild phase extraction method from aqueous water solution is thermodynamically stable with a wide extent of pH (Krasnod bska-Ostr ga et al. 2013; Xiao et al. 2018).

Apart from the choice of a suitable method of Tl determination, it is critical to preserve Tl species in collected river water and sediment samples. The Tl (I) species is more stable than the Tl (III) species, so spontaneous reduction of Tl (III) to Tl (I) (Eh (Tl^{3+}/Tl^+) = +1.26 V) and also hydrolysis of Tl (III) at pH < 7 can be observed. The reduction potential of Tl (III) is exaggerated by pH and complexing agents like in 1 M HCl, where the potential drops to 0.77 V because it is strongly complexed with chloride compared with Tl (I), (Fergusson 1990; Jia et al. 2018). The Tl (III) is prone to precipitated as Tl (OH)$_3$ at pH < 7 (K_{sp} = 1.68 × 10^{-44} 25 °C); also, Tl (OH)$_2^+$ and Tl (OH)$_2^-$ would shape even at pH~2 (Couture et al. 2011; Sadowska et al. 2016; Campanella et al. 2017). For instance, Tl (III) at normal levels is efficiently reduced to Tl (I) (Eh^o = 1.28 V), the latter would overwhelm in ecological waters (Kaplan and Mattigod 1998). Such that a stable Tl (III) complexes in solution is needed for the chemical speciation analyses at higher pH, where hydroxide structures are dominant if no treatment is used (Lin and Nriagu 1999; Xiao et al. 2018).

Regarding the Tl ligands such as the chlorides (log β [TlCl$_4^-$] = 17) or acetate (log β [Tl (CH$_3$CO$_2$)$_4^-$] = 15.4), the trivalent species may happen in natural samples (Das et al. 2007). To avoid hydrolysis and reduction of Tl (III), diethylene triamine pentaacetic acid (DTPA) can be added to the samples. Thereby Tl (III)-DTPA complex is basically extremely stable (log β [Tl (III)-DTPA] = 46) (Smith and Martell 1989), although DTPA does not intricate Tl (I) and the stability of the complex is essentially free of pH or on the presence of others ions (Karlsson et al. 2006; Krasnodebska-Ostrega et al. 2008). Notably, the reduction rate of Tl (III) to Tl (I) was decreased up to 80% in the presence of acetate, while 40% was observed in the existence of chlorides and even to only 3% in the presence of DTPA (Nowicka et al. 2014). Therefore, the addition of DTPA can greatly enhance the stability of the Tl (III) species (Xiao et al. 2018).

Several studies on the Tl speciation at ultra-trace levels have been published in waters, soils, and river sediments (Twiss et al. 2004; Jia et al. 2018; Xiao et al. 2018) Previously, mostly researcher used anion exchange chromatography technique for Tl speciation, which is very time consuming. Whereas, the more rapid method for Tl speciation analysis using cation exchange chromatography has never achieved universal agreement for the complex systems such as mine water (Krasnodebska-Ostrega et al. 2008; Karlsson et al. 2006). Among the reported techniques for Tl speciation, solid-phase extraction (SPE) is easy to implement and reproducible, allowing determination of Tl in samples below the limit of detection due to preconcentration. Also, it could be combined with various testing methods. Furthermore, portable experimental equipment and reagents make it possible for in situ fresh samples testing. The anion exchange resin of AG1-X8 has been extensively used in preconcentration of Tl isotope measurement (Baker et al. 2009), and for the separation of Tl (I) or Tl (III) in seawater (Batley and Florence 1975; Xiong 2009). However, it lacks a confirmatory experiment with a standard solution and without stable reagent for Tl (III), and its procedure is hard to put into practice for other samples. Thus, owing to the upgrade, this procedure combing AG1-X8-based SPE and the DTPA-Tl (III) separation may be helpful to the confirm and assess the Tl species in stream water and sediments samples accumulated from the Tl-rich mineralized Lanmuchang district, Southwest Guizhou, China. Therefore, the fundamental objective of this study was to establish a basic methodology for analyzing the separation of Tl (I) and Tl (III)-DTPA in stream water and sediment pore water samples based on the AG1-X8 resins and the ICP-MS measurement. This method could work well in a wide range of pH, avoiding the change in the valence of Tl during adjusting solution pH. The findings of this study provide an economical, simple, fast, and sensitive method for separation of Tl species, and also gain an insight into the in-depth understanding of the geochemical cycling of Tl.

Material and methods

Site description

The present study area for sampling is located in Lanmuchang southwest Guizhou, China. The Lanmuchang district has been widely used for farming and residential purposes. The altitude is typically higher in the northwest and lower in the southeast. The height above sea level is 1000–1600 with a relative relief of 200–600 m. The karstic geology is depicted by tops, valleys, karstic holes, karstic underground rivers, and sinkholes. The Tl mineralized area in southwest Guizhou originates from the natural weathering of Tl sulfide–rich (red Tl ore, realgar, orpiment, cinnabar, etc.) ores and the human activities in

mining. The nearby soil, water, sediment, and crops are rich in Tl, and neighborhood residents had a serious health risk (Xiao et al. 2012; Jia et al. 2013). There is an area from north to south of the river surface (Qingshui stream) that goes through the mineralized zone, downstream into a natural wetland. The study area Lanmuchang climate could be characterized as a continental sub-tropical monsoon climate. It is humid and warm with a yearly precipitation of 1200–1500 mm, and it is highest from June to August. The average temperature is about 14 °C per year, and the maximum temperature happens (30–35 °C) from July to August. In an agricultural point of view, the main crops are grown in the present study area incorporated with wheat, rice, vegetables, and corn, whereas most profitable crops are fruits, rapeseed, buckwheat, and vegetables. The crops grown in the study area are only enough for the local people, but some fruits can be transported outside the village. The people there used drinking water from springs, dug wells, and karstic caves, but the water treatment plant was unavailable in the study area. The local people live very close to Tl-rich sulfide mineralized environment, its mining and smelting processes directly affect the local people health directly. The diseases produced in study area people are hair loss, blindness, body-aches, and joint pain due to the high concentration of Tl in vegetables and drinking water from Tl mining processes.

