

Sorption of Sb(III) and Sb(V) to Goethite: Influence on Sb(III) Oxidation and Mobilization[†]

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Antimony is an element of growing interest for a variety of industrial applications, even though Sb compounds are classified as priority pollutants by the Environmental Protection Agency of the United States. Iron (Fe) hydroxides appear to be important sorbents for Sb in soils and sediments, but mineral surfaces can also catalyze oxidation processes and may thus mobilize Sb. The aim of this study was to investigate whether goethite immobilizes Sb by sorption or whether Sb(III) adsorbed on goethite is oxidized and then released. The sorption of both Sb(III) and Sb(V) on goethite was studied in 0.01 and 0.1 M KClO₄ M solutions as a function of pH and Sb concentration. To monitor oxidation processes Sb species were measured in solution and in the solid phase. The results show that both Sb(III) and Sb(V) form inner-sphere surface complexes at the goethite surface. Antimony(III) strongly adsorbs on goethite over a wide pH range (3–12), whereas maximum Sb(V) adsorption is found below pH 7. At higher ionic strength, the desorption of Sb(V) is shifted to lower pH values, most likely due to the formation of ion pairs K₂Sb(OH)₆^o. The sorption data of Sb(V) can be fitted by the modified triple-layer surface complexation model. Within 7 days, Sb(III) adsorbed on goethite is partly oxidized at pH 3, 5.9 and 9.7. The weak pH-dependence of the rate coefficients suggests that adsorbed Sb(III) is oxidized by O₂ and that the coordination of Sb(III) to the surface increases the electron density of the Sb atom, which enhances the oxidation process. At pH values below pH 7, the oxidation of Sb(III) did not mobilize Sb within 35 days, while 30% of adsorbed Sb(III) was released into the solution at pH 9.9 within the same time. The adsorption of Sb(III) on Fe hydroxides over a wide pH range may be a major pathway for the oxidation and release of Sb(V).

Introduction

Antimony (Sb) is consumed in large quantities (>100 000 tons annually worldwide) in a variety of industrial products, e.g., Sb(III) in flame retardants and elemental Sb in alloys for storage batteries and ammunition (1–3), although Sb and its compounds are considered as pollutants of priority interest (ref 4 and references therein).

Elevated concentrations of Sb in soils have been detected around mining and smelter areas, at shooting ranges, and along roadsides (dust from brake pads and tires) (4–6). However, very little is known about the mobility of Sb in the environment (4, 5). In oxic waters, Sb(V) predominates as Sb(OH)₆⁻ (4, 7), which forms oxides (Sb₂O₅) that are more soluble than oxides of Sb(III) (Sb₂O₃) (3). Antimony(III) occurs as Sb(OH)₃ in aqueous solutions and is more stable under anoxic conditions (7). Sorption processes to mineral phases may control the mobility of Sb.

Only very few sorption studies of Sb on natural sorbents have been reported to date ((8) and reference therein). Both Sb(III) and Sb(V) appear to bind strongly to hydroxides of Fe and Mn and only weakly to clay minerals (9). Extended X-ray adsorption fine structure (EXAFS) measurements of soils from shooting ranges provide evidence for a strong preference of Sb binding to Fe hydroxides (6). However, the binding mechanism is still unclear. According to the five studies dealing with Sb sorption to Fe hydroxides known to the authors, both surface coverage and pH have a strong influence on Sb(III) and Sb(V) sorption (9–13). The sorption maxima of Sb(V) on Fe hydroxides was generally reported at low pH values and extended up to pH 7 at low surface coverage (9–11, 13). Only a single study investigated the pH-dependence of Sb(III) adsorption on amorphous Fe hydroxides in the absence of organic ligands, namely tartrate and acetate, indicating that Sb(III) sorbs strongly in the pH range 6–10 (10). However, in that study a high Sb(III) concentration (41 μM) was used. In order to assess the binding potential of Fe hydroxides for Sb, both Sb(III) and Sb(V) sorption data at low Sb concentrations (<5 μM) over a wide pH range is needed but is not available in literature.

Mineral surfaces in aqueous systems not only bind metal ions, but can also accelerate redox reactions, such as the oxygenation of Fe(II), Mn(II), and VO²⁺ (14–16). The metal ions are bound to oxygen donor ligands of the surface in an inner-sphere coordination, which has a similar effect as hydrolysis for homogeneous reactions (17). Since the hydrolyzed species Sb(OH)₄⁻ is the reactive species for the Sb(III) oxidation by O₂ and H₂O₂ (18, 19), it could be expected that adsorption of Sb(III) on Fe hydroxides accelerates the oxidation of Sb(III). Indeed, there is one study, showing that Sb(III) is oxidized in the presence of amorphous Fe hydroxides in the pH range 5–10 with a pH-independent rate coefficient (20). This result indicates that adsorption may influence the Sb(III) oxidation rate, but it remains unknown whether Sb(V) is sorbed or released after oxidation.

