



Barium concentrations and speciation in surface waters collected from an active barium mining area in Guizhou Province, southwestern China

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Abstract

Barium (Ba) is a toxic element and can cause serious health effects. Humans have experienced increased exposure to Ba due to its intensive usage in industrial areas and daily life. Anthropogenic activities of Ba mining and the manufacture of Ba containing products introduce the element into surrounding areas, posing environmental concerns. Concentrations of total Ba (TBa) and dissolved Ba (DBa) in water samples collected from active Ba mines in Tianzhu, east Guizhou Province, southwestern China were measured to show the regional dispersion of Ba contamination. Aqueous Ba species in water were calculated using the PHREEQC program. The results showed that TBa and DBa concentrations ranged from 6.7 to 483.1 µg/L and from 7.5 to 222.7 µg/L, respectively. TBa concentrations presented a high average value of 126.6 µg/L and greatly exceeded the reported common value of 10 µg/L Ba in surface water set by the Ministry of Environment Protection of China. PHREEQC results indicated that Ba species in water were present as Ba²⁺, BaSO₄, BaHCO₃, BaCO₃, and BaOH⁺. The distribution of Ba species in water is controlled by pH and total organic carbon (TOC), and the lower pH (pH < 7) the higher the dissolved fractions. The log *K_d* values (*K_d*, dissolved-particulate distribution coefficients) varied from 2.41 to 6.32. Significant correlations were observed among Ba²⁺ and K⁺, Na⁺, Cl⁻, NO₃⁻, with Pearson correlation coefficients of 0.425, 0.531, 0.853, 0.612, and 0.329, respectively (*p* < 0.01). Elevated Ba concentrations in water indicated that the Ba contamination and its distribution pattern in local aquatic ecosystems are derived from Ba mining sites in the Tianzhu area.

Keywords Barium · Species · Multivariate statistical analysis, PHREEQC Program, mining activities

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Introduction

Barium (Ba), an alkaline earth heavy metal element, was discovered by Dr. Humphrey Davy in 1808 (Schroeder et al. 1972), and belongs to Group 2 in the periodic table of elements. Humans have experienced elevated levels of Ba exposure due to the intensive usage of Ba compounds in industrial production and in daily life, such as drilling fluids, oil industry, glass, paper, explosives, fire extinguishers, soaps, and insecticides (Brooks 1986; Kravchenko et al. 2014; Weast 1969). However, Ba is not an essential element for the biota (Schroeder et al. 1972) and is known to be toxic at a certain concentration (Lamb et al. 2013; Mohammed and Ismail 2017). Humans' intake Ba via breathing, eating, and drinking, and drinking water is the primary intake path (Padilla et al. 2010). Brenniman et al. (1979) reported that human exposure to Ba above 2 ppm might result in gastrointestinal disturbances and muscular weakness, and a positive correlation between cardiovascular disease death rates and concentrations of Ba in drinking water was observed. Padilla et al. (2010) reported that Ba might affect public health when associated positively with body mass index (BMI) and waist circumference (WC). Recently, Ohgami et al. (2012) found severe hearing loss caused by drinking water contaminated with Ba. Yajima et al. (2012) observed low levels of Ba can even promote arsenic-mediated cancer toxicity. Nordberg et al. (2014) found that free Ba^{2+} can cause muscular paralysis by blocking K^+ channels in cell membranes.

Barium can enter and be widely distributed in aquatic ecosystems with Ba^{2+} , $BaSO_4$, $BaHCO_3$, $BaCO_3$, $BaOH^+$, $BaNO_3$, BaF^- , $BaCl^+$, $BaB(OH)_4^+$, and $Ba(CH_3COO)_2$ (McGrath et al. 1989; Merkel et al. 2005; Dupré et al. 1996; Frančišković-Bilinski et al. 2007). It is capable of bioconcentration and bioaccumulation (Hope et al. 1996; Jabłońska et al. 2016), posing health risks throughout the food chain. Walther and Thorrold (2006) found that water deposition rather than food consumption was the main source of Ba in otoliths of marine fish. The World Health Organization (WHO 2011) regarded Ba as a chemical contaminant and recommended the maximum acceptable Ba concentration of 700 $\mu\text{g/L}$ in drinking water. The Agency for Toxic Substance and Disease Registry (ATSDR 2007) declared that fish and aquatic organisms can accumulate Ba and might increase potential health risks for humans.

