

Redox reactions of antimony in the aquatic and terrestrial environment

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Zusammenfassung

Antimon (Sb) ist ein toxisches Element mit ähnlichen chemischen Eigenschaften wie Arsen. Der Einsatz von Sb in industriellen Produkten, insbesondere in Flamm- schutzmitteln und als Additiv in Bleilegierungen, z.B. in Batterien und Munition ge- winnt zunehmend an Bedeutung. In der Umwelt kommt Sb in den zwei Oxida- tionszuständen Sb(III) und Sb(V) vor. In aquatischen Systemen ist Sb(V) die vorherrschende Spezies, welche als Hydroxidkomplex $\text{Sb}(\text{OH})_6^-$ vorliegt. Nur ein kleiner Teil des gelösten Sb liegt im dreiwertigen Zustand als neutraler Hydroxidkomplex $\text{Sb}(\text{OH})_3$ vor. Es wird vermutet, dass die Löslichkeit von Sb(III) entweder durch die Sorption an Fe-, Mn- und Al-Oxiden oder durch die Ausfällung als Oxid stärker als für Sb(V) kontrolliert wird. Daher kann Sb durch Oxidationsprozesse in der Umwelt mobilisiert werden. Ein besseres Verständnis der Bedingungen, unter welchen Sb oxidiert, ist daher notwendig um potentielle Risiken für Mensch und Umwelt beurteilen zu können.

Ziel dieser Arbeit war es, die Reaktionsbedingungen und -kinetiken der Oxidation von Sb(III) zu Sb(V) mit natürlichen Oxidationsmitteln zu bestimmen. Der Einfluss von Eisenhydroxiden auf die Mobilität von Sb wurde untersucht, da diese sowohl als Sorptionsmittel als auch als Oxidationsmittel für Sb wirken können. Extraktions- methoden für Böden wurden an verschiedenen Sb Verbindungen sowie kontaminierten Böden getestet, um eine Methode zu entwickeln, die gleichzeitig Informationen über den Oxidationszustand und die Bindungsart von Sb im Boden liefert.

Die Sb(III) Oxidation mit O_2 war sehr langsam und konnte nur in alkalischen Lö- sungen gemessen werden. Bei pH 10.9 wurde eine Halbwertszeit von 230 Tagen und bei pH 12.9 von 3 Tagen bestimmt. Für umweltrelevante Bedingungen (pH 8.5) erhält man durch Extrapolation eine Halbwertszeit von 170 Jahren.

H_2O_2 ist ein stärkeres Oxidationsmittel als O_2 , welches bei der Reduktion von O_2 entsteht. Die Ratenkoeffizienten für die Sb(III) Oxidation mit H_2O_2 nahmen mit sin- kender H^+ Konzentration im pH Bereich von 8.1 bis 11.7 zu. Oberhalb von pH 11.7 waren die Ratenkoeffizienten pH unabhängig. In Oberflächengewässern bei pH 8 wur- den Halbwertszeiten von 117 Tagen für eine 10^{-6} M und 32 Jahren für 10^{-8} M H_2O_2 Konzentration berechnet.

Während der Reaktion von Fe(II) mit O_2 werden reaktive Zwischenprodukte, wie z.B. $\text{O}_2^{\cdot-}$, H_2O_2 und Fe(IV) gebildet, welche Sb(III) sehr schnell bei neutralen pH- Werten oxidierten. In der Gegenwart von Fe(II) folgten die Ratenkoeffizienten für die Sb(III) Oxidation dem gleichen Trend wie jene der Fe(II) Oxidation und nahmen mit steigendem pH zu. Die Halbwertszeiten für Sb(III) betrugen 35 Stunden bei pH 5 und 1.4 Stunden bei pH 6.2. In der Gegenwart von Fe(II)+ H_2O_2 wurde Sb(III) bei pH 3 7000 mal und bei pH 7 20 mal schneller oxidiert als mit Fe(II)+ O_2 . Experimente mit 2-

Propanol haben gezeigt, dass bei tiefen pH-Werten $\cdot\text{OH}$ -Radikale an der Sb Oxidation beteiligt sind. Bei neutralen pH-Werten ist ein anderes Zwischenprodukt, möglicherweise Fe(IV), an der Sb(III) Oxidation beteiligt.

Anhand von Adsorptionsexperimenten an Goethit mit Sb(III) und Sb(V) wurde untersucht, ob Sb an Eisenhydroxide gebunden oder oxidiert und dann freigesetzt wird. Beide Sb Spezies bilden innersphärische Komplexe an der Goethitoberfläche. Während Sb(V) an Goethit nur unterhalb von pH 7 stark adsorbierte, band Sb(III) an Goethit über den ganzen pH-Bereich von 3-12. Eine schwache Desorption (<15%), die durch die Oxidation von Sb(III) zu Sb(V) verursacht wurde, konnte oberhalb von pH 7 in den Adsorptionsexperimenten mit Sb(III) gemessen werden. Zeitreihen bei verschiedenen pH-Werten (3, 5.9 und 9.7) zeigten, dass mindesten 38% vom adsorbierten Sb(III) innerhalb von 7 Tagen oxidierte. Die Oxidationsratenkoeffizienten waren pH-unabhängig, die Menge an gebildetem Sb(V) nahm jedoch mit steigendem pH zu. Durch die Oxidation wurden >30% der totalen Sb Konzentration bei pH 9.7 freigesetzt, während bei den beiden tieferen pH-Werten keine Freisetzung von Sb(V) festgestellt wurde. Die Abhängigkeit der Sb(III) Oxidation von der Desorption weist daraufhin, dass nur ein kleiner Anteil der Oberfläche bezüglich der Sb(III) Oxidation reaktiv ist.

Die Extraktionsmittel Wasser, Oxalat und Oxalat-Ascorbinsäure wurden an elementarem Sb, Sb_2O_3 , $\text{KSb}(\text{OH})_6$ und Goethit, an dem Sb(III) oder Sb(V) adsorbiert war, sowie an Bodenproben von Schiessanlagen getestet. Extraktionen von Bodenproben mit Wasser zeigten, dass ein Wasser zu Festphasenverhältnis von 100:1 geeignet war, um eine Sättigung bezüglich Sb zu vermeiden. Der wasserlösliche Anteil in den Bodenproben betrug bis zu 15% des totalen Sb Gehaltes. Die Oxalatextraktion erwies sich als nicht geeignete Methode zur Bestimmung von gebundenem Sb an amorphen Eisenhydroxiden, da Oxalat elementares Sb oxidierte und Sb von kristallinen Eisenhydroxiden desorbierte. Dagegen konnte die Oxalat-Ascorbinsäure Extraktion zur Bestimmung von gebundenem Sb an amorphen und kristallinen Eisenhydroxiden verwendet werden. Zusätzlich blieb die Spezierung von Sb(III) und Sb(V) während der Extraktion erhalten. Gemäss dieser Extraktion sind über 75% des totalen Sb Gehaltes in kontaminierten Böden gebunden an Eisenhydroxiden.

Diese Arbeit zeigt, dass Sb(III) in Oberflächengewässern wahrscheinlich mit H_2O_2 oder $\text{Fe}(\text{II})+\text{H}_2\text{O}_2$ oxidiert wird. In oxischen Böden und Sedimenten führt hauptsächlich die Adsorption von Sb an Eisenhydroxiden zur Oxidation. Die Reaktion mit $\text{Fe}(\text{II})$ und O_2 ist an Grenzschichten zwischen aeroben und anaeroben Bedingungen von Bedeutung. Aus diesen Ergebnissen wird geschlossen, dass Sb(III) in der Umwelt leicht oxidiert. Dies erklärt warum Sb(V) die dominante Spezies in Gewässern und Böden ist. Zukünftige Studien zu Sb Kontaminationen könnten sich daher schwerpunktmässig mit der Geochemie von Sb(V) befassen.

Summary

Antimony is an element widely used in industrial products. The main applications are in flame retardant formulations and in lead alloys for lead-acid batteries and ammunition. Very little is known about its toxicity and geochemistry but it is assumed to have a similar behavior to Arsenic (As). In the aquatic environment, the oxidation states Sb(III) and Sb(V) commonly occur. Under oxic conditions, the more soluble species Sb(V) predominates and is present as Sb(OH)_6^- . It appears that Sb(III) has a stronger affinity for Al, Mn and Fe (hydr)oxides and that its oxide (Sb_2O_3) is less soluble than that of Sb(V). This indicates that oxidation processes may lead to the mobilization of Sb in the environment and that an understanding of Sb(III) oxidation reactions is important in order to assess the risk posed to humans and the environment.

The main aim of this thesis was to investigate whether and how quickly Sb(III) is oxidized by naturally-occurring oxidants. The potential of Fe (hydr)oxides to immobilize Sb due to sorption or to mobilize it by oxidation was the main focus. To assess the binding of Sb and its oxidation state in soils, common extraction methods were tested on different Sb compounds and applied to contaminated soil samples.

The oxidation of Sb(III) by O_2 was very slow and only occurred in alkaline solutions. Half-lives ranged from 230 days to 3 days at pH values between 10.9 and 12.9. For environmentally relevant conditions (pH 8.5), the half-life was extrapolated to 170 years.

A more powerful oxidant for Sb(III) is H_2O_2 , which is produced by reduction of O_2 . The pseudo-first-order rate coefficients of Sb(III) oxidation by H_2O_2 increased inversely proportional to the H^+ concentration in a pH-range of 8.1 to 11.7. Above pH 11.7 no pH-dependence was observed. In sunlit surface waters, estimated half-lives vary from 32 years to 117 days at pH 8 for H_2O_2 concentrations of 10^{-8} and 10^{-6} M, respectively.

During the oxidation of Fe(II) by O_2 , Sb(III) was quickly oxidized by reactive intermediates at neutral pH values. The pseudo-first-order rate coefficients increased with increasing pH and followed a similar pH trend as those of the Fe(II) oxidation reaction. Half-lives of Sb(III) were 35 and 1.4 h at pH 5.0 and pH 6.2, respectively. The Sb(III) oxidation in the presence of Fe(II) and H_2O_2 (Fenton reaction) was about 7000 and 20 times faster at pH 3 and 7 than in the presence of Fe(II) and O_2 . Experiments with 2-propanol showed that $\cdot\text{OH}$ radicals were involved in the Sb(III) oxidation at low pH values and other intermediates, possibly Fe(IV), were more important at neutral pH values.

Whether Sb(III) and Sb(V) are sorbed and immobilized on Fe (hydr)oxides, or whether Sb(III) is oxidized and released, was investigated in the presence of goethite. Antimony(V) was strongly adsorbed on goethite in the pH range 3 -7, while desorption

occurred above pH 7. In contrast, Sb(III) strongly sorbed to goethite over a wide pH range 3-12. Weak desorption of Sb (<15%) above pH 7 was the result of Sb(III) oxidation and subsequent release of Sb(V). Time series showed that adsorbed Sb(III) was partly oxidized with weakly pH-independent rate coefficients at pH 3.0, 5.9 and 9.7, respectively. At these pH values, 35, 50 and 90%, respectively, of Sb(III) was oxidized within 7 days. Below pH 7.3, no desorption of Sb occurred within 35 days, whereas 30% of total Sb was released into the solution at pH 9.9. More Sb(III) was oxidized when desorption occurred, indicating that only a small percentage of the goethite surface is reactive with respect to Sb(III) oxidation.