Sample collection, treatment, and preservation

Two field surveys were carried out in May 2016 and July 2017, respectively. Twenty one freshwater samples were collected from the studied area (Fig. 1). Two types, namely the filtered and unfiltered water samples, were sealed in pre-cleaned 60-ml Nalgene1 bottles from each site, one with DTPA of final concentration 5 mmol/L was added to all samples to fix Tl (III) in situ. In May 2016, three additional water samples were collected with DTPA for stable Tl (III) from Lanmuchang study area. All the water samples were filtered on the sampling site by using Millipore Strives syringe capsules containing 0.45-µm cellulose acetate filters. In each site, water replicate (500 ml) were collected from the stream into a Nalgene polyethylene bottle. The parameters of water such as temperature, pH, dissolved oxygen (DO), oxidation-reduction potential (Eh), and electrical conductivity (EC) were measured in situ. Three buffer solutions (pH = 4, 7, and 10) were used to calibrate the pH electrodes. A field duplicate was collected at every 10th location. The fresh sediment samples by grabbing from bottom of the Qingshui stream of Lanmuchang (approximately 500 g) were collected at the same point as water samples using a portable Ekman grab sampler, repeated three times, and stored in polyethylene bags as well as approximately 50 g in Nalgene1 tubes with added 5-mM DTPA for fixed Tl (III). All samples were sealed with screw caps and stored in coolers at 4 °C and then shipped to the laboratory where they

were kept in the refrigerator at the same temperature. The sediment pore water samples were collected in the lab by Rhizons MOM sampler. Rhizons MOM was installed into test tubes, with 10-mL syringes used to create a vacuum, and after 5 h of incubation at room temperature, solution around 10 to 15 ml was collected. In extracted sediment pore water, pH, Eh, and EC were was measured by a calibrated HACH HQ30d pH meter (HACH, Loveland, USA) after equilibrating by standing 30 min in the lab.

Reagents, standards, and solutions

In the present experiment for thallium speciation through chemical method, we used some reagents, standards, and solutions, such as Pure MQ water (18.2 MΩ cm) obtained from Milli-Q50 system (Millipore, USA), $CH_3COONa.3H_2O$ ($M = 136.08$ g/L), pro purely check (Chempur, www.chempur.pl), ethanol 96% ($d = 0.808$ g/L), check up from expert (Poch, www.poch.com.pl), 68% nitric acid ($d = 1.42$ g/L), ultranal (Cheman, www.ciechtrading.com), 96% CH_3COOH ($d = 1.06$ g/L), suprapur (Merk, www.merckgroup.com), 30%NaOH ($d = 1.33$ g/L), suprapur (Merk, www.merckgroup.com), DTPA ($M = 393.35$ g/mol), pure check analysis (Sigma-Aldrich, www.sigmaaldrich.com) and Tl $(NO_3)_3.3H_2O$ (444.44 g/mol), and purum (Sigma-Aldrich, www.sigmaaldrich.com). The DTPA solution 5 mmol/L was prepared by mixing 5 g of DTPA into the 1000-ml flask and diluting it with MQ water. The standard solution of Tl (I) was prepared by dissolving $TlNO_3$ (Sigma-Aldrich) in 0.5 mmol/L HNO_3 and diluted with MQ water up to required concentrations. The standard solution of Tl (III) was set up by dissolving Tl $(NO_3)_3$ in 10 mmol/L DTPA + 5 mmol HNO_3 solution, adding immersed bromine water to oxidate it for 15 min, at that point warming to vapid. Saturated NaCl solution was prepared by adding 100 g of NaCl per 100 mL of MQ, stirring at water bath 60° heating, dissolved at room temperature after cooling supernatant. Whereas 0.1 M HCl with 5% SO_2 take 180 ml 0.1 M HCl in a container, placed on the balance of leveling, for dissolving 5% by weight approximately 9 g SO_2 gas in 0.1 M HCl to form a solution (Xiao et al. 2018).

Preparation of the sorbent and microcolumn procedure

The sorbent was prepared: first, take the resin volume of 3 times the saturated brine, the resin placed in saturated NaCl solution, shake resin with a salt solution, stay for 24 h, after that the discharge of water without yellow. Wash resin used MQ water more than 5 times. Accordingly, resin with 1 mol/L NaOH for 8 h, then let off the solution, wash with MQ water to neutral, and then preserve resin with 0.1 mol/L HCl solution for further use (Fig. 2). SPE tube can rinse with ultrapure water and place

