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Influence of reducing conditions on the release of antimony and arsenic from a tailings sediment

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Abstract

Purpose Burial treatment is a frequently used technology for contaminated solid materials, but little is known about the effect of redox changes on the mobility of metals and metalloids. Here, sediment contaminated by historical tailing slurry from an antimony (Sb) mine was incubated with sodium ascorbate solution (SAS), so as to gain insights into the remobilization of Sb and arsenic (As) under reducing conditions.

Materials and methods Anaerobic incubation of a tailing sediment was incubated with SAS and high-purity water (HPW) as a comparison for 20 day. Metals and metalloids in various chemical fractions of the sediment were quantified by sequential extraction. Dissolved Sb and As species in the HPW and SAS over the incubation period were quantified by hydride generation atomic fluorescence spectrometry.

Results and discussion In the tailing sediment, 30.8 % of iron (Fe) was found in Fe(III) oxyhydroxides, which hosted 26.7 % of Sb and 32.8 % of As. The water-soluble and exchangeable fractions of Sb (0.09 and 2.0 %) were approximately 10-fold that of As (0.01 and 0.2 %). When the sediment was incubated with the HPW, the behavior of manganese (Mn) was active and Sb was found to be concomitant with Mn. In the SAS, As was first released more weakly than Sb, but later released more strongly than Sb. The release of Sb before 72 h was approximately 2.6-fold that of As, and after 72 h the release of As was approximately 8.8-fold that of Sb. It was deduced that Sb and As were bound differently to Fe phases, with Sb mainly bound to the early dissolved Fe phases whereas As was mainly bound to the later-dissolved Fe phases.

Conclusions This work indicated that both Mn and Fe phases played an important role on the behavior of Sb, and Fe phases played an important role on the behavior of As. Under reducing conditions, the reductive dissolution of Mn and Fe phases resulted in a strong release of Sb in the early stage and a strong release of As in the later stage, because Sb and As exhibited different chemical associations in the tailing sediment.

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1 Introduction

Antimony (Sb) and arsenic (As) are toxic, nonessential metalloids of growing interest for a variety of industrial applications. They have s^2p^3 outer orbital electron configurations, and both occur as oxyanions (Filella et al. 2009; Wilson et al. 2010). They can occur in four oxidation states (−3, 0, +3, and +5) but are mostly found in two oxidation states (+3 and +5) in the environment (Filella et al. 2002; Smedley and Kinniburgh 2002). The geochemical behavior of Sb and As in soil–water systems is highly dependent on their oxidation states (Laintz et al. 1992; Sun and Doner 1998), and trivalent Sb and As are more toxic than their pentavalent species (Filella et al. 2002; Wang and Mulligan 2009).

Tailings from mining of sulfidic metal ores are important Sb and As sources because some residual sulfide

minerals (e.g., stibnite, arsenopyrite, realgar, orpiment, and pyrite) contain high levels of Sb and As (Smedley and Kinniburgh 2002; Casiot et al. 2007; Zhang et al. 2009). Also, high Sb concentrations are generally associated with high As concentrations in sulfide ores (Filella et al. 2002). In many cases, mine tailings have been improperly disposed in river courses, and accordingly, the sediment is mostly composed of tailings. When exposed to air, sulfides in the tailings are oxidized and metals and metalloids are released from the mineral lattice (Fanfani et al. 1997; McCarty et al. 1998; Dold 2003), resulting in serious pollution.

A simple and effective method for remediating mine-impacted streams is the physical removal of stream sediments. These sediments might be deposited into an impoundment or repository (Butler 2011). However, the oxidation–reduction status of the dredged sediments postdisposal is likely to be switched from aerobic to anaerobic by indigenous bacterial activity, organic matter, oxygen consumption, or deterioration of sediment physical properties (Barcelona and Holm 1991; Heron et al. 1994; Chatain et al. 2005a). The labile metals and metalloids may be released by simple desorption or reductive dissolution of Fe and Mn phases (Davranche and Bollinger 2000; Chatain et al. 2005a; Pareuil et al. 2008; Hockmann et al. 2014a, b). Therefore, research on the change of Sb and As mobility under reducing conditions is important, especially for risk assessment of contaminated sites.

Relevant research on the influence of reducing conditions on the mobility of Sb has been mostly focused on soil (Mitsunobu et al. 2006; Hockmann et al. 2014a, b, 2015), water or solution (Casiot et al. 2007; Polack et al. 2009), and mineral phases (Mitsunobu et al. 2008; Liu et al. 2015). However, the mobility of Sb and As in sediment that is predominantly composed of mine tailings has rarely been examined. Compared to soil, mine tailings usually exhibit low organic matter content and high Mn content (Lu et al. 2014). Organic matter may affect the mobility of metals and metalloids through competition for sorption sites, formation of complexes, and electrostatic interactions (Wang and Mulligan 2009), and Mn phases may significantly affect the behavior of Sb (Thanabalasingam and Pickering 1990; Hockmann et al. 2014b).

In the present study, we investigated the release of Sb and As from a tailing sediment under imposed reducing conditions through the addition of ascorbate. The sediment was historically contaminated by tailing slurry from an Sb mine and had been exposed to oxidizing conditions for more than 10 years. The aims of this study were to (i) achieve insights into the mobility of Sb and As in a tailing sediment under reducing conditions and (ii) elucidate the mechanisms involved. Moreover, the behavior of Sb under reducing conditions was compared with that of As.

2 Materials and methods

High-purity deionized water (HPW) (resistivity 18.2 MΩ·cm) was prepared with a Milli-Q system (Millipore, Bedford, MA, USA). All chemicals were of analytical grade, except hydrogen peroxide, HCl, HNO_3, and HF, which were guaranteed grade. Moreover, HCl, HNO_3, and HF were purified by a DST-1000 Sub-Boiling Distillation System (Savillex, Minnetonka, USA). All glassware and plasticware were soaked in 10 % HNO_3 (v/v) for 24 h and rinsed three times with HPW before use.