The extraction agents water, oxalate and oxalate/ ascorbic acid were evaluated with elemental Sb, Sb_2O_3 , $\text{KSb}(\text{OH})_6$, goethite with adsorbed Sb(III) or Sb(V) and with soils, contaminated by Sb due to ammunition. A water to solid ratio of 100:1 was found to be appropriate to avoid saturation effects during extraction. The mobile fraction of Sb in soils ranged between 3 and 15%. Since elemental Sb was completely extracted by oxalate due to oxidation of Sb(0) to Sb(III), and Sb(III) and Sb(V) were desorbed from goethite during oxalate extraction, oxalate extractions proved inadequate to determine the Sb fraction associated with amorphous Fe oxides. The oxalate-ascorbic acid extraction was found to be a reasonable method to determine the fraction of Sb bound to amorphous and crystalline Fe (hydr)oxides. In addition, the speciation of Sb remained unaltered during this extraction procedure. According to oxalate-ascorbic acid extraction a large fraction of total Sb (>75%) was associated to amorphous and crystalline Fe oxides in soils from shooting ranges.

In conclusion, it is probable that Sb(III) oxidation by both H_2O_2 and the Fenton reaction occurs in sunlit surface waters. In soils and sediments, Fe oxidizes Sb(III) irrespectively of the oxidation state of Fe. In oxic soils, Sb(III) adsorbed on Fe (hydr)oxides is oxidized, whereas at the oxic-anoxic interface the Fe(II) oxidation occurs and co-oxidizes Sb(III). The results indicate that Sb(III) is susceptible to oxidation in most environmental compartments and thus provide an explanation as to why such low Sb(III) concentrations are found in water and soils. Future studies on geochemical properties of Sb with regard to contamination will therefore need to focus on Sb(V).

Chapter 1

Introduction

1.1 INTRODUCTION

Antimony (Sb) is coming into use in ever increasing quantities in a variety of industrial products. In total, 140'000 t were mined worldwide in 2001. In that year, Sb was the 9th most consumed metal after Fe, Al, Cu, Pb, Zn, Cr, Ni and Sn in the United States (1). Approximately 60% of Sb, as Sb₂O₃, is used as a synergist in combination with halogenated hydrocarbons in flame retardant formulations for plastics and textiles (1). Therefore, different products such as electric wire insulation, computer cabinets, telephone cases and interiors of planes and cars contain 2-6 wt% of Sb (2). Other important applications for Sb(III) compounds are in brake pads, lubricants or as a catalyst in plastics (e.g. PET bottles) (3). Large quantities of elemental Sb are used in lead-alloys for acid-lead batteries, accumulators and ammunition to increase the strength and inhibit corrosion. In rubber products, such as in car tires, Sb₂S₅ is employed as a vulcanizing agent (1, 4, 5).

In Switzerland, the major emission pathways of Sb to the environment are via shooting practice (~16.5 t in 2001) at shooting ranges and via the abrasion of car brake pads and tires along road sides (18 t in 2001) (3). Another possible source of groundwater contamination is leaching from landfill ashes, which are enriched in Sb (6). This source will gain importance with increasing Sb concentration in consumer products.

Antimony compounds are classified as priority pollutants by the European Union (7, 8) and the Environmental Protection Agency of the United States (9). The World Health Organization has set a provisional drinking water guideline of 5 µg/L for Sb (10). It is assumed that the toxicity of Sb is similar to that of As, i.e. Sb(III) compounds are approximately 10 times more toxic than Sb(V) compounds (5, 11). There is evidence that Sb₂O₃ is genotoxic and possibly carcinogenic (10, 11). Yet very little is known about the ecotoxicity of Sb. In

order to be able to assess the risk posed to humans and the environment, the geochemical behavior of Sb must be better understood.

1.1.1 Antimony species in the aquatic environment

Typical background concentrations of Sb in natural waters are in the range of 0.03-10 ng/L in freshwaters, 10-300 ng/L in estuarine waters and 120-430 ng/L in seawater (12-18). Elevated Sb concentrations of a few $\mu\text{g/L}$ were measured in waters close to industrial or mining areas ((13) and references therein). High natural Sb concentrations are found in geothermal waters, where concentrations of up to 1.5 mg/L can occur (19).

The prevalent oxidation states of Sb in the environment are Sb(III) and Sb(V). Generally, more than 90% of the total dissolved Sb concentration is Sb(V) in the oxic aquatic environment and occurs as $\text{Sb}(\text{OH})_6^-$ above pH 2.7 (13, 20). Antimony(III) is present either as a neutral hydroxo complex, $\text{Sb}(\text{OH})_3$, or as methylated species in natural waters (12, 13, 16, 17, 20-22). Concentrations of methylated Sb(III) species are smaller than 1% of the total dissolved Sb(III) concentration.

Very little is known about other dissolved Sb complexes in the environment. There is evidence that Sb(III) favors complexation with humic acids (23, 24) and it is estimated that approximately 30% of dissolved Sb(III) is bound to humics under environmental conditions (23). A few classical studies have shown that Sb(III) forms complexes with oxalic acid, ethylenediamine tetraacetic acid (EDTA) and organic ligands containing thiol groups (25, 26). Inorganic complexes of Sb(III) are formed with sulphides and chlorides, which are stable only under alkaline and acidic conditions, respectively (19, 27). Antimony(V) may also form weak complexes with chlorides and sulphides, but it appears that Sb(V) is more commonly found as hydroxo complex $\text{Sb}(\text{OH})_6^-$.

The low concentrations of Sb(III) and the high percentage of dissolved Sb(V) in natural waters either indicate that the solubility of Sb(III) is stronger

controlled by precipitation and sorption compared to Sb(V) or that Sb(III) is rapidly oxidized to Sb(V).

1.1.2 Processes that control the solubility of Sb in the environment

Natural minerals containing Sb, in particular Sb(III), are sulphides (e.g. stibnite (Sb_2S_3), tetrahedrite $(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$), jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$), boulangerite ($\text{Pb}_5\text{Sb}_4\text{S}_{11}$), pyrrargyrite (Ag_3SbS_3)) and oxides (e.g. senarmonite (Sb_2O_3), stibiconite ($\text{Sb}^{+3}\text{Sb}_2^{+5}\text{O}_6(\text{OH})$), kermesite ($\text{Sb}_2\text{S}_2\text{O}$), bindheimite ($\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O,OH})$) (19). Stibnite is the predominant Sb mineral, which is mined commercially (1, 5, 19). The above mentioned minerals are associated with ore bodies. Secondary minerals that form in sediments and soils under ambient conditions and may control the solubility of Sb are less known. It is possible that the solubility of Sb(III) is limited by Sb_2O_3 to 60 $\mu\text{g/L}$ under oxic conditions (20) and this may explain the low Sb(III) concentrations found in natural waters. In contrast, Sb(V) concentrations range up to 20 mg/L in equilibrium with Sb_2O_5 (20). Thermodynamically more stable phases, which might control the solubility of Sb(V), are likely to be Ca and Fe antimonates ($\text{Ca}[\text{Sb}(\text{OH})_6]_2$ and $\text{FeSb}(\text{OH})_8$) (28, 29). Tripuhyite (FeSbO_4), a Fe antimonate, has been identified in association with ore bodies (30) and leaching experiments of contaminated soils from shooting ranges suggest that Ca-antimonates can play a role (29).

Sequential extractions according to Zeien and Brümmer applied to Sb contaminated soils have shown that Sb is mainly found in the fractions of amorphous and crystalline Fe (hydr)oxides (31-33). Up to 90% of the total Sb was measured in the two fractions, indicating the association of Sb to Fe (hydr)oxides in soils. Additional leaching experiment with organic chelating ligands, such as amino acids, showed that the solubility of Sb did not increase. However, the addition of ascorbic, citric or tartaric acids increased the leachability of Sb, most likely by dissolving poorly crystalline Fe oxides (33). It

appears that Fe (hydr)oxides are important natural sorbents and influence the solubility of Sb in sediments and soils.

The few sorption studies available in the literature show that Sb binds to Fe, Mn and Al oxides (33-37). Results from sorption isotherms show that both Sb(III) and Sb(V) strongly sorb to Fe (hydr)oxides and only weakly to clay minerals at neutral pH values (33). The sorption capacity of Sb(III) on goethite and hematite was 13 and $>15 \mu\text{mol}/\text{m}^2$, respectively (33). For Sb(V), the sorption capacities were approximately 3 times smaller than for Sb(III), with values of 4 and $3.4 \mu\text{mol}/\text{m}^2$ on goethite and hematite, respectively (33). There is only one study that investigated the adsorption of Sb(III) on Fe (hydr)oxides as a function of pH in the absence of organic ligands (35). It is expected that the presence of organic ligands, such as tartrate and acetate strongly influences the sorption behavior on Fe (hydr)oxides. The study without organic ligands indicates that Sb(III) adsorbs strongly on amorphous Fe oxides in the pH range 6 to 10 (35). Compared to Sb(III), it appears that pH has a large influence on the sorption of Sb(V) to Fe (hydr)oxides. Sorption maxima of Sb(V) occur at low pH values which extend up to pH 7 depending on surface coverage, and desorption of Sb rapidly increases above pH 7 (34, 35, 37). Most studies used very high surface loadings of Sb to simulate conditions in waste water treatment. To assess the binding mechanisms to Fe (hydr)oxides in nature, sorption data with low surface coverage of Sb(III) and Sb(V) are necessary since these are not available in the literature.

According to this review, it appears that Sb(III) is less available than Sb(V) and this implies that oxidation processes are critical with regard to mobilization of Sb.