The aim of the present study was to determine whether Fe hydroxides immobilize Sb by sorption or increase dissolved concentrations by oxidation to Sb(V). The sorption of low concentrations of Sb(III) and Sb(V) on goethite, a widespread and thermodynamically stable Fe hydroxide in natural soils, as a function of ionic strength and pH, was investigated. Oxidation processes of Sb(III) and the release of Sb(V) was monitored by distinguishing redox species in solution and the solid phase.

Experimental Section

Reagents and Materials. All chemicals were used as received and of at least analytical grade (pro analysi (p.a.), for details, see the Supporting Information).

Mineral Sorbent. Goethite was prepared as described elsewhere (21) (for details, see the Supporting Information).

Antimony Sorption Experiments. All experiments were carried out with a background electrolyte of 0.01 or 0.1 M KClO₄ (Fluka, puriss p.a.) at 25 °C and in light λ > 550 nm

[†] This article is part of the Emerging Contaminants Special Issue.

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to avoid photochemical reactions. All experiments were performed as triplicates in a glove box (Mecaplex) equipped with a CO₂-scrubber (pCO₂ < 2 ppm, DMP Ltd.) to avoid pH drifts around neutral conditions due to CO₂ uptake. Sorption of Sb(V) and Sb(III) on goethite was initiated by the addition of Sb(III) and Sb(V) stock solutions to solid suspensions at different pH values, adjusted with HClO₄ (Merck) or KOH (Merck, Titrisol). The final solid concentration was 0.5 g L⁻¹. Suspensions were shaken on a rotary shaker (125 rpm). Preliminary experiments showed that an equilibration time of 7 days is appropriate for Sb(V). A shorter equilibration time of 2 days for Sb(III) was chosen to minimize oxidation reactions of Sb(III). After the desired reaction time, suspensions were centrifuged and the supernatant filtered to 0.45 μm (Infochroma AG, nylon filter, Titan2). The pH value at the end of the experiment, measured in the filtrate, was reported. Samples for total Sb (Sb_{tot}) and Sb(III) determinations were stored in 3% HCl (Merck, Suprapur) and in 0.5 M disodium hydrogen citrate (Fluka, Ultra) at 4 °C prior to analysis. The amount of Sb sorbed to goethite was calculated by difference.

Sorption Isotherms on goethite were conducted to estimate the maximum sorption density. The experiments were performed at pH 3.0 for Sb(V) and at pH 4.0 for Sb(III), corresponding to the pH values of maximum sorption of the antimony species (Figure 1B, C). However, the final pH of the Sb(III) experiments with increasing Sb(III) concentrations decreased to pH 2.5 probably due to the acidic stock solution.

Oxidation of Sb(III) to Sb(V) in the presence of goethite was investigated at pH 3.0, pH 7.3, and pH 9.9 under oxic conditions. After filtration, pH, Sb(III), and total Sb were measured in solution. *Oxygen-free experiments* at pH 12 in the presence (duplicates) and absence (singles) of goethite were prepared and samples were taken under N₂ in an anaerobic chamber (Vacuum/Atmospheres Company). Glass bottles for batches were sealed in order to shake them outside of the glove box. The same experiments were carried out under oxic conditions to compare the results. The *desorption behavior* of Sb(V) was investigated at pH 9.9. Antimony(V) was first equilibrated with goethite at pH 6.9 for 7 days, after which the suspensions were centrifuged and the supernatant withdrawn. Then, a 0.01 M KClO₄ solution at pH 9.9 was added to the goethite and suspensions were again equilibrated up to 2 days.

Additional Sb(III) Oxidation in the presence of goethite (similar to oxidation experiments at pH 3.0, 7.3 and 9.9) were carried out in duplicate at pH 3.0, 5.9, and 9.7 under normal atmospheric conditions, after separating the supernatant from the solid by centrifugation. The remaining suspension of supernatant and goethite (5 mL) was dissolved in 25 mL of 0.2 M NH₄-oxalate buffer/0.1 M ascorbic acid solution at pH 3.25 and 96 °C within 30 min. Both solutions, the supernatant and the oxalate/ascorbic acid extract, were filtered and analyzed for Sb(III) and Sb_{tot}. Adsorbed concentrations of Sb are those that are measured in the extract minus the dissolved Sb concentrations in 5 mL. Preliminary experiments extracting Sb₂O₃, KSb(OH)₆, adsorbed Sb(III) and adsorbed Sb(V) on goethite have shown that goethite was completely dissolved and speciation of Sb(III) and Sb(V) remained during the extraction procedure (22). The pseudo-first-order rate coefficients were calculated as described elsewhere (18), and the errors are the twofold standard errors of the linear regressions.