Fig. 1 The map showing the location of stream sediment pore water and water samples of the Lanmuchang study area, southwest Guizhou
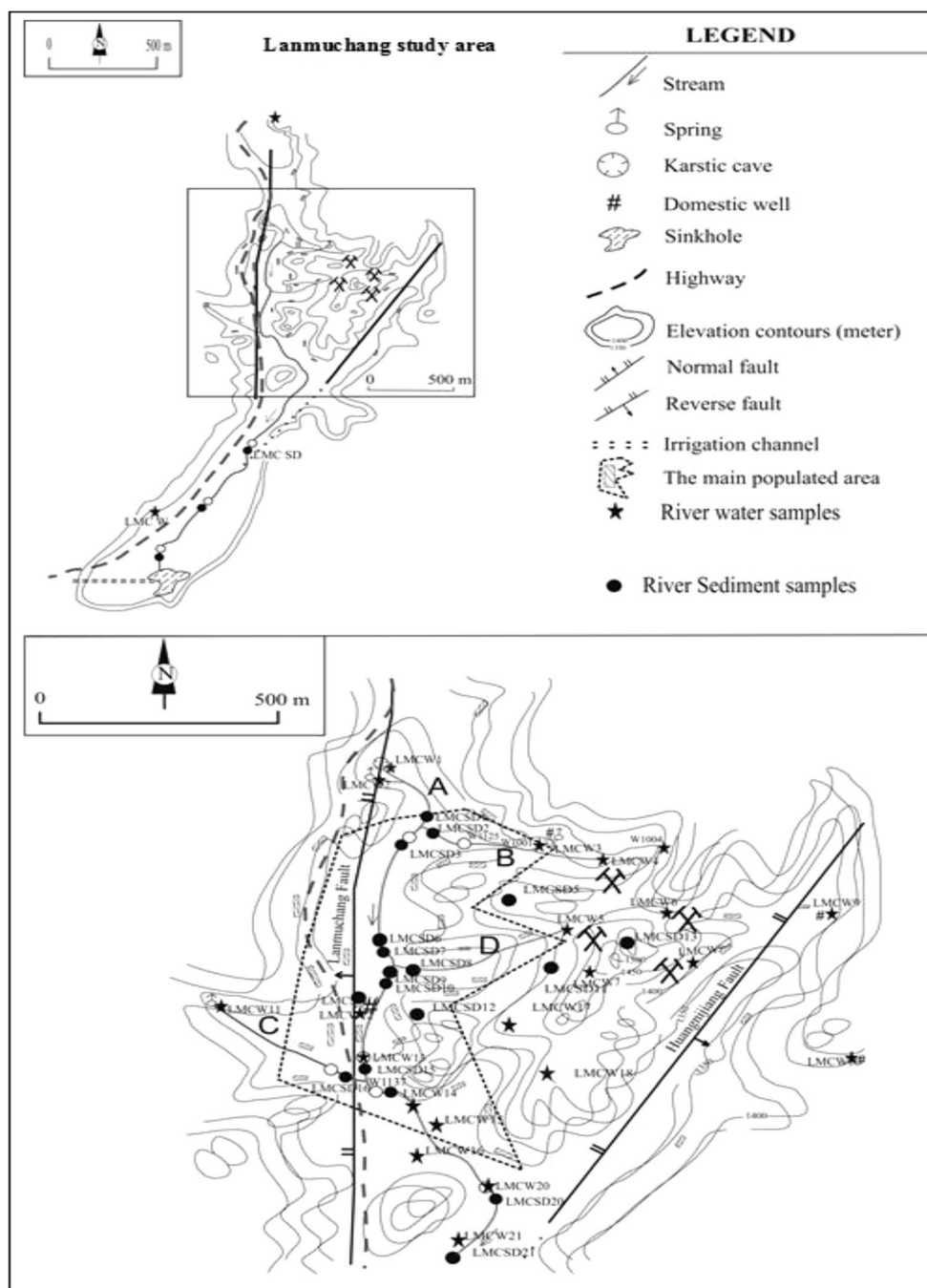
in 1 M HCl for 2–3 days. After that, use the pipette to add 2 ml of AG1X8 (200–400 mesh) anionic resin to the SPE tube and the resin was kept in 0.1 mol/L HCl solution for wet balance. Then add 5 ml water slowly to wash, so as not to disturb the resin. Open the tube and allow the resin to precipitate naturally. Accordingly, in the first step, we add 10 ml original sample (each time 2 ml) into microcolumn for getting Tl (I), and the speed of the sample to get through the microcolumn was controlled at 2.0 ml/min by a peristaltic pump. At the end of the sample, add 10 ml MQ water to wash the co-retain Tl (I) on the microcolumn. The complex of Tl (III)-DTPA is retained on the resin. Tl (I) is un-retained on the SPE resin and is eluted from the cartridge and collected for analysis. Continuously, to elute the Tl (III)-DTPA complex from the column, 15 mL of a 0.1 M HCl-SO2 solution were laden on the SPE (3 mL aliquots each time) and the eluent collected for Tl (III) analysis (Xiao et al. 2018). Nevertheless, to check the retention of Tl (I) and Tl (III) on AG1-X8 resin, different levels standard solutions were prepared for SPE through diluting them to required concentrations with 5-mM DTPA solution. Spiked samples were set up by using a similar method. So, we decide the final volume of 10 ml for ICP-MS analysis, which was easier to collect the