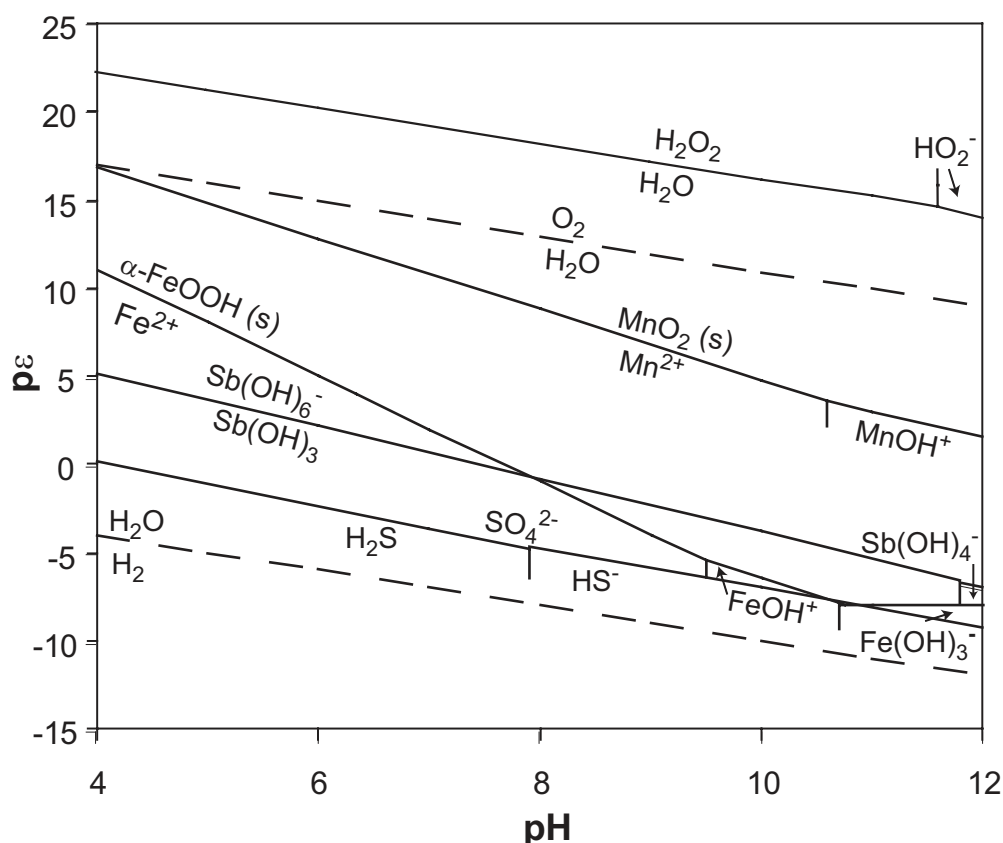


Fig. 1.1: pE - pH diagram for Sb species compared to other redox couples in natural waters. The solid phase for manganese is birnessite (MnO_2) and for goethite (α - $FeOOH$). For the calculations, following concentrations were assumed: $[H_2O_2] = 10^{-7}$ M, $p(O_2) = 0.2$, $[Mn(II)] = 10^{-6}$ M, $[Fe(II)] = 10^{-7}$ M, $[Sb(III)] = 10^{-10}$ M, $[Sb(V)] = 10^{-8}$ M and $[S(-II)] = [S(VI)]$. The ionic strength was assumed to be 0.

1.1.3 Redox processes

Oxidation of Sb(III) to Sb(V) has been observed (21, 38). However, the kinetics and mechanisms received little attention. The redox potential of the redox couple Sb(III)/Sb(V) is compared to the potentials of other redox couples H_2O_2/H_2O , O_2/H_2O , $Fe(II)/Fe(III)$, $Mn(II)/Mn(IV)$ and $S(-II)/S(VI)$ in Fig. 1.1. According to the thermodynamic estimates, a reduction of Sb(V) to Sb(III) by S(-II) is possible in the pH range 3 to 12, whereas H_2O_2 , O_2 and Mn oxides appear to be relevant oxidants. The reaction of Sb(III) with O_2 appears to be slow since no oxidation of Sb(III) was observed within 7 days (39). Oxidation of

Sb(III) to Sb(V) by Mn oxides has been observed under both oxic and anoxic conditions (33, 39). Depending on pH, Fe may act as reducing or as oxidizing agent. In anaerobic, alkaline solutions Fe(II) has been observed to reduce Sb(V) to Sb(III) (40), whereas Fe(III) (hydr)oxides may oxidize Sb(III) under oxic, acidic conditions. In the presence of amorphous Fe oxides, Sb(III) oxidation has been reported to occur irrespectively of pH in the pH range 5 to 10 (39). This indicates that adsorption may catalyze the Sb(III) oxidation by O₂ (41). However, it remains unknown whether Sb(V) is sorbed or released after oxidation. It is also possible that Sb(III) is oxidized indirectly by Fe(II) as the latter is oxidized to Fe(III) by O₂ as was reported for As(III) (42). The Fe(II) oxidation by O₂ produces reactive intermediates, such as H₂O₂, [•]OH radicals and possibly Fe(IV). For As(III), it is suggested that [•]OH radicals oxidize As(III) under acidic conditions, whereas at neutral pH values, another oxidant, possibly Fe(IV), plays a major role (42). Iron oxides are very common in sediments and soils. However, to date the role of Fe as a sorbent or an oxidant for Sb is unclear. Therefore, Fe could both immobilize and mobilize Sb in the environment.

1.2 SCOPE OF THIS STUDY

The literature review above has shown that key processes, influencing the mobility of Sb in the environment are most probably linked to the oxidation of Sb(III) to Sb(V) and the sorption behavior of Sb to Fe (hydr)oxides. This Ph.D. thesis aimed at investigating the oxidation reactions of Sb(III) in the presence of the natural oxidants, O₂, H₂O₂, Fe(III) (hydr)oxides. Additionally, the reaction of Sb(III) in the presence of Fe(II) oxidation was determined. These studies should help to answer the following questions:

- Under which conditions is Sb(III) oxidized by O₂ and how does O₂ compete with other oxidants in the environment?
- Is H₂O₂ a potential oxidant for Sb(III) in surface waters?
- Does Fe(II) oxidation, which produces reactive intermediates such as [•]OH radicals, mediate the Sb(III) oxidation?
- Can surface complexes of Sb(III) on goethite be oxidized and is Sb afterwards released from the surface?
- How is Sb associated in contaminated soils?

To address these questions, the following studies were carried out within this dissertation:

Oxidation of Sb(III) to Sb(V) by O₂ and H₂O₂ in aqueous solution (Chapter 2). Oxygen is the primary oxidant in environmental systems, though reactions with O₂ are often kinetically hindered. Therefore, it is important to know whether Sb(III) oxidation by O₂ is significant. The study was extended to investigate the influence of H₂O₂ on Sb(III) oxidation since the latter is another powerful oxidant in natural surface waters and an intermediate product of the reduction of O₂. The rate law for the oxidation reaction of Sb(III) with O₂ and H₂O₂ in dilute solutions were investigated over a wide pH range (pH 8-13). The pH-dependence and possible reaction mechanisms were investigated and the relevance of these reactions in natural waters was assessed.

Iron-mediated oxidation of antimony(III) by oxygen and hydrogen peroxide compared to arsenic(III) oxidation (Chapter 3). In aquatic systems, Fe(II) is produced either by photochemical reduction in surface waters or by anaerobic, microbial respiration in anoxic waters and sediments. During Fe(II) oxidation by O₂, reactive intermediates, such as superoxide, H₂O₂ and [•]OH radicals are formed. These intermediates may have an effect on Sb(III) oxidation. To better understand the reaction pathways and kinetics, the reactions of Sb(III) in the

presence of Fe(III), Fe(II) and O_2 , and Fe(II) and H_2O_2 as a function of pH and Fe(II) concentrations in aqueous solutions were investigated and compared to those of As(III).

Sorption of Sb(III) and Sb(V) to goethite: Influence on Sb(III) oxidation and mobilization (Chapter 4). It appears that Fe (hydr)oxides are important natural sorbents for both Sb(III) and Sb(V). However, it is expected that adsorption catalyzes the oxidation of Sb(III) by O_2 . It is still unclear to what extent oxidized Sb remains at the surface or is released. Therefore, the sorption of low concentrations of Sb(III) and Sb(V) on goethite, a widespread and thermodynamically stable Fe oxide in natural soils was investigated as a function of ionic strength and pH. Concentrations of Sb(III) and total Sb were measured in solution and in the solid phase in order to assess both oxidation processes of Sb(III) and mobilization.

Development of extraction methods for Sb species in soils (Chapter 5). In Switzerland, the largest emissions to the environment are via shooting practice and car brake pad and tire erosion. Therefore, the knowledge of the Sb speciation and binding in soils is of great interest for the assessment of oxidation and mobilization processes in soils, in light of the geochemical findings discussed in chapter 2-4. The goal of this study was to evaluate known extraction methods with different Sb compounds and contaminated soils in order to find a suitable extraction procedure for Sb and to use the methods in selected soils.

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Oxidation of Sb(III) to Sb(V) by O₂ and H₂O₂ in aqueous solutions

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Abstract: The rates of Sb(III) oxidation by O₂ and H₂O₂ were determined in homogeneous aqueous solutions. Above pH 10 the oxidation reaction of Sb(III) with O₂ was first order with respect to the Sb(III) concentration and inversely proportional to the H⁺ concentrations at a constant O₂ content of 0.22·10⁻³ M. Pseudo-first-order rate coefficients, k_{obs}, ranged from 3.5·10⁻⁸ s⁻¹ to 2.5·10⁻⁶ s⁻¹ at pH values between 10.9 and 12.9. The relationship between k_{obs} and pH was: $\log k_{obs} = 1.0(\pm 0.3)pH - 18.5(\pm 3.4)$ $R^2 = 0.89$. No significant Sb(III) oxidation by O₂ was observed between pH 3.6 and 9.8 within 200 days.

Oxidation of Sb(III) by H₂O₂ was found to be first order with respect to the total Sb(III), H₂O₂ and inversely proportional to the H⁺ concentrations in a pH-range of 8.1 to 11.7. Above pH 11.7 no pH-dependence was observed. The rate law for the pH range 8.1 to 12.9 was determined to be:

$$-\frac{d[Sb(III)]_{tot}}{dt} = k \cdot [Sb(III)]_{tot} \cdot [H_2O_2]_{tot} \text{ and } k = k_3 \cdot \frac{K_{a1}}{K_{a1} + [H^+]} = k_4 \cdot \frac{K_{a2}}{K_{a2} + [H^+]}$$

where K_{a1} and K_{a2} are the deprotonation constants of Sb(OH)₃ and H₂O₂, respectively and k₃ (= 365 M⁻¹ s⁻¹) and k₄ (= 342 M⁻¹ s⁻¹) are the specific second-order rate coefficients.

The results indicate that the rate-limiting step below pH 11.7 involves one deprotonated species, either Sb(OH)₄⁻ or HO₂⁻. Since the pK_a-values of Sb(OH)₃ and H₂O₂ are very close (11.8 and 11.6, respectively) it was not possible to determine which species is involved. Varying the ionic strength between 0.001 and 1.0 M at pH 10 and between 0.01 and 1.0 M at pH 12 resulted in a less than twofold increase in k_{obs}. In both cases, the increase was attributed to a shift in pK_a-values as a function of the ionic strength. It could be concluded that O₂ was unlikely to be a significant oxidant in homogenous solution but that H₂O₂ might be responsible for the oxidation of Sb(III) in natural waters since half-lives could vary from 32 years to 117 days at pH 8 with H₂O₂ concentrations between 10⁻⁸ M and 10⁻⁶ M, respectively.

2.1 INTRODUCTION

Antimony (Sb) and its compounds have been declared as pollutants of priority interest by the Environmental Protection Agency of the United States (USEPA) and the Council of the European Communities ((1) and references therein). Approximately 140'000 tons of Sb are mined annually and utilized in many different industrial products, mainly as Sb(III) in flame retardants and in elemental form in alloys for storage batteries and ammunition (2-4).

