



# Fate and removal of antimony in response to stringent control activities after a mine tailing spill

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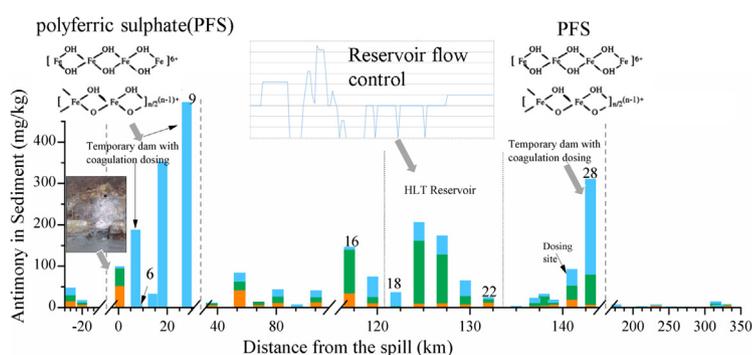
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## HIGHLIGHTS

- Reservoir regulation and temporary dam both remarkably reduced Sb level in water.
- Reservoir regulation in spill led to high level of Sb in sediments and pore water.
- Temperature alternations caused fluctuation of coagulation treatment efficiency.

## GRAPHICAL ABSTRACT



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## ABSTRACT

When tailing spill accidents occur, the risk of contamination by antimony (Sb) tailings into adjacent rivers, sediments, aquifers and soil environments is high. The Sb concentrations in water and sediment under different stringent control activities were investigated for 60 days in the Jialing River basin after a tailing spill accident. Both reservoir regulation and the construction of a temporary dam with coagulation dosing remarkably reduced the Sb levels in the river water. The increase in dissolved Sb caused by the spill was reduced from  $\sim 400 \mu\text{g/L}$  in the inflow to  $\sim 200 \mu\text{g/L}$  in the outflow by reservoir regulation. Moreover, reservoir regulation led to a high concentration of Sb in the reservoir sediment, which was difficult to remove and may cause subsequent unpredictable long-term ecological and health risks. In contrast, the Sb-enriched deposition inside the temporary dam was convenient to remove. Notably, temperature alternations between day and night in winter resulted in a large fluctuation in coagulation efficiency, which may cause the failure of stringent control projects. The results of this study suggest potential improvements to stringent control activities after mine tailing accidents to mitigate environmental impacts and prevent secondary risks.

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## 1. Introduction

Antimony (Sb) is the ninth most mined element in the world (Courtin-Nomade et al., 2012). Human exposure to Sb leads to accumulations in vascularized organs and results in cardiovascular, liver and

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respiratory diseases (Gebel, 1997; Feng et al., 2013). Consequently, as a global dilemma, the mobility, transport and fate of Sb are substantial concerns worldwide (Herath et al., 2017).

Mining waste is commonly stored in tailing pools in safe places to avoid the environmental risks of mining activities (Lacal et al., 2003). The Sb in tailings also remains largely immobile because the mobility of Sb is restricted by oxyhydroxide cover and the acidification of tailing particles, and the released portion can move only centimetres (Wilson et al., 2004). As a result, the majority of Sb in tailings is retained in impoundments under stable circumstances and does not migrate into adjacent environments despite the high concentration of Sb in tailings (Wilson et al., 2004; Majzlan et al., 2011). However, when spill accidents occur, the Sb in tailings may go beyond the range of mining regions due to river flow transport, physical disturbances and the relatively higher pH of water (Del Río et al., 2002), which affects the ecosystem downstream. The migration of Sb is greatly accelerated at temporal and spatial scales in situations where tailings are released into river water that has a higher pH than that of the tailing ponds (Wilson et al., 2004) because the bound Sb is loosened (Langmuir, 1997). Hence, tailing spill accidents are an especially important pathway for Sb to enter aquatic environments downstream. Sb-enriched tailing spills cause a high degree of Sb pollution in soil (Simón et al., 2001; Nakamaru and Martín Peinado, 2017) and sediment pollution in long river channels (Cooke et al., 2016) and have potential effects on wild animal populations (Gil-Jiménez et al., 2017). The bio-availability of Sb should be enhanced when pore water migrates upwards from Sb-enriched sediment caused by spills (Fawcett et al., 2015).

The migration and destination of contaminants in spill accidents are significantly affected by urgent preventive and mitigating actions. For example, walls constructed in the Aznalcóllar mine tailing accident in Spain prevented toxic floods from entering a branch river (Grimalt et al., 1999). The heavy metal concentration in plants in a remediated area was lower than that in a non-remediated region (Madejón et al., 2002; Liu et al., 2005). Most previous studies on Sb have focused on the environmental and health impacts of the spills themselves (Draves and Fox, 1998; Madejón et al., 2002; Martín Peinado et al., 2015), and the results have suggested that remediation activities using organic amendments should improve the bio-availability of Sb (Clemente et al., 2010; Nakamaru and Martín Peinado, 2017). A few studies have reported the initial assessment of Sb migration and the fate during a spill (Cooke et al., 2016). However, there is still a research gap in the mechanism of Sb migration and the fate of Sb in tailing spills, especially concerning the effects of Sb transportation with stringent control activities.

In this study, spill data as well as the effects of stringent control activities, including building temporary dams, regulating the reservoir, and adding ferric salt coagulant in the upper reaches of the Yangtze River were recorded in detail, and a distinct opportunity to gain knowledge about how to address Sb-enriched tailing spill accidents occurred. The main objectives of the study were the following: (1) to investigate the temporal and spatial variation in the Sb plume after a mine tailing spill accident; (2) to analyse the influences of stringent control activities on the migration and fate of Sb; and (3) to propose an optimized solution for Sb tailing spill accidents.

## 2. Materials and methods

### 2.1. Sampling

On November 23, 2015, a catastrophic spill of 25,000 m<sup>3</sup> of Sb mine water and tailings occurred as a consequence of catchpit failure in the Jialing River basin, which discharges into the Yangtze River. The mining site is exploited for stibnite mineral (Sb<sub>2</sub>S<sub>3</sub>) and tailings with high level of Sb are deposited in the tailings pond. This sudden release of mine tailings and effluent flowed directly into the Taishi River, flooded 46.59 ha of farmland, and travelled approximately 400 km downstream to the

Tingzikou Reservoir, which is the drinking water source for half a million people. The tailings contained high concentrations of Sb. Stringent control activities, including building temporary dams, regulating the reservoir, and adding ferric salt coagulant, were carried out as soon as possible to prevent pollutant migration. The clean-up actions included the removal of tailings, the upper layer of polluted sediment and the soil and sludge from the settling tanks formed by the dams.