Fig. 2 Flowchart states new method for separation of Tl (I) and Tl (III) in samples based on AG1-X8 and ICP-MS
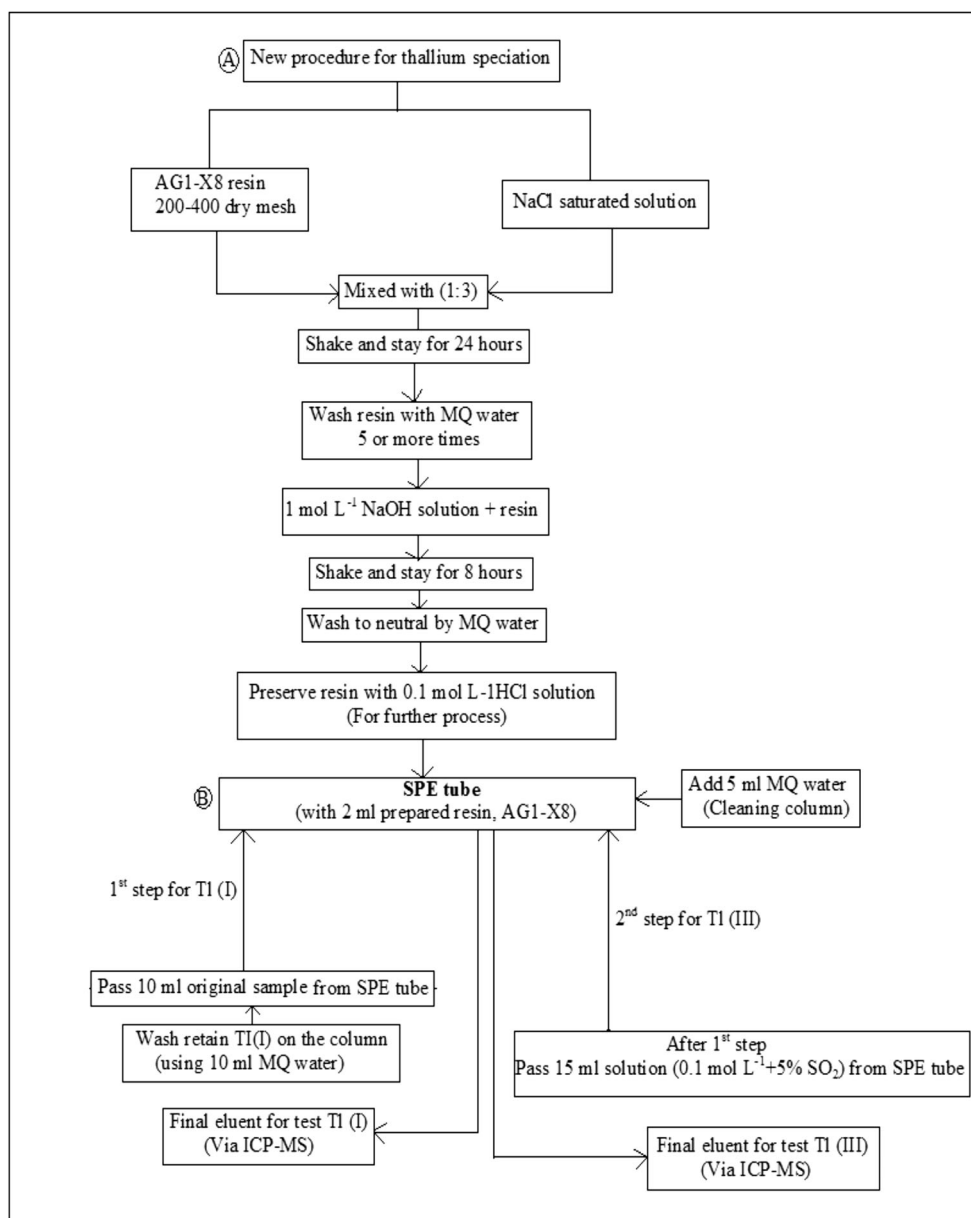
eluates in 10 ml vials. The detailed of this method was well reported by (Xiao et al. 2018).

Stability of Tl (III)

Thallium (III) is unstable in a solution and endures a quick reduction to Tl (I). To prepare Tl (III) solutions, it is obligatory to stabilize the trivalent form by the addition of complexing agents. The normally used regents are DTPA and chlorides. Therefore, the standard solution or sample, with known concentration of Tl (III), is probably higher around 10 mg/L, and the regent Tl (Cl)4 is effectively surviving. Whereas the solutions with a very low concentration is almost below mg/L; in such case, DTPA can be used and the decline of Tl (III) is seen 20–30%, (Nolan et al. 2004; Karlsson et al. 2006;

Krasnodebska-Ostrege et al. 2011). In this method, the Tl (III)-DTPA complex is remarkably stable in weakened solutions and moreover within the sight of various particles. The dependability of this complex is on a very basic level autonomous of pH (perfect pH go from 5 to 8). In our present studies, Tl (III) is easy to be reduced to Tl (I), thus DTPA is employed. However, Tl (III) may still be reduced in the processing of weighing and dissolving of Tl $(NO_3)_3$. Without oxidation, about 32% of Tl (III) would reduce to Tl (I) in our experiment. Therefore, saturated bromine water was applied for the oxidation of Tl as mentioned in the previous section.

The Tl (III) reduction rate was twice in smaller samples, as fast as in the larger, and the rate was double when the samples were exposed to fluorescent light. Therefore, acidification of samples with HNO_3 and storage in the dark are critical to

safeguard the original species dispersion at environmentally applicable concentrations. Promptly after collecting fresh samples encasing Tl (III) species, it is important to include complexing agents. Often, DTPA solution as in extraction technique of Tl species from sediment pore water (Lin and Nriagu 1999) and water sample (Karlsson et al. 2006) allied to keep the decrease of Tl (III). It is difficult to include the solution of DTPA; in this way, the solid DTPA was checked in the oxidation procedure of Tl (I); it demonstrates that the solid DTPA has a similar capacity like the solution of DTPA and the solid DTPA is already applied in the protection of Tl (III) in real samples (Campanella et al. 2017).