China is the largest Ba producing country in the world, which is attributed to abundant barite resources (Li et al. 2010). Several of the world's largest Ba mines are in Dahebian, Gongxi, and Banbi. Intensive industrial mining activities released Ba into the surroundings, posing environmental concerns. Compared to other heavy metals, such as Cd, Hg, Pb, and As, little attention has been paid to Ba contamination in China. To date, no reports on Ba in aquatic ecosystems, especially in mining areas, are available.

In the present study, the Dahebian mine, the world's largest Ba mine, in Tianzhu County, east Guizhou Province, southwestern China was selected to investigate impacts on water due to intensive Ba mining activities. Water samples were collected for the determination of total Ba (TBa) and dissolved Ba (DBa), as well as other parameters. This was the first report on the distribution of Ba in an aquatic system in mining areas in China.

Materials and methods

Study area

Tianzhu County is located in east Guizhou province, southwestern China, covering an area of 2201 km^2 with latitude ranging from $26^\circ 41'$ to $27^\circ 09'$ N, and longitude from $108^\circ 54'$ to $109^\circ 36'$ E. This county had a population of 0.43 million in 2016. The study area has a subtropical humid monsoon climate. The average yearly temperature is 16°C and annual precipitation is 1280 mL. The major river is Jianjiang River with tributaries the Mibei, Langjiang, and Yuanjiang River, a tributary of the Yangtze River.

The barite reserves in Tianzhu County total 178 million tons, accounting for more than 70% of the total in China. It consists of numerous barite mines, most of which are located in the Fuluo River watershed. Intensive mining activities occurred at the Dahebian Ba mine during the study period. The primary ore mineral in the Dahebian Ba mine is barite, with minor amounts of dolomite and calcite. Gangue minerals are mostly quartz, illite, and potash feldspar, with minor amounts of pyrite (Hou et al. 2014).

Sample collection and preparation

A total of 63 water samples (including five groundwater samples) was collected from the Ba mining areas in Tianzhu county in May, August, and September 2016, respectively, for total Ba (TBa), dissolved Ba (DBa), anions and cations, total organic carbon (TOC), and total suspended solid (TSS) analyses. The sampling sites are shown in Fig. 1.

Unfiltered samples for the determination of TBa were directly collected into 100-mL borosilicate bottles. Filtered samples for DBa, anions, and cations were passed through a 0.45- μm membrane (Millipore Durapore membrane filters) with a pre-cleaned syringe. Water samples other than anions were acidified (0.4%, v/v) in situ with ultra-pure HNO_3 . Samples for TSS and TOC were directly collected into 1-L plastic bottles and 30-mL brown glass bottles without acidification, respectively. After collection, all samples were shipped to a laboratory and stored in a refrigerator at 4°C .

The borosilicate and brown glass bottles were pretreated by cleaning with alkali detergent, soaking overnight in nitric acid,