Immediately after the spill, a monitoring and emergency disposal plan was formed that aimed to slow contaminant diffusion, alleviate environmental and socio-economic influences and prevent potential health risks. Plume tracking was accomplished by monitoring the dissolved Sb concentration in the rivers at 2–12-hour intervals.

A more detailed investigation was carried out between 24 December 2015 and 13 January 2016. Sediment and water samples from 38 locations, including 3 reference locations (Fig. 1), were collected with a gravitational piston core sampler. Thirty-five groundwater samples were collected from drinking water wells two months after the spill (between 26 and 28 January 2016). Statistical data of only 218 drinking water samples from wells that were collected and dissolved Sb was determined one month after the spill (between 23 and 28 November 2015) were provided by the local centre for disease control.

### 2.2. Bulk analysis

The water samples were filtered with a 0.45 µm membrane filter to measure the dissolved concentrations and were digested after acidification with 4%(v/v) HNO<sub>3</sub> using a microwave digestion device (CEM3100) to measure the total concentrations.

The bulk sediment samples were centrifuged in Teflon centrifugal tubes (Corning, USA) at 8000 rpm for 10 min to isolate the pore water. After centrifugation, the sediment samples were freeze-dried, ground and sieved through a 0.15 mm plastic sieve. Then, total 50.0 mg sediment sample was digested with 1 mL HF, 2 mL HCl and 5 mL HNO<sub>3</sub> by using microwave digestion device.

The Sb content was determined by hydride generation-atomic fluorescence spectrometry (HG-AFS, Millennium Excalibur System, Kent, United Kingdom). The atomic fluorescence equipment was operated using a wavelength of 217.6 nm. A 0.5 mL volume of reducing agent, which consisted of 50% (m/v) KI and 10% (m/v) ascorbic acid (both purchased from Sinopharm Chemical Reagent Co.,Ltd) and 15 mL hydrochloric acid (12 mol/L, Beijing Chemical Works) were added to 5 mL of filtered water. The carrier solution of HCl (1.8 mol/L) and NaBH<sub>4</sub> solution (0.8%) for HG-AFS was prepared with ultrapure hydrochloric acid and dissolving powdered NaBH<sub>4</sub> in 0.4% NaOH solution, respectively (both purchased from Tianjin Fuchen Chemical Reagents Factory). Hydride generation was performed with a Millennium P.S. Analytical-10.055. Standard solutions with concentrations from 0 to 20 µg/L were prepared by diluting standard stock solutions (stored at 4 °C), which were obtained by dissolving appropriate amounts of antimony potassium tartrate (K(SbO)C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) (Sinopharm Chemical Reagent Co.,Ltd).

Quality control included method blanks, blank spikes, matrix spikes and blind duplicates. CRM (certified reference standard) of stream sediments (Chinese National Standard, GSD-12) were used in the determination of total Sb. The recoveries of total Sb was 97–104%. Standard solutions of total Sb were prepared daily and calibrated with standard curves, in which coefficients of determination (r) were >0.999. Limits of detection (LOD) of total Sb were 0.72 µg/L. Relative standard deviations (RSDs) of duplicated samples in waters and sediments were <6%.

## 3. Results

### 3.1. Sb plume tracking

After the spill, the velocity of the concentration peak in the plume generally decreased. The average velocity of peak approach was 1.53 km/h in the AB area (from the spill location to the first confluence)

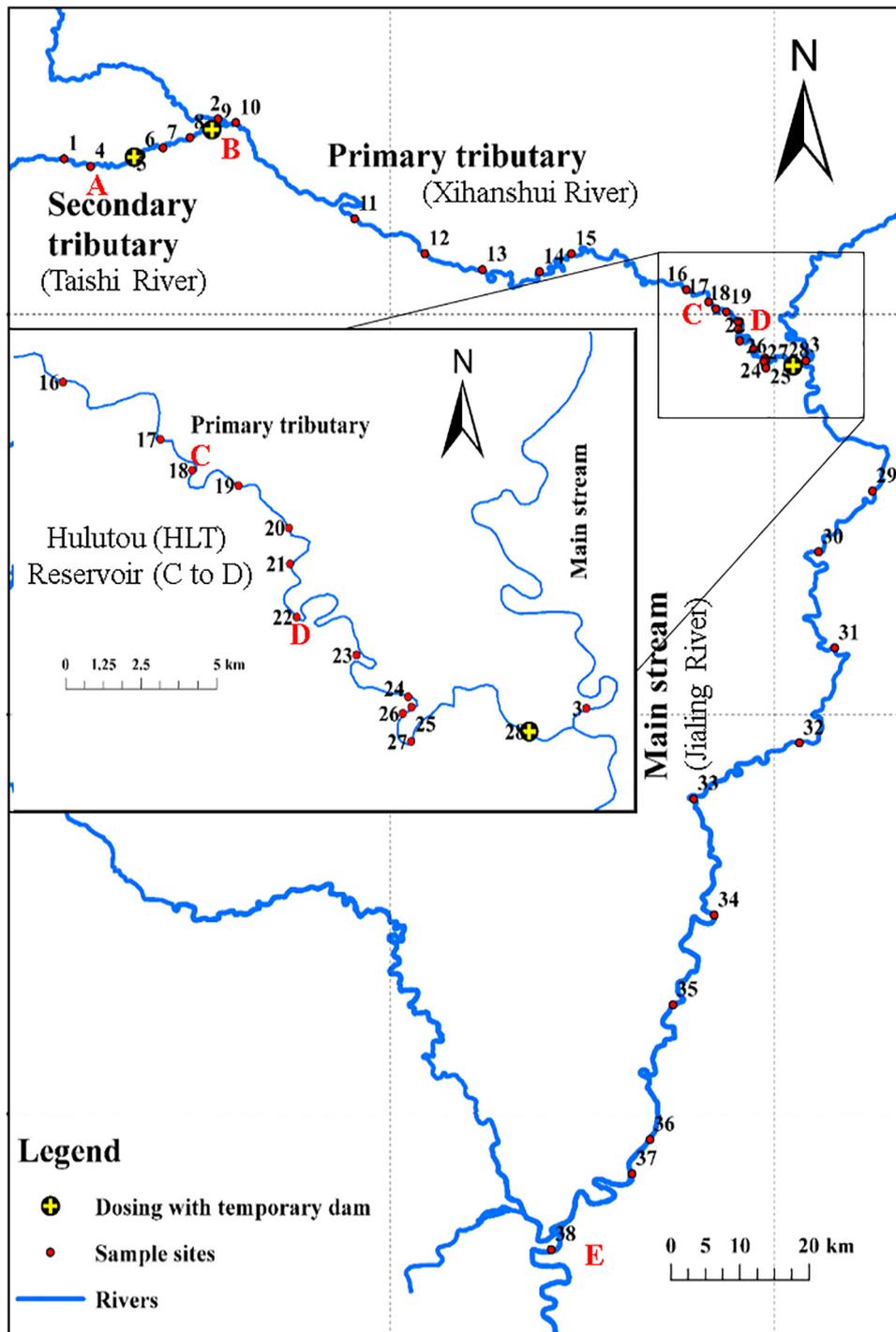
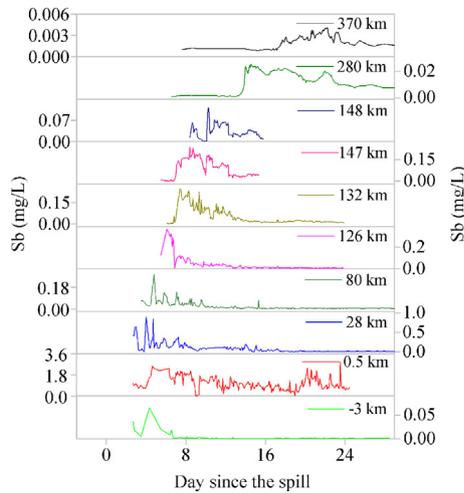