Analysis. Antimony(III) and total Sb were selectively analyzed using a hydride generation atomic fluorescence spectrometer (Millenium Excalibur-System, PSA 10.055, PS Analytical Ltd) as described elsewhere (18). The pH of the solutions (±0.1 units) was measured using a pH meter (Metrohm 713) and a combined glass electrode (Metrohm 6.0222.100), which was calibrated with buffer solutions (Merck). The reproducibility of the adsorbed Sb concentration

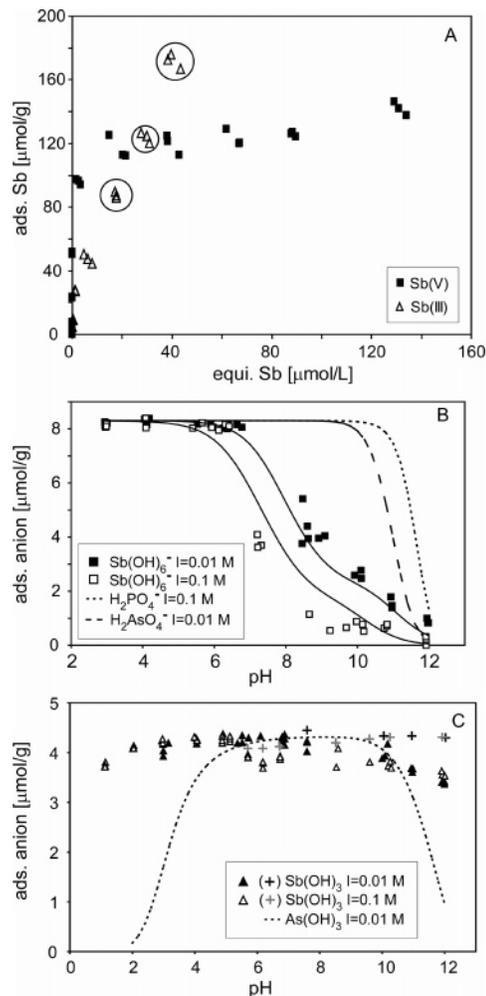


FIGURE 1. A: Sorption isotherms of Sb(III) (triangles) and Sb(V) (squares). Experimental conditions for Sb(V): [Sb(V)]₀ = 2–200 μM, 0.5 g/L goethite, I = 0.01 M pH 3.0 and for Sb(III): [Sb(III)]₀ = 2–127 μM, 0.5 g/L goethite, I = 0.1 M pH 4–3. For the data points in circles, initial Sb(III) concentrations were above the solubility product of Sb₂O₃ (7). **B, C: Sorption edges of Sb(V) (squares) and Sb(III) (triangles) on goethite at I = 0.01 M (solid symbols) and I = 0.1 M (open symbols).** Experimental conditions: [Sb(V)]₀ = 4.15 μM or [Sb(III)]₀ = 2.2 μM, 0.5 g/L goethite, 25 °C. Solid lines in B represent fits of the modified TLM model (Table S1). Dashed lines show predicted adsorbed phosphate, arsenate and arsenite concentrations for the same initial concentrations of anions and goethite calculated from refs 29 and 33. **C: crosses show corrections for Sb(III) oxidation.**

on goethite or in solution between triplicate or duplicate experiments was 8% on average.

Surface Complexation Model. The modified triple-layer model (TLM), which includes surface ion-pair formation with the background electrolyte ions, was used to describe the antimonate sorption edges (23). Constants for protonation of the surface hydroxyl groups and aqueous species were taken from the literature (Table S1). Surface complexes used for fitting sorption data are given in Table S1. The program Fit 2.5 was used to obtain the intrinsic Sb(V) surface complexation constant (24), while forward calculations were carried out with the chemical speciation program ECOSAT 4.7 (25). Solution speciation was taken into account, adopting stability constants from references (7, 26). The surface site density was set to 2.4 sites nm⁻², which was obtained from Sb(V) sorption isotherm experiments in this study. Activity coefficients of aqueous species were calculated using the Davies equation (27).

Results and Discussion

Sorption Isotherms on Goethite. The maximum sorption density for Sb(V) was $136 \pm 8 \mu\text{mol g}^{-1}$ or 2.4 sites nm^{-2} at pH 3 (Figure 1A). The isotherm follows a H-type curve, which indicates a strong affinity of Sb(V) for the goethite surface. This corresponds well with the edge-sharing surface complex for Sb(V), which was found by EXAFS measurements for the same goethite (6). Edge linkage sites are considered to be high-energy sites, which are preferentially occupied at low surface coverage (28).