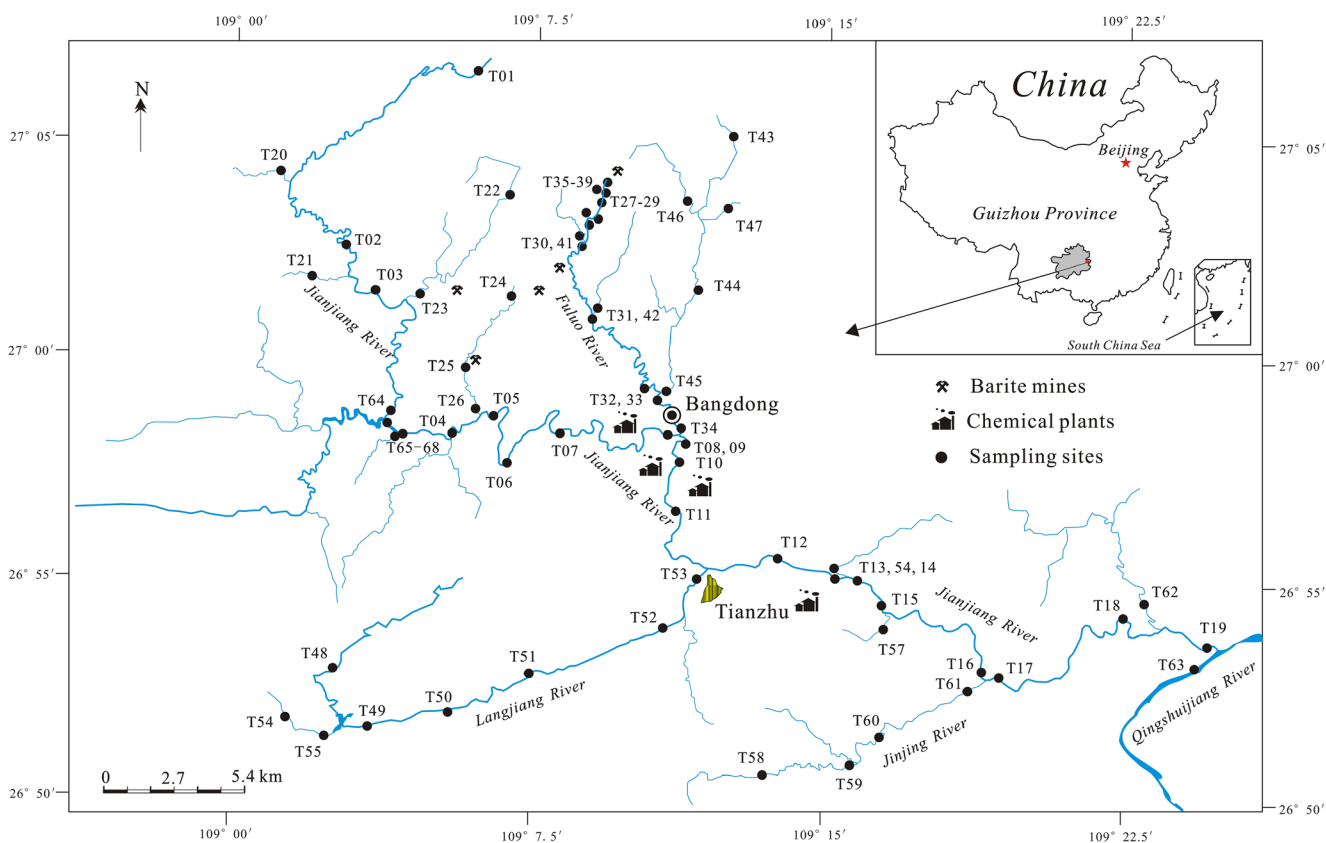


Fig. 1 Map of the study area and sampling sites

later cleaning with double-deionized water (DDW), and finally heating in an oven at 105 °C to evaporate water. Plastic bottles were cleaned with alkali detergent and DDW. Prior to water sample collection, all vessels were rinsed at least three times.

Experimental methodology

Concentrations of TBa and DBa in water samples were determined by ICP-MS (Agilent HPLC 1290-7700x, USA) according to METHOD 200.8 (Long and Martin 1994). Quality control was monitored by analyzing a diluted Ba standard stock solution of 255.45 µg/L (ICP-MS-04N-0.1X-1, AccuStandard) for every ten samples during analysis. Recoveries of standard stock solution samples were between 97.6 and 99.9%.

Concentrations of anions and cations in samples were determined using Wasst-mapx (Agilent company, USA) and DIONEX ICS-90 (DIONEX company, USA), respectively. TOC in water was measured using Vario MACRO Cube (Elementar Company, Germany) with method NPOC (Federation and Association 2005). TSS in water samples was measured by weighing by difference (Michaud 1994). TDS and pH were directly measured in situ using a portable pH meter (pH-100A) and TDS meter (BTDSSCAN 20).

PHREEQC (Parkhurst and Appelo 1999), a general geochemical program, was used for simulating Ba species in water samples.

Results and discussion

Ba in water

TBa and DBa

TBa concentrations exhibited extreme variations, ranging from 6.7 to 483.1 µg/L with an average of 126.6 µg/L (Table S1). The highest TBa concentration was found in sample T09 located downstream of Bangdong Town, which was significantly higher than the reported value of 10 µg/L Ba in surface water in China (Ministry of Environment Protection of China 2002). Several chemical plants, such as the Liuhe Chemical Plant (LH), Jiujia Chemical Plant (JJ), and Xingfa Chemical Plant (XF) that produce Ba containing products, are located in the region. These anthropogenic activities might account for the high concentrations of Ba in water. Sample T38 collected adjacent to the Dahebian Ba mining site exhibited a high TBa concentration of 458.5 µg/L as well, suggesting impacts from nearby intensive Ba mining activities. However, much lower concentrations of TBa were observed

in samples isolated from the Ba mining sites; for instance, samples T48, T49, T50, T51, and T52 collected from the Langjiang River ranged from 14.2 to 22.2 µg/L, with an average of 15.9 µg/L, which might be considered as the background Ba concentration for water bodies in the study area.

TBa concentrations in groundwater collected from wells in the study area ranged widely from 5.6 to 440.3 µg/L. The peak was observed in T38 located upgradient of the mining area, indicating that the groundwater was contaminated with Ba in the mining region due to the intensive anthropogenic activities. The alternative reason would be attributed to the geological background. The lowest level was found in T55, which was isolated from the mining area, and might be considered as the background value of Ba in groundwater in the region.