2.1 Sediment sampling

A tailing sediment sample was collected at the bank of a stream (24° 50′ 41″ N, 107° 37′ 45″ E) that drains the Chashan Sb (in the form of stibnite) mine in Nandan County, Guangxi Autonomous Region, China. This stream received a large amount of Sb mine tailing slurry approximately 10 years ago. At the sampling location, the stream bank was composed of predominantly milled tailing and a small amount of ordinary sediment. The bank was dry for most of the year and was occasionally waterlogged during flooding. The color of the sediment was reddish brown because of the long-term oxidation of the tailings. Sediments (0–30 cm) at two locations (spacing ~1 m) on the bank were collected and evenly mixed (1:1, v/v), and finally, a bulk sample of ~5 kg was obtained. In the laboratory, the sediment was air-dried at room temperature (20 ± 5 °C), sieved to <2 mm by a stainless steel sieve, and homogenized and stored at 4 °C until use.

2.2 Characterization of the tailing sediment

The sand (20–2000 μm), silt (2–20 μm), and clay (<2 μm) fractions of the sediment were measured by a Mastersizer 2000 laser diffractometer (Malvern Instruments, Malvern, UK). The mineralogical composition of the sediment was analyzed by X-ray diffraction (XRD) (D-MAX 2200, Rigaku Co., Japan). Morphology and chemical composition of mineralogical phases were identified by scanning electron microscopy (SEM) (JSM 6460, JEOL, Japan) in the back-scattered electron (BSE) mode coupled with an energy-dispersive spectrometer (EDS) (accelerating voltage = 25 kV, EDAX Genesis, USA). Prior to SEM-EDS analysis, the sediment was coated with conductive carbon. The major element concentrations of the sediment were measured by XRF (Axios PW4400, PANalytical Co., The Netherlands). The pH of the sediment was determined in a 1:2.5 (w/v) sediment-deionized water suspension after a 2-h agitation. Total sulfur (S) of the sediment was detected by the Eschka method (ISO 334 1992). The total organic carbon (TOC) content was determined with an elemental analyzer (PerkinElmer 2400-11, Germany) after decarbonation. The sediment was digested by HNO_3 and HF in a

Teflon crucible (sealed within a stainless steel bomb) at 170 °C (internal pressure ca. 7.9 bar). This digestion method was modified from Liang et al. (2000) and is described in detail by Zhang et al. (2009). After digestion of the sediment sample, the determination of trace elements was assessed using a certified reference material of soil (GBW07404, China National Research Center for CRM, Beijing, China). The concentrations of Sb and As ($n = 3$) in the reference soil sample were 6.2 ± 1.5 and 60 ± 5 mg kg^{-1}, compared with the certified values of 6.3 ± 1.1 and 58 ± 6 mg kg^{-1}, respectively. The precision of the measurement of elements was generally better than 5 %. To determine the chemical associations of metals and metalloids, a sequential extraction procedure adapted from Dold (2003) was used. This procedure was developed for the dissolution of secondary and primary minerals in mine tailings from sulfide ore deposits, and in this procedure, the focus is secondary Fe(III) oxyhydroxide phases. The secondary Fe(III) oxyhydroxides were proposed to be important for the behavior of Sb and As (Chatain et al. 2005a; Hockmann et al. 2014a, b). The sequential chemical extraction of the sediment was conducted in triplicate, and seven fractions (Table 1) were examined. In the sequential extraction, Mn oxides and Fe(III) oxyhydroxides dissolved simultaneously in the third step, and metals and metalloids adsorbed to solid phases were extracted in the exchangeable fraction (Dold 2003).

2.3 Sediment incubation

Sediment incubation was performed at a solid concentration of 100 g l^{-1} (100 g of sample in 1 l of solution) in a three-necked, round-bottomed flask (1 l). The reductive condition was obtained with 0.1 mol l^{-1} sodium ascorbate solution (SAS) (Changsha Kangwang Biological Technology Co., Ltd., China). In addition, an experiment under more natural conditions was conducted with HPW for comparison. Ascorbate was considered a suitable reducing agent for the incubation experiments. It is a mild reducing agent with a standard redox potential of +390 mV (versus normal hydrogen electrode (NHE)) that is lower than the potential (1000 mV) for the Fe(III)/Fe(II) redox couple, so it has been used widely as a reducing agent for reduction of Fe and Mn oxyhydroxides (Deng 1997; Chatain et al. 2005a; Pareuil et al. 2008, 2011). Sodium ascorbate can provide a broad Eh range, while the pH of the soil suspension was only slightly modified (less than ±0.5 pH unit, depending on the concentration) and was expected to minimize the risks of precipitation or complexation associated with metals and metalloids (Chatain et al. 2005a; Pareuil et al. 2008). Duplicate incubation experiments were performed at room temperature (15 ± 3 °C) in an N$_2$-saturated glove box (MT012-C, Changsha Mitr Instrument Equipment Co. Ltd., China). The pH was free to change during the experiment. The sediment was maintained in

suspension by continuous electromagnetic stirring at 200 rpm. A gentle flow of pure N$_2$ (pure grade, >99.99 %) was continuously blown into the flask to ensure the anaerobic condition of the experiment. This flow of N$_2$ also kept a continuous flow of N$_2$ into the glove box and helped avoid the permeation of air. A 10-ml suspension was taken at various periods of 1, 2, 3, 5, 10, 24, 48, 72, 120, 168, 240, 360, and 480 h. Two milliliters of nonfiltered suspension was used for the measurement of pH and Eh. The remaining suspension was immediately filtered through a 0.45-μm membrane filter (Millipore, USA) and then divided into several aliquots. The aliquots for the determination of Fe, Mn, Sb, and As were acidified to 1 % HCl, whereas the aliquots for the determination of SO$_4^{2-}$, Sb(III), and As(III) were not acidified. The sampling and filtration of the suspension were conducted in the glove box under an N$_2$ atmosphere.