The Sb(III) isotherm is linear for low surface coverage (Figure 1A). No maximum sorption density can be determined since precipitation of Sb_2O_3 occurs at initial Sb(III) concentrations above $63 \mu\text{M}$ (7).

Maximum sorption density for Sb(V) on goethite was similar to values of 2.4 and 2 sites nm^{-2} reported for sorption densities of Sb(V) on goethite and hematite, respectively, at pH 7 (9). Blay (2000) also found a linear sorption isotherm for Sb(III) for initial concentrations below $25 \mu\text{M}$ (9).

For both As(V) and As(III), similar maximum sorption site densities on goethite of 2.0 sites nm^{-2} were found (29).

Antimonate Sorption Edge on Goethite. Between pH 3 and 6, the sorption of Sb(V) was above 96% at both ionic strengths (0.01 and 0.1 M, Figure 1B). Adsorption of Sb(V) decreased at pH values of 6.8 and 6.1 at an ionic strength of 0.01 and 0.1 M, respectively. EXAFS spectra of adsorbed Sb(V) on goethite, which we prepared similarly to the batch experiments (pH 3.5), showed that a Sb(V) octahedron ($\text{Sb}(\text{OH})_6^-$) shares an edge with an $\text{Fe}(\text{OH})_6$ octahedron and forms an edge-sharing inner-sphere sorption complex at the goethite surface (6). Above pH 6, the influence of ionic strength on the sorption of Sb(V) was strong and resulted in a lower adsorption of Sb(V) at higher ionic strength. This trend could not be predicted by the modified TLM using either outer-sphere surface complexes alone or a combination of inner-sphere and outer-sphere surface complexes. The opposite effect would be expected if an outer-sphere surface complex was involved: Increasing the ionic strength decreases the negative charge of the surface at higher pH values and adsorption increases at higher ionic strength as it has been observed for phosphate (30). However, the influence of ionic strength on Sb(V) adsorption can be modeled if an inner-sphere surface complex and the formation of ion pairs of $\text{KSb}(\text{OH})_6^\circ$ in solution is assumed. The $\text{KSb}(\text{OH})_6^\circ$ ion pairs reduce the activity of $\text{Sb}(\text{OH})_6^-$ in solution and thus adsorption is decreased at higher ionic strength. Formation of ion pairs for Sb(V) has not been reported so far to the authors' knowledge. However, ion pairs between K^+ or Na^+ and other anions, such as acetate or the halides do exist, though they are quite weak ($\log K \approx -0.2$ to -0.5 (31)).

A simultaneous fit of the surface complexation constant of Sb(V) (K_{adsSb}) and the stability constant of $\text{KSb}(\text{OH})_6^\circ$ ($K_{\text{KSb}(\text{OH})_6^\circ}$) for both ionic strengths yielded a $\log K_{\text{adsSb}}$ of 6.7 and a questionably high value for $\log K_{\text{KSb}(\text{OH})_6^\circ}$ of 3.7 (data not shown). According to Stumm and Morgan, estimated $\log K$ values for stability constants of ion pairs, based on Coulombic interactions between the ions, are expected to be in the range of 0–1 at $I = 0$ M for ion pairs with opposite charge of 1 (27). Therefore, the surface complexation constant was estimated in a fit for the data of both ionic strength with a fixed value of 1 for $\log K_{\text{KSb}(\text{OH})_6^\circ}$. This results in a lower $\log K_{\text{adsSb}}$ value of 4.77. The trend of less adsorption of Sb(V) at higher ionic strength is visible, however the effect is less marked and does not fit our data (Figure S1). Assuming a fixed value of 2 for $\log K_{\text{KSb}(\text{OH})_6^\circ}$ and a fit for the data of both ionic strength yield a log value of 5.21 for $\log K_{\text{adsSb}}$ (Table S1, Figure 1B). With this data set, the influence of ionic strength on Sb(V) sorption is better reproduced than with the lower stability constant of $\text{KSb}(\text{OH})_6^\circ$. This indicates that

in our experiments ion pairs for Sb may have a strong influence and decrease the adsorption of Sb. The complexation constant is higher than is usual for monovalent species (see above) but then it must be noted that Na and K antimonates are relatively insoluble compared to other alkali salts (32).