Concentrations of DBa in samples ranged from 7.5 to 222.7 µg/L with an average of 86.4 µg/L, displaying a similar distribution pattern to TBa. Sample T09 collected from Bangdong Town exhibited the highest concentration of DBa, and samples from distances far away from the mining sites, such as from the Langjiang River, showed low DBa concentrations. High ratios of DBa to TBa were obtained in most samples, reaching up to 90% in samples T03, T46, and T60. The toxicity of Ba is correlated positively with solubility, and soluble Ba compounds are more toxic than insoluble compounds (Miner 1969). Hence, high ratios of DBa to Tba in the present study area might result in more deleterious effects than other regions of comparable concentrations.

Compared to Ba concentrations of 3.0 to 80 µg/L in river waters worldwide (Table 1), most samples in the study area were higher, indicating that humans living in the Tianzhu mining area might have increased health risks from Ba exposure. Samples collected from the Jianjiang River and its tributary the Fuluo River flowing through the Dahebian Ba mining area exceeded the maximum value of 100 µg/L for the quality of drinking water recommended by the Council of European Communities (Lagas et al. 1984) (Fig. 2). However, compared with the guideline value of 700 µg/L recommended by WHO (2011), TBa concentrations of all samples from the Tianzhu Ba mining region were low.

Both surface water and groundwater in the study area were contaminated with Ba, the Jianjiang River in particular, which might result in a potential health risk for local populations. High Ba concentrations in water samples from the tributary of the Fuluo River can be considered the major source of Ba in the aquatic ecosystems of the region. High TBa concentration obtained from wells indicated that the groundwater in the mining area was contaminated with Ba as well, but further studies are necessary.

Effects of pH and TOC

The pH values in all samples ranged from 6.22 to 9.32, exhibiting an alkaline condition (Table S1). Although a negative correlation between Ba solubility and pH was

Table 1 Comparison of Ba in water environment from Tianzhu Ba mining region, Guizhou Province, southwestern China and other aquatic systems worldwide

Oceans	Range/average	References
Eastern Pacific	5–23 µg/L	Bernat et al. 1972
Mediterranean	10–12.1 µg/L	
Atlantic	10.1 µg/L	
Coastal areas		
St. Georges Harbor	15–18 µg/L	Chow and Patterson 1966
Bay of Bengal	35–113 nmol/kg	Singh et al. 2013
Pearl River	11.8–119.9 µg/L(dissolved)	Ouyang et al. 2006
Rivers		
Guangxi of China	5.4–69.5 µg/L (dissolved)	Wang and Yan 2013
Guangzhou of China	0 to 55.1 µg/L	Xu et al. 2010
Hunan of China	20–50 µg/L	Li 2009
Tibet area of China	13–32 µg/L	Li et al. 2007
Northwestern of China	6.2–12.2 µg/L	Zhou and Dong 2002
Aba area in Sichuan of China	24.9 µg/L	Shi et al. 2015
Western of China	43.6–161 µg/L	Li and Zhang 2010
Italian	7–1160 µg/L (groundwaters)	Lanciotti et al. 1989
Guidelines for surface water		
CEC (guideline value)	100 µg/L	Lagas et al. 1984
WHO (standard value)	700 µg/L	WHO 2011
CHINA(surface water value)	10 µg/L	Ministry of Environment Protection of China, 2002

Fig. 2 The distribution patterns of total barium and dissolved barium in the aquatic systems: **a** mainstream the Jianjiang River (T01-T19) and its tributary Fuluo River (T27-T33) and **b** the average values in mainstream and tributaries (MX, Maixi; DT, Datian; FL, Fuluo; MB, Mibei; LJ, Langjiang; JJ, Jinjing; JJZ, Jianjing)