2.4 Analysis of the supernatant

The pH and Eh of the supernatant of the sediment incubation were measured by a Denver UB-7 pH meter combining pH and redox electrodes, respectively. The E values measured by redox electrodes were converted into Eh values versus the NHE by addition of a value (e.g., 214 mV at 10 °C) in each Eh determination (Nordstrom and Wilde 2005). The SO$_4^{2-}$ concentration in solution (filtered suspension) was analyzed by barium chromate spectrometry (MEPC 2007), and the concentrations of Fe and Mn in solution were analyzed by ICP-MS.

Trivalent Sb and As were analyzed using modified methods from Fuentes et al. (2003) and Liao and Deng (2006), respectively. Citric acid (1 g l^{-1}) and 8-hydroxyquinoline (18 g l^{-1}) were promptly added into two aliquots of supernatant to mask the signals from Sb(V) and As(V), respectively. The concentrations of Sb(III) and As(III) were immediately (within 40 min) determined by hydride generation-atomic fluorescence spectrometry (HG-AFS) (AFS-2202E, Haiguang Instruments Corp., Beijing, China). The addition of citric acid was shown to increase the stability of Sb(III) (Zheng et al. 2001; Fuentes et al. 2003), and the addition of HCl before AFS analysis could increase the stability of As(III) in the presence of high Fe concentrations (Gault et al. 2005). Our results showed that Sb(III) and As(III) in solution were stable for at least 4 h. For the simultaneous analysis of total Sb and As, ascorbic acid (10 g l^{-1}) and thiourea (10 g l^{-1}) were added to reduce pentavalent Sb and As to trivalent species and to mask the interference of metals (Zhang et al. 2006). The concentrations of Sb(V) and As(V) were calculated as the difference between the concentrations of total Sb and As and that of the trivalent species. Regarding the HG-AFS determination, the detection limits for total Sb and As, Sb(III), and As(III) were 0.004, 0.01, 0.05, and 0.03 μg l^{-1} (calculated as their concentrations equivalent to a signal three times the standard deviation of a blank

Table 1 Sequential chemical extraction used in this study (modified from Dold 2003)

Fractions	Extraction procedures
Water-soluble	1.0 g sample into 50-ml deionized H_2O, shaken for 1 h
Exchangeable	1 M NH_4 acetate, pH 4.5, shaken for 2 h
Fe(III) oxyhydroxides	0.2 M NH_4 oxalate, pH 3.0, shaken for 1 h in darkness
Fe(III) oxides	0.2 M NH_4 oxalate, pH 3.0, heated in water bath 80 °C for 2 h
Organic and supergene sulfides	35 % H_2O_2, heated in water bath for 1 h
Primary sulfides	$KClO_3$ and HCl, followed by 4 M HNO_3 boiling
Residual and silicates	HF and HNO_3 digestion

solution, $n = 11$), and the relative standard deviation was 0.5, 0.6, 0.6, and 3.1 %, respectively.

2.5 Statistical analysis of data

SPSS 16.0 software (SPSS Inc., New York, USA) was used for the calculation of correlation coefficients between elements.

3 Results and discussion

3.1 Characterization of the sediment

The granulometric analysis showed that the tailing sediment consisted of 51 % sand, 32 % silt, and 17 % clay. The XRD analysis indicated the presence of quartz, montmorillonite, illite, gypsum, kaolinite, calcite, and dolomite (Fig. 1). The SEM-EDS analysis revealed the presence of gypsum, pyrite, arsenopyrite, and Fe and Mn oxydroxides (Fig. 2). The presence of water-soluble gypsum could be identified in the sample most likely because the sample location was dry most of the time. Gypsum can be observed as a secondary mineral in mine tailings because sulfuric acid is generated during the oxidation of sulfide minerals (Garrels and Thompson 1960) and reacts with carbonate minerals (calcite and dolomite). The organic carbon content of the tailing sediment was 0.3 %.

The sediment had a pH value of 7.8 and an Eh value of 339 mV. The major and trace element concentrations of the sediment sample are presented in Table 2. Silicon, Fe, Ca, Al, and S were the dominant major elements, and Zn, As, Pb, and Sb were the dominant trace elements in the sediment.

The results from the sequential chemical extractions of the sediment are shown in Fig. 3. Iron was found mainly in Fe(III) oxyhydroxides (30.8 %), Fe(III) oxides (22.3 %), and primary sulfides (32.7 %). The secondary phases of Fe were assumed to be caused by long-term weathering and oxidation of pyrite. Manganese was mainly present in the exchangeable fraction (53.3 %) and as Mn oxides (31.3 %), which were simultaneously dissolved with Fe(III) oxyhydroxides in the extraction (Stone 1987; Dold 2003).