A similar pH-dependence of Sb(V) adsorption on goethite was shown with higher initial Sb(V) concentrations (10–400 μM) and NaNO_3 as background electrolyte (10), though with increasing Sb(V) concentration, adsorption decreased and shifted to lower pH values. The best fits for all data, using the modified TLM, were obtained assuming a combination of an outer-sphere ($\text{FeOH}_2^+ \text{-Sb}(\text{OH})_6^-$) and an inner-sphere surface complex ($\text{Fe-OSb}(\text{OH})_5^-$) for Sb(V) sorption. However, for the lowest Sb(V) concentration, which corresponds to an Fe:Sb ratio similar to the one in this study, the inner-sphere surface complex, with a log value of the surface complexation constant of 6, was sufficient to predict the data. No significant influence of ionic strength was observed in the range between 0.001 and 0.01 M NaNO_3 , which would be in agreement with our model. A similar pH dependence for Sb(V) adsorption on hematite has also been reported in the pH range between 2 and 10 at 50 °C in 0.25 M LiCl solution (11). No pH-dependence of Sb(V) sorption was observed at higher initial Sb(V) concentration (200 μM) and a lower goethite concentration (0.125 g L^{-1}) in the pH range of 2–10 (9). However, at this high surface coverage either surface precipitation or polymerization of Sb(V) may occur (7).

Antimonate, phosphate, and arsenate are all reported to be bound inner-spherically to the goethite surface (ref 28 and references therein). However, the adsorption of arsenate and phosphate on goethite is less pH-dependent and maximum sorption occurs over a wide pH range of 3–10 (Figure 1B, (29, 33)). The stronger adsorption of phosphate and arsenate over a wider pH-range could be ascribed to the fact that phosphoric acid and arsenic acid are triprotic acids with high $\text{p}K_a$ values for the second and third deprotonation reaction, whereas antimonate is a monoprotic acid (7). The main mechanism for inner-spherically-bound anion is ligand exchange. The surface hydroxyl is exchanged by a ligand of the anion and the formation of surface complexes is favored by lower pH values due to protonation of surface hydroxyl groups (27). Since arsenate and phosphate occur as HAsO_4^{2-} and HPO_4^{2-} at pH values greater than 7, surface hydroxyl groups could still be protonated by the third proton of arsenate and phosphate, permitting ligand exchange to take place. Antimonate is deprotonated at pH values above 2.7 (7), and thus favors protonated surface groups for adsorption.

Antimonite Sorption Edge on Goethite. The pH-dependence of Sb(III) sorption was weaker than that of Sb(V) sorption, and >80% of Sb(III) was adsorbed between pH 1 and 12 (Figure 1C). At low pH values, adsorption of Sb(III) decreased with increasing concentrations of $\text{Sb}(\text{OH})_2^+$ (Table S1), whereas at pH values above 6, adsorption of Sb(III) decreased due to Sb(III) oxidation and desorption of Sb(V). The Sb(III) adsorption was corrected by the released Sb(V) concentrations in solution indicating that Sb(III) sorption is strong over a wide pH range under anoxic conditions (Figure 1C crosses). Ionic strength has no influence on Sb(III) sorption over the whole pH range, indicating that Sb(III) forms inner-sphere surface complexes at the surface (e.g., ref 23). According to EXAFS spectra, Sb(III) forms a bidentate, corner-sharing inner-sphere complex at the goethite surface (6). Since there is no significant decrease in adsorption over the whole pH range, it is difficult to estimate the surface complexation constants by modeling.

A similar pH-independence of Sb(III) adsorption on amorphous Fe hydroxides was observed in the pH range 6–10 for short equilibration times (10). Arsenite also forms binuclear inner-sphere surface complexes at the goethite

surface. However, if the sorption of antimonite and arsenite are compared for the same initial concentrations of anion and goethite, the binding of the former is strong over the whole pH range, while the arsenite is estimated to have a maximum sorption between pH 4 and 10 (Figure 1C (29)). Antimonite is a stronger Lewis base than arsenite. The surface sites can be considered as Lewis acids, which explains the stronger binding of Sb(III) over the whole pH range. Arsenite adsorption increases with increasing pH and increased concentration of $\text{As}(\text{OH})_4^-$, which is a stronger Lewis base than $\text{As}(\text{OH})_3$. In analogy, $\text{As}(\text{III})$ binds more weakly to humic acids than $\text{Sb}(\text{III})$ (34, 35), where binding sites are also oxygen bridges of carboxylic or phenolic functional groups (35).