Instrumentation

The content of Tl was determined by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent, 7700x, California, USA) at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry Chinese Academy of Science. The certified reference liquid materials (SLRS-5), its producer national research council of Canada (NRC-CNRC), and internal standards (Rh at 500 mg/L) were used during the measuring process. The SRM 1640a (NIST, USA) was utilized as analytical quality control. Accuracy and precision were monitored using in-house quality control solutions. All the samples were examined in duplicate. The analytical accuracy decided in light of the standard quality control techniques, utilizing universally confirmed reference materials (OU-6, AMH-1, and GBPG-1), duplicates, and reagent blanks, was better than to $\pm 10\%$. All calculation was acquired utilizing Microsoft Excel, variant 2010. Statistical Package for the Social Sciences (SPSS) version 17 was used for descriptive state analysis. For mapping of sampling points, CorelDraw 12 was being utilized.

Results and discussion

Standard solution recovery and validation

The capability of sorbent in speciation of Tl was investigated by processing standard synthetic solution with a mixture of T1(I) and T1(III) and the adsorption capacity of the sorbent in the presence of DTPA was also considered. Standard solution of Tl (I) at concentration 40.9 μg/L and Tl (III) at concentration 40.9 μg/L was prepared in the presence of DTPA (Table 1). The results showed that the sample made with only Tl (I) standard solution (10 ml) at concentration 40.9 μg/L enclosing Tl (I) recovery was $96.75 \pm 1.74\%$ and Tl (III) recovery was $2.2 \pm 0.044\%$, respectively (Table 1). Likewise in another sample with only Tl (III) standard solution (10 ml) at concentration 40.9 μg/L containing Tl (III), recovery was $97.11 \pm 1.64\%$ and Tl (I) recovery was $3.8 \pm 0.051\%$,

Table 1 Determination of Tl species from samples prepared by synthetic standard solution

Thallium concentrate	% Recovery	
Tl (I) + Tl (III) (μg/l)	Tl (I)	Tl (III)
10.0 + 0	96.75 ± 1.74	2.2 ± 0.04
0 + 10.0	3.8 ± 0.05	97.11 ± 1.64
1.0 + 10.0	9.8 ± 4.52	99.67 ± 1.41
10.0 + 1.0	101.34 ± 1.81	6.6 ± 0.08
2.5 + 2.5	101.12 ± 1.92	96.8 ± 1.81
5.0 + 5.0	102.67 ± 2.22	101.22 ± 2.1
10.0 + 100.0	97.3 ± 1.05	99.6 ± 1.31

Samples contain 40.9 μg/l Tl (I) and Tl (III) of 1, 2.5, 5, 10, and 100-folds in 10 ml samples

Mean and S.D. of three independent measurements

respectively, while concentration of 409.5 μg/L of Tl (I) and 409.5 μg/L Tl (III) of standard solution with 2.5 ml at the ratio (1:1) of Tl (I)/Tl (III) showed Tl (I) recovery was $101.12 \pm 1.92\%$ and Tl (III) recovery was $96.8 \pm 1.81\%$, resulting in Tl (I) higher improvement may be due to too high standard concentration, and after the sample was diluted, 10-fold were tested and average recovery was little low (Table 1). The recoveries of Tl (I) or Tl (III) were around 100% in all prepared standard solution.

Samples were spiked with Tl standard solution immediately after their collection. In the situation of adding DTPA, Tl (III) would form an anion group with DTPA. But Tl (I) could not form a complex. Thus, Tl (I) and Tl (III) could be separated by anion exchange resin of AG1-X8. Spiked samples values of Tl (I) and Tl (III) are reported in (Table 2). The recovery of Tl (III) spiked into sediment pore water sample (SDS9) was satisfactory (13.80%), while lower Tl (III) recovery observed for in SDS17 (10.85%) is shown (Table 2). The average spiking recoveries of Tl (I) and Tl (III) in sediment-spiked pore water samples were $99.80 \pm 0.9\%$ and $100.17 \pm 1.1\%$, respectively. The highest percent spike recovery of Tl (III) in a water sample (WSF1) was found with 74.80%, while lowest spike recovery 42.34% was found in sample WFS9, respectively (Table 2). Similarly, in the sample, WNS17 percent spike recovery for Tl (I) and Tl (III) was observed 52.77% and 47.22%, respectively (Table 2). The average spiking recoveries of Tl (I) and Tl (III) in water samples were $99.88 \pm 1.05\%$ and $101.17 \pm 1.2\%$, respectively. However, proposed method was successful for separation of Tl (I) and Tl (III) in the freshwater and pore sediment water samples with the presence of DTPA. The adsorption capacity of the sorbent in the DTPA presence was also considered. These outcomes indicated the existences of substances in the affected site sediments that decrease Tl (III) but are absent in all areas. This type of matrix in the pore water implies that Tl (III) ingenuity in the pore water system together the acid mine

Table 2 Recovery of spiked samples (added standard solution with original sample) during total thallium analysis