Antimony was identified predominantly present in the residual and silicate fraction (35.4 %) and associated with Fe(III) oxyhydroxides (32.8 %), Fe(III) oxides (19.5 %), and primary sulfides (10.2 %). Arsenic was identified predominantly associated with primary sulfides (61.6 %) and Fe(III) oxyhydroxides (26.7 %). In addition, a small proportion of As was associated with Fe(III) oxides (6.6 %) and present in the residual and silicate fraction (4.7 %). The SEM-EDS analysis also showed the association of Sb and As with Fe oxyhydroxides (Fig. 2b, d). Both Sb and As were closely associated with Fe(III) oxyhydroxides because Fe(III) oxyhydroxides were proven to be an important host phase for trace elements due to the presence of functional groups and a high surface area (Dzombak and Morel 1990; Dold 2003; Richmond et al. 2004). For example, Sb and As, once released from a mineral lattice, show a high affinity to Fe(III) oxyhydroxides (Manning et al. 1998; Bose and Sharma 2002; Leuz et al. 2006). The association of Sb and As with sulfides could be attributed to the remaining sulfide minerals of Sb and As as well as pyrite in the tailings. Pyrite has been proven to usually contain abundant As (Smedley and Kinniburgh 2002; Zhang et al. 2003) and other trace elements (Alastuey et al. 1999). Although the water-soluble and exchangeable fractions
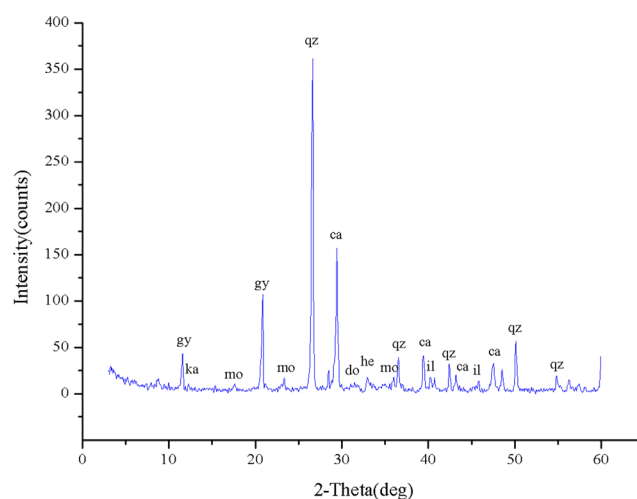
Fig. 1 X-ray diffraction (XRD) results for the tailing sediment (*ca* calcite, *do* dolomite, *gy* gypsum, *il* illite, *ka* kaolinite, *mo* montmorillonite, *qz* quartz)

Fig. 2 Scanning electron microscope (SEM) photographs of the tailing sediment. Backscattered electron images of **a** Fe and Mn oxyhydroxide; **b** pyrite and As-bearing Fe oxyhydroxide; **c** arsenopyrite; **d** Sb-bearing Fe oxyhydroxide; **e** calcite; **f** gypsum
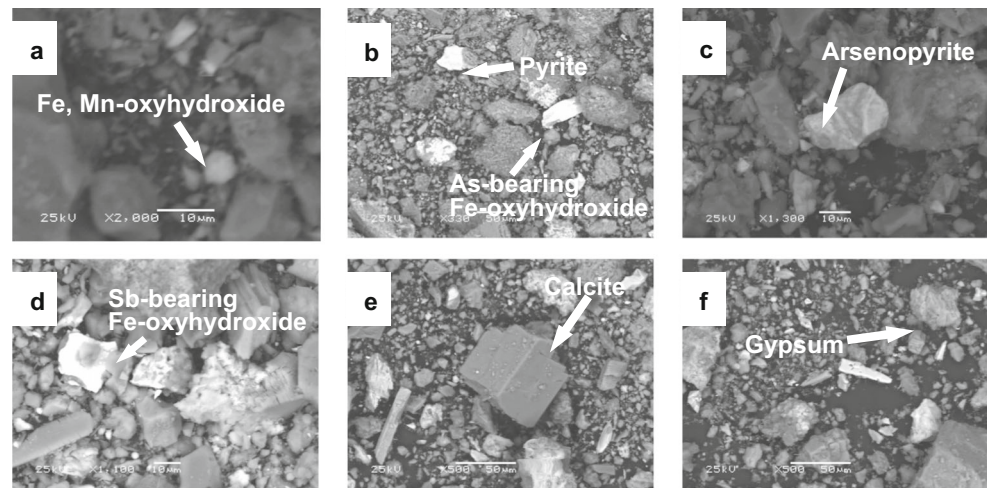
of both Sb and As were small, it should be noted that the water and exchangeable fractions of Sb (0.09 and 2.0 %) were approximately 10-fold that of As (0.01 and 0.2 %).

3.2 General variations in the two treatments

The variations in pH, Eh, and other variables of the HPW and SAS according to the incubation period are shown in Figs. 4 and 5, respectively. In general, the pH value varied slightly in the ranges of 7.4–8.2 and 7.3–8.7 for the HPW and SAS, respectively. The pH declined slightly in both the HPW and SAS before 24 h, probably because the dissolution of soluble secondary sulfate salts containing Fe^{2+}, Mn^{2+}, Fe^{3+}, and Al^{3+} has a potential for producing acidic conditions through hydrolysis reactions (Khorasanipour 2015). The increase of pH after 24 h was likely caused by the consumption of the produced acid by buffering minerals such as calcite and dolomite in the sediment. The Eh of the SAS decreased from −4 to −292 mV, which was much more reducing compared to the Eh range of 342 to −44 mV of the HPW.