Influence of O_2 on Oxidation of Adsorbed $\text{Sb}(\text{III})$ at pH 12. At pH 12 oxidized Sb should be released according to the sorption experiments (Figure 1B). Within 23 days, 26% of total Sb was released in the absence of measurable O_2 (<1 mg/L), while 58% was released in the presence of approximately 6.6 mg/L O_2 (Figure 2A). At 23 days, the fraction of $\text{Sb}(\text{III})$ in solution was smaller than 1% in the presence of O_2 , while $\text{Sb}(\text{III})$ concentrations varied in the duplicates between 9 and 39% in the absence of measurable O_2 . The results indicate that the oxidation of adsorbed $\text{Sb}(\text{III})$ on goethite at pH 12 was faster in the presence of O_2 . The question arises as to why $\text{Sb}(\text{III})$ is oxidized in the absence of measurable oxygen since $\text{Fe}(\text{III})$ as $\alpha\text{-FeOOH}$ has a lower redox potential than $\text{Sb}(\text{III})$ as $\text{Sb}(\text{OH})_4^-$ at pH 12 and no other oxidant is present in the system. The only explanations are that either traces of O_2 diffused into the bottles for the experiments without O_2 or O_2 was sorbed to the surface particles and are responsible for the $\text{Sb}(\text{III})$ oxidation in the presence of goethite.

Without goethite and O_2 , $\text{Sb}(\text{III})$ remained constant for 23 days (data not shown). In the presence of O_2 , the oxidation rate for dissolved $\text{Sb}(\text{III})$ was similar to that of adsorbed $\text{Sb}(\text{III})$ (18). Either $\text{Sb}(\text{III})$ is oxidized in solution and released from the surface by re-equilibration, or, and this is probable, the environment around the $\text{Sb}(\text{III})$ atom in solution at pH 12 is similar to that of $\text{Sb}(\text{III})$ adsorbed to goethite. The similarity could be the result of an increased electron density on the Sb atom, derived from additional electron-donor ligands, either as a result of hydrolysis or specific binding to surface oxide ions (27).

Influence of Adsorption on $\text{Sb}(\text{III})$ Oxidation in the pH range 3–10. The concentrations of adsorbed $\text{Sb}(\text{III})$ on goethite remained constant for 35 days at pH 3.0 and 7.3 (Figure 2B). During this time period, no significant amount of $\text{Sb}(\text{V})$ (<0.2%) was measured in solution at these pH values. At pH 9.9, adsorption of Sb decreased by 30% within 7 days and remained constant thereafter. After 1 day, 77% of the dissolved Sb was $\text{Sb}(\text{V})$, and after 2 days, no significant amounts of $\text{Sb}(\text{III})$ were measured in solution. This indicates that adsorbed $\text{Sb}(\text{III})$ on goethite was oxidized at pH 9.9 and that $\text{Sb}(\text{V})$ was then released into solution. At pH 3.0 and 7.3, either no $\text{Sb}(\text{III})$ oxidation had occurred within 35 days or the $\text{Sb}(\text{V})$ was still adsorbed on the surface and could not be measured.

The desorption experiment at pH 9.9 shows that within 7 h 22% of $\text{Sb}(\text{V})$ was released into solution, but subsequently desorption began to slow down, and within 2 days, only 34% of adsorbed $\text{Sb}(\text{V})$ had been released (Figure 2C). Applying these observations to the oxidation experiments, it becomes clear that measuring species in solution only does not give a complete picture.

Additional oxidation experiments, in which goethite was dissolved in oxalate–ascorbic solution after filtration, showed that $\text{Sb}(\text{V})$ was found in the solid phase at pH 3.0 and 5.9 (Figure 3). The amount of total $\text{Sb}(\text{V})$ appears to be pH-dependent: 35, 50, and 90% of $\text{Sb}(\text{III})$ were oxidized within 7 days at pH 3, 5.9, and 9.7, respectively. After 7 days no