In unpolluted aquatic environmental systems total Sb concentrations are generally below $1 \mu\text{g L}^{-1}$ and the oxidized Sb(V) species, $\text{Sb}(\text{OH})_6^-$, is the predominant dissolved species (1, 5). This appears to be related to the differing geochemical properties of the two redox states found in the environment, namely Sb(III) and Sb(V). Little is known of the geochemical properties of Sb in the environment, but studies have indicated that Sb(III) sorbs more strongly to surfaces than Sb(V), primarily to Fe(III) and Mn(IV) (hydr)oxides (6, 7). Also, the oxide of Sb(V) (Sb_2O_5) is more soluble than the oxide of Sb(III) (Sb_2O_3) (4). The greater solubility of Sb(V) means that oxidation processes are critical with regard to the mobility of Sb in the aqueous environment.

Qualitative studies have indicated which oxidants may be important for the oxidation of Sb(III) but to date virtually no quantitative data is available in the literature (8). The oxidation of Sb(III) to Sb(V) by unspecified oxidants has been reported to occur within 6 hours in waste waters (9), within 260 days in saline waters (10) and within 25 days in aqueous solutions containing humic acids (11). No significant oxidation of Sb(III) was observed in solution with O_2 in the pH range of 5 to 10 within 7 days (12). Antimony(III) was converted to Sb(V) within 10 min in sea water during photooxidation treatments (13, 14) and iodate was suggested as a possible oxidizing agent (14). In addition, there is some evidence for the oxidation of Sb(III) by Fe(III) and Mn(IV) (hydr)oxides (7, 12, 15). Average pseudo-first-order rate coefficients for synthetic Fe(III) and Mn(IV)

(hydr)oxides were 0.887 day^{-1} and 2.35 day^{-1} , respectively (12). Lyalikova (1974) reported the existence of bacteria in ore deposits that can oxidize Sb(III) to Sb(V) (16). From the investigations to date, it appears that photooxidation products and Fe(III) and Mn(IV) (hydr)oxides could play a major role in the oxidation process. However, there is little kinetic data to be able to assess the relative importance of these oxidants. Further, it is not known whether or not and under which conditions O_2 is a relevant oxidant for Sb(III).

Oxygen is a strong oxidant from a thermodynamic point of view with a redox potential of $E_{\text{H}} = +0.8 \text{ V}$ at pH 7 in natural oxic waters (17). However, it appears that oxidation reactions involving dissolved O_2 are generally slow (18). The oxidation of As(III), another group 15 element, with O_2 is slow with a half-life of 1 to 3 years in freshwaters (19). Another potential oxidant for Sb(III) in surface waters is H_2O_2 . Hydrogen peroxide is the intermediate reduction product of O_2 and is more reactive than O_2 . It is produced by photochemical reactions in surface waters and occurs at concentration levels between 10^{-6} and 10^{-8} M (20, 21). Pettine et al. (1999) estimated that As(III) is oxidized by $2 \cdot 10^{-7} \text{ M}$ H_2O_2 in surface waters within 2 to 3 months between pH 8 and 9 (21). A study has been recently carried out to determine the rate law between Sb(III) and H_2O_2 in saline solutions in the pH range between 8 to 9.7 and under highly acidic conditions (22). Antimony(III) oxidation rates are estimated to be slightly lower than As(III) at pH 8.5 in saline solutions.

The aims of this study were to determine the rate law for the oxidation reaction of Sb(III) with O_2 and H_2O_2 over a wide pH range (pH 8-13) in dilute solutions, to determine the pH-dependence and possible reaction mechanisms and to assess the relevance of these reactions in natural waters.

2.2 EXPERIMENTAL PROCEDURES

2.2.1 Materials

All chemicals were at least of pro analysi (p.a.) grade. Hydrochloric acid (30 % Suprapur), H_2O_2 (30 %), NaCl, KCl, KOH solution (1 M, Titrisol) and the Sb(III) standard solution (1000 mg/L Sb_2O_3 , CertiPUR) in 2 M HCl were purchased from Merck. Ascorbic acid (vitamin C, puriss p.a.), KI (puriss p.a.), NaBH_4 (puriss p.a.), NaOH (Ultra) and di-Sodium-hydrogen-citrate sesquihydrate ($\text{C}_6\text{H}_6\text{Na}_2\text{O}_7 \cdot 1.5 \text{H}_2\text{O}$ purum p.a.) were bought from Fluka.

Ultra pure water (resistivity $> 18 \text{ M}\Omega\cdot\text{cm}$, Millipore) was used for the preparation of solutions and rinsing processes. All glassware, polyethylene bottles and sample vessels used for the experiments and analyses were leached in acid solutions (0.3 M HCl, Merck) and rinsed 3 times with ultra pure water prior to use.

2.2.2 Analytical Methods

Solution pH measurements were carried out using a pH meter (Metrohm 713) with a glass combination electrode (Orion 81-72BN and Metrohm 6.0222.100). The pH meter was calibrated with Merck buffer solutions (pH 4, 7, 9, 10, 11 and 12) and freshly prepared 0.1 M KOH. The average slope of the electrodes was 0.94.

Dissolved O_2 was measured using an O_2 sensor (DurOx 325 WTW) connected to a digital O_2 pocket meter (Oxi 315i WTW). Calibration was performed in water vapor-saturated air using an air calibration vessel (OxiCal-D). The relative slope of the sensor was 0.89. The measurement accuracy was 10 % for an incident flow of 2.5 cm/s.

Samples for Sb(III) analysis (10 mL) were stabilized by mixing with 1 M di-sodium-hydrogen-citrate solutions (10 mL) in order to prevent further oxidation

and samples for Sb_{tot} ($Sb_{tot} = Sb(III) + Sb(V)$) determination were stabilized by adjusting the solutions to 3 M with respect to HCl. All samples were stored at 4°C and samples that were kept for longer than 3 days prior to analysis were frozen at -20°C. Concentrations of Sb(III) and total Sb were measured with a hydride generation atomic fluorescence spectrometer (Millenium Excalibur-System, PSA 10.055. PS Analytical LTD) using the method adapted from PS Analytical. Antimony(III) was converted to SbH_3 by mixing with $NaBH_4$ (0.19 M, dissolved in 0.1 M NaOH, flow rate 4.5 mL min⁻¹) introduced by flow injection into the carrier solution (0.5 M di-sodium-hydrogen-citrate, flow rate 9 mL min⁻¹) and the sample (flow rate 9 mL min⁻¹). Total Sb was analyzed by reducing Sb(V) to Sb(III) with KI-ascorbic acid solution (0.06 M KI, 0.01 M ascorbic acid) in 3 M HCl prior to analysis (23-25). Inorganic Sb(III) was determined in 0.5 M di-sodium-hydrogen-citrate at pH 4.7 (23, 24). The total Sb concentration remained constant and equal to the initially added Sb(III) concentrations in all experiments. Thus, the concentration of Sb(V) was calculated from the difference of Sb_{tot} and Sb(III) concentrations. The determination limit ($\pm 2\sigma$) of the instrument is 0.1 µg/L and 0.04 µg/L for Sb(III) and Sb_{tot} , respectively. Precision determined by duplicate measurements ranged between 1 % and 20 %.

2.2.3 Oxidation experiments

All oxidation experiments were conducted in single bottles (polyethylene, 500 mL) in the dark at 25 °C. Therefore, the bottles were covered in aluminum foil and kept on a rotary shaker (175 rpm). The aqueous solutions contained an initial O_2 concentration of 0.22 ± 0.02 mM. The solutions were not buffered, in order to avoid unwanted reactions with buffers. If required, the pH was adjusted using HCl and NaOH below pH 11. Above pH 11, KOH was used as a base in

order to avoid the precipitation of NaSb(OH)_6 (26). The ionic strength (I) of 0.001 M was adjusted with NaCl and with KCl for higher ionic strengths.

The oxidant was added in excess to work under pseudo-first-order conditions in all oxidation experiments. Oxidation rate coefficients were then calculated using the following equation:

$$\ln[\text{Sb(III)}]_{\text{tot}} = -k_{\text{obs}} \cdot t + \ln[\text{Sb(III)}]_{\text{tot},0} \quad (1)$$

where $[\text{Sb(III)}]_{\text{tot}}$ is the total concentration of Sb(III) (sum of the concentrations of the species Sb(OH)_3 and Sb(OH)_4^-) at any time, t , $[\text{Sb(III)}]_{\text{tot},0}$ is the total Sb(III) concentration at $t = 0$ and k_{obs} is the observed pseudo-first-order rate coefficient that relates to the consumption of $[\text{Sb(III)}]_{\text{tot}}$.

Oxidation of Sb(III) with O_2 . Duplicate oxidation experiments with O_2 were performed at pH 12.9 (I = 0.1 M), pH 12.8 (I = 0.1 M), pH 12.1 (I = 0.01M), and single ones at 12.1 (I = 0.1 M) and pH 11.9 (I = 0.1 M). Additional single experiments were carried out at pH 10.9, 9.8, 9.6, 9.3, 8.1 and 3.6 at an ionic strength of 0.001 M. Initial concentrations of Sb(III) varied between 0.7 and 0.9 μM in the experiments. Total Sb concentrations and pH were measured at the beginning and at the end of each experiment. Duplicate samples (2 mL) for Sb(III) analysis were removed over a period of 200 days for the experiments between pH 3.6 and pH 9.8, 420 days for the experiment at pH 10.9, 120 days for the experiments at pH ~ 12 and 7 days for the experiments at pH ~ 13 .

Oxidation of Sb(III) with H_2O_2 . For all oxidation experiments with H_2O_2 , solutions containing twice the initial Sb(III) concentration (250 mL) and twice the initial H_2O_2 concentration (250 mL) were rapidly mixed in order to avoid locally higher concentrations of oxidant during initial mixing. Samples for Sb(III) measurements were removed at appropriate time intervals to obtain between 6 and 10 data points for the determination of the pseudo-first-order rate coefficient in each experiment. Samples were taken in duplicate where sampling

intervals allowed (>50 s). Fresh H_2O_2 solutions were prepared before each experiment and the concentration of stock solutions were tested with KMnO_4 titration before each set of experiments.

The dependence of the oxidation reaction on the initial Sb(III) concentration was investigated with 5 single batch experiments at pH 10.0, with an H_2O_2 content of 20 μM and an ionic strength of 0.001 M. Initial Sb(III) concentrations were 0.08, 0.7, 0.8, 1.0 and 1.7 μM . The pH was measured at the beginning of the experiment, after 50 min and at the end. The dependence of the oxidation reaction on the initial H_2O_2 concentration was determined as described above in 14 batch experiments. The initial Sb(III) concentration was between 0.8 and 1.0 μM and the H_2O_2 concentrations used were 5, 10, 20, 30, 40 and 50 μM . The pH dependence of the Sb(III) oxidation reaction was investigated in 28 single batch experiments in the pH range between pH 8.1 and 12.9 with 20 μM H_2O_2 . The ionic strength was 0.001 M below pH 11 and 0.1 M above pH 11. Additional duplicate experiments at $I = 0.1$ M were carried out at pH 10.6 and 10.9. Initial concentrations of Sb(III) varied between 0.35 and 1.0 M, because the freshly prepared Sb(III) stock solution of 100 mg/L was not stable. The pH was measured at the beginning and at the end of the experiment. The influence of the ionic strength on the Sb(III) oxidation rate coefficients was determined at pH ~10 and pH 12.0 in experiments as described above. The investigated ionic strengths were (0.001 M), 0.01 M, 0.1 M, 0.5 M and 1.0 M. Triplicate experiments were carried out at each ionic strength.