The Fe concentration in the HPW was <0.53 mg l^{-1} (Fig. 4c). In the SAS, the Fe concentration showed an approximately linear increase from 3.0 mg l^{-1} at the beginning to 105 mg l^{-1} at 360 h (Fig. 5c), indicating a generally constant dissolution rate in this period. A similarly linear increase in Fe concentration has also been previously observed in a shallow sandy aquifer in Denmark (Larsen et al. 2006) and in a soil

that was incubated with lactate (Hockmann et al. 2014a). The maximum Fe concentration (105 mg l^{-1}) at 360 h corresponded to only 1.5 % of the total Fe or 4.7 % of Fe(III) oxyhydroxides. This suggests that only a very small fraction of Fe oxyhydroxides was reductively dissolved under this condition. Hockmann et al. (2014a) also reported the dissolution of a similar percentage of ~2 % of total Fe in a contaminated soil. Because the pH of the suspension was in a slightly alkaline range (7.3–8.7) and could not cause acidic dissolution of Fe phases, the increase of Fe in the SAS must have been caused by the reductive dissolution of labile Fe phases in the sediment. Under the reducing conditions induced by ascorbate, Fe(III) oxyhydroxides have been proven to be no longer stable and can be partially dissolved (Davranche and Bollinger 2000; Petrunic and Al 2005; Leuz et al. 2006). Previously, Fe (hydr)oxides were predicted to be reduced at redox potentials <0 mV in neutral to alkaline soils (Kirk 2004), which coincided with the Eh range (−4 to −292 mV) of this work.

In the HPW, the Mn concentration increased from 0.2 to 7.1 mg l^{-1} before 120 h and then attenuated to 2.4 mg l^{-1} at 480 h (Fig. 4c). In the SAS, the Mn concentration instantly reached a high level of 20 mg l^{-1} at the very beginning of the incubation and remained in the range 20 to 25 mg l^{-1} up to 48 h, followed by a gradual decrease (Fig. 5c). The maximum Mn concentration in the HPW (7.1 mg l^{-1}) and SAS (25 mg l^{-1}) corresponded to 3.2 and 10.8 %, respectively, of

Table 2 Concentrations of major and trace elements in the sediment

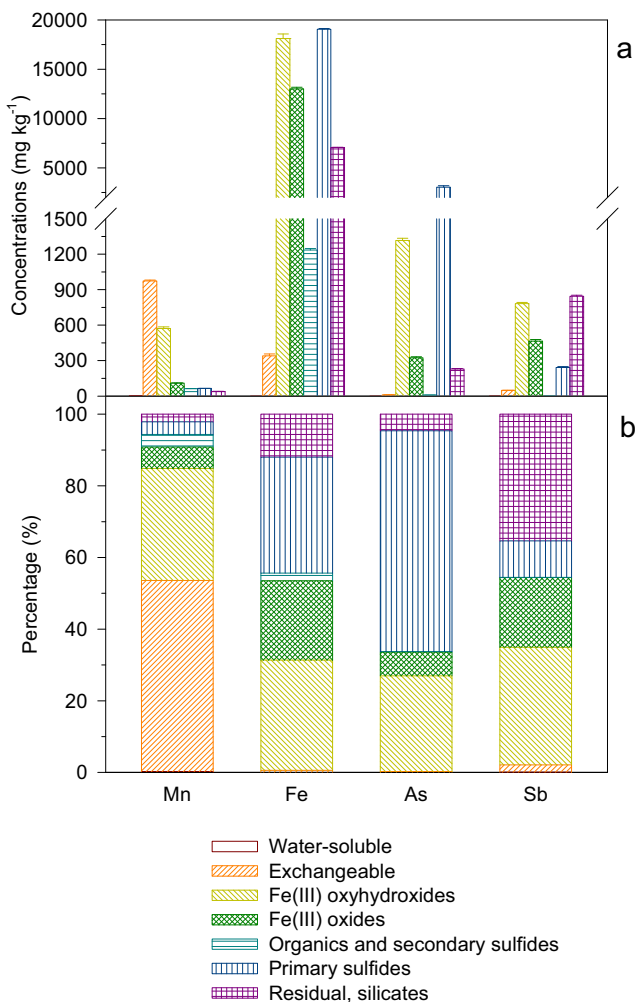| Major elements (%)	Si	Al	Fe	Mn	Ca
	21.5 ± 0.34	0.77 ± 0.03	5.71 ± 0.29	0.19 ± 0.01	9.6 ± 0.54
	Na	K	Mg	Ti	S
	0.27 ± 0.02	0.54 ± 0.01	0.28 ± 0.01	0.09 ± 0.01	4.1 ± 0.03
Trace elements (mg kg^{-1})	As	Sb	Zn	Pb	Cd
	5145 ± 325	2249 ± 130	7327 ± 528	3312 ± 235	81 ± 4

Fig. 3 Chemical associations of Mn, Fe, As, and Sb in the sediment expressed as concentrations (**a**) and percentages (**b**)

the total Mn in the sediment. The increase of Mn in HPW before 120 h could be associated with the dissolution of Mn-containing secondary sulfate salts and possibly a fraction of adsorbed Mn (McGregor et al. 1998; Khorasanipour 2015) that was included in the exchangeable fraction. The increase of Mn in the SAS at the very beginning of incubation could also be associated with the superimposing of the reductive dissolution of Mn oxides that could occur instantly owing to the high redox potential of MnO_2/Mn^{2+} (James and Bartlett 1999). The decrease of dissolved Mn in the HPW and SAS was assumed to be caused by possible precipitation of secondary rhodochrosite ($MnCO_3$). It was previously reported that the dissolution of Fe and Mn oxyhydroxides and calcite in a freshwater aquifer system may lead to the precipitation of rhodochrosite and siderite (Saunders and Swann 1992). In field studies, it has often been reported that the ion activity products of carbonate minerals in many natural anaerobic aquatic systems are highly supersaturated with respect to carbonate minerals such as $MnCO_3$ (Jensen et al. 2002). Moreover, the high proportion of Mn (53.3 %, Fig. 3) in the

exchangeable fraction (mainly as carbonate) also implied a high potential for $MnCO_3$ precipitation in the tailing sediment.

