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ORIGINAL PAPER

Geochemical behaviors of antimony in mining-affected water environment (Southwest China)

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Abstract Antimony (Sb) is a harmful element, and Sb pollution is one of the typical environmental issues in China, meaning that understanding of the geochemical behaviors of Sb is the key to control the fate of environmental Sb pollution. Sb tends to migrate in soluble form in the water–sediment system, but the fate of dissolved Sb is poorly known. Duliujiang river basin, located in southwest China, provided us with a natural aqueous environment to study the transport of Sb because of its unique geological and geographical characteristics. Physicochemical properties (pH, EC, Eh, DO, Flux), trace elements (Sb, As, Sr) and main ions (Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$) concentrations in mining-impacted waters were measured in order to determine their distribution and migration potential. There are three types of water samples; they are main stream waters (pH of 7.33–8.43), tributary waters (pH of 6.85–9.12) and adit waters with pH values ranging from 7.57 to 9.76, respectively. Results showed that adit waters contained elevated concentrations of Sb reaching up to 13350 μg L^{-1} from the abandoned Sb mines, and mine wastes contained up to 8792 mg kg^{-1} Sb from the historical mine dumps are the important sources of Sb pollution in the Duliujiang river basin. Dissolved Sb had strong migration ability in streams, while its attenuation mainly depended on the dilution of tributary water with large flow rate. In the exit section of the Duliujiang river basin, which had only 10 μg L^{-1} of average Sb concentration. The simple deionized water extraction was designed to investigate the ability of Sb likely to dissolve from the mine wastes. The results indicated that a greater solubility of Sb in alkaline (pH of 7.11–8.16) than in acid (pH of 3.03–4.45) mine wastes, suggesting that mine wastes contained high Sb concentrations, could release Sb into solution in the natural river waters. Furthermore, the fate of Sb pollution depends on the comprehensive treatment of abandoned adit waters and mine wastes in the upper reaches of the drainage basin.

Keywords Antimony · Migration · Adit water · Mine waste

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Introduction

Antimony (Sb) is a toxic element and a global environmental contaminant (Shotyk et al. 2005) that is found throughout the environment as a result of natural processes and human activities. Sb and its compounds are considered as pollutants of primary control by the United States Environmental Protection Agency (USEPA 1979) and the Council of the European Communities (EU 1976) because of their toxicity (Hockmann and Schulin 2012; Filella et al. 2002). The permissible limits for Sb in drinking water recommended by the USEPA and EU are 6 μg L^{-1} and 5 μg L^{-1}, respectively; this guideline value recommended by the World Health Organization (WHO) is 10 μg L^{-1} (Herath et al. 2017). Nevertheless, Sb is an important mineral material widely used in modern industrial societies (He et al. 2012). The limitations of global Sb resources and the wide use of Sb in our daily life have made Sb as a critical raw material with maximum supply risk and maximum vulnerability (Glöser et al. 2015). Hence, Sb, as a global dilemma, has recently attracted increasing attention from both scientific and public community (Herath et al. 2017).

China is the largest Sb reserves in the world with productivity on top of the world (USGS 2018). By 2010, the identified Sb deposits are concentrated in southwest of China, which accounted for more than 90% of the total Sb reserves in China (Wang et al. 2013; Ding et al. 2013). With the rapid development of national economy and the demand of industries and mankind lives, the increasing use of Sb and its compounds has resulted in the increasing inputs of Sb into the environment. Sb pollution has become one of the typical environmental issues in China (He et al. 2012).

In general, average Sb concentrations are 1.0 μg L^{-1} in world rivers (Filella et al. 2002), and most of Sb in unpolluted waters at levels less than 1.0 μg L^{-1} in China (He et al. 2012). However, the elevated concentrations of Sb in natural rivers ranged from 10 × to 10^3 × μg L^{-1}, which are usually resulted from anthropogenic activities, and particularly high Sb concentrations are detected in the waters from mining areas and smelter sites (Mykolenko et al. 2018; Zhang et al. 2018; Li et al. 2017; Fu et al. 2016; Macgregor et al. 2015; Liu et al. 2010). Elevated Sb contents were found in the aqueous phase due to the lower affinity of Sb for the stream sediments and hydrous ferric oxides (HFOs) in a natural water–sediment system (Sharifi et al. 2016; Asaoka et al. 2012; Hiller et al. 2012). Even in a natural water-suspended particulate matter (SPM) system, Sb has a strong hydrophilicity compared to other heavy elements (Li et al. 2018; Masson et al. 2009; Casiot et al. 2007). Those studies suggested that Sb has a potential mobility with dissolved phase in rivers, while most of the natural river systems are water–SPM–sediment systems. The adsorption or co-precipitation of Sb for SPMs and sediments resulted in that researchers cannot observe the migration of Sb in a natural aqueous environment.

In the Duliujiang river basin of China, there are abundant identified Sb resources (e.g., Banpo Sb deposit in Guizhou) with the long-term exploitation and smelting of Sb deposits. Most of Sb deposits were closed and abandoned so far, but mining activities have produced amounts of waste drainages and tailings which contribute to the Sb pollution of the Duliujiang river (Sun et al. 2016b). However, the water environment of Duliujiang river is different from other Sb mine water environment. It has a wide channel, turbulent river and shallow riverbed composed with a large number of massive rocks, which make it difficult to collect sediment samples in Duliujiang river (Sun et al. 2016a; Xiao et al. 2016). In other words, the Duliujiang river provides us with a natural water environment to study the migration behavior of Sb in liquid phase. Furthermore, due to the Duliujiang river is an important support for industrial and agricultural production in that drainage basin and is the headwaters of Liujiang river which is the sources of drinking water in Liuzhou city and other regions in Guangxi Zhuang Autonomous Region, the government pays great attention to the Sb pollution in the Duliujiang river basin. In recentl years, the local environmental protection departments and related enterprises have begun to implement a series of environmental remediation projects in the area for guaranteeing the water quality safety of the drainage basin.

The objectives of this study are: (1) to investigate the spatial distribution characteristics of Sb in the water environments; (2) to reveal migration of Sb in the mining-impacted water environments. The outputs of this study will get clear understanding for the sources and geochemical behaviors of Sb in a natural aqueous environment and provide implication of Sb pollution remediation and management in the Duliujiang river water environment.