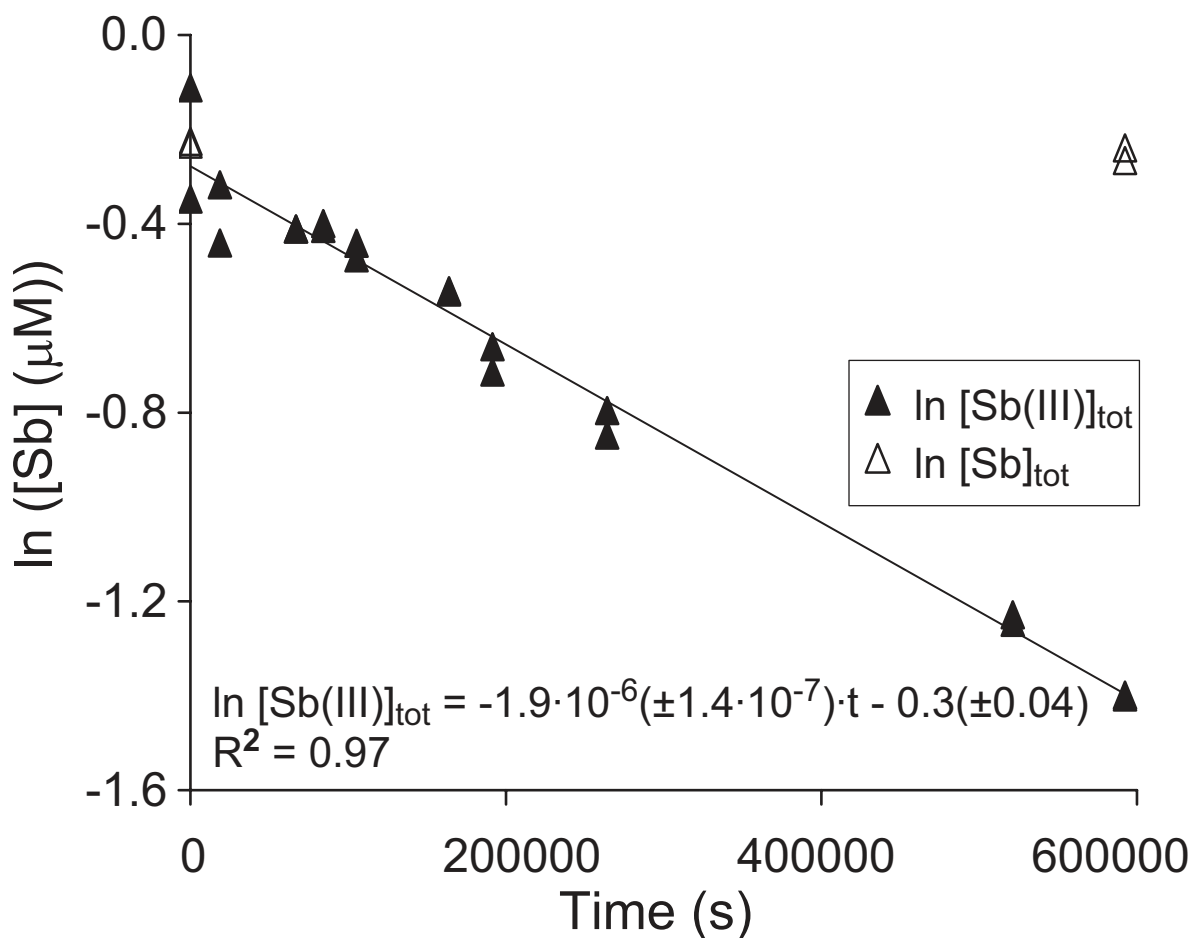


Fig. 2.1. Natural logarithmic values of the $[Sb(III)]_{tot}$ and $[Sb]_{tot}$ concentration as a function of time at pH 12.8 and 25°C ($[Sb(III)]_{tot,0} = 0.8 \mu M$, $O_2 = 0.22 \text{ mM}$, $I = 0.1 \text{ M}$). Data points at the same time are duplicates. The line represents a linear fit of $\ln [Sb(III)]_{tot}$ versus time, t .

2.3 RESULTS AND DISCUSSION

2.3.1 Oxidation of Sb(III) with O_2

Significant oxidation of Sb(III) was observed at a pH range between 10.9 and 12.9 within 3 to 420 days. The linear decrease of Sb(III) concentration at pH 12.8, illustrated in Fig. 2.1, indicates that the oxidation reaction with O_2 is pseudo-first-order with respect to Sb(III) concentrations in this pH range (Eqn. 1). The average pseudo-first-order oxidation rate coefficient, k_{obs} , ranges from

$2.5 \cdot 10^{-6} \text{ s}^{-1}$ at pH 12.9 to $3.5 \cdot 10^{-8} \text{ s}^{-1}$ at pH 10.9 (Table 2.1). The corresponding half-lives are estimated to be between 3.3 and 229 days for pH 12.9 and 10.9, respectively. The differing values for k_{obs} at pH 12.1, cannot be explained. However, a linear fit of $\log k_{\text{obs}}$ and pH results in a slope close to 1 and indicates that the faster oxidation rates at pH 12.1 are closer to the expected value. The influence of ionic strength on the oxidation rates is not significant (Table 2.1). The rate coefficients, k_{obs} , of the experiments carried out at pH 12.1 and at

Table 2.1. Pseudo-first-order rate coefficients, k_{obs} , and half-lives for the oxidation of Sb(III) with O_2 at different pH values at 25°C in the dark. The twofold standard error of the slope of the linear regression for calculating k_{obs} is shown as 2σ .

pH	k_{obs} [s ⁻¹]	2σ [s ⁻¹]	half-life [d]	I [M]
12.9	$2.7 \cdot 10^{-6}$	$\pm 7 \cdot 10^{-7}$	3.0	0.1
12.9	$2.2 \cdot 10^{-6}$	$\pm 1 \cdot 10^{-7}$	3.6	0.1
12.8	$2.0 \cdot 10^{-6}$	$\pm 3 \cdot 10^{-7}$	4.0	0.1
12.8	$1.9 \cdot 10^{-6}$	$\pm 1 \cdot 10^{-7}$	4.2	0.1
12.1	$3.5 \cdot 10^{-7}$	$\pm 5 \cdot 10^{-8}$	22.9	0.1
12.1	$2.8 \cdot 10^{-7}$	$\pm 4 \cdot 10^{-8}$	28.7	0.01
(12.1	$0.9 \cdot 10^{-7}$	$\pm 9 \cdot 10^{-9}$	89.1	0.01)
11.9	$2.3 \cdot 10^{-7}$	$\pm 5 \cdot 10^{-8}$	34.9	0.1
10.9	$3.5 \cdot 10^{-8}$	$\pm 6 \cdot 10^{-9}$	229.2	0.001

Initial concentrations of O_2 and Sb(III) were 0.22 mM and 0.8-0.9 μM , respectively. A linear fit of $\log k_{\text{obs}}$ and pH results in: $\log k_{\text{obs}} = 1.0 (\pm 0.3) \text{ pH} - 18.5 (\pm 3.4)$ ($R^2 = 0.89$).

pH 11.9 with an ionic strength of 0.1 M are in the same order of magnitudes as the experiments carried out at pH 12.1 with an ionic strength of 0.01 M. No significant oxidation of Sb(III) with O_2 , within the range of 20 % of measurement uncertainty, was measured within 200 days at initial pH values of

3.6, 8.1, 9.3, 9.6 and 9.8 (data not shown). If the trend of pH dependence determined at pH values > 10 is extrapolated to lower pH values, an average half-life of ~ 220 years at pH 8.5 would be expected. These results suggest that the oxidation of Sb(III) with O_2 as sole oxidant is very slow in homogenous aqueous solutions under environmental conditions and this reaction was therefore not further investigated.

The increase of the oxidation rate coefficient with pH indicates that the reaction rate may be associated with the pH-dependent speciation of Sb(III). The species $Sb(OH)_3$ with a pK_a -value of 11.8 hydrolyses to $Sb(OH)_4^-$ (5). The free energy of the two half-reactions of the oxidation of $Sb(OH)_3$ to $Sb(OH)_6^-$ and $Sb(OH)_4^-$ to $Sb(OH)_6^-$ are $+110.6 \text{ kJ}\cdot\text{mol}^{-1}$ and $+45.8 \text{ kJ}\cdot\text{mol}^{-1}$, respectively (27). This indicates that from a thermodynamic point of view $Sb(OH)_4^-$ is more easily oxidized to $Sb(OH)_6^-$ with the same oxidant than $Sb(OH)_3$. The additional OH^- ligand may donate electron density to Sb(III), which results in an increased metal basicity and in an increased reducing power. An additional effect may be the stabilization of Sb(V) by OH^- ligands as it is reported for Fe(II) oxidation (17, 28-31). Acceleration of oxidation reactions due to hydrolysis has also been reported for other metal such as V(IV), Cr(III), Mn(II) and Fe(II) oxidation (28, 29, 31-33). Therefore, the reactive species is suggested to be $Sb(OH)_4^-$. The question remains as to why there is such a strong pH-dependence when the concentrations of $Sb(OH)_4^-$ approach 50% at pH values close to the pK_a of $Sb(OH)_3$ of 11.8.

A similar investigation was carried out by Eary and Schrapke (1990) with As(III) and O_2 in aqueous solutions between pH 7 and pH 11 (19). They found that the oxidation rate of As(III) increased with increasing pH between pH 5.5 and pH 9 and that the oxidation rates depend on the concentration of the more hydrolyzed species, $H_2AsO_3^-$. Half-lives for As(III) oxidation with O_2 ($[O_{2(aq)}] = 0.25 \cdot 10^{-3} \text{ M}$) were calculated in the range of 1 to 3 years between pH 7 and pH

11. The oxidation rate of As(III), calculated by Cherry et al. (1979) was an order of magnitude lower at pH 7 in O₂-saturated water ($[O_{2(aq)}] = 0.22 \cdot 10^{-3} \text{ M}$) (34). The oxidation of As(III) at pH 7 is therefore approximately 4 orders of magnitudes faster than that of Sb(III). This may be partly due to the fact that As(III) deprotonates at a lower pH value.

Table 2.2. Initial oxidation rates and pseudo-first-order rate coefficients, k_{obs} , for the Sb(III) oxidation with 20 μM H₂O₂ in 0.001 M NaCl solutions as a function of initial Sb(III) concentrations, $[Sb(III)]_{tot, 0}$ at pH 10.0 and 25°C. The twofold standard error of the slope of the linear regression for calculating k_{obs} is shown as 2σ .