Fig. 1. Map of study region.

and decreased to 1.30 km/h in segment BC before the peak arrived at the Hulutou (HLT) reservoir; the velocity then declined to 0.78 km/h in segment DE from the HLT reservoir to the termination point (the section where the Sb concentration was below 20 µg/L and at a safe level for drinking water (WHO, 2011)). The magnitude of dissolved Sb in the plume decreased along the river. The dissolved Sb in the tailing exudation fluid was ~2000 µg/L and increased from the background level to ~1000 µg/L in the section before the first confluence (23 km from the spill location). The increase of dissolved Sb level decreased to ~400 µg/L when the plume arrived at the middle of the HLT reservoir (site

20, 126 km from the spill), and it took 26 h for the plume to pass through the reservoir (characterized by the full width at half maximum, Fig. 2). After 210 h, the plume had travelled 284 km from the spill location, and the dissolved Sb level declined to ~23 µg/L. The location of the termination point of the stringent control activities where the concentration never exceeded 5 µg/L was 354 km from the spill location.

The mean, 75% quartile and maximum dissolved Sb concentrations at site 9 at night were remarkably higher than the values in daytime at the second stage (days 12–19) when only polyferric sulfate (PFS) was dosed as a coagulant (Fig. 3b). Moreover, the values were more



**Fig. 2.** Dissolved antimony concentration within rivers since the spill on 24th December 2015. Determination on 2 h to 12 h intervals.

discrete at night. Nevertheless, the data from the first stage (days 4–11), when no coagulant was dosed, did not show the day/night alternation pattern (Fig. 3a).

### 3.2. Detailed investigation of the water and sediment one month after the spill

#### 3.2.1. Water quality

Surface water, interface water, sediment and pore water in the sediments were collected one month after the spill to assess long-term influences. The water samples were analysed to determine the water quality and potential risk to human health. The pH values of the river

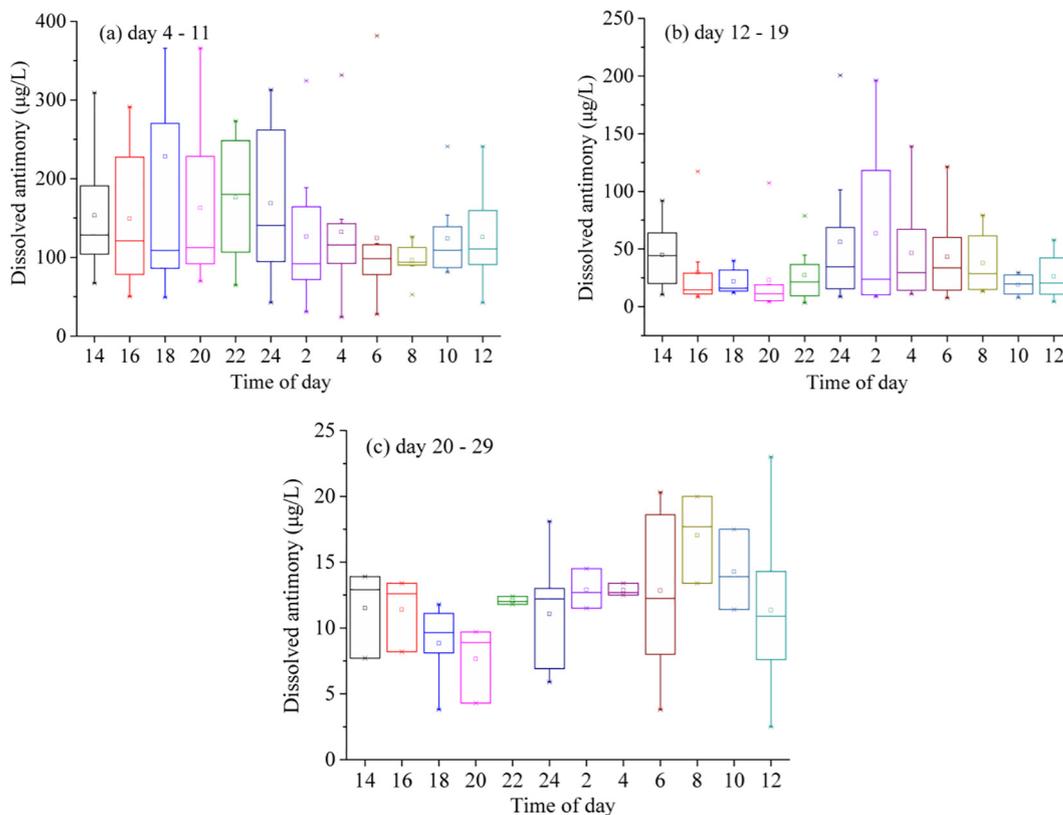
sites were in the same range (between 8.07 and 8.78), except those at the dosing sites (between 5.87 and 6.88), while the dissolved oxygen (DO) values of all sites ranged from 9.10 to 11.77 mg/L.