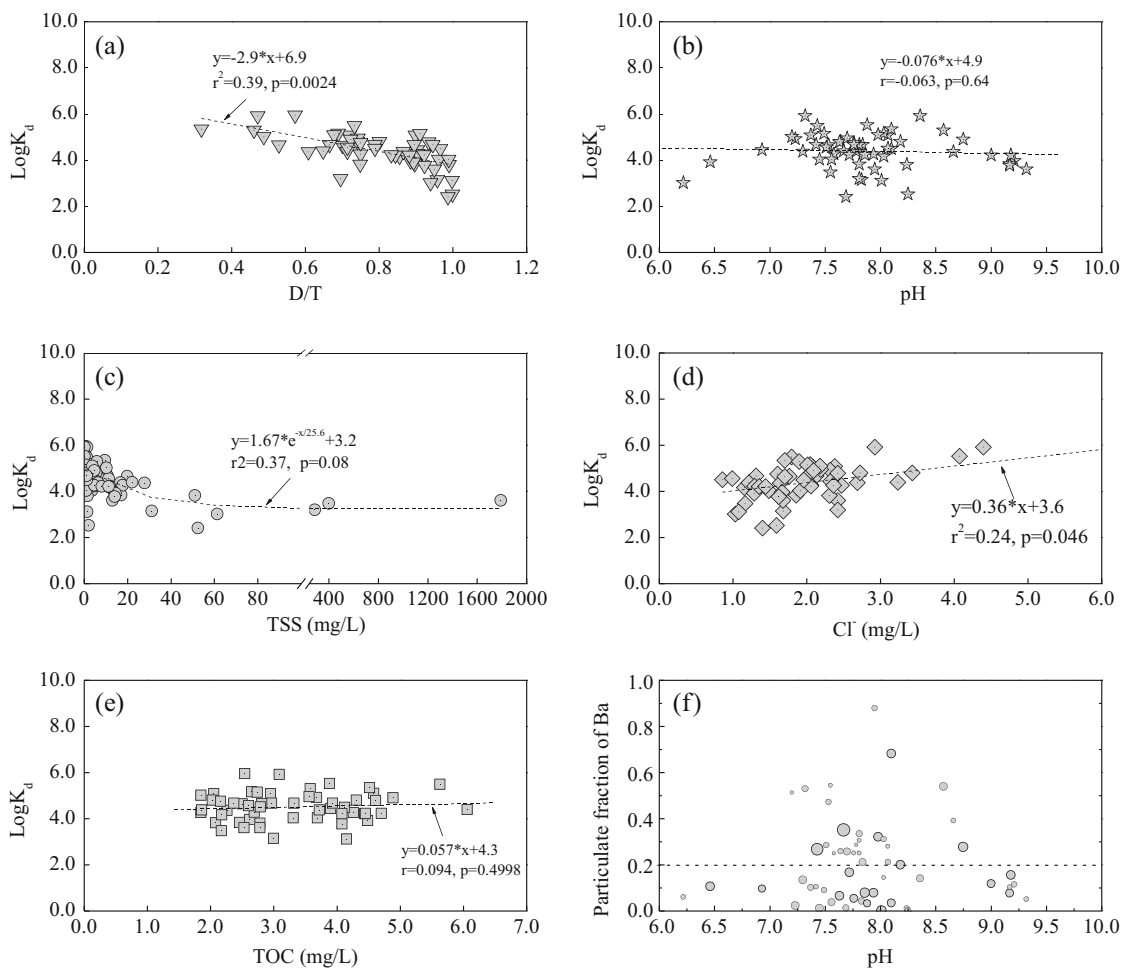
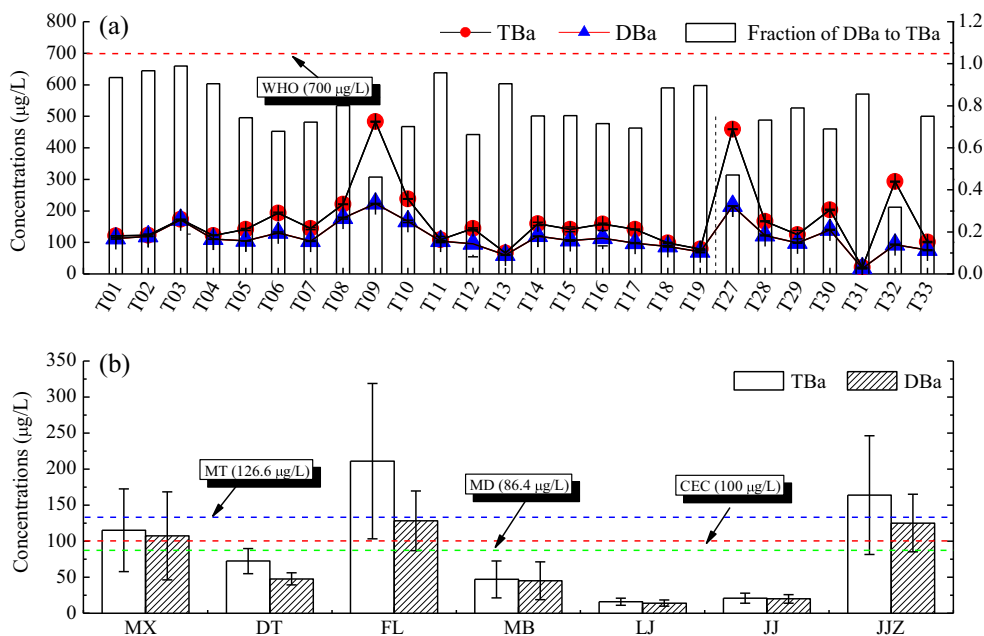