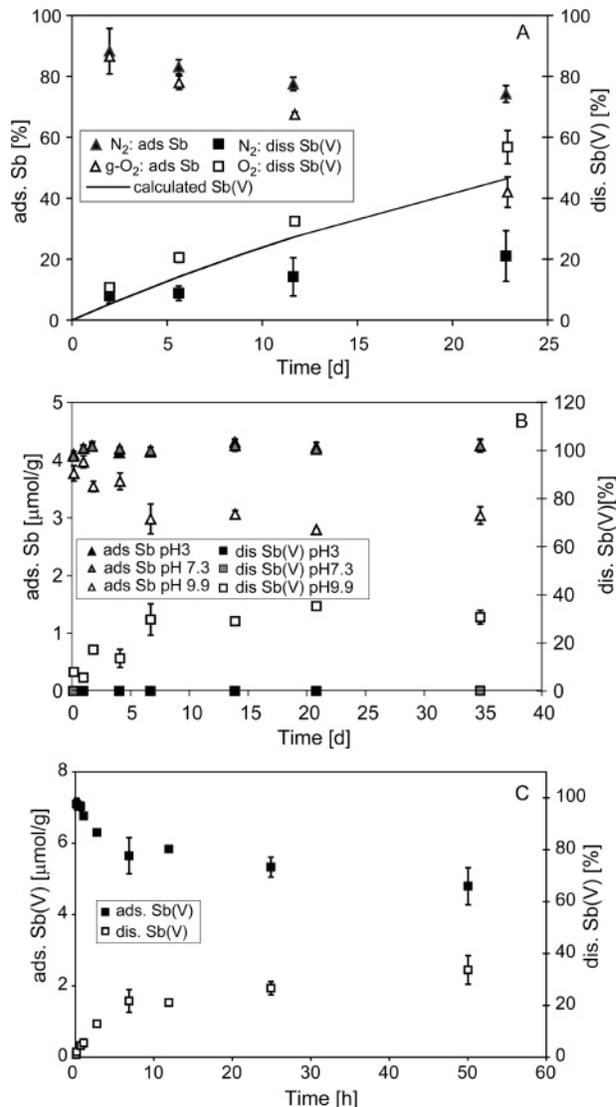


FIGURE 2. A: Oxidation of adsorbed $\text{Sb}(\text{III})$ on goethite ($[\text{Sb}(\text{III})]_0 = 2.3 \mu\text{M}$) at pH 12.0 in the presence (O_2) and absence (N_2) of measurable oxygen. Homogeneous oxidation of $\text{Sb}(\text{III})$ at pH 12, calculated from ref 18 is represented by the line. **B:** Adsorption of $\text{Sb}(\text{III})$ on goethite as a function of time in the pH range 3–10. Initial Sb concentration was $2.2 \mu\text{M}$ and 0.5 g/L goethite at 25°C and $I = 0.01 \text{ M KClO}_4$. **C:** Desorption of $\text{Sb}(\text{V})$ at pH 9.9: $4.2 \mu\text{M}$ of $\text{Sb}(\text{V})$ was adsorbed at pH 7 and then goethite was equilibrated at pH 9.9 in 0.01 M KClO_4 at 25°C . Error bars are the standard deviation of duplicates or triplicates and within the symbols of some data points.

significant amount of $\text{Sb}(\text{III})$ was further oxidized. This could be explained if only a small percentage of the goethite surface sites were available for $\text{Sb}(\text{III})$ oxidation. At pH 9.7, $\text{Sb}(\text{V})$ desorption occurs and reaction sites can be recycled, whereas sites remain occupied at pH 3 and 5.9 due to strong adsorption of $\text{Sb}(\text{V})$. The pseudo-first-order rate coefficients for the total $\text{Sb}(\text{III})$ oxidation were 0.9×10^{-6} ($\pm 0.1 \times 10^{-6}$), 1.2×10^{-6} ($\pm 0.2 \times 10^{-6}$) and 5×10^{-6} ($\pm 0.7 \times 10^{-6}$) s^{-1} at pH 3.0, 5.9 and 9.7, respectively. If $\text{Fe}(\text{III})$ were the oxidant, a different relationship between pH and the oxidation rate coefficients would be expected, since $\text{Fe}(\text{III})$ has a higher redox potential than $\text{Sb}(\text{III})$ only below pH 7.5 and would only be able to oxidize $\text{Sb}(\text{III})$ in acidic solutions. Instead, the weak pH-dependence of the rate coefficients could be related to the fact that the environment around the $\text{Sb}(\text{III})$ atom when sorbed to goethite does not vary strongly with pH.

Similar experiments were carried out with adsorbed $\text{Sb}(\text{III})$ on amorphous $\text{Fe}(\text{III})$ hydroxides at an $\text{Fe}:\text{Sb}$ ratio of