Fig. 4 illustrates the changes in the total and dissolved Sb levels in the surface water along with the distance from the spill location. The vast majority of the Sb values in both the surface water (92.5%) and interface water (100%) did not exceed the guidelines for drinking water (WHO, 2011). The maximal values of total and dissolved Sb in the surface water were recorded at site 5 (7 km from the spill and just before the dosing site). Moreover, the concentrations at site 6 (directly downstream of the dosing site) showed peak valleys due to coagulation and precipitation. However, the surface water levels at sites 7 and 8 were above the guidelines (20  $\mu\text{g/L}$ ) again. The total fraction was caused by the disturbance of tailing particles deposited on the riverbed, while the dissolved fraction originated from the re-dissolving of flocs and leaching from tailing particles.

The majority of Sb was the dissolved fraction in this study (Table 2). The dissolved fractions in the surface and interface waters were of the same magnitude ( $<0.01$ – $28.37 \mu\text{g/L}$  and  $<0.01$ – $14.23 \mu\text{g/L}$ , respectively). However, the dissolved Sb in the pore water was remarkably higher ( $\sim 1$  to  $\sim 125 \mu\text{g/L}$ ), and 52.27% of the samples were above the guideline level. Moreover, the fluctuation among sites was greater. A total of 16.51% (36 of 218) of the groundwater samples collected one month after the spill exceeded the guideline, and the dissolved Sb concentration in the samples exceeding guideline was  $48.20 \pm 55.02 \mu\text{g/L}$ . The proportion declined to 2.86% (1 of 35) two months after the spill, with a concentration of  $28.57 \mu\text{g/L}$ .

#### 3.2.2. Impacts on sediment

Table 3 shows the mean, standard deviation, and minimum and maximum Sb concentrations in the sediments of the three channel segments and the tailings. The levels decreased considerably from upstream to downstream. The level declined from  $180.33 \pm$



**Fig. 3.** Antimony concentration at different time of day of three coagulation situations: (a) no coagulation used; (b) polymeric ferric sulfate (PFS) used as coagulant only; and (c) PFS used with  $\text{Na}_2\text{S}$ .

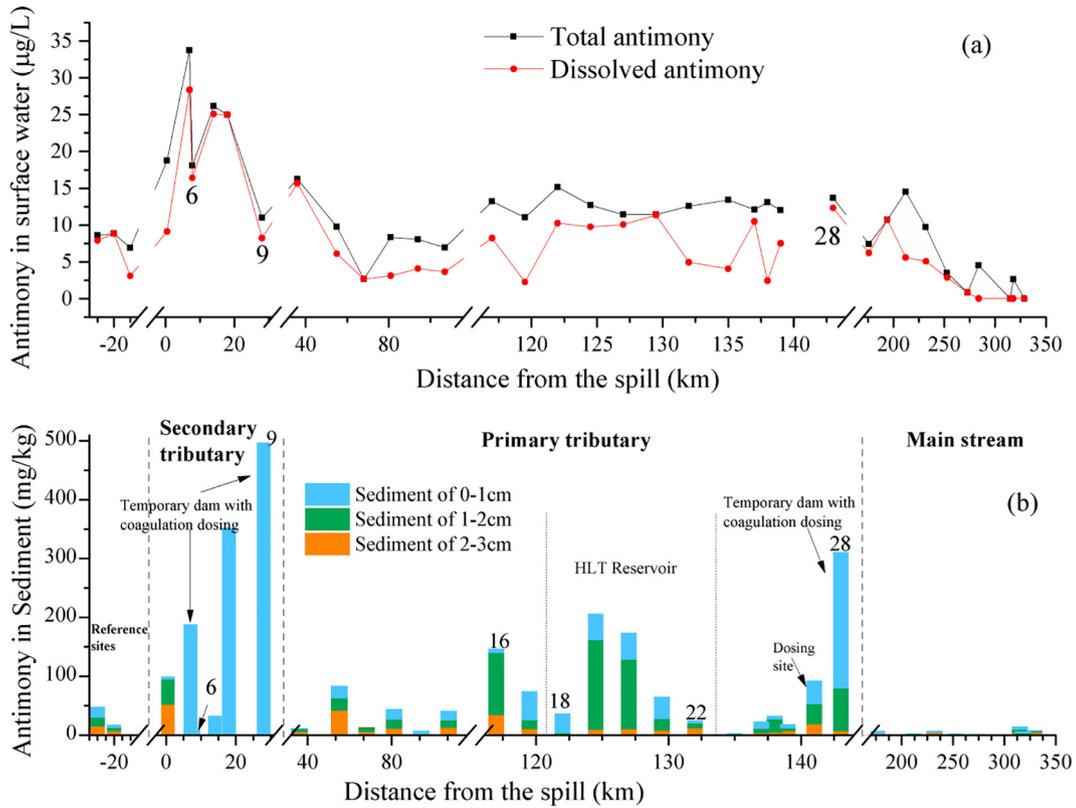


Fig. 4. Spatial changes of total and dissolved antimony concentrations in surface water and vertical distribution of antimony levels in sediment.

206.13 mg/kg in the secondary tributary to  $30.72 \pm 51.29$  mg/kg in the primary tributary and dropped further to  $2.33 \pm 1.89$  mg/kg in the mainstream of the Jialing River.