$[Sb(III)]_{tot, 0}$	oxidation rate v	k_{obs}	2σ
$[\mu\text{M}]$	$[\mu\text{M s}^{-1}]$	$[\text{s}^{-1}]$	$[\text{s}^{-1}]$
0.08	$1.1 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-5}$
0.68	$1.3 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$1.5 \cdot 10^{-5}$
0.80	$1.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$7.5 \cdot 10^{-6}$
1.03	$1.7 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$
1.73	$2.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$	$1.1 \cdot 10^{-5}$

2.3.2 Oxidation of Sb(III) with H₂O₂

Reaction order with respect to Sb concentration. The initial rates of Sb(III)_{tot} oxidation, v , were determined from the slope of the plots of $[Sb(III)]_{tot}$ against time within the first 20 % of the oxidation reaction (Eqn. 2). A linear fit of $\log v$ versus $\log [Sb(III)]_{tot, 0}$ yields the intercept, k_{obs} , and a slope of n , the dependence of the oxidation rate on Sb(III)_{tot} concentration, according to the following equation (35):

$$v = -\frac{d[Sb(III)]_{tot}}{dt} = k_{obs} \cdot [Sb(III)]_{tot, 0}^n \quad (2)$$

Pseudo-first-order rate coefficients, k_{obs} and values of v are reported for different Sb(III) concentrations in Table 2.2. Using this data, a plot of $\log v$ against $\log [\text{Sb(III)}]_{\text{tot}, 0}$ resulted in the following linear fit:

$$\log v = 1.04(\pm 0.1) \cdot \log [\text{Sb(III)}]_{\text{tot}, 0} - 3.8(\pm 0.1) \quad \text{with } R^2 = 0.99 \quad (3)$$

with values in brackets being the twofold standard error of the slope and the intercept, and R^2 is the coefficient of determination. Thus n appears to have a value very close to 1 and k_{obs} has an average value of $1.6 \cdot 10^{-4} \text{ s}^{-1}$. This shows that the rate of Sb(III) oxidation with H_2O_2 is 1st order with respect to $[\text{Sb(III)}]_{\text{tot}}$. The estimated k_{obs} of $1.6 \cdot 10^{-4} \text{ s}^{-1}$ represents the average value of all experiments at pH 10.0 and 25°C reported in Table 2.2.

Reaction order with respect to H_2O_2 concentration. The second-order rate law may now be written as:

$$-\frac{d[\text{Sb(III)}]_{\text{tot}}}{dt} = k \cdot [\text{Sb(III)}]_{\text{tot}} \cdot [\text{H}_2\text{O}_2]_{\text{tot}}^m \quad (4)$$

where k is the second-order rate coefficient and m represents the order of the reaction with respect to the total concentration of H_2O_2 , (including H_2O_2 and HO_2^-). The pseudo-first-order rate coefficient, k_{obs} , is related to k by the following equation (35):

$$k = \frac{k_{\text{obs}}}{[\text{H}_2\text{O}_2]_{\text{tot}}^m} \quad (5)$$

A linear fit of the log values of the oxidation rate coefficients, k_{obs} , and $\log [\text{H}_2\text{O}_2]_{\text{tot}}$ yielded a slope of 1.01 (Fig. 2.2). This shows that the rate of $\text{Sb(III)}_{\text{tot}}$ oxidation with H_2O_2 at pH 10 is 1st order with respect to total H_2O_2 concentrations according to Eqns. 4 and 5. The intercept yields an average value for k of $7.9 \cdot 10^{-6} \text{ }\mu\text{M}^{-1} \text{ s}^{-1}$ at pH 10 and 25°C.

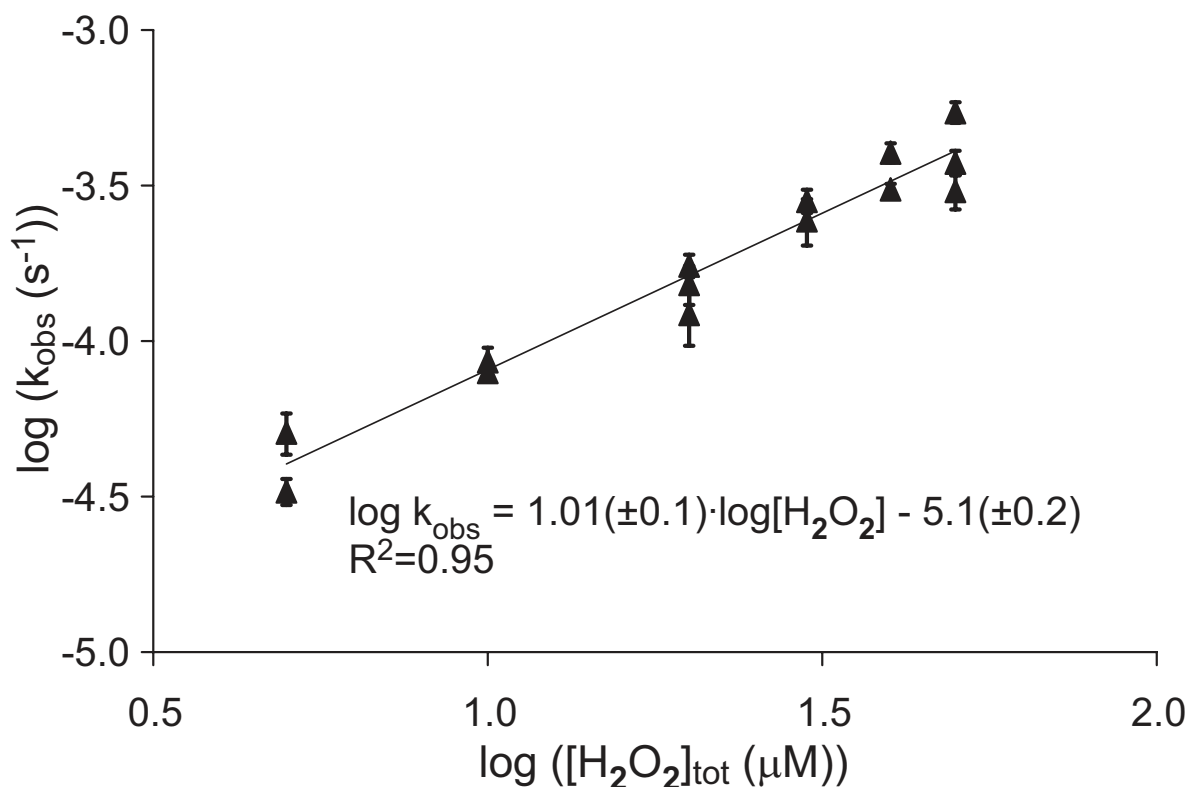
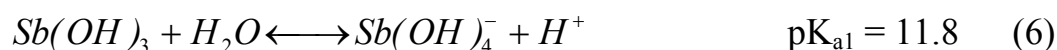


Fig. 2.2. Log values of the pseudo-first-order oxidation rate coefficients, k_{obs} , as a function of logarithmic concentration of H_2O_2 (5-50 μM). All experiments were performed at pH 10, $[Sb(III)]_{tot,0} = 0.8-1.0 \mu M$, $I = 0.001 M$ at $25^\circ C$ in the dark. The line represents the linear fit between $\log k_{obs}$ and $\log [H_2O_2]_{tot}$. Values in brackets are the twofold of standard error of slope and intercept, respectively, and R^2 is the coefficient of determination. Error bars of the oxidation rate coefficients are within the symbols of some data points.

The pH dependence of the reaction. The second-order rate coefficient, k , for the oxidation of Sb(III) with H_2O_2 is strongly pH dependent below a pH value of approximately 11.7 (Fig. 2.3). This corresponds to the dissociation constants for the two species, of 11.8 and 11.6, respectively (Eqns. 6 and 8; (5, 36)).



$$[Sb(III)]_{tot} = [Sb(OH)_3] + [Sb(OH)_4^-] = [Sb(OH)_4^-] \cdot \left(\frac{K_{a1} + [H^+]}{K_{a1}} \right) \quad (7)$$

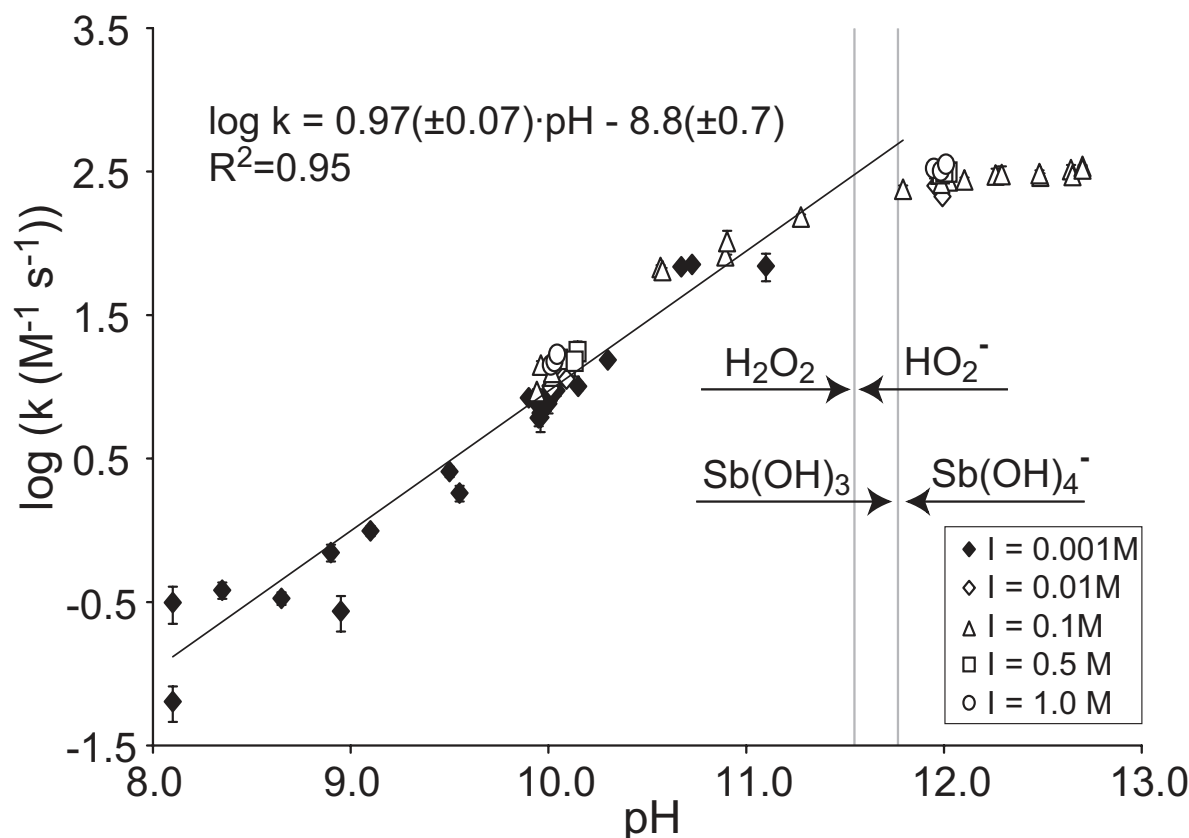


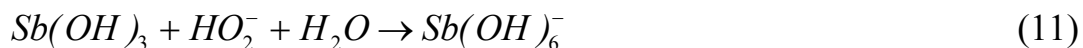
Fig. 2.3. Log values of second-order rate coefficients, k , for the oxidation of Sb(III) with H_2O_2 as a function of pH. All experiments were performed at 25°C in the dark. Initial concentration of Sb(III) varied between 0.35-1.0 M. The black line is the linear fit between $\log k$ and pH in the pH range of 8.1 to 11.7 with values in brackets being the twofold of standard error of slope and intercept, respectively, and R^2 is the coefficient of determination. Gray lines show the pK_a -values of $Sb(OH)_3$ and H_2O_2 at $I = 0$. Error bars of the oxidation rate coefficients are within the symbols of most data points.



$$[H_2O_2]_{tot} = [H_2O_2] + [HO_2^-] = [HO_2^-] \cdot \left(\frac{K_{a2} + [H^+]}{K_{a2}} \right) \quad (9)$$

The slope of curve in Fig. 2.3 is close to 1 at pH values below the pK_a -values. Either one or partially both of the following reactions could be responsible for the rate limiting step below a pH value of approximately 11.7:





Unfortunately, since these reactions have the same pH dependence and the reactive species have similar pK_a -values, the reactions cannot be distinguished kinetically. Above pH 11.7, where $Sb(OH)_4^-$ and HO_2^- are the predominant aqueous species, the reaction appears to be zero order with respect to pH. This observation may be explained by the reaction of one charged species (either $Sb(OH)_4^-$ or HO_2^-) upon which the rate limiting step depends, with either species of the respective reactant.