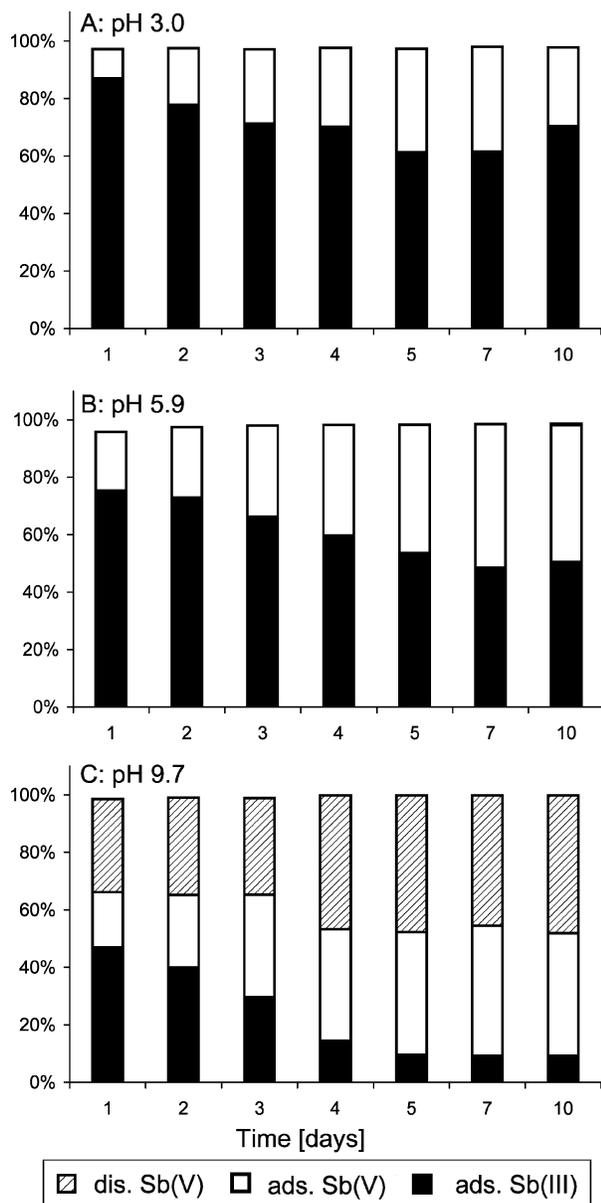


FIGURE 3. A–C: Distribution of adsorbed Sb(III), adsorbed Sb(V) and dissolved Sb(V) as a function of time during oxidation. Experimental conditions: $[Sb(III)]_0 = 2.2 \mu M$, 0.5 g/L goethite at 25 °C and $I = 0.01 M KClO_4$. Dissolved Sb(III) concentrations were <5% of the total Sb concentration and are not shown.

4500:1 in the pH range 5–10 (20). Antimony(III) was completely oxidized (>96%) within 5 days and a pH-independent pseudo-first-order rate coefficient of $1 \times 10^{-5} (\pm 0.2 \times 10^{-5}) s^{-1}$ was found. The rate coefficients were approximately 4 times larger than in this study, probably due to a larger surface area for amorphous Fe hydroxides.

For As(III), the oxidation of adsorbed As(III) on Fe hydroxides, ferrihydrite and goethite was also observed (36–38). Between 50 and 75% of adsorbed As(III) on amorphous Fe hydroxides were oxidized at a rate independent of pH in the pH range 4.7–10.2 within 2 days at an Fe:As ratio of 3400:1 (36). At an Fe:As ratio of 75:1, 10–20% of adsorbed As(III) on goethite was oxidized at pH 5 within 4 days (38).

For As(III) oxidation processes in the presence of Fe hydroxides, the effect of preparation of Fe hydroxides from Fe(II) or Fe(III) salts is discussed in the literature (36, 39). The experiments of the present study show clearly that Sb(III) is also oxidized in the presence of goethite, which is

prepared from Fe(III) salts, and thus does not contain traces of Fe(II). However, compared to the oxidation rate coefficients in the presence of Fe(II), the oxidation rate coefficients are approximately 6 and 8000 times slower at pH 5 and 7, respectively (40).

Environmental Significance. Analyses of Sb in aquatic systems have usually shown that Sb(V) predominates and Sb(III) is only found at low concentrations under oxic conditions (4). The reason for this may be that Sb(III) sorbs strongly to Fe hydroxides, as this and the other study (10) show, but that this also results in oxidation and release, particularly in calcareous soils and water. It is possible that this contributes to Sb(III) concentrations being very low in oxidizing environmental compartments. There is evidence to support this. Antimony speciation in shooting range soils by EXAFS spectroscopy showed that Sb(III) compounds were not prevalent and only elemental Sb from the bullets and Sb(V) associated to Fe hydroxides, occur. The EXAFS spectra of the Sb(V) species were similar to the spectra of adsorbed Sb(V) on goethite (6). Investigations of soils, contaminated by Sb and Sb_2O_3 smelter emissions also found that Sb(V) is the predominant species and that oxidation processes must occur in the soil environment (41).

Acknowledgments

We thank the Swiss National Science Foundation for funding and R. Kretzschmar and I. Christl for their advice and support in modeling the surface complexation constants.

Note Added after ASAP Publication

There was an error in the Antimonate Sorption Edge on Goethite section in the Results and Discussion due to a production error in the version posted ASAP on August 30, 2006; the corrected version was published ASAP on October 18, 2006.

Supporting Information Available

Details of the reagent and materials, the mineral sorbent, aqueous and intrinsic Surface complexation constants (Table S1), and sorption edges of Sb(V) on goethite with the fits of the modified TLM model with $\log K K_{Sb(OH)_6} = 1$ and $\log K_{ads,Sb} = 4.8$ (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review May 29, 2006. Revised manuscript received August 2, 2006. Accepted August 2, 2006.

ES061284B