The Sb content in the sediment showed high spatial variability. Emergency disposal activities were one of the most important factors. The first emergency disposal activities, including coagulant dosing, channel precipitation and precipitate removal, were carried out in the secondary tributary before the first confluence. As a result of the removal activities, only one layer of sediment was collected at most sites in the secondary tributary. The mean Sb content was 10.0 times higher than that at the reference site.

The first type of removal activity was applied in the primary tributary in the section before the second confluence. Meanwhile, the second type of emergency disposal activity utilized in the segment was reservoir regulation. Compared to the reference site that was not affected by the spill, the levels in the secondary tributary were 5.6-fold, 6.8-fold and 1.5-fold higher in the 0–1 cm, 1–2 cm and 2–3 cm layers, respectively, suggesting that the 2–3 cm layer could adequately describe the situation before the spill. The 1–2 cm layer could record the impacts of the plume, while the 0–1 cm layer could indicate the continued consequences of the spill and the disposal activities.

#### 4. Discussion

##### 4.1. Impacts of reservoir regulation on the migration and fate of Sb

The migration velocity and magnitude of Sb elevation caused by the tailing spill generally declined as the plume was transferred downstream, which was in accordance with the characteristics of another spill in Canada (Cooke et al., 2016) into a river in a similar watershed that transitioned from a mountainous to a lowland area in winter. The observed decline in dissolved Sb with the passage of time may be due to three main causes: (1) dilution effects resulting from confluences; (2) the sorption of Sb by sedimentary particles and settlement in the

gentle river segment; and (3) turbulent flow and complicated riverbed composition stretching the plume (Cooke et al., 2016).

However, in this study, the HL reservoir (segment CD) was the segment where the plume passed with the lowest velocity (0.31 km/h, see Table 1). Furthermore, the dissolved Sb level was reduced from ~400 µg/L to ~200 µg/L directly after leaving the HL reservoir. The passage time of dissolved Sb peak (characterized by the full width at half maximum, Fig. 2) rose from 26 h to 104 h. This result is consistent with the release optimization of Tono Dam after a small flood event, which effectively reduced the total suspended solids in the lake through the operating policy (Castelletti et al., 2013). Outflow control was also implemented in this study. The sluice gate was closed for 10 h when the plume reached the HL reservoir to slow down the plume and allow time for stringent control activities downstream. Small flows were then drawn off intermittently for project safety and contaminant peak control considerations. The delay, decline and broadening of the pollution peaks were due to reservoir regulation activities.

Hydraulic regulation is one of the most important in-lake techniques to improve the water quality of reservoirs (Chang et al., 1996; Chaves and Kojiri, 2007). The optimal operation of reservoir outflows, such as optimizing outflow rates and timing controls, has been indicated to be

Table 1

Plume travelling velocity of each river segment (A, B, C, D, and E are shown in Fig. 1). A is the spill spot. B is the spot of first confluence. C is the spot before Hulutou (HLT) Reservoir. D is the section after HLT Reservoir. E is the termination point.

River segment	Travelling distance/km	Time/h	Average velocity/km/h
Secondary tributary (AB)	23	15	1.53
Primary tributary before HLT Reservoir (BC)	94	72.5	1.30
HLT Reservoir (CD)	15	48	0.31
Main stream (DE)	212	272	0.78

**Table 2**  
Summary statistics of the Sb concentrations ( $\mu\text{g/L}$ , DL = 0.01  $\mu\text{g/L}$ ) in surface water, interface water and pore water samples.

	Surface water		Interface water		Pore water		
	Total Sb	Dissolved Sb	Total Sb	Dissolved Sb	0–1 cm	1–2 cm	2–3 cm
$N_{\text{total}}^{\text{a}}$	38	38	22	22	20	14	10
$N_{\text{nd}}^{\text{b}}$	1	1	1	3	0	0	0
Mean	11.20	7.89	10.16	6.41	52.16	45.87	35.33
S.D.	7.06	6.95	4.93	4.49	45.03	53.20	39.91
Median	11.00	6.19	10.22	6.55	38.62	15.02	19.88
Range	n.d. <sup>c</sup> – 33.72	n.d. <sup>c</sup> – 28.37	n.d. <sup>c</sup> – 19.34	n.d. <sup>c</sup> – 14.23	1.46–125.91	0.72–125.53	3.51–125.24

<sup>a</sup>  $N_{\text{total}}$  is the total number of samples.

<sup>b</sup>  $N_{\text{nd}}$  indicates the number of samples with non-detected values.

<sup>c</sup> n.d. indicates non-detected values.

effective for optimizing the water quality of reservoirs and downstream areas (Castelletti et al., 2013; Giuliani et al., 2014; Weber et al., 2017). However, the fractional contaminants that are removed from water are deposited into sediments. The 1–2 cm layer recorded the impacts of the plume (See 3.4). The values of the 1–2 cm layer (Fig. 4) in the middle section of the HLT reservoir ( $135.40 \pm 24.49$  mg/kg) were considerably higher than those in the sections upstream ( $22.04 \pm 31.91$  mg/kg) and downstream ( $28.31 \pm 27.59$  mg/kg) of the primary tributary. Moreover, the pore water in the 0–1 cm and 1–2 cm layer sediments of the same section contained high levels of dissolved Sb (Fig. 5). The high concentration of Sb in the reservoir sediment was due to a decreasing plume velocity and an increasing sediment residence time. High levels of heavy metals were also detected in the sediments of another reservoir that was affected by mining activities, while the water quality did not exceed the WHO standard (except for Cr) (Kapia et al., 2016). Thus, outflow regulation activities will likely lead to high concentrations of contaminants being deposited in mining-affected reservoirs while promoting water quality to provide sufficient hydraulic detention time for the sedimentation of contaminants. Physical disturbances and DO increases at the sediment-water interface caused by convection with season alternation as well as human disturbances such as dredging (van den Berg et al., 2001) may lead to heavy metal releases from sediments. Therefore, hydraulic regulation should be cautiously assessed when taking sediment safety into account when the process is used in reservoirs affected by mining activities.