Fig. 3 The correlations among $\log K_d$, D/T, pH, TSS, Cl^- , and TOC, as well as the particulate fraction of Ba at different pH values and TOC (the size of the radius represents the content of the TOC)

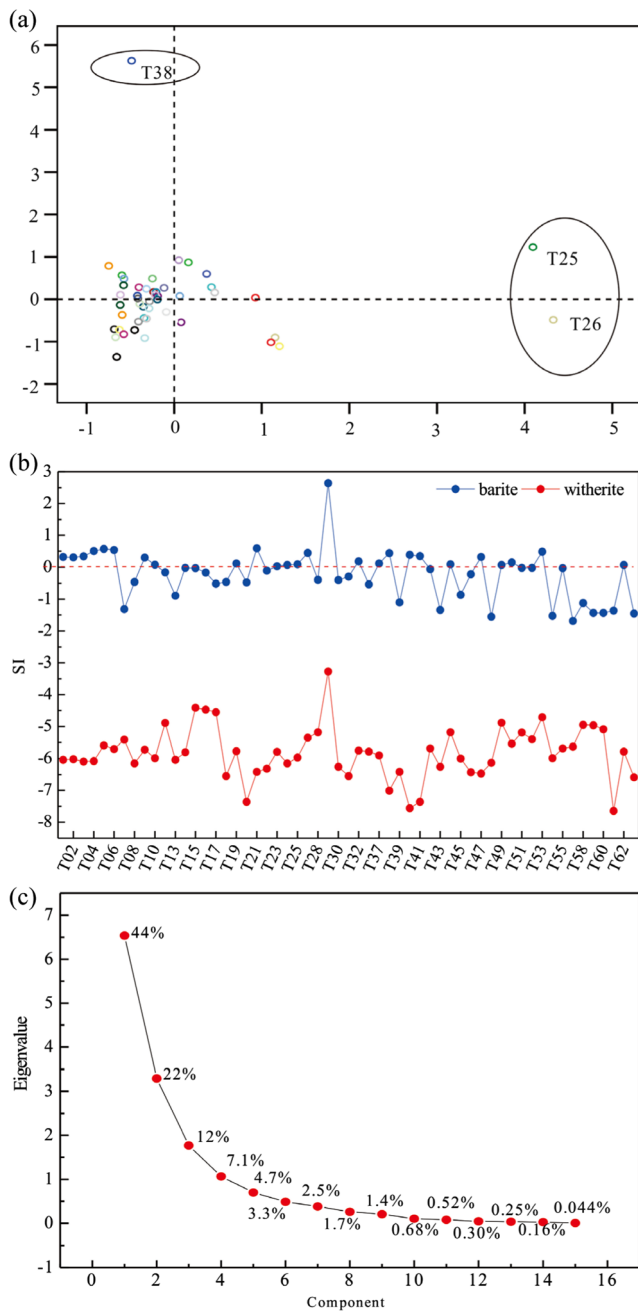


Fig. 4 The results for PCA analysis: **a** scree plot, **b** score plot and the distribution of the saturation indexes (SI), and **c** the SI values of barite and witherite

demonstrated by Frančišković-Bilinski (2006), no significant correlation between DBa and pH was observed among samples in the study, probably attributed to the narrow variation of pH values. In the present study, only three samples, T04, T39, and T49, showed acidic pH values. In addition, in these sites, less than 15% of particle fractions were observed (Fig. 3f), confirming that hydrogen ions might replace the Ba absorbed onto particles at low pH to reduce the particulate fraction of Ba (Gundersen and Steinnes 2003).

The TOC values varied widely from 1.85 to 6.06 in water (Table S1). High particulate fractions were found at the sites of high TOC concentrations (T07, T25, T28), but no significant correlations between TOC and particulate Ba were observed. Due to a strong affinity for metals, TOC may influence the Ba fraction mainly by a chelating mechanism in those samples (Gundersen and Steinnes 2003). Samples with high TOC concentrations, such as T01, T02, and T60, exhibited low particulate fractions. Generally, high organic matter can induce more bacteria due to the presence of electron donors and nutrition for heterotrophic bacteria, some of which can solubilize Ba. Baldi et al. (1996) found that Ba was dissolved from barite by sulfate-reducing bacteria, which was a good candidate for Ba solubilization. It can be observed that TOC might play dual roles for speciation distribution of Ba in water body.