Assuming only the reaction between $Sb(OH)_4^-$ and H_2O_2 (Eqn. 10) to be relevant, the rate law for the decrease of $Sb(III)_{tot}$ concentration can be formulated as (combining Eqns. 4, 6 and 7)

$$-\frac{d[Sb(III)]_{tot}}{dt} = k \cdot [Sb(OH)_4^-] \cdot [H_2O_2] \cdot \left(\frac{K_{a1} + [H^+]}{K_{a1}} \right) \quad (12)$$

The rate of the oxidation of Sb(III) is therefore dependent on the molar fraction of $Sb(OH)_4^-$ and the specific second-order rate coefficient, k_3 , is then:

$$k_3 = k \cdot \frac{(K_{a1} + [H^+])}{K_{a1}} \quad (13)$$

According to Eqn. 13 it is possible to calculate k_3 for the reaction (10). A linear fit of k vs $K_{a1}/(K_{a1} + [H^+])$ yields k_3 as the slope of the linear regression. From the slope of the plot of Fig. 2.4a, a value of $365 \text{ M}^{-1} \text{ s}^{-1}$ was obtained. Only the data below $I = 1.0 \text{ M}$ were used, because the K_{a1} values were corrected with the Davies Equation (28).

A similar procedure was carried out assuming reaction (11) as main mechanism. The rate law can be expressed by the following equation (combining Eqns. 4, 8 and 9):

$$-\frac{d[Sb(III)]_{tot}}{dt} = k \cdot [Sb(OH)_3] \cdot [HO_2^-] \cdot \left(\frac{K_{a2} + [H^+]}{K_{a2}} \right) \quad (14)$$

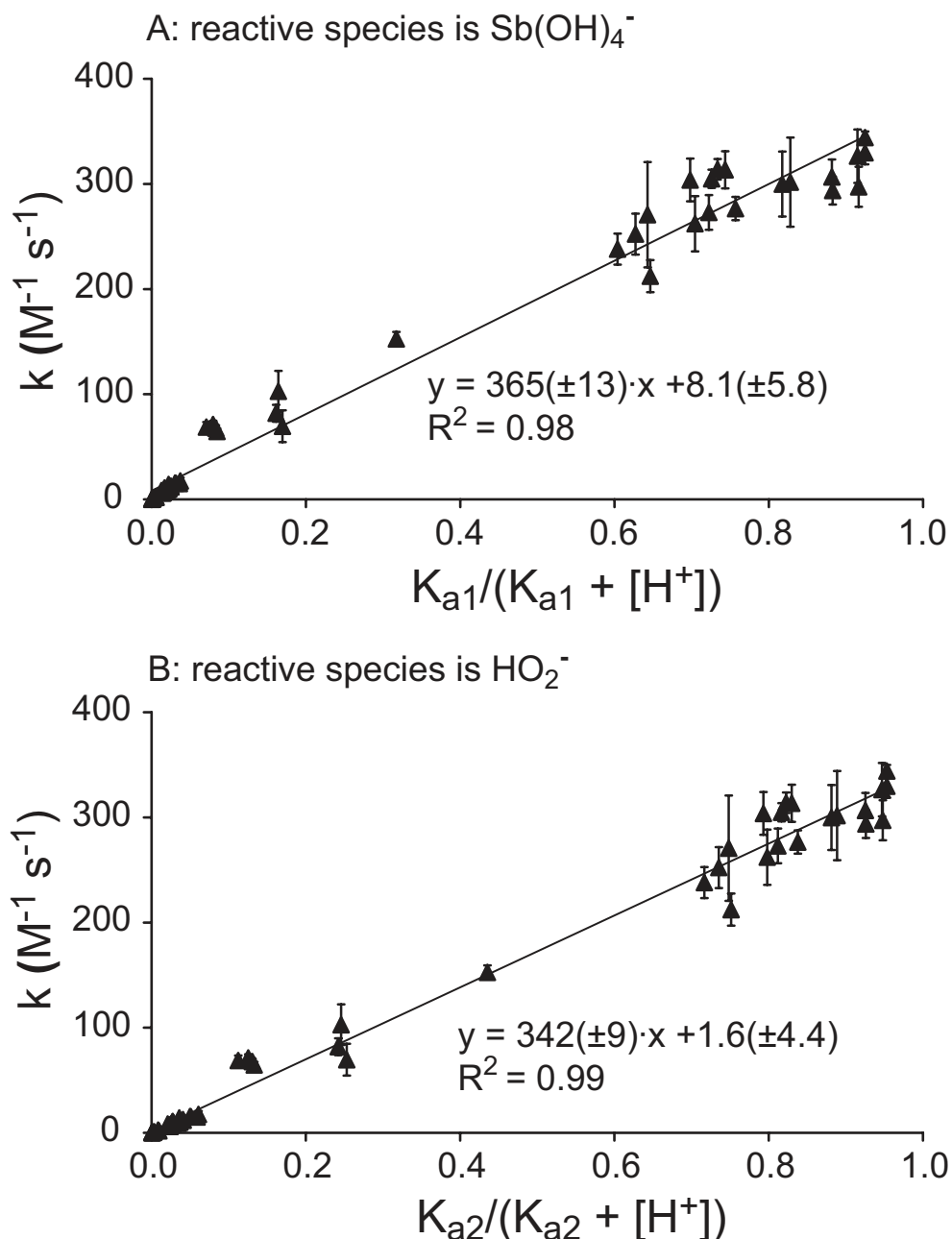


Fig. 2.4. Linear plot of the measured second-order rate coefficients, k , for the Sb(III) oxidation with H_2O_2 versus the molar fraction of (A) $\text{Sb}(\text{OH})_4^-$ and (B) HO_2^- relative to the total concentrations of Sb(III) and H_2O_2 , respectively. According to Eqns. 13 and 15, the slopes of the linear regressions correspond to the specific second-order rate coefficients k_3 and k_4 , respectively.

The specific rate coefficient for the reaction, k_4 , is in this case formulated as follows:

$$k_4 = k \cdot \frac{(K_{a2} + [H^+])}{K_{a2}} \quad (15)$$

A linear plot of k against $K_{a2}/(K_{a2} + [H^+])$ yields $k_4 = 342 \text{ M}^{-1} \text{ s}^{-1}$ as the slope of the straight line in Fig. 2.4b. Thus the overall rate equation (Eqn. 4) can also be formulated with the specific rate coefficients as follows:

$$-\frac{d[Sb(III)]_{tot}}{dt} = 365 \cdot \frac{K_{a1}}{(K_{a1} + [H^+])} \cdot [Sb(III)]_{tot} \cdot [H_2O_2]_{tot} \quad (16)$$

$$-\frac{d[Sb(III)]_{tot}}{dt} = 342 \cdot \frac{K_{a2}}{(K_{a2} + [H^+])} \cdot [Sb(III)]_{tot} \cdot [H_2O_2]_{tot} \quad (17)$$

Both reactions (10) and (11) are possible as they cannot be distinguished by our kinetic measurements. Thermodynamic calculations do not clarify the situation since both $Sb(OH)_4^-$ and HO_2^- are more reactive species than $Sb(OH)_3$ and H_2O_2 , respectively. Arguments in support of the reaction of $Sb(OH)_4^-$ with H_2O_2 (Eqn. 10) are the change in electron density of Sb(III) resulting from hydrolysis and the possible stabilizing effect of OH^- ligands on Sb(V) as stated in section 3.1. It is also possible that the negatively charged species, $Sb(OH)_4^-$, donates electrons more easily than $Sb(OH)_3$, and that the neutral species, H_2O_2 , accepts electrons more easily than HO_2^- .

Quentel et al. (2004) have recently found a similar rate law for the oxidation of Sb(III) with H_2O_2 in the pH range between 8-9.7 in a 0.5 M NaCl solution (22). They also observed a 1st order dependence on pH. In a similar investigation of the oxidation of As(III) with H_2O_2 , Pettine et al. (1999) found that the dependence of the oxidation coefficient on the pH was 1.4 in the pH range from 7.5 to 10.3, suggesting that two species, possibly $AsO(OH)_2^-$ and AsO_3^{3-} , were the reactive ones in this reaction (21). Neither Quentel et al. (2004) or Pettine et al. (1999) considered the deprotonated species of H_2O_2 as a possible reactive species (21, 22).