#### 4.2. Impacts of temporary dam building with coagulation dosing

##### 4.2.1. Impacts of temporary dams

The Sb levels of the surface water after dosing the sites were low (Fig. 4), and the surface sediments in front of the temporary dam (i.e., site 9 and site 28) contained extremely high concentrations of Sb (Fig. 4). The low values detected in the surface sediment, such as

those at site 4 (spill location), were due to remediation actions, such as the removals of precipitate and the original contaminated sediment after coagulating sedimentation. This finding suggests that coagulant dosing combined with the construction of temporary dams effectively removed Sb from the surface waters of the river. However, the Sb levels in the surface water rose again a few kilometres downstream (i.e., site 7 and site 10). This finding may be due to two mechanisms: a) some flocs were dissolved again in the turbulent flow with a relatively higher pH; and b) water travelled into and through the hyporheic zone (Hancock, 2002) and then influxed back to the surface water at a location downstream. This result coincides with the effect of subsurface processes that were observed a few kilometres downstream in Sycamore Creek (Dent et al., 2001).

Moreover, temporary dams also affected the quality of the groundwater. No values exceeding the drinking water standard were recorded in the well water before the spill, while the level rose to 16.51% one month after the spill and dropped to 2.86% two months after the spill. Bedrock fissure water is the main groundwater type in this study region. The primary groundwater recharge pattern is meteoric water infiltration. After being recharged, the groundwater influxes to the river channel from high to low areas with the terrain. Consequently, channel water level rises caused by temporary dam building lead to lateral groundwater recharge from river water. Under these circumstances, the exploitation of wells along the river will accelerate the penetration of polluted river water through the hyporheic zone, resulting in a steep rise in pollutant concentrations in well water (Mauclair and Gibert, 1998). In conclusion, temporary dam building is a valid approach to contain and remove contaminants in tailing spill accidents. However, this remediation action will increase the risk of groundwater pollution. Therefore, well water exploitation should be controlled accordingly to restrict the negative effects.

Temporary dam building and reservoir regulation were carried out under significantly different geographical and hydrological conditions.

**Table 3**  
Summary statistics for the sediment samples and tailing samples. Values below the DL were changed to the DL for the calculation of the summary statistics. DL = 0.005 mg/kg.

	$N_{\text{total}}^{\text{a}}$	$N_{\text{nd}}^{\text{b}}$	Mean	SD	Minimum	Median	Maximum	Reference sites
River TS								
0–1 cm	6	0	180.33	206.13	4.48	110.59	496.84	18.07
1–2 cm	1	0	43.08	–	43.08	43.08	43.08	14.58
2–3 cm	1	0	51.78	–	51.78	51.78	51.78	15.49
River XHS								
0–1 cm	19	1	30.72	51.29	<0.005	16.26	231.02	5.42
1–2 cm	18	0	34.71	45.58	0.29	15.15	152.72	5.00
2–3 cm	18	1	11.27	10.78	<0.005	8.46	41.51	7.16
River JIJ								
0–1 cm	10	0	2.33	1.89	0.22	2.17	5.51	0.47
1–2 cm	9	4	1.37	1.86	<0.005	0.45	5.32	<0.005
2–3 cm	7	1	2.61	1.97	<0.005	2.54	4.99	<0.005
Tailing								
	3	0	2493.33	381.36	2070.00	2600.00	2810.00	

<sup>a</sup>  $N_{\text{total}}$  is the total number of samples.

<sup>b</sup>  $N_{\text{nd}}$  indicates the number of samples with non-detected values.

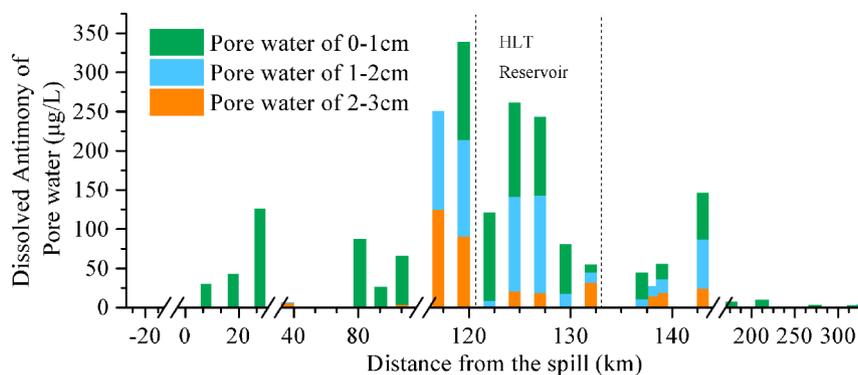


Fig. 5. Spatial changes of total and dissolved antimony concentrations of antimony levels in pore water samples.

Temporary dams were built in a flat and open area that was connected to roads, which was convenient for engineering vehicle operation. Consequently, the contaminants gathered by coagulation in front of the dams could be removed and harmlessly treated expediently. However, the reservoir was in a canyon and was positioned between mountains, and the water depth and sediment thickness made it extremely difficult to remove the polluted surface sediments. If the release of Sb from the sediment caused by the disturbance occurred after the emergency disposal plan ended, the water quality may not be detected in a timely manner. Notably, this risk would be more unpredictable and harder to control.

#### 4.2.2. Influence of low temperature on PFS coagulation

The day and night alternation patterns at site 9 (Fig. 3b) indicated that the Sb removal function through PFS coagulation was more effective and stable in the daytime, while the function was restricted at night. One possible cause is that the workers in charge of the dosing treatment were insufficiently performing their duties at night and avoided inspection. However, temperature differences are the most likely explanation, as the patterns of day and night alternations were consistent with differences in the Sb values.

The water temperature of rivers can notably influence the rate and extent of the hydrolysis of Fe(III) coagulants and adsorption rates (Kang and Cleasby, 1995). The PFS used in this study could be considered the half-completed status of the slow formation stage of large polymers (Dousma and Bruyn, 1976) in the ferric hydrolysis process, with massive polymers in the solution while pH values were dropped to 2.0 and 3.0. The slow formation of large polymers continued after being injected into the river (pH = 6.0). Lower water temperatures at night significantly increase the oxidation and growth time of large polymers (Dousma and Bruyn, 1976), leading to a lower adsorption capacity of  $\text{SbO}_3^{3-}$  and resulting in higher Sb levels in river water. The physical effects of water temperature on flocculation are also distinct (Kang and Cleasby, 1995). Poor rapid-mixing conditions (Francois and Bekaert, 1986) and the inhomogeneous distribution of Fe(III) species (Kang and Cleasby, 1995) caused by low temperatures will result in a low aggregation rate (Xiao et al., 2009), which is disadvantageous for Sb removal through coagulation. Moreover, the floc of ferric sulfate coagulant was much weaker at 5 °C than at 20 °C (Hanson and Cleasby, 1990; Xiao et al., 2009), meaning that floc tended to break up and Sb was released back into river water at low temperatures.