The sulfate in the solution was considered to originate from the dissolvable salts (e.g., gypsum) in the tailings. The marked decline of sulfate concentration (Fig. 5d) in the SAS after 168 h implied that sulfate reduction might have occurred due to possible microbial activity. For example, sulfate-reducing bacteria can be widely present in mine tailings (Fortin et al. 2000), and these bacteria can transform sulfate to hydrogen sulfide (Sanchez-Andrea et al. 2014) followed by precipitation with metals. The activity of indigenous bacteria can be accelerated under reducing conditions and in the existence of lactate as a carbon source (Chatain et al. 2005b; Hockmann et al. 2014a). In the SAS, a dark color developed while sulfate strongly decreased, possibly meaning the formation of Fe sulfides (Butler 2011). The slight decrease of dissolved Fe and As in the SAS from 360 to 480 h (Fig. 5c) might be explained by the possible formation of Fe sulfides, because As exhibits a high affinity to Fe sulfides (Smedley and Kinniburgh 2002; Zhang et al. 2003). The color of the HPW remained yellow, but the Eh decreased with time (Fig. 4b). Therefore, development of bacteria might also have occurred in the HPW but was not strong possibly due to the low organic matter content in the suspension.

3.3 Mobilization of Sb and As in the sediment

The two treatments resulted in the release of Sb and As to different degrees. During the incubation, the concentrations of Sb and As in the SAS ranged between 932 and 2115 and between 116 and 2758 $\mu g\ l^{-1}$, respectively, much higher than 60.2 and 126 and 30.3 and 230 $\mu g\ l^{-1}$, respectively, in the HPW (Figs. 4e and 5e). This indicates that, in contrast to the HPW, a much larger amount of Sb and As was released into the SAS under reducing conditions. Over the incubation period, the Sb(III)/Sb(V) and As(III)/As(V) ratios were 0.05 to 0.18 (mean 0.12) and 0.03 to 0.89 (mean 0.21), respectively, in the HPW, and 0.02 to 0.15 (mean 0.07) and 0.11 to 0.52 (mean 0.26), respectively, in the SAS. This finding indicates that Sb and As in both the HPW and SAS were dominated by Sb(V) and As(V), although the treatment in the SAS was under imposed reducing conditions. Similarly, it was previously reported that As(V) can dominate in anoxic hypolimnetic waters (Kuhn and Sigg 1993; Aurilio et al. 1994), and Sb(V) was identified as the main species in the liquid phase even at reducing conditions that should not favor Sb(V) (Mitsunobu et al. 2006; Okkenhaug et al. 2012). Additionally, Sb was present exclusively as the oxidized form Sb(V) over a wide redox range in reducing sediment pore water (Cutter 1992).

In the HPW, the Sb concentration increased from 60.2 $\mu g\ l^{-1}$ at the beginning to 126 $\mu g\ l^{-1}$ at 72 h followed by a gradual decrease to 43.9 $\mu g\ l^{-1}$ at 480 h. This variation

Fig. 4 Evolution of chemical variables in the liquid phase of sediment—high-purity water (HPW)
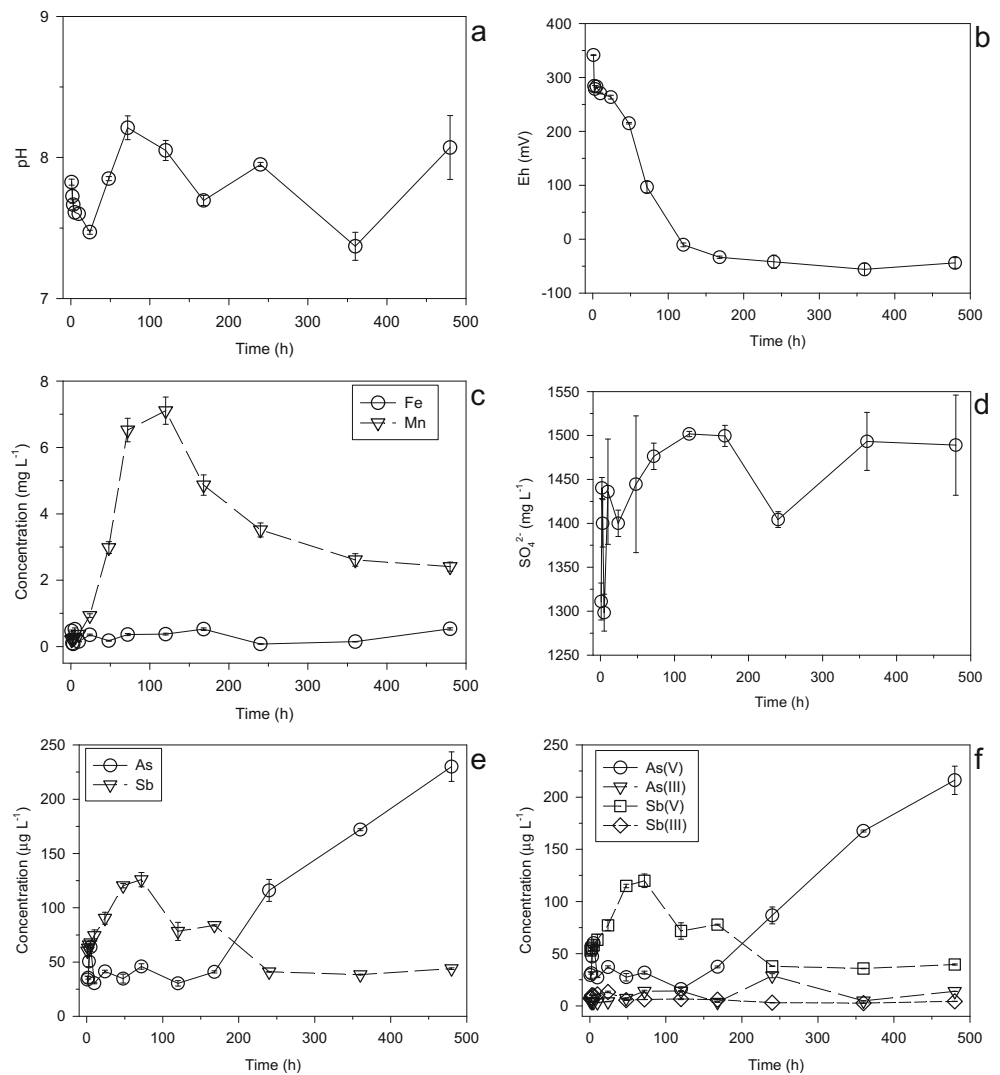