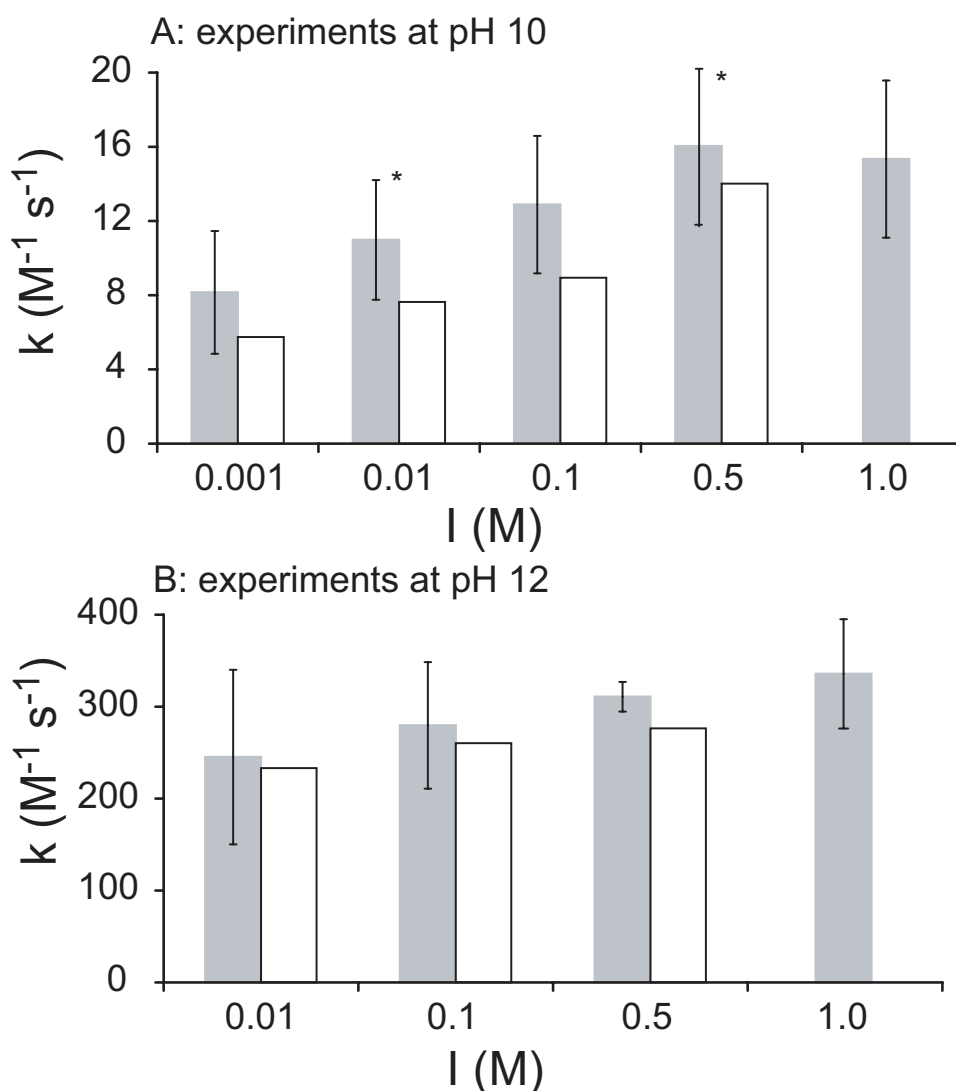


Fig. 2.5. Measured average second-order rate coefficients, k , for the Sb(III) oxidation with 20 μM H_2O_2 (■) as a function of ionic strength at pH ~ 10 (A) and at pH 12.0 (B). Values estimated using Eqn. 16 (□) to take account of shifts in pK_a with ionic strength using the David Equation (28). For rate coefficients marked with asterisk (*) the pH was 10.1. The error bars are the standard deviation of triplicates corrected by using the student distribution ($1-\alpha=0.95$).

The influence of ionic strength. The rate coefficients for Sb(III) oxidation with H_2O_2 increase by a factor of ~ 1.4 at pH 12 between ionic strengths of 0.01 to 1.0 M and by a factor of ~ 1.9 at pH 10 between ionic strengths of 0.001 M to 1.0 M (Fig. 2.5). There are generally two mechanisms that may cause such effects. Firstly, an increased ionic strength may have a shielding effect that reduces

repulsive interactions between ions of the same charge (such as $\text{Sb}(\text{OH})_4^-$ and HO_2^-). Secondly, a higher ionic strength also results in a shift of pK_a to lower pH values, which increases the fraction of the deprotonated species at a given pH. Using the transition state theory and correcting the activity coefficient with the Debye-Hückel Equation (35), a 10-fold change in rate coefficient is to be expected with every unit increase in the square root of ionic strength for a reaction involving two monovalent species as a result of the shielding effect. This was indeed observed by Pettine et al. (1999) for As(III) oxidation with H_2O_2 (21). The increase in rate coefficients in our Sb(III) oxidation experiments were much lower at both pH values. The shift of pK_a -values could be described quite well by the observed increase as a function of ionic strength (Fig. 2.5), particularly at pH 12, and is thus suggested to be the predominant effect resulting from a change in ionic strength. Quentel et al. (2004) also found a similar dependence on ionic strength up to $I = 1.0 \text{ M}$ at pH 8.2 and 9 (22).

2.4 CONCLUSIONS

Antimony(III) is oxidized by both O_2 and H_2O_2 and both reactions are pH dependent. The oxidation of Sb(III) to Sb(V) with O_2 as sole oxidant appears to be extremely slow under neutral conditions in homogenous solutions. Assuming an O_2 concentration of $0.28 \cdot 10^{-3} \text{ M}$, the half-life of Sb(III) at pH 8.5 was estimated to be 170 years. By comparison the oxidation reaction with H_2O_2 is much faster. The estimated half-lives of Sb(III) in the pH range from pH 7 to pH 9 with H_2O_2 concentrations between 10^{-6} M and 10^{-8} M , typical for surface waters, are presented in Table 2.3 and give an overview of the half-lives of Sb(III) under different conditions. The estimated half-lives range from 11 days to over 330 years indicating that H_2O_2 is a potential oxidant under certain conditions. Such long half-lives might explain why the concentration of Sb(III)

Table 2.3. Estimated half-lives for the oxidation of Sb(III) with H₂O₂ at typical pH values for surface waters (Eqn. 13 with I = 0.01 M).

	pH 7	pH 8	pH 9
k [M ⁻¹ s ⁻¹]	6.8·10 ⁻³	6.8·10 ⁻²	6.8·10 ⁻¹
t _{1/2} [years] with 10 ⁻⁸ M H ₂ O ₂	324.2	32.4	3.2
t _{1/2} [years] with 10 ⁻⁶ M H ₂ O ₂	3.2	0.32	0.03

in surface waters exceeds the thermodynamic equilibrium prediction of 10⁻¹⁸ for the ratio of Sb(III)/Sb(V) by several orders of magnitude (1, 24, 37). Furthermore, the oxidation of Sb(III) with O₂ and H₂O₂ appears to be significantly slower than the published experimental values determined for oxidants, such as Mn(IV) and Fe(III) (hydr)oxides. Complexation could also stabilize Sb(III) in solutions but there is little data to support this hypothesis. Nevertheless, the oxidation rates determined here provide a valuable basis for the further study of Sb(III) oxidation in the environment.

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Iron-mediated oxidation of antimony(III) by oxygen and hydrogen peroxide compared to arsenic(III) oxidation

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Abstract. Antimony is used in large quantities in a variety of products, though it has been declared as a pollutant of priority interest by the Environmental Protection Agency of the United States (USEPA). Oxidation processes critically affect the mobility of antimony in the environment since Sb(V) has a greater solubility than Sb(III). In this study, the co-oxidation reactions of Sb(III) with Fe(II) and both O₂ and H₂O₂ were investigated and compared to those of As(III). With increasing pH, the oxidation rate coefficients of Sb(III) in the presence of Fe(II) and O₂ increased and followed a similar pH trend as the Fe(II) oxidation by O₂. Half-lives of Sb(III) were 35 and 1.4 h at pH 5.0 and pH 6.2, respectively. The co-oxidation with Fe(II) and H₂O₂ is about 7000 and 20 times faster than with Fe(II) and O₂ at pH 3 and pH 7, respectively. For both systems, •OH radicals appear to be the predominant oxidant below approximately pH 4, while at more neutral pH values, other unknown intermediates become important. The oxidation of As(III) follows a similar pH trend as the Sb(III) oxidation, however, As(III) oxidation was roughly 10 times slower and only partly oxidized in most of the experiments. This study shows that the Fe(II)-mediated oxidation of Sb(III) can be an important oxidation pathway at neutral pH values.

3.1 INTRODUCTION

Antimony (Sb) and its compounds have been declared as pollutants of priority interest by the Environmental Protection Agency of the United States (USEPA) and the Council of the European Communities ((1) and references therein) and is consumed in large quantities (>100'000 tons annually worldwide) in a variety of industrial products, e.g. Sb(III) in flame retardants and in elemental form in alloys for storage batteries and ammunition (2-4).

Naturally occurring concentrations of Sb are below 1 µg/L in aquatic systems. In the oxic aqueous phase, the oxidized species Sb(V) predominates as $\text{Sb}(\text{OH})_6^-$ (1, 5), which sorbs less well than Sb(III) species to Fe and Mn (hydr)oxide surfaces (6, 7) and forms oxides (Sb_2O_5) that are more soluble than oxides of Sb(III) (Sb_2O_3) (4). Due to the greater solubility of Sb(V), oxidation processes are critical with regard to the mobility of Sb in the environment.

Very little is known so far about oxidation processes, and kinetic studies, in particular, are rare (8). Oxidation of Sb(III) by O_2 as the sole oxidant appears to be extremely slow. The reaction was only observed at pH values in the range of 11 to 13, where the rates were inversely proportional to H^+ concentrations. Extrapolating this trend to neutral pH values yields a half-life of 170 years at pH 8.5 in homogeneous solutions in the dark ((9)/Chapter 2). Oxidation of Sb(III) by H_2O_2 is much faster, with a half-life of 118 days at 1 µM H_2O_2 and pH 8 ((9)/Chapter 2). The reaction is again inversely proportional to H^+ concentrations in the pH ranges of 8-11 and 8-9.5 in 0.001 and 0.5 M NaCl solutions, respectively ((9, 10)/Chapter 2). There is evidence that humic acids (5 mg/L DOC) oxidize Sb(III) to Sb(V) with a half-life of 17 min at pH 7.2 in sunlight (11). Other reported oxidants are Mn(IV) and Fe(III) (hydr)oxides, with average pseudo-first-order rate coefficients of 2.35 d^{-1} and 0.887 d^{-1} between pH 5 and 10, respectively (12). In the case of Fe(III) (hydr)oxides, the exact oxidation reaction is not fully understood. Traces of incorporated Fe(II) in Fe(III)

(hydr)oxides could increase oxidation rates, as has been observed for As(III) (13, 14).

The co-oxidation of As(III), another group 15 element with a similar geochemistry to Sb, by Fe(II) and O₂ or H₂O₂ has been observed. During Fe(II) oxidation by O₂, reactive intermediates such as O₂^{•-}, HO₂[•], H₂O₂, [•]OH and possibly Fe(IV), are formed ((15, 16) and references therein). In the presence of H₂O₂, [•]OH is one of the predominant radicals (17). Arsenic(III) competes with Fe(II) and is partially oxidized within hours at neutral pH conditions (15). In the presence of Fe(II) and H₂O₂, As(III) is even more quickly oxidized under similar conditions (15, 18).

The aim of this study is to determine the rate law of the Sb(III) oxidation in the presence of Fe(II) and O₂, and Fe(II) and H₂O₂ as a function of pH in aqueous solutions, to determine possible reaction mechanisms, to compare these reactions with those of As(III) and to assess the relevance of these reactions in natural waters.

3.2 EXPERIMENTAL SECTION

3.2.1 Reagents and materials

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

3.2.2 Analysis

Arsenic(III), As_{tot}, Sb(III), and Sb_{tot} were selectively analyzed using a hydride generation atomic fluorescence spectrometer (Millenium Excalibur-System, PSA 10.055. PS Analytical LTD) as described elsewhere ((