The water temperature was extremely low (frequently below 2 °C) at night, while it was approximately 11 °C in the daytime in this study. As a result, the plummeting of water temperature during the night time was the major limiting factor on flocculation. In contrast, the flocculation efficiency was high enough to accomplish Sb removal in the daytime with a relatively higher water temperature. Hence, the effect of temperature on the coagulation efficiency was hidden in the noise of other variables, such as the Sb concentrations upstream,

hydraulic parameters, etc. Therefore, the Sb levels after coagulation were remarkably higher at night than during the daytime (Fig. 3). In the third stage (from day 20 to day 29),  $\text{Na}_2\text{S}$  was added as a flocculation aid, and the pattern of day and night alternation in the mean, maximum and discreteness values was no longer observed. Addition of  $\text{Na}_2\text{S}$  will provide  $\text{S}^{2-}$  lead to the reduction of Sb(V) to Sb(III) with oxidation of  $\text{S}^{2-}$  to S or  $\text{SO}_4^{2-}$ , and removal capacities of Sb(III) by PFS is remarkably more than Sb(V) (Wu et al., 2010; Guo et al., 2018). Internal and surface adsorption on hydrous ferric oxide was the major mechanism of Sb(V) removal by ferric coagulation, while Sb(III) could incorporate into nanocrystalline hydrous ferric oxide and be removed by coprecipitation (Wu et al., 2010). Moreover, solid ( $\text{Sb}_2\text{S}_3$ ) produced due to addition of  $\text{Na}_2\text{S}$  will be removed through sweeping by precipitate enmeshment (Gannon and Wilson, 1986; Jiang, 2001). This finding suggests that the limitation of temperature on the Sb removal function was lifted. Therefore, flocculation aids should be used based on water temperature alternations to optimize the treatment effect of temporary dams with coagulation and minimize the secondary pollution caused by chemical dosing.

## 5. Conclusions

In summary, the comprehensive disposal of tailings from a spill that occurred in the low flow season provided a unique opportunity to study the migration and fate of Sb after dam failures, which have serious effects on ecosystem and human health worldwide. Significant influences on the migration and fate of Sb due to control activities were observed and analysed in this research. Temporary dam building combined with coagulant dosing was an effective solution for treating mine tailing spills into rivers in a low flow period. Nevertheless, raising the river water level promotes the migration of pollution to the groundwater. The drinking of water from wells near the dam should be ceased or limited accordingly. Although PFS works well in cold river water, the method is ineffective when the water temperatures are lower than a threshold (2 °C in this case). Coagulation aids should be added in this situation, and special attention should be paid to day and night alternations in winter. Reservoir regulation can buffer the peak of spills and benefit the protection of watersheds and waterworks downstream. However, reservoir sediments store high levels of contaminants, which may cause potential unpredictable risks. This type of activity should be evaluated cautiously before implementation. This research enhances the understanding of Sb environmental behaviours in spill accidents and our ability to optimize disposal activities and minimize environmental impacts.