paralleled that of Mn concentration (Fig. 4c, e). The correlation coefficient between Sb and Mn concentrations was calculated for the periods of 0 to 72 and 120 to 480 h, respectively, because it was proposed that different processes accounted for the increase of dissolved Mn from 0 to 72 h and the decrease of dissolved Mn from 120 to 480 h (see above). The correlation coefficient was 0.90 ($p < 0.01$, $n = 8$) and 0.84 ($p < 0.05$, $n = 5$) for the periods of 0 to 72 and 120 to 480 h, respectively. This finding indicates that the behavior of Sb was significantly associated with Mn. The relationship between Sb and Mn phases was also proposed in previous studies (Thanabalasingam and Pickering 1990; Hockmann et al. 2014b). Before 72 h, Sb in soluble and adsorbed fractions and associated with Mn oxides could be released. After 72 h, Sb concentration attenuated possibly because Sb became bound to the precipitation of $MnCO_3$. Unlike Sb, As concentration in the HPW fluctuated slightly between 30.3 and 63.6 μg l^{-1} from the beginning to 168 h and then increased

to 230 μg l^{-1} at 480 h (Fig. 4e). No close association could be found between the concentration of As and that of Mn or Fe. The increase of As after 168 h could not be explained.

The reductive dissolution of Fe secondary phases was shown to be an important mechanism for the release of metals and metalloids, such as the release of Sb from a contaminated soil (Hockmann et al. 2014a); the release of As from a mining soil (Chatain et al. 2005a) and contaminated calcareous floodplain soils (Parsons et al. 2013); the release of Fe, Mn, Ni, and Zn from contaminated soils (Pareuil et al. 2008); and the release of Mn from a Mn-rich slag (Pareuil et al. 2011). In general, the As concentration in the SAS showed a parallel variation to the Fe concentration and exhibited significant correlation with the Fe concentration ($r = 0.95$, $p < 0.01$), indicating that the release of As from the sediment was closely associated with the dissolution of Fe phases. However, corresponding to the approximately linear increase of Fe before 360 h, As concentration only increased to 770 μg l^{-1} at

Fig. 5 Evolution of chemical variables in the liquid phase of sediment—sodium ascorbate solution (SAS)
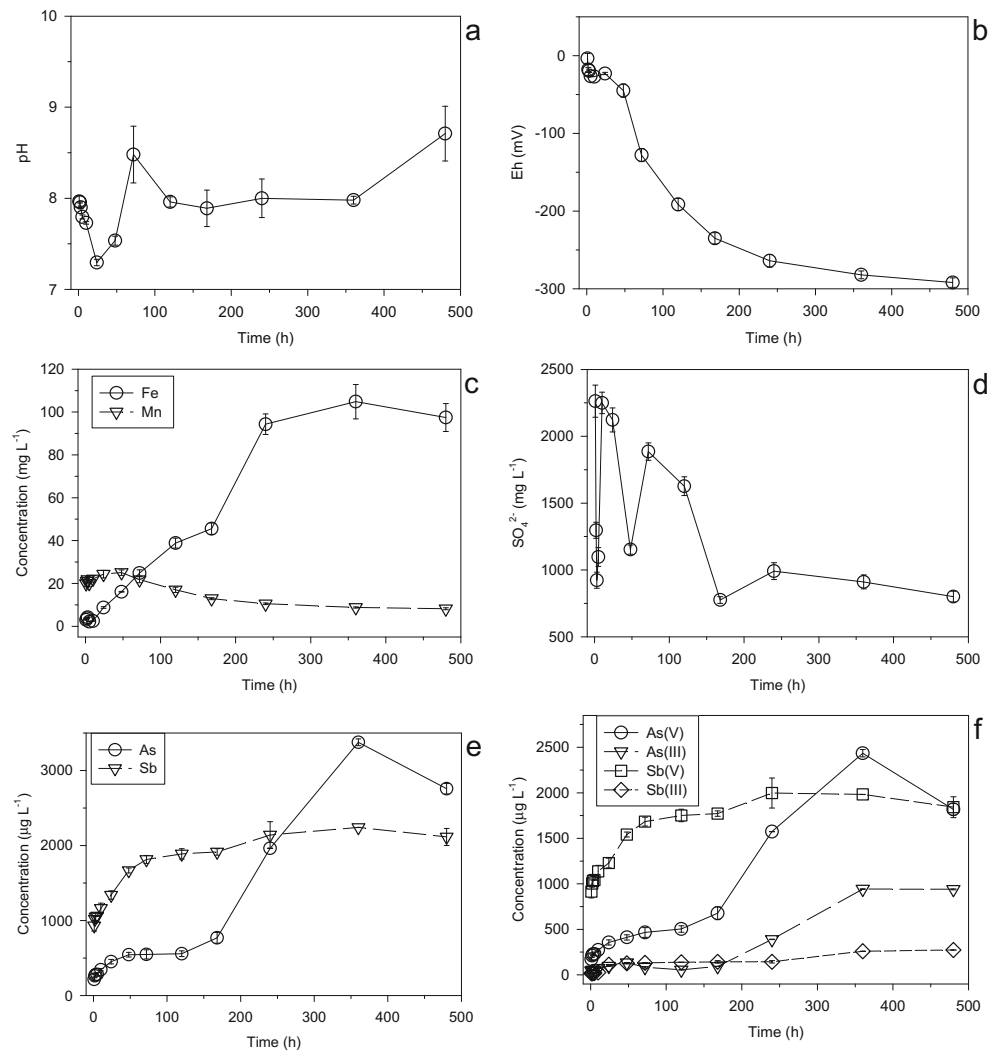
168 h but strongly increased from 770 µg l^{-1} at 168 h to 3377 µg l^{-1} at 360 h. This contrast possibly means that As was mainly hosted by the later-dissolved Fe phases.