Spike sample number	Total Tl (µg/l)	% Recovery	Tl (I) (µg/l)	% Recovery	Tl (III) (µg/l)	% Recovery
WFS1	134.8	101.10%	34.29	25.40%	100.85	74.80%
WFS9	72.55	99.88%	41.71	57.53%	30.69	42.34%
WNS17	28.99	99.99%	15.32	52.77%	13.69	47.22%
SDS9	48.98	99.80%	42.13	86.11%	6.76	13.80%
SDS17	20.22	100.17%	18.06	89.32%	2.19	10.85%

drainage (AMD) is not likely, as it is rapidly being decreased to Tl (I) (Al-Najar et al. 2003; Vanek et al. 2010a, b). Since AMD effluent is known to be high in sulfides (Bajza and Vrcek 2001; Escudero et al. 2013), and effluents were released straightforwardly to a Qingshui stream with reducing/oxidizing conditions, the sediment could be especially rich in sulfides mineral in the study area. Similarly, in some sediment pore water and fresh water–spiked samples, Tl (I) recovery greater than 100% may be due to mining and smelting activity in the study area.

Consequence of physicochemical parameters

The physicochemical parameters were measured in samples collected from acid mine drainage (AMD), stream water and sediment pore water of sulfide-rich thallium mineralized area Lanmuchang. The physicochemical properties of the river sediment pore water and water samples are summarized in (Tables 3 and 4). The pH was significantly higher in upstream water samples ranging from 7.56 to 7.72, midstream water samples ranging from 3.37 to 7.51, and downstream water samples ranging from 7.23 to 7.55 respectively (Table 3). Likewise in sediment pore, water samples pH varied from 4.33 to 7.65 in upstream, while in midstream samples varied from 7.14 to 7.83 as well as in downstream samples varied from 7.03 to 7.82 respectively (Table 4). The EC was significantly higher in upstream sediment pore water samples ranging from 400 to 1316 µS/cm, then midstream and downstream samples, respectively, whereas in water samples EC higher value found in downstream samples ranging from 268.2 to 365. 1 µS/cm respectively. The Eh was relatively high across all water samples (ranged 288.9 to 629.3 mV in upstream, 213.6 to 346.9 mV in midstream, and 268.2 to 365.1 mV in downstream, respectively), indicating that relative oxic environments prevailed in these sites. Similarly, the redox potential (Eh) values of sediment pore water were varied between 131.1 to 252.9 mV in the upstream, while in midstream samples values were varied between − 23.4 and 23.6 mV and varied between − 8.3 and 15.3 mV in the downstream samples, respectively (Table 4). The pH and EC of the studied samples have an important role in the deposition and recovery of the standard solution. The pH would affect the dissociation of DTPA in water (Xie and Tremaine 1999; Nolan et al. 2004;

Dorazio and Vezzoni 2016), and therefore may affect the stability of Tl (III)-DTPA complex, and the pH may also affect the adsorption properties of the resin. So the solutions containing T l(I) and Tl (III) of different pH values were tested. The chemical gradients of pH, EC, and Eh along the stream sediment and water may influence the bio-accessibility and redox speciation of Tl (Amin et al. 2009; Vanek et al. 2010a, b).

Extraction and separation Tl (I) and Tl (III) in stream water samples

The speciations of Tl extraction by DTPA measured in the stream water are summarized in (Table 3). The retention times for the Tl (III)-DTPA complex and Tl (I) on the AG1X8 columns were the same in the fresh stream water samples as in the standard solutions and total Tl was earlier measured by ICP-MS. Table 3 shows the outcomes of total and speciation examination of Tl from stream water samples accumulated in May 2016 and July 2017. In AMD samples LMCW1 and LMCW169, total Tl concentration ranges between 71.08 and 66.58 µg/L. Similarly, Tl (I) concentration near AMD sample LMCW1 is 61.47 µg/L, while Tl (III) concentration is 9.73 µg/L, with Tl (I) recoveries 85% and Tl (III) recoveries 14%, respectively (Table 3). In the upstream water sample, Tl reaches concentration ranges from 0.315 to 71.1 µg/L at the top of the sequence (samples LMCW2–7), as well as Tl (I) concentration ranges from 0.012 to 1.91 µg/ L with recoveries about 5.33 to 85.1%, whereas Tl (III) recoveries from 12.53 to 97.6%. Accordingly, in midstream water samples (LMCW8–14), total Tl varied from 1.08 to 3.86 µg/L, with Tl (I) ranges varied up to 0.82 to 3.398 µg/L (recovery range around 77.2 to 93.1%), while Tl (III) concentration ranging from 0.223 to 0.546 µg/L with recoveries 6.74 to 27.87%, respectively (Table 3). Similarly in downstream water samples (LMCW15–21), total Tl decreases range from 3.55 to 5.96 µg/L, although Tl (I) varied from 3.15 to 4.2 µg/L with average recovery rate 90%, as well as in Tl (III) concentration varied from 0.353 to 2.79 µg/L with average recovery rate 47%, respectively (Table 3). Two water samples (W1623 and W161) were also collected in 2016 from the Lanmuchang thallium rich mineralized area; the total Tl concentration varied between 2.799 and 2.99 µg/L, while Tl (I)

Table 3 The physicochemical parameters and concentration of total Tl, Tl (I), and Tl (III) in stream water samples collected in May 2016 and July 2017