Distribution of coefficients (K_d)

Dissolved-particulate distribution coefficients (K_d) represent the distribution of metals at equilibrium between the particulate and dissolved forms, describing the solid-dissolved form of metals in water (Hatje et al. 2003). The K_d value was calculated based on the concentrations of TBa, DBa, and TSS using the following equation (Allison and Allison 2005):

$$K_d = \frac{(T-D)/TSS}{D} \tag{1}$$

where

- T total Ba concentration ($\mu\text{g/L}$)
- D dissolved Ba ($< 0.45 \mu\text{m}$) concentration ($\mu\text{g/L}$)
- TSS total suspended solid concentration (mg/L)

The K_d values were presented as $\log K_d$ and are listed in Table S1. The values of $\log K_d$ varied from 2.41 to 6.32, with an average of 4.7, similar to the value of 4.0 reported by Allison and Allison (2005). Similar $\log K_d$ data might indicate similar Ba species distributions between the study area and other regions worldwide. The decline of $\log K_d$ values followed increasing TSS concentrations (Fig. 3c), consistent with previous reports and proving “particle concentration effects” (Mishra et al. 2004). The $\log K_d$ values provide the empirical information on the combined effects of heterogeneous reactions on the solid-solution distribution of metals. The differences in the speciation of metals might affect the rate of transport in aquatic system (Allison and Allison 2005). Generally, high- $\log K_d$ values indicate that metals are transported with a solid phase, and low values indicate that metals are in the dissolved form in the environment (Hamad et al. 2012; Lannuzel et al. 2011).

In the present study, ratios of DBa to TBa (D/T) in water were negatively correlated with $\log K_d$ values (Fig. 3), suggesting that Ba might be transported in ionic form at those

Table 2 Pearson correlation coefficients of ions in water in this study

	Al ³⁺	Ca ²⁺	Fe ³⁺	K ⁺	Mg ²⁺	Mn ²⁺	Na ⁺	SiO ₂	Si ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ba ²⁺
Al ³⁺	1													
Ca ²⁺	0.252*	1												
Fe ³⁺	0.117	-0.272*	1											
K ⁺	0.327**	0.650**	-0.136	1										
Mg ²⁺	0.280*	0.921**	-0.285*	0.622**	1									
Mn ²⁺	0.233	0.729**	0.02	0.440**	0.742**	1								
Na ⁺	-0.434**	-0.317**	0.280*	-0.260*	-0.335**	-0.108	1							
SiO ₂	-0.395**	-0.383**	0.388**	-0.352**	-0.358**	-0.133	0.788**	1						
Si ²⁺	0.311*	0.893**	-0.224	0.485**	0.810**	0.628**	-0.259*	-0.363**	1					
F ⁻	0.568**	0.850**	-0.166	0.561**	0.833**	0.764**	-0.371**	-0.418**	0.757**	1				
Cl ⁻	-0.049	0.260*	-0.226	0.641**	.136	-0.147	-0.16	-0.365**	0.247*	0.099	1			
NO ₃ ⁻	-0.051	0.103	-0.189	0.546**	-0.014	-0.13	-0.156	-0.238	0.037	-0.085	0.706**	1		
SO ₄ ²⁻	0.355**	0.919**	-0.195	0.610**	0.935**	0.839**	-0.228	-0.237	0.770**	0.862**	-0.003	-0.019	1	
Ba ²⁺	0.137	0.162	-0.275*	0.425**	0.145	-0.118	-0.531**	-0.583**	0.167	0.142	0.612**	0.329**	-0.018	1

sites of low log K_d with higher ratios. However, an abnormal phenomenon was found in T53. The ratio of particulate Ba was reached 88%, but its log K_d value was relatively low. The highest TSS of 1793.4 mg/L may be a dilutive effect on the log K_d value at this site. The log K_d value was related to chloride ion concentrations in the aquatic system with certain correlations (Fig. 3d). The reason for the chloride ion effect on log K_d is unknown and further study is needed. No significant correlations between log K_d and pH were observed (Fig. 3b), probably due to the narrow range of pH in the present study mentioned above (Hatje et al. 2003).