In the SAS, Sb concentration was as high as 931 µg l^{-1} at the beginning of incubation (1 h) and increased to 1816 µg l^{-1} at 72 h (Fig. 5e). The Sb associated with labile Mn phases should have been released early, because Mn concentration was 20 mg l^{-1} at 1 h and reached a maximum of 25 mg l^{-1} at 48 h. Moreover, the dissolution of Mn phases seemed not likely to cause such a strong release of Sb because in the HPW the release of Sb in soluble and adsorbed fractions and associated with labile Mn phases caused a maximum Sb concentration of only 126 µg l^{-1}. Therefore, the Sb released in the SAS before 72 h was suggested to originate not only from the mobilization of Sb in soluble and adsorbed fractions and associated with labile Mn phases but also from the dissolution of Fe phases because Fe concentration was elevated to 3 mg l^{-1} at 1 h and increased linearly to 25 mg l^{-1} at 72 h (Fig. 5c). The release of Sb before 72 h was stronger compared to the period of 72–360 h, in which Sb concentration increased from 1816

to only 2241 µg l^{-1}. This possibly means that Sb was mainly hosted by the early dissolved Fe phases. Generally, Sb and Fe exhibited a significant correlation ($r = 0.89$, $p < 0.05$, $n = 13$), indicating that the release of Sb was associated with the dissolution of Fe(III) oxydroxides, which has been previously reported as an important mechanism for Sb release (Scheinost et al. 2006; Ackermann et al. 2009).

Compared to the Sb concentration, the As concentration in both the HPW and SAS was lower before 240 h but higher afterwards (Figs. 4e and 5e). The relationship between dissolved Sb and As in the SAS differed in the early and later stages of the incubation (Fig. 6). Based on a linear regression calculation, the release of Sb before 72 h was approximately 2.6-fold ($r = 0.97$, $p < 0.01$, $n = 8$) that of As, and after 72 h the release of As was approximately 8.8-fold ($r = 0.93$, $p < 0.01$, $n = 5$) that of Sb. This finding indicates that, with decreasing Eh, there is a stronger release of Sb than As first but a stronger release of As than Sb later. Similarly in a creek draining the Bournac Sb mine in France, As exhibited a lower mobility than Sb under oxic conditions but a higher mobility than Sb
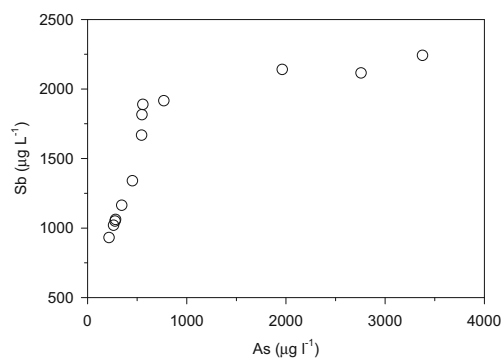
Fig. 6 Relationship between dissolved Sb and As in the liquid phase of sediment—sodium ascorbate solution (SAS)

under anoxic conditions (Casiot et al. 2007). Compared to As, Sb in the sediment was more significantly present in the water-soluble fraction and associated with Mn oxides and early dissolved Fe phases. This could explain the stronger release of Sb than As in the early stage of incubation. On the other hand, As was mainly hosted by the later-dissolved Fe phases. This likely explains the stronger release of As than Sb in the late stage of incubation.

The behavior of early dissolved Fe phases and later-dissolved Fe phases is very possibly associated to crystallinity of Fe phases (crystal structure and size distribution) that can be dissolved in SAS. The reactivity of Fe phases will change as the assemblage of Fe(III) oxydroxide particles becomes partially dissolved (Larsen et al. 2006).

4 Conclusions

When the tailing sediment was incubated with water, the behavior of Mn was active and Sb was found to be concomitant with Mn. This means that the strong Mn cycling in surface environment may lead to mobilization or immobilization of Sb. Because some mine wastes contain high contents of Sb, these processes associated with Mn and Sb would be of significance in the mine environment.

When the tailing sediment was incubated with SAS, a large amount of Sb and As was mobilized. With decreasing Eh, As was first released more weakly than Sb, but was later released more strongly than Sb. It was deduced that Sb and As were bound to Fe phases differently, with Sb mainly bound to the early dissolved Fe phases whereas As was mainly bound to the later-dissolved Fe phases. The Sb in the water-soluble fraction, and associated with Mn phases and early dissolved Fe phases, contributed to the strong release of Sb in the early stage of incubation. In contrast, the As associated to the later-dissolved Fe phases contributed to the strong release of As in the later stage. Consequently, both Mn and Fe phases played an important role on the behavior of Sb, and Fe phases played an important role on the behavior of As.

Reburial is a common practice for the treatment of mine wastes that contain high contents of Sb and As, but the reducing conditions after reburial may lead to the dissolution of Mn and Fe phases followed by a release of Sb and As. Our results showed that Sb release would occur first and that As release would get stronger with time. It is suggested that the potential influence of the metalloid release on groundwater would be a concern.

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