Sample ID	Temp °C	pH	Eh (mV)	EC (µS/cm)	DO (mg/L)	Total Tl (µg/L)	%Recovery	Tl (I) (µg/L)	Tl (I)%	Tl (III) (µg/L)	Tl (III)%
Upstream											
LMCW1	26	3.37	629	238.2	1.41	71.08	98.75	61.46	85.06	9.73	13.69
LMCW2	26	6.38	289	677	3.72	1.07	99.93	0.70	65.31	0.37	34.62
LMCW3	25	7.03	385	265	7.8	0.25	102.9	0.01	5.33	0.24	97.57
LMCW4	16.4	7.23	394	221.2	7.09	0.24	100.57	0.01	5.78	0.23	94.79
LMCW5	19	7.41	366	262.5	7.81	0.32	100	0.04	13.52	0.27	86.6
LMCW6	18.6	7.51	344	214.4	8.39	1.82	100.53	1.03	56.88	0.79	43.65
LMCW7	18.9	7.39	338	336.2	7.16	2.18	99.95	1.91	87.42	0.27	12.53
Midstream											
LMCW8	17.1	7.55	347	307.5	7.21	1.21	99.22	0.93	77.19	0.27	22
LMCW9	17.2	7.46	263	311.7	7.06	1.12	100	0.89	80	0.22	19.95
LMCW10	17.5	7.23	328	321.5	6.9	1.08	103	0.82	75.58	0.29	27.43
LMCW11	17.8	7.26	291	325.5	7.62	3.44	99.98	2.89	84.11	0.55	15.87
LMCW12	18	7.31	214	328.7	6.9	3.19	100.3	2.86	89.59	0.34	10.7
LMCW13	18.3	7.35	267	334.2	6.04	3.87	94.66	3.39	87.92	0.26	6.74
LMCW14	18.6	7.44	254	326.2	6.05	3.61	99.79	3.36	93	0.25	6.69
Downstream											
LMCW15	19.6	7.72	292	350.4	6.4	4.41	99.83	3.83	86.83	0.57	13
LMCW16	19.9	7.61	268	352.2	5.82	4.09	100.98	3.60	88	0.53	12.88
LMCW17	20.3	7.56	332	358.1	4.55	4.82	100.23	4.20	87.14	0.64	13
LMCW18	20.4	7.6	348	198	5.38	3.95	97.46	3.26	82.69	0.58	14.77
LMCW19	20.6	7.57	344	357.1	5.6	3.555	100.92	3.23	90.97	0.35	9.94
LMCW20	20.7	7.57	359	358.3	4.59	4.16	99.9	3.54	84.97	0.63	14.93
LMCW21	20.8	7.57	365	357.2	4.3	5.97	99.8	3.15	52.84	2.79	46.77
Samples (2016)											
LMCW191	20.8	7.93	47	44.21	2.43	2.99	99.75	1.143	38.22	1.84	61.54
LMCW169	21.2	2.65	432	154.6	2.22	66.58	99.96	62.465	93.82	4.09	6.14
LMCW1623	18.6	7.1	− 64.8	57.5	6.61	2.79	99.89	2.469	88.21	0.33	11.68

varied from 1.134 to 2.469 µg/L with averaged recovery 60%, but in Tl (III) range from 0.327 to 1.84 µg/L with averaged recovery 36%, respectively (Table 3). Contrariwise, raised Tl (III) concentrations were found in samples gathered along the stream, and these samples situated toward the start of the upstream, which was because of the impact of mine smelting and sulfide mineral activities close to upstream in Lanmuchang research area (Lis et al. 2003; Xiao et al. 2004; Sadowska et al. 2016). The presence of Tl (III) in Qingshui stream waters suggests that the Tl (I) that depicted the AMD must oxidize in the noticeable aquatic condition. In the present investigation territory, the presence of Tl (III) is might be a result of the high substance of manganese in the water from mines, weathering of sulfide metal, and the relationship of Tl with Mn hydroxides is known and same revealed in the literature (Lis et al. 2003; Petrini et al. 2016). Tl (III) is more noxious than Tl (I) and this is more unsafe for human health and sea species. Our results of unique water samples agree with standard-prepared solution results, which demonstrate that Tl would subdue

species at the Eh-pH conditions of the deliberated waters (Coetzee et al. 2003; Biagioni et al. 2017).

Tl speciation in river sediments pore water

The speciations of Tl extraction by DTPA measured in the stream sediment pore water are summarized in (Table 4). The total Tl concentration in upstream sediment samples (SD1–7) varied from 10.35 to 264.75 µg/L, while Tl (I) concentration ranged from 8.5 to 245.48 µg/L with averaged recovery 61% and Tl (III) concentration ranged from 0.594 to 29.95 µg/L, with averaged recovery 29%, respectively (Table 4). The highest Tl (I) and Tl (III) concentrations were found in LMCSDP1, with the recovery of Tl (I) 92.3% and Tl (III) is 8%, with total recovery 100.3% which was near to AMD in Lanmuchang study area. Whereas, in midstream sediment pore water samples, Tl concentrations were 1.43 to 14.22 µg/L, while Tl (I) ranged between 1.32 and 13.96 µg/L, as well as the Tl (III) concentration ranged

Table 4 Physicochemical parameters, total Tl, Tl (I) and Tl (III) concentrations in sediment pore water samples (all concentrations in μg/L)