Description of study area

The Duliujiang river basin is located on the southern nonferrous metal deposit belt in China with full length of 310 km. The drainage area is 11,326 km^2, and the topography of the drainage basin decreases from northwest to southeast (Fig. 1). The Duliujiang river originated from Dushan County, south of Guizhou Province belongs to Pearl River system, flows through Sandu, Rongjiang and Congjiang County, southeast of Guizhou Province and Sanjiang County, north of Guangxi Zhuang Autonomous Region, China, and then flows into Xijiang river which is one of the important main streams in the Pearl River system (Fig. 2). Geologically, the Duliujiang river basin consists of various rocks from Precambrian metamorphic rocks to Quaternary fluvial sediments. Limestone is widely distributed, and karst is well developed in the basin.

Particular geological structure and physiognomic characteristics bring up much abundant mineral resources in this basin, especially for Sb mineral resources. There are two types of Sb deposits distributed in the Duliujiang basin. The one is detrital rock-type Sb deposit with hydrothermal vein, particularly in Dushan Banpo Sb deposit (Fig. 3a); the other one is light metamorphic rock-type Sb deposit with mesothermal hydrothermal vein, particularly in Rongjiang Bameng Sb deposit (Fig. 3c) (Wang et al. 2013).

Figure 2 shows the locations of mine areas and monitoring sections. The studied mine sites are mainly distributed in Dushan, Sandu and Rongjiang County, and the five monitoring sections are situated in Banian Town (D1) and Panjiawan Town (D2) of Dushan County, Xinghua Town (D3) and Baji Town (D4) of

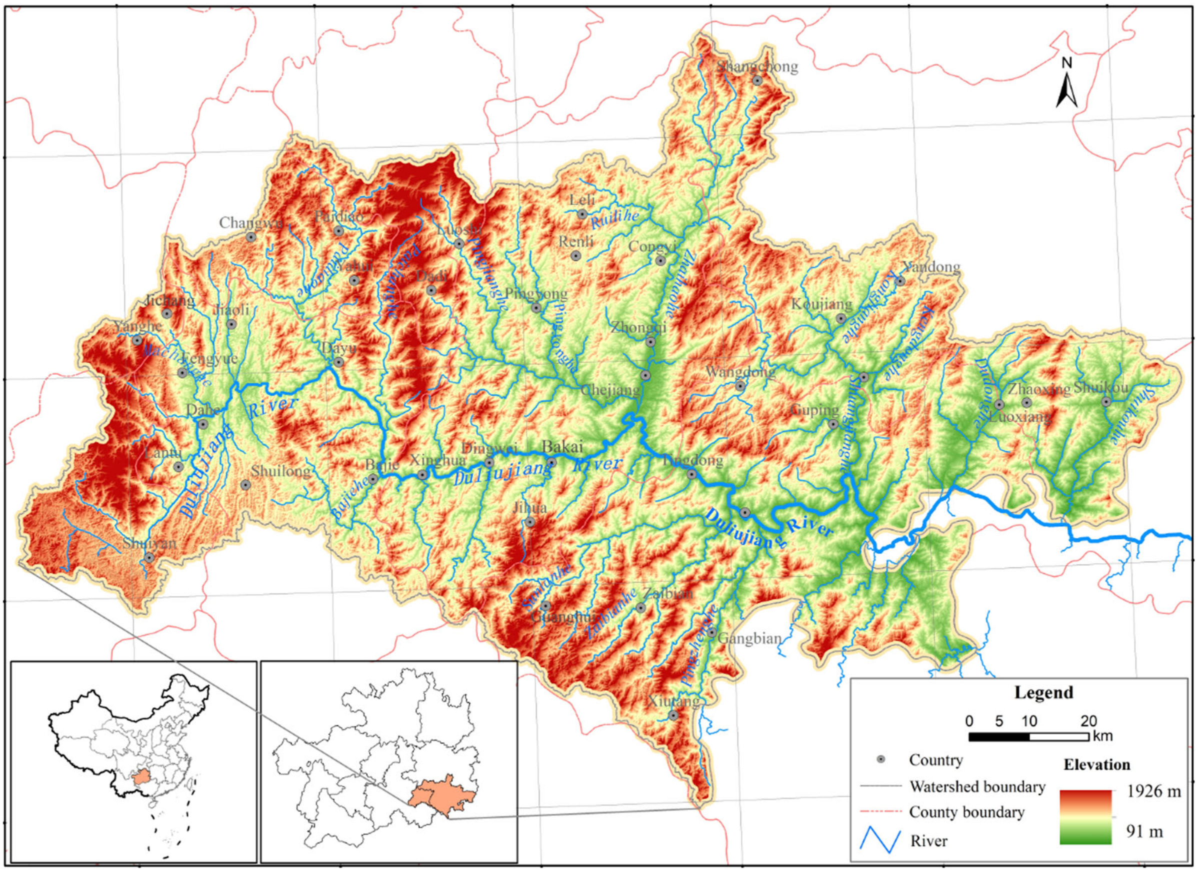


Fig. 1 Location and topography of study area

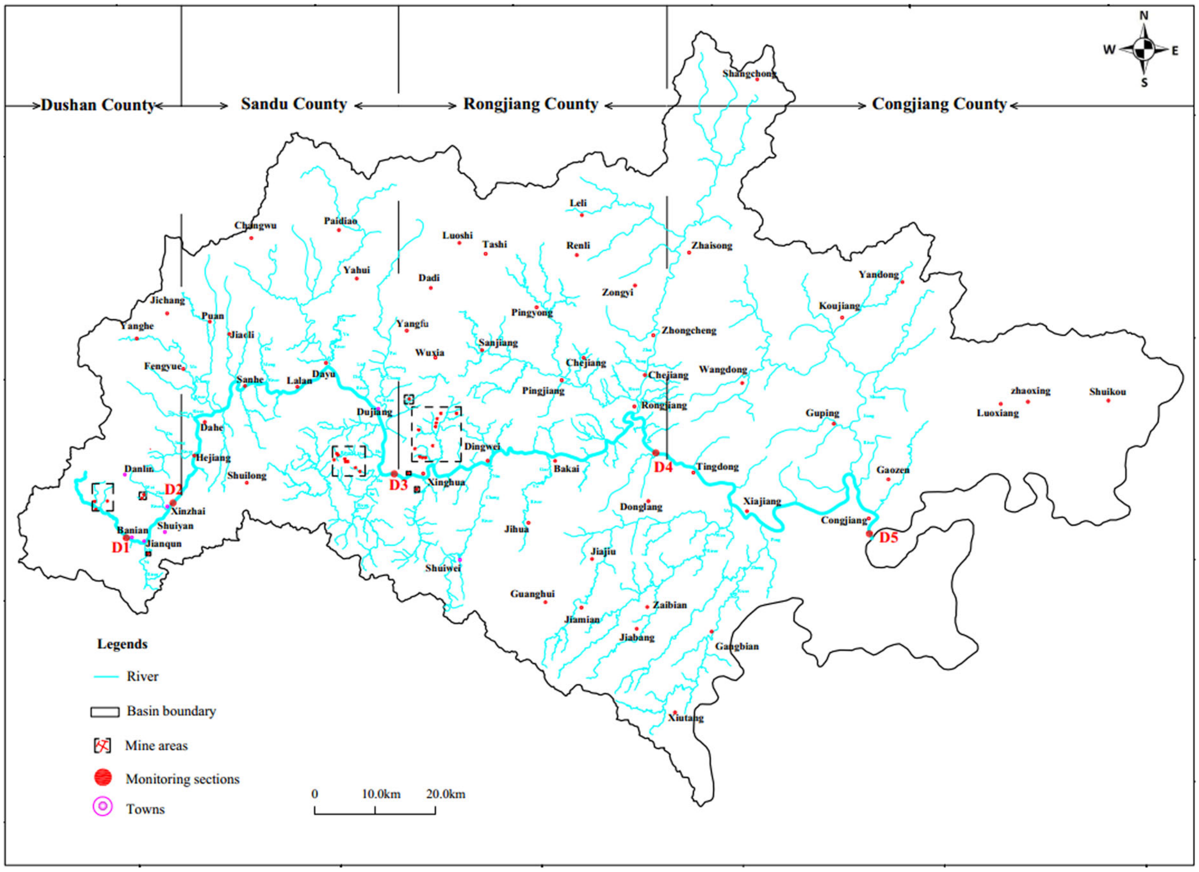


Fig. 2 Locations of mine areas and monitoring sections in Duliujiang River basin

Rongjiang County and Congjiang Bridge (D5) of Congjiang County. Dushan Sb ore field is one of the important components of the South China metallogenic belt of Sb, which is located between the southeastern margin of the Yangtze Platform and the South China fold belt (Luo et al. 2014).There are two proved Sb deposits in Dushan County, the one is Banpo large-scale Sb deposit and the other one is Banian medium-sized Sb deposit (Fig. 3a). The ore-forming elements of Dushan ore field are mainly Sb with a little of As, Hg, Pb, Zn and Au. The devonian system is widely distributed in this area, and the major rock types include sandstone, carbonate and mud rock (Cui et al. 1995). In Sandu County, there are mainly closed and abandoned Sb deposits located in Dujiang Town about 40–60 km from the downstream of county (Fig. 3b). The area is drained by two streams called Bahui and Bajie river, which flows into Duliujiang river. Bameng Sb ore field is a typical "fracture-type" Sb located on the Leishan–Rongjiang belt of Sb ore, which is situated in the upstream of Rongjiang County (Fig. 3c). The ore is characterized by a unitary lithology, simple ore composition and wall rock alteration. Stibnite interstitial crystals, together with quartz, form vein-type antimony deposit. Antimony is the main component of Bameng Sb ore and has a small amount of Au, Pb and As (Chen et al. 1991). The mine site is very close to the Duliujiang river directly receiving mine wastes and waters from the abandoned adits and tailing dumps, which has had a serious impact on the Duliujiang river. The river in Congjiang County belongs to the Pearl River system. The main stream of Duliujiang river runs from north to south, through the cross section of Congjiang bridge (D5), and it finally flows into Guangxi Province. There is no historical Sb residue and abandoned adit in Congjiang County (Fig. 3d). The local government and the environmental protection departments have carried out a variety of environmental pollution control projects since 2011, due to the impacts of the long-

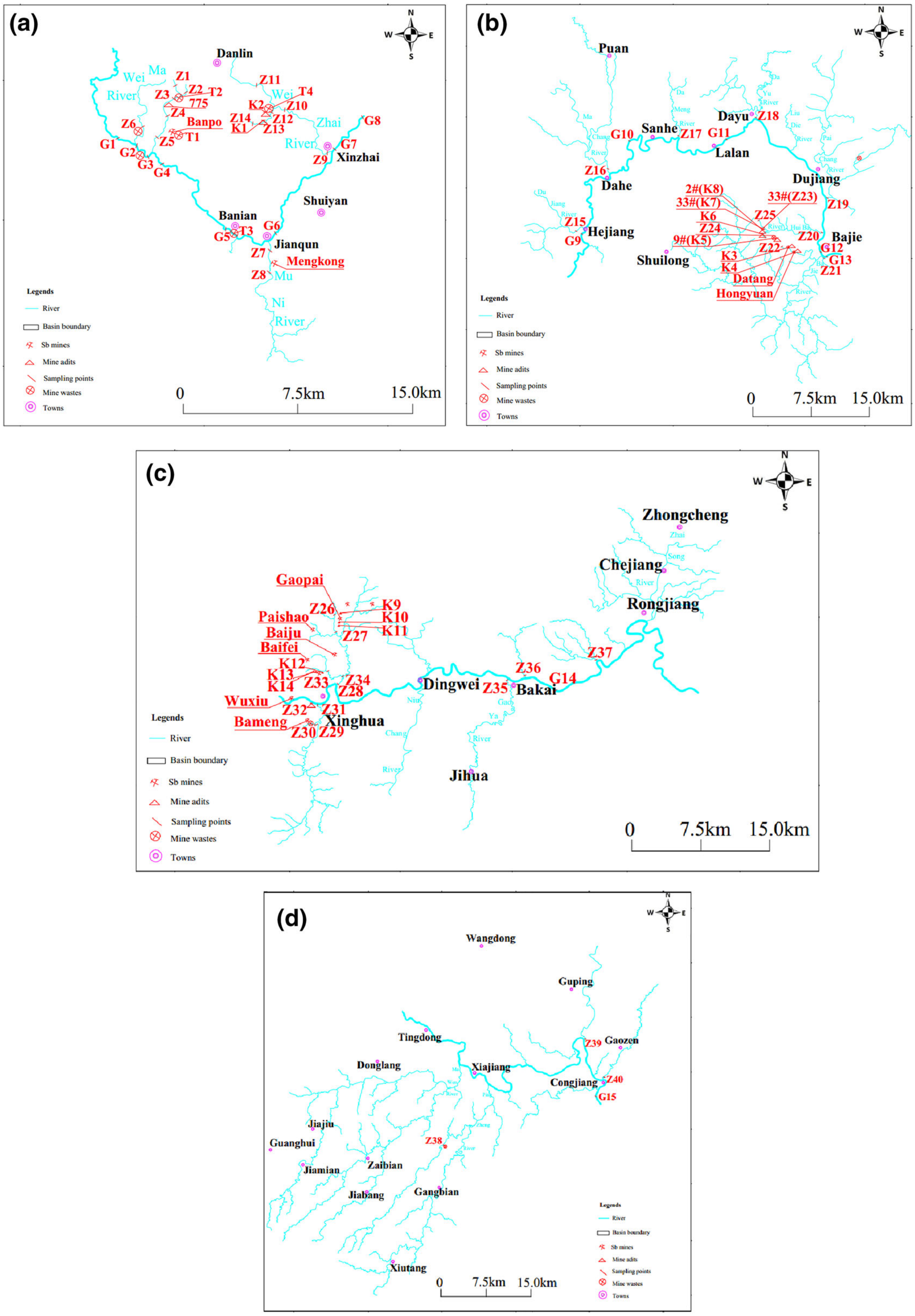


Fig. 3 Sampling locations in Duliujiang River basin. **a** Dushan County, **b** Sandu County, **c** Rongjiang County, **d** Congjiang County

term Sb mining and smelting activities in the Duliujiang river basin.

Materials and methods

Waters

Sampling points are shown in Fig. 3a–d. The locations of sampling points were determined by Global Positioning System (GPS). Water was collected at intervals along the main polluted streams, the adjacent non-impacted streams upstream of the point where they receive mining-impacted waters, and the downstream sections of these streams where they flow into the Duliujiang river. According to the actual conditions of the study area, the sampling sites of water can be divided into three groups: (1) main stream water samples of Duliujiang river, G1 to G15; (2) tributary water samples located in the tributaries streams of Duliujiang river, Z1 to Z39; (3) adit water samples, K1 to K14.

Water samples were collected in duplicate at each site in 500 mL acid-washed high-density polyethylene (HDPE) bottles in May 2017, immediately filtered through 0.22 μm membrane filter paper to remove SPM (Li et al. 2018). The one was acidified with HNO_3 and then stored in a cool box (< 4 °C) for elements analysis, and the other one was directly stored in a cool box for anions analysis. The pH, Eh, dissolved oxygen (DO) and electrical conductivity (EC) of the waters were measured in situ using portable multi-parameter water quality analyzer (WTW, Multi-3430). Five routine monitoring sections (D1 to D5) are shown in Fig. 2. The monthly average Sb contents of these sections from 2013 to 2016 were collected, which was provided by the local environmental protection department.

Mine wastes

Total of 12 mine waste samples were collected in December 2017. We collected the surface tailing sample (T1) from the fresh concentrator tailing, the vertical profile tailing samples (T2, T3) from two historical mining residue heaps and the residual tailings sample (T4) from a historical adit. Actually, these historical mining residue heaps are only exposed to the surface environment during the dry season, because they are abandoned in the river course. Once the season is full of rain, they are drowned in the river. So we collected these profile tailing samples in the dry season. The locations of mine dumps were recorded by GPS.

The mine wastes were sampled using a stainless steel trowel and sealed in precleaned polythene bags (Guo et al. 2018). Prior to digestion, each sample was air-dried at 25 °C and then milled so that it passed through a 150-μm sieve. Then, 0.01 g milled sample was placed in a PTFE (polytetrafluoroethylene) crucible to which 1 mL HNO_3 and 0.5 mL HF were added. The crucible was sealed with a stainless steel gland bush and heated at 170 °C (internal pressure: ca. 7.9 bar) for 12 h. The gland bush was then opened, and the solution was heated to dryness. A further 1 mL of HNO_3 was added and evaporated to dryness. Finally, the residue was re-dissolved in 1 mL of HNO_3 and diluted to 100 mL by deionized water (Milli-Q, 18.2 M cm). The solution was decanted into polystyrene test tubes and analyzed for trace elements. In addition, 10 g dry mine waste sample was stirred with 25 mL deionized water and analyzed for the pH value (Tan et al. 2018; He, 2007).

Leaching experiment

Leaching experiments were designed to investigate the ability of Sb likely to dissolve from the mine wastes. The simple deionized water extraction was preferred for quick estimate of dissolved Sb as described previously (Ettler et al. 2007; Flynn et al. 2003). Briefly, 2 g of dry sample was shaken with 20 mL deionized water for 2.5 h, centrifuged at 10,000 rpm for 10 min, filtered through 0.22 μm membrane filter paper and analyzed for trace elements.

Analytical method

Trace elements (i.e., Sb, As and Sr) were determined by ICP-MS (NexION 300X, PE), cations (i.e., Ca^{2+} and Mg^{2+}) were determined by ICP-OES (Wasstmpx), and anions were determined by ion chromatography (ICS-90, DIONEX).

Reagents and quality control

Deionized water produced by a Milli-Q system (Millipore, Bedford, MA, USA) was used throughout the sample preparation, digestion and determination. Sub-boiling distilled (DST-1000, Savillex, USA) nitric acid and hydrofluoric acid were used for sample digestions. Multielement standard solutions (AccuTrace ICP-MS Calibration Standard, 10 μg mL^{-1} each element) for ICP-MS analysis were purchased from AccuStandard Incorporation, New Haven, USA.

All reagents were analytical grade. Rigorous quality control procedures included analysis of reagent blanks, water blanks, filter paper blanks, replicate samples and certified national reference material of sediment (GBW07305. China National Research Center of CRM's). The precision of determination of elements was better than 5%.

Results

Dushan County

There were 24 water samples included 2 adit waters, 14 tributary waters and 8 main stream waters collected in Dushan County (Fig. 3a; Table S1). The two adit waters (K1 and K2) were slightly alkaline with small amount of water discharge, which were located nearby Weizhai mine, and flowed into Weizhai river. Tributary water samples were neutral to alkaline, pH values ranging from 7.49 to 9.12, and EC values were 49–506 μs cm^{-1}. The highest pH value comes from Z5 situated in the downstream of an Sb mine sewage plant, which was resulted from the sewage treatment plant use lime to treat the wastewater of the mine. In the water samples of main stream, the average pH and EC values were 8.17 ± 0.21 and 337 ± 42 μs cm^{-1}, respectively.

As shown in Table S1, adit water samples had the highest Sb and Sr concentrations. In the Banpo Sb deposit, Z1 and Z2 were the upstream waters with low Sb contents, but Z3, Z4 and Z5 showed elevated Sb due to the mine wastes distributed at the bottom of the riverbed and on both sides of the river. Z4 showed the highest level of SO_4–Ca–Mg–Sr in the tributary of Dushan County compared to other sites. In the Banian Sb deposit, there is a regular monitoring section of D1 with higher Sb concentrations than other sections (Figs. 2, 4). Field investigations found that about 2.6 million m^3 of abandoned antimony tailing were deposited on both sides of the river and riverbed, and the main stream of river water flows through the waste residue area. In Muni river, there was a small smelter distributed between Z8 and Z7, causing the elevated Sb and As were detected in Z7. In Weizhai river, Z11 and Z14 were upstream waters with low Sb contents. However, K1 and K2 were untreated adit waters from the abandoned mine directly discharged into the river, which lead to elevated concentrations of Sb in the downstream of this tributary. After the tributary flows into the main stream of the Duliujiang river, there is a second regular monitoring section D2 (Fig. 2). According to the monthly average Sb concentrations of the monitoring sections (Fig. 4), the content of Sb in D2 section is almost above 100 ppm. There is an intercepting reservoir between G7 and G8, the Sb concentration of G8 was higher than the G7. With the impact of mining activities, Sb concentrations ranged from 8.27 to 281.30 μg L^{-1}, and Sr values varied from 62.34 to 140.20 μg L^{-1} in river water samples of main stream.

There were 12 mine waste samples collected in Dushan County. The concentrations of Sb and As, and their concentrations in the leachates are shown in Table 1. T1 and T2 were sampled in Banpo Sb deposit, which were characterized by acidic pH values. T3 was collected in Banian Sb deposit, which was characterized by neutral to alkaline pH values. T4 was a residual tailing sample collected from the adit K2, which showed a circumneutral pH value.

Sandu County

There were 22 water samples that included 6 adit waters, 11 tributary waters and 5 main stream waters collected in Sandu County (Fig. 3b; Table S1). Water samples were neutral to alkaline, pH values ranging from 7.51 to 9.76. The highest pH value appeared at K3 which is the outfall of the Datang adit water treatment. Accordingly, the highest EC also appeared at K3 with the value of 988 μs cm^{-1}. In the water samples of main stream, the average pH and EC values were 8.08 ± 0.19 and 271 ± 71 μs cm^{-1}, respectively.

With the impact of river waters from Dushan County, G9 is as the entry section of Sandu County in Duliujiang river, still having elevated Sb

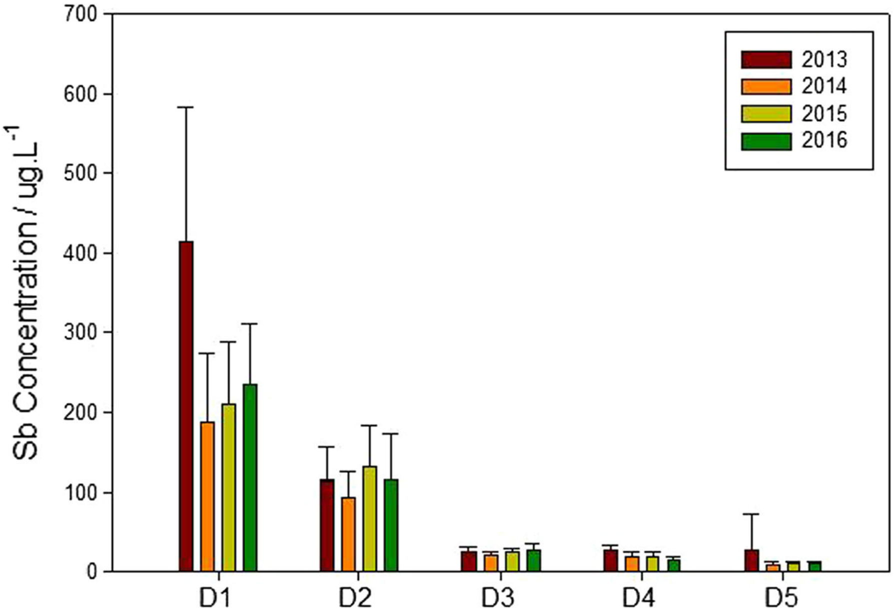


Fig. 4 Monthly average Sb concentrations of the monitoring sections in Duliujiang River basin (from 2013 to 2016)

Table 1 Concentrations of Sb and As in mine wastes and their concentrations in leachates

Sample	pH	Depth (cm)	Sb (mg/kg)	As	Sb (μg/L)	As	Sb (% of total)	As
T1	3.03	–	145	80	14	19	0.098	0.237
T2-1	4.45	10	8792	46	241	1.0	0.027	0.018
T2-2	3.81	25	3270	46	8.0	0.3	0.003	0.006
T2-3	7.11	40	2334	44	936	1.0	0.401	0.020
T2-4	4.21	55	2476	40	27	0.3	0.011	0.008
T2-5	3.73	140	785	39	8.0	0.2	0.010	0.006
T2-6	3.77	160	2271	41	20	0.4	0.009	0.009
T3-1	8.16	10	5898	988	2336	169	0.396	0.171
T3-2	7.82	25	2671	1098	700	2.0	0.262	0.002
T3-3	7.89	100	247	150	485	2.0	1.968	0.011
T3-4	7.78	160	1606	443	972	3.0	0.605	0.006
T4	7.31	–	484	538	335	6.0	0.694	0.011

–, Surface sample with a depth of 5 to 10 cm

concentration of 101.4 μg L^{-1}. In the mainstream (from G9 to G13) of Sandu County, the concentrations of Sb and Sr gradually decreased, but As concentration increased (Table S1). The abandoned Sb mines mainly distributed in the upper reaches of Bahui river and Bajie river. Z25 is the headwater of Bahui river, which had Sb concentration of 7.51 μg L^{-1}. However, with the inputs of adit waters (K8, K7, K6 and K5), the exit section (Z20) of Bahui river contained elevated Sb concentration of 579.4 μg L^{-1}. In contrast, the flow of Bajie river is much larger than that of the Bahui river, and the flux of former is 15 times higher than that of the latter. The Sb concentrations of adit waters in Bajie river showed an elevated levels (K3: 13,350 μg L^{-1}; K4: 1096 μg L^{-1}), but the exit section (Z21) of Bajie river had only 19.07 μg L^{-1} of Sb. As a whole, adit water and the tributary water affected by it all showed elevated levels of Sb–As–Sr–SO_4 contents.

Rongjiang County

The abandoned Sb mines are distributed in the upstream area of Rongjiang County. There were 19 water samples containing 6 adit waters, 11 tributary waters and 2 main stream waters collected in Rongjiang County (Fig. 3c; Table S1). Adit water samples with relatively low flux showed slightly alkaline characteristic (pH of 7.57–8.54), but EC values ranged between 53 and 904 μs cm^{-1}. The pH values of tributary water samples with relatively high flux ranged from 6.85 to 8.30, but EC varied widely with values ranging from 54 to 916 μs·cm^{-1}. The highest EC value was determined for the sample from Z32; Z32 is a culvert nearby the Bameng Sb deposit. Wastewater (Z32) from Sb ore field is discharged directly into the main stream of Duliujiang River without any treatment; it showed the highest levels of SO_4–Ca–Mg–Sr–Sb–As compared to other water samples.

In Rongjiang County, Z29 is the headwater of an important tributary in the south of the Duliujiang River, which contained only 4.35 μg L^{-1} of Sb. Before the tributary reaches the Duliujiang River, the water sample from Z31 showed the content of Sb is 26 μg L^{-1}. There is a small tributary Z30 flowing through the Bameng Sb mining area, flows into the tributary of Z29 to Z31. The Sb concentration in Z30 was as high as 799.5 μg L^{-1}. There are also many abandoned Sb deposits on the northern side of the Duliujiang River main stream. In this study, there are three abandoned open adits in the upper reaches of Z33, where the untreated adit waters (K12, K13 and K14) are directly discharged into the tributary of Z33. At the same time, a large amount of historical tailing was deposited in the course of Z33 tributary. Affected by the adit waters and the long-term leaching of tailings, the content of Sb in Z33 was 1648 μg L^{-1}. Z34 is located in the lower reaches of the Gaopai Sb mine area. Some of abandoned Sb mines and adits are distributed around the tributary Z34. Three adit waters (K9, K10 and K11) near this tributary were collected and showed the elevated concentrations of Sb, Sr, As and SO_4^{2-}. Z34 and Z33 are the main tributaries of Z28, and Z28 is located before the tributary flows into the Duliujiang River. Affected by the mine waters of Z33 and Z34, Z28 contained 467 μg L^{-1} of Sb. There are two perennial monitoring sections on the main stream of Duliujiang River in Rongjiang County, D3 is the section connecting Sandu County and Rongjiang County, D4 is the section of the main stream leaving Rongjiang County. According to Fig. 4, the monthly average Sb contents in section D3 increased slightly from 2013 to 2016, and the monitoring values of Sb concentrations in section D4 decreased year by year.

Congjiang County

There are no Sb ore field and Sb-related enterprises in Congjiang County (Fig. 3d). All of water samples were slightly alkaline with pH values ranging from 7.14 to 7.63, and EC values were in the range 61–203 μs cm^{-1}. In this study, water samples of Z38 and Z39 from two tributaries were collected, containing 0.21 μg L^{-1} and 0.41 μg L^{-1} of Sb, respectively. G15 is the water sample collected from the main stream of Duliujiang River, and its Sb content is 10.50 μg L^{-1}. There is also a routine monitoring section D5 at the exit of Congjiang County on the main stream of Duliujiang River. The results (Fig. 4) showed that the monthly average Sb content has been decreasing year by year since 2013, and it has dropped to 10.30 ± 1.80 μg L^{-1} by 2016, which is similar to the Sb concentration of water sample collected by this study.

Discussion

Sources and spacial distribution of Sb pollution

Generally, Sb mainly exists in nature as stibnite (Sb_2S_3) and valentinite (Sb_2O_3) by the form of ores (Filella et al. 2002). Once the Sb ore is mined, the Sb in the ore will be dissolved and released, causing environmental Sb pollution (He et al. 2012).

In the mine water environment, Sb mainly comes from the oxidative dissolution of sulfur-bearing Sb minerals (such as stibnite). Ashley et al. (2003) has reported that the dissolution of stibnite in oxidized circumneutral natural waters can occur by two principal pathways, the first one is direct oxidative dissolution, the second one is indirect oxidative dissolution. The result of oxidative dissolution of the Sb sulfide minerals is the formation of sulfate ions and acid mine drainage (AMD). In fact, oxidation and dissolution of Sb sulfide minerals or oxides are the most common geochemical mechanisms for the release of Sb into the environment (He et al. 2018; Zhou et al. 2017; Herath et al. 2017; Hu et al. 2017a, b; Wen et al. 2016; Nyirenda et al. 2015; Ritchie et al. 2013).

As showed in the distribution of Sb and sulfate in the different types of water samples of the study area (Fig. 5), it can be found that the adit waters had the

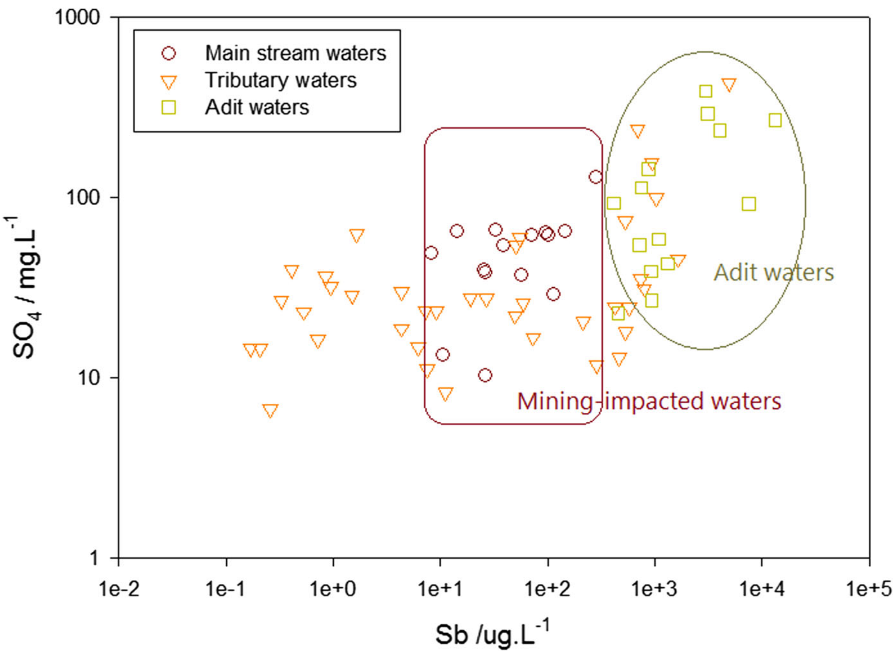


Fig. 5 Distribution of Sb and sulfate in different types of water samples of the study area

highest levels of Sb and SO_4^{2-} concentrations comparing to the other water samples. With the input of adit waters, significant elevated dissolved Sb and SO_4^{2-} concentrations were found in the main stream and other mining-impacted waters. AMD can, however, also be neutral or even basic, depending on the mineralogy of the site (Lindsay et al. 2009). If rocks or minerals are carbonates such as calcite and dolomite, acid drainage can be naturally attenuated, which results in formation of neutral mine drainage (NMD) (Heikkinen et al. 2009). Actually, NMD is found in our study area. The pH values of the adit water samples with elevated Sb and SO_4^{2-} concentrations were neutral to alkaline (Table S1), because of the abundant carbonates geological background, and acid neutralization by the abundant carbonates. As a result, adit water from the abandoned Sb mines is one of the main sources of Sb pollution. In the study area, adit waters are mainly distributed in Banpo Town of Dushan County, the upper reaches of Bahui River and Bajie River in Sandu County, and Gaopai Town of Rongjiang County, which are the main contributors of Sb pollution in Duliujiang river basin.

Oxidation and dissolution of Sb sulfide minerals or oxides may also occur in mine wastes, because mine wastes usually contain a large number of Sb-bearing sulfide mineral residues (Hiller et al. 2012). In the study area, mine wastes contained up to 8792 mg kg^{-1} Sb and 1098 mg kg^{-1} As, and the highest concentrations of both metalloids in leachates were 2336 μg L^{-1} and 169 μg L^{-1}, respectively (Table 1). Through on-site investigation and exploration, it is found that the existing abandoned mine wastes in Dushan County, upper reaches of the drainage basin, are about 6.27 million m^3, with an area of about 4.42 km^2. Due to early disorderly mining and management, a large number of historical residues were randomly piled in the riverbed or on both sides of the river. Once the season is full of rain, mine wastes are drowned in the river, or washed into the downstream area. In this case, mine wastes distributed in riverbeds or channels, like sediments, releases Sb into the water environment under water–sediment interactions (Ren et al. 2016). So, the mine wastes contained high Sb concentrations could release Sb into water environments, which should be another significant source of Sb pollution in the Duliujiang river basin.

Formation and attenuation of Sb pollution

Mobility of Sb in mine wastes

In the study area, we collected the total of 12 mine waste samples. Leaching tests were designed to investigate the ability of Sb likely to dissolve from the mine wastes. As shown in Fig. S1a, for the profile of acid mine wastes, from the surface to the bottom of the mine dump, only the tailing with high leaching Sb content was found in the sample located at 40 cm of the profile because the pH value of this sample was weak alkaline, while the leaching Sb contents from other mine residues in the profile were not high, and it is also related to the acidic characteristics of mine wastes. However, for the profile of alkaline mine wastes (Fig. S1b), it can be found that leaching Sb contents were common elevated in these mine wastes. Results indicated that the mobility of Sb in mine wastes depends on the acidity and basicity of environment. This just explains that Sb in acid tailings contaminated by high Sb has relatively low plant availability (Anawar et al. 2011), while higher concentrations of extractable Sb were detected in soil polluted by Sb with the characteristic of neutral to weak alkaline (Yang et al. 2015). The alkaline environment is favorable for the release of Sb from mine wastes into the water environment, which means that the mine wastes piled up in riverbed or river course has a huge and long-term risk of Sb pollution to the water environment of the drainage basin.

Considering the similar chemical properties of Sb and As (Wilson et al. 2010) and the elevated content of Sb and As detected in mine wastes, we will discuss the mobility of Sb with As in this part of the study. Previous studies have revealed that Sb displayed higher mobility than As under oxidizing conditions (Hiller et al. 2012; Casiot et al. 2007). Actually, all of mine waste samples of this study are exposed to the surface environment with oxidizing conditions. According to the relationship between pH values and leaching Sb and As percentage from the mine waste samples (Fig. 6), it is obviously that the leaching percentage of Sb and As in acidic mine wastes were similar, but the leaching percentage of Sb in alkalescent mine wastes was significantly higher than those of As. The Sb/As ratios were higher in the leachates derived from the alkalescent mine wastes than in the solid samples (Fig. S2), indicating again that there is a higher mobility of Sb compared with As in alkaline than in acid mine wastes under oxidizing conditions.

Migration of Sb in the mining-impacted waters

The migration of contaminated elements in river systems usually depends on their distribution and occurrence patterns among water, suspended particulate matter (SPM) and sediment (Li et al. 2018; Sharifi et al. 2016; Fawcett et al. 2015). In the study area, we haven't been able to collect the SPMs from our water samples, because the stream or river waters are almost clear, especially the adit waters are more clear. At the same time, because the drainage basin is wide, shallow water depth, the Duliujiang river mainly distributes a number of different sizes of rocks (Sun et al. 2016a), and part of the tailings washed down from the upstream. Actually, it was very hard to collect real river sediment samples in the middle of river channels. Therefore, we may only conclude that the migration of Sb in waters of Duliujiang river basin was attributed to its dispersion as dissolved forms. Similar results have been reported in a number of studies (Gil-Díaz et al. 2018; Li et al. 2018; Zhou et al. 2017; Sharifi et al. 2016; Cidu et al. 2014), although a very small number

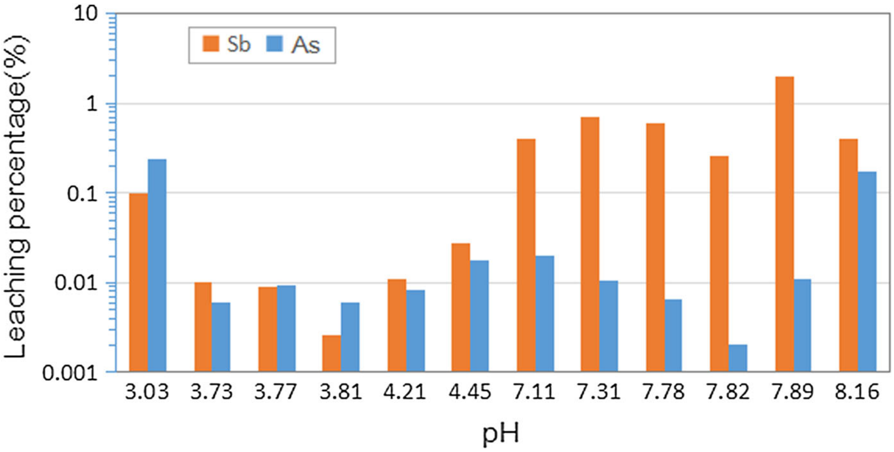
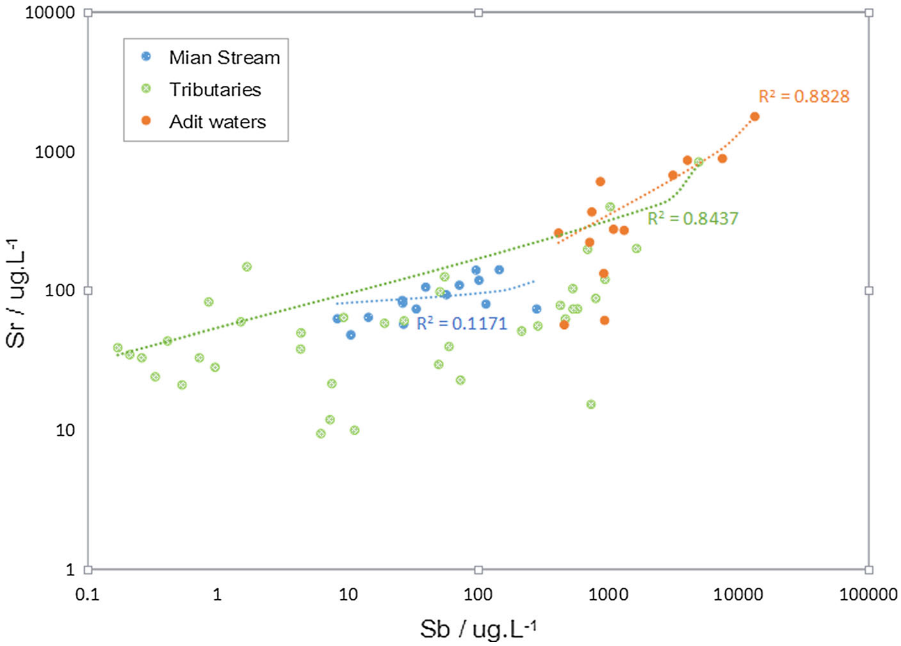


Fig. 6 Relationship between pH values and leaching percentage in the mine waste samples

Fig. 7 Correlations between Sb and Sr in different types of waters



of studies have suggested that Sb has a higher affinity for the particulate phase than for the aqueous phase (Wang et al. 2011).

There are five monitoring sections in this drainage basin. According to the monthly average Sb concentrations of these monitoring sections from 2013 to 2016 (Fig. 4), it is obviously that Sb concentrations decreased from upstream to downstream of the drainage basin year by year. D5 is the exit section of the Duliujiang river basin, which had only 10 µg L^{-1} of average Sb concentration in 2016. Furthermore, in the three selected tributaries containing adit water streams, the concentration of Sb decreased significantly from upstream to downstream under the dilution of river water with large water flow, although affected by adit water with high Sb content (Fig. S3). Therefore, field characterization showed that Sb was attenuated by dilution and removed from the dissolved phase in downstream transportation.

Dissolved Sb originated from the oxidation and dissolution of Sb-bearing sulfide mineral, which resulted in the release of large amounts of dissolved SO_4^{2-} from sulfide mineral, and the acidification and dissolution of carbonate rocks widely distributed in the study area. Strontium is enriched in carbonate rocks resulting from its similar ion radius with Ca (Liu et al. 1984). The elevated of Sr were detected in the mining-impacted waters. Duliujiang river is located in the upper reaches of the Pearl River system. The average Sr content in the upstream of Pearl River is 175 µg L^{-1} (Liu et al. 2007), while the average Sr content in the mine water in the study area is 624 ± 670 µg L^{-1}. In the study area, there was a good positive correlation between Sb and Sr in adit waters and tributary waters impacted by mine activities (Fig. 7), indicated that the release of Sb leads to a strong release of Sr in water environments of mining area. Wen et al. (2016) used Sr isotope method to study the mine waters of Xikuangshan mining area in Hunan Province, which also showed that Sb and Sr in the waters had a common contamination source. Moreover, mine activities accelerated the weathering degree of carbonate rocks in the Duliujiang river basin.

Remediation implication of Sb pollution in Duliujiang river basin

Based on the results of this study and the monitoring of Sb contents in the routine monitoring sections of the Duliujiang river basin from 2013 to 2016, it is concluded that the Sb concentrations in the sections D1 and D2 were relatively high and the decreasing trends were not obvious after the corresponding control measures taken by relevant government departments and enterprises for the Sb pollution of the drainage basin, while the Sb contents were decreasing year by year in the other sections. Both D1 and D2 sections are located in Dushan County, and they are also the upper reaches of the whole drainage basin. This indicated that the upstream water environment is facing serious risk of Sb contamination. Considering the analysis of the sources of Sb pollution in the drainage basin, the study concludes that the future prevention and control of Sb pollution should focus on the abandoned mine wastes in the upper reaches of the drainage basin, the mine residues piled on the riverbed or the river side, and three relatively concentrated adit water outcropping areas. At the same time, effective supervision over the Sb production enterprises in the drainage basin should be strengthened.

Conclusions

Antimony pollution is one of the typical environmental issues of China. The geochemical behaviors of Sb were investigated in mining-impacted water environment, Southwest China. Adit waters contained elevated concentrations of Sb reaching up to 13,350 μg L^{-1} from the abandoned Sb mines and mine wastes contained up to 8792 mg kg^{-1} Sb from the historical tailing piles are the important sources of Sb pollution in the Duliujiang river basin.

Due to its unique geological and geographical characteristics, the Duliujiang river basin provided us with a natural water environment to study the release, migration and fate of dissolved Sb. With the input of adit waters, significant elevated dissolved Sb, Sr and SO_4^{2-} concentrations were found in the mining-impacted waters. Dissolved Sb had strong migration ability in streams, while its attenuation mainly depended on the dilution of tributary water with large flow rate. In the exit section of the Duliujiang river basin, which had only 10 μg L^{-1} of average Sb concentration.

Mine wastes contained high Sb concentrations could release Sb into solution under the surface environment with oxidizing conditions, which suggested that the leachate derived from the mine waste is one of the significant contributors for the Sb pollution in natural rivers. The higher dissolved Sb contents were found with the higher pH of mine wastes, indicating that a greater solubility of Sb in alkalescent than in acid mine wastes. The Sb/As ratios of the leachates were commonly higher than of the solid samples, suggesting that there is a higher mobility of Sb released from the mine wastes compared with As under oxidizing conditions.

The monitoring results of monthly average Sb content in Duliujiang river section from 2013 to 2016 showed that the control of Sb pollution in recent years is effective, and the impact of Sb pollution on the environment is mainly concentrated in the upper reaches of the river basin. Combined with the work of this study, the key to the management of the Sb pollution depends on the comprehensive treatment of abandoned adit waters and mine wastes in the upper reaches of the drainage basin.

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