Multivariable statistics analysis

Concentrations of Ba²⁺, anions, and cations were analyzed by principal component analysis (PCA), which is commonly employed to group related chemical constituents and to identify potential sources (Heidam 1982). The results are presented in Table S2. Four components had eigenvalues greater than 1 and were 6.5, 3.2, 1.8, and 1.1, respectively. The major three components were extracted, contributing 43.6, 22.0, and 11.8%, with a total percentage of 77.4% for all variances in the dataset. The first component with high loadings of Ca²⁺ and Mg²⁺ might indicate a natural geological background source. Ba had significantly higher loadings in the second principal component. Almost all water samples in our study contained high levels of Ba, suggesting sources from Ba mining and retorting.

All sampling sites were defined by the first two principal components. Groundwater sample T38 exhibited high loadings of the second principal component and low on the first principal component (Fig. 4b). Samples T24 and T25, which were impacted by intensive Ba mining activities, had high loadings on the first principal component and low loadings on the second principal component. Other samples had similar features, having moderate loadings on the first two principal components.

The results of the Pearson correlation analysis between Ba²⁺ and other ions are shown in Table 2. Correlation coefficients ($p < 0.01$) for (Ba²⁺, K⁺), (Ba²⁺, Na⁺) (Ba²⁺, Pba) (Ba²⁺, Cl⁻), and (Ba²⁺, NO₃⁻) were 0.425, 0.531, 0.853, 0.612, and 0.329, respectively. Ba²⁺ and K⁺ showed a significant correlation. The results from a previous study showed that Ba²⁺ usually follows K⁺ due to fairly similar ionic radii in the geochemical process (Kabata-Pendias 2011). The correlation for (Ba²⁺, Cl⁻) was more significant than for (Ba²⁺, NO₃⁻), which agrees with the theoretical knowledge that Ba chloride is more easily dissolved than Ba nitrate. However, Ba²⁺ and SO₄²⁻ are not correlated (coefficient value: -0.018). Ba²⁺ combines with SO₄²⁻ to generate a precipitate, which is insoluble in an aquatic environment.

Speciation of Ba and saturation index

In the present study, a geochemical speciation model, PHREEQC, was selected to calculate the chemical species of Ba in water. The PHREEQC program evolved from the Fortran program PHREEQE, which was applied to simulate aqueous equilibrium speciation, batch chemical reactions, and one-dimensional reactive transport in aqueous environments (Parkhurst and Appelo 2013). The input parameters in the study consisted of Ba^{2+} , pH, temperature, and a total of 14 other anions and cations. Simultaneously, the saturation index (SI) was calculated to characterize the thermodynamic state of a mineral relative to a solution. SI values less than zero indicate the mineral is in a dissolving state, while SI values higher than zero indicate a precipitation state, and values close to zero indicate an equilibrium of dissolving and precipitation. The SI value was calculated by Eq. 2:

$$\text{SI} = \log_{10}(\text{IAP}/K) \quad (2)$$

where

IAP ion activity product
 K equilibrium constant

The simulated results of the PHREEQC program indicated that five forms of Ba species existed in water, including Ba^{2+} , BaSO_4 , BaHCO_3 , BaCO_3 , and BaOH^+ . Ba^{2+} had the highest percentage, reaching 89%. Among species, BaSO_4 might cause few harmful health effects, since it has the lowest solubility and does not dissolve in the stomach. However, BaHCO_3 , BaCO_3 , and BaOH^+ can dissolve in the stomach and cause harmful health effects (ATSDR 2007). The results of SI values for barite ranged from -1.68 to 2.64 and were closely distributed near zero (Fig. 4c), indicating that the water was saturated with barite. However, SI values for witherite were much less than zero, indicating that the water was under-saturated with witherite and was capable of further dissolving.

Our results for Ba species and SI values were comparable with that reported for waters from central Romania (Tudorache et al. 2010). Similar SI values were obtained for barite. However, SI values for witherite in the present study were far below that observed in waters from central Romania.

Conclusions

Results revealed that Ba contamination was predominantly in a dissolved form in waters collected from the Tianzhu Ba mining area in southwestern China, and the pH and TOC played important roles on Ba species in water. The PCA analysis showed three main factors influencing the amounts of all anions, cations, and TBa in the surface water of Ba mining

area, with the K^+ , Na^+ , Cl^- , NO_3^- , and Ba^{2+} exhibiting significant correlations. The PHREEQC program calculated out the species of Ba^{2+} , BaSO_4 , BaHCO_3 , BaCO_3 , and BaOH^+ present in water, and SI values indicated an equilibrium of barite and under-saturated witherite in aquatic ecosystems. Elevated concentrations of Ba^{2+} might result in a threat to human health and aquatic ecosystems. The intensive Ba mining activities were considered the major Ba source for local aquatic systems. The impacts of Ba contaminated water on aquatic inhabitants and their potential health risks are needed for further studies.

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