Sample ID	Temp (°C)	pH	EC (μS/cm)	Eh (mV)	Total Tl (μg/L)	%Recovery	Tl (I) (μg/L)	Tl (I)%	Tl (III) (μg/L)	Tl (III)%
Up stream										
LMCSDP1	18.3	4.33	1316	253	264.7	100.3	245.48	92.72	20.92	7.59
LMCSDP2	18.2	6.32	447	163	73.8	97.85	42.27	57.28	29.95	40.58
LMCSDP3	18.4	6.21	400	152	16.28	99.98	8.32	51.11	7.96	48.88
LMCSDP4	17.9	5.26	436	162	25.88	103.9	8.5	32.84	18.38	71.1
LMCSDP5	18.5	7.08	744	139	10.36	99.9	9.76	94.25	0.59	5.74
LMCSDP6	18.5	7.65	528	131	66.53	100	51.42	77.29	15.11	22.71
LMCSDP7	18.3	7.03	773	136	39.11	99.78	38.08	97.37	0.95	2.42
Midstream										
LMCSDP8	18.3	7.62	1223	−23.4	1.43	100.6	1.32	92.44	0.11	8.18
LMCSDP9	18.8	7.47	362	12.3	2.15	100.5	2.016	93.94	0.14	6.54
LMCSDP10	19	7.36	1213	23.6	4.68	100	4.58	97.92	0.11	2.31
LMCSDP11	18.9	7.83	1045	−29.3	3.82	97	3.62	94.86	0.09	2.55
LMCSDP12	18.8	7.65	915	18.3	4.38	100	4.28	97.67	0.11	2.34
LMCSDP13	18.9	7.21	1227	−5.4	14.22	99	13.96	98.17	0.16	1.14
LMCSDP14	19	7.14	761	−11.2	10.19	99	9.96	97.76	0.13	1.26
Down stream										
LMCSDP15	19.6	7.45	1054	9.5	14.26	100	13.96	97.88	0.31	2.18
LMCSDP16	19.3	7.22	134	15.3	2.99	100	2.9	97.15	0.09	2.86
LMCSDP17	19.2	7.31	519	2.9	12.37	99.2	11.96	96.72	0.31	2.47
LMCSDP18	19.8	7.58	1076	4.4	1.87	100	1.81	96.42	0.07	3.58
LMCSDP19	19.9	7.14	591	−5.5	7.37	100	7.24	98.24	0.14	1.9
LMCSDP20	19.2	7.03	753	2.3	8.54	100	8.32	97.39	0.23	2.64
LMCSDP21	19	7.82	915	−8.3	7.92	99.9	7.78	98.26	0.13	1.62

between 0.097 and 0.14 μg/L respectively (Table 4). In midstream pore, water samples' averaged recovery of Tl (I) is 98% and Tl (III) is 8% respectively, (Table 4). However, in downstream sediment samples, total Tl concentration varied from 2.98 to 12.37 μg/L, whereas Tl (I) concentration ranged between 1.81 and 13.96 μg/L and Tl (III) concentration ranged between 0.128 and 0.31 μg/L, respectively, below the upstream and midstream sediment samples. But Tl (I) averaged recovery is 97% and Tl (III) averaged recovery is 3% in downstream sediment pore water. The percentage recoveries of Tl (III) has raised slightly in upstream sediment samples than the midstream and downstream. This may be due to the influence of mining and smelting activities around upstream in the study area. This result is similar to others reported (Nolan et al. 2004; Scheckel et al. 2007; Krasnodebska-Ostrega et al. 2008; Kersten et al. 2014; Ospina-Alvarez et al. 2015). Thus, our Tl speciation analyses show that pore water of stream sediment mainly present Tl (I) from sediment and accumulate Tl (I) in the stream water. The results are important because they clearly demonstrate that an active enrichment of Tl (I) enriched isotopic-ally light Tl in the sediment. The more oxidized form of Tl (III) has been identified as being ~ 50,000 times more toxic than Tl (I) to the common alga Chlorella (Ralph and Twiss 2002) and also much more toxic to *Daphnia magna* (Lan and Lin 2005), although Tl (III) is much less bioavailable. Therefore, our current results demonstrate that in some sediment pore water samples, Tl (III) concentration is higher, which is more toxic to human and aquatic life. In addition, the rummaging of Tl (I) and its oxidation to Tl (III) by birnessite are reported in marine ferromanganese precipitates (Twining et al. 2003; Peacock and Moon 2012; Nielsen et al. 2013; Voegelin et al. 2015).

Conclusions

The present study provided encouraging insights into the speciation of Tl in stream sediment pore water and fresh water from a Tl-rich sulfide mineralized contaminated area. The main advantage of the proposed method is simple and easy to implement with high reproducibility and selectivity for separation, and this methodology can be used for in situ Tl speciation analysis. This method not only could be applied to a wide range of pH but also could be tolerant to the high ratio of Tl (I)/Tl (III). This method was successfully applied in the case of studied analyzed pore water and real water samples. The results

show that high Tl (III) levels were detected upstream sediment pore water near AMD sampling location. Speciation analysis with DTPA showed the lower detectable concentration of Tl (III) in stream waters, indicating that only Tl (I) is present. The total recoveries of Tl speciation in contaminated sediment pore water samples are 101% as well as in water samples are 100%, such high levels of recoveries may be the influence of mining and smelting activities in study area Lanmuchang. The elevated Tl (III) levels in samples near AMD and scaling these latter measurements according to the percent spike recovery and standard solution. Results show that the Tl (III) concentration of some studied water samples may be above the Chinese standards for the protection of aquatic life and may pose potential risk to the local ecosystem and human health. Therefore, it is clear that we must need to pay more attention to the field automated procedures for monitoring both total Tl and the respective Tl (I) and Tl (III) species.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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