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## References

- van den Berg, G.A., Meijers, G.G.A., van der Heijdt, L.M., Zwolsman, J.J.G., 2001. Dredging-related mobilisation of trace metals: a case study in the Netherlands. *Water Res.* 35, 1979–1986.
- Castelletti, A., Yajima, H., Giuliani, M., Soncini-Sessa, R., Weber, E., 2013. Planning the optimal operation of a multioutlet water reservoir with water quality and quantity targets. *J. Water Resour. Plan. Manage.* 140, 496–510.
- Chang, N.-B., Wen, C., Chen, Y., Yong, Y., 1996. A grey fuzzy multiobjective programming approach for the optimal planning of a reservoir watershed. Part A: theoretical development. *Water Res.* 30, 2329–2334.
- Chaves, P., Kojiri, T., 2007. Deriving reservoir operational strategies considering water quantity and quality objectives by stochastic fuzzy neural networks. *Adv. Water Resour.* 30, 1329–1341.
- Clemente, R., Hartley, W., Riby, P., Dickinson, N.M., Lepp, N.W., 2010. Trace element mobility in a contaminated soil two years after field-amendment with a greenwaste compost mulch. *Environ. Pollut.* 158, 1644–1651.
- Cooke, C.A., Schwindt, C., Davies, M., Donahue, W.F., Azim, E., 2016. Initial environmental impacts of the Obed Mountain coal mine process water spill into the Athabasca River (Alberta, Canada). *Sci. Total Environ.* 557–558, 502–509.
- Courtin-Nomade, A., Rakotoarisoa, O., Bril, H., Grybos, M., Forestier, L., Foucher, F., Kunz, M., 2012. Weathering of Sb-rich mining and smelting residues: insight in solid speciation and soil bacteria toxicity. *Chem Erde-Geochem* 72, 29–39.
- Del Río, M., Font, R., Almela, C., Vélez, D., Montoro, R., Bailon, A.D.H., 2002. Heavy metals and arsenic uptake by wild vegetation in the Guadiamar river area after the toxic spill of the Aznalcóllar mine. *J. Biotechnol.* 98, 125–137.
- Dent, C.L., Grimm, N.B., Fisher, S.G., 2001. Multiscale effects of surface–subsurface exchange on stream water nutrient concentrations. *J. North. Am. Benthol. Soc.* 20, 162–181.
- Dousma, J., Bruyn, P.L.D., 1976. Hydrolysis-precipitation studies of iron solutions. I. Model for hydrolysis and precipitation from Fe (III) nitrate solutions. *J. Colloid Interface Sci.* 56, 527–539.
- Draves, J.F., Fox, M.G., 1998. Effects of a mine tailings spill on feeding and metal concentrations in yellow perch (*Perca flavescens*). *Environ. Toxicol. Chem.* 17, 1626–1632.
- Fawcett, S.E., Jamieson, H.E., Nordstrom, D.K., McCleskey, R.B., 2015. Arsenic and antimony geochemistry of mine wastes, associated waters and sediments at the Giant Mine, Yellowknife, Northwest Territories, Canada. *Appl. Geochem.* 62, 3–17.
- Feng, R., Wei, C., Tu, S., Ding, Y., Wang, R., Guo, J., 2013. The uptake and detoxification of antimony by plants: a review. *Environ. Exp. Bot.* 96, 28–34.
- Francois, R., Bekaert, N., 1986. Influence of mixing parameters and water quality on the flocculation of kaolinite with aluminium sulphate. *Studies in Environmental Science*, vol. 29. Elsevier, pp. 273–296.
- Gannon, K., Wilson, D.J., 1986. Removal of antimony from aqueous systems. *Sep. Sci. Technol.* 21, 475–493.
- Gebel, T., 1997. Arsenic and antimony: comparative approach on mechanistic toxicology. *Chem. Biol. Interact.* 107, 131–144.
- Gil-Jiménez, E., Manzano, J., Casado, E., Ferrer, M., 2017. The role of density-dependence regulation in the misleading effect of the Aznalcollar mining spill on the booted eagle fecundity. *Sci. Total Environ.* 583, 440–446.
- Giuliani, M., Galelli, S., Soncini-Sessa, R., 2014. A dimensionality reduction approach for many-objective Markov Decision Processes: application to a water reservoir operation problem. *Environ. Model. Softw.* 57, 101–114.
- Grimalt, J.O., Ferrer, M., Macpherson, E., 1999. The mine tailing accident in Aznalcollar. *Sci. Total Environ.* 242, 3–11.
- Guo, W., Fu, Z., Wang, H., Liu, S., Wu, F., Giesy, J.P., 2018. Removal of antimonate (Sb (V)) and antimonite (Sb (III)) from aqueous solutions by coagulation-flocculation-sedimentation (CFS): dependence on influencing factors and insights into removal mechanisms. *Sci. Total Environ.* 644, 1277–1285.
- Hancock, P.J., 2002. Human impacts on the stream-groundwater exchange zone. *Environ. Manag.* 29, 763–781.
- Hanson, A.T., Cleasby, J.L., 1990. The effects of temperature on turbulent flocculation: fluid dynamics and chemistry. *Journal-American Water Works Association* 82, 56–73.
- Herath, I., Vithanage, M., Bundschuh, J., 2017. Antimony as a global dilemma: geochemistry, mobility, fate and transport. *Environ. Pollut.* 223, 545–559.
- Jiang, J., 2001. Development of coagulation theory and pre-polymerized coagulants for water treatment. *Sep. Purif. Methods* 30, 127–141.
- Kang, L.-S., Cleasby, J.L., 1995. Temperature effects on flocculation kinetics using Fe (III) coagulant. *J. Environ. Eng.* 121, 893–901.
- Kapia, S., Rao, B.K.R., Sakulas, H., 2016. Assessment of heavy metal pollution risks in Yonki reservoir environmental matrices affected by gold mining activity. *Environ. Monit. Assess.* 188, 586.
- Lacal, J., da Silva, M.P., García, R., Sevilla, M.T., Procopio, J.R., Hernández, L., 2003. Study of fractionation and potential mobility of metal in sludge from pyrite mining and affected river sediments: changes in mobility over time and use of artificial ageing as a tool in environmental impact assessment. *Environ. Pollut.* 124, 291–305.
- Langmuir, D., 1997. *Aqueous environmental*. Prentice Hall, Upper Saddle River, NJ.
- Liu, H., Probst, A., Liao, B., 2005. Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Sci. Total Environ.* 339, 153–166.
- Madejón, P., Murillo, J., Marañón, T., Cabrera, F., López, R., 2002. Bioaccumulation of As, Cd, Cu, Fe and Pb in wild grasses affected by the Aznalcóllar mine spill (SW Spain). *Sci. Total Environ.* 290, 105–120.
- Majzlan, J., Lalinská, B., Chovan, M., Bláß, U., Brecht, B., Göttlicher, J., Steining, R., Hug, K., Ziegler, S., Gescher, J., 2011. A mineralogical, geochemical, and microbiological assessment of the antimony- and arsenic-rich neutral mine drainage tailings near Pezinok, Slovakia. *Am. Mineral.* 96, 1–13.
- Martín Peinado, F.J., Romero-Freire, A., García Fernández, I., Sierra Aragón, M., Ortiz-Bernad, I., Simón Torres, M., 2015. Long-term contamination in a recovered area affected by a mining spill. *Sci. Total Environ.* 514, 219–223.
- Mauclair, L., Gibert, J., 1998. Effects of pumping and floods on groundwater quality: a case study of the Grand Gravier well field (Rhône, France). *Hydrobiologia* 389, 141–151.
- Nakamaru, Y.M., Martín Peinado, F.J., 2017. Effect of soil organic matter on antimony bio-availability after the remediation process. *Environ. Pollut.* 228, 425–432.
- Simón, M., Martín, F., Ortiz, I., García, I., Fernández, J., Fernández, E., Dorransoro, C., Aguilar, J., 2001. Soil pollution by oxidation of tailings from toxic spill of a pyrite mine. *Sci. Total Environ.* 279, 63–74.
- Weber, M., Rinke, K., Hipsey, M., Boehrer, B., 2017. Optimizing withdrawal from drinking water reservoirs to reduce downstream temperature pollution and reservoir hypoxia. *J. Environ. Manag.* 197, 96–105.
- WHO, 2011. *Guidelines for Drinking-water Quality*. Fourth edition. 38. World Health Organization, pp. 104–108 chronicle.
- Wilson, N., Craw, D., Hunter, K., 2004. Antimony distribution and environmental mobility at an historic antimony smelter site, New Zealand. *Environ. Pollut.* 129, 257–266.
- Wu, Z., He, M., Guo, X., Zhou, R., 2010. Removal of antimony (III) and antimony (V) from drinking water by ferric chloride coagulation: competing ion effect and the mechanism analysis. *Sep. Purif. Technol.* 76, 184–190.
- Xiao, F., Huang, J.H., Zhang, B., Cui, C., 2009. Effects of low temperature on coagulation kinetics and floc surface morphology using alum. *Desalination* 237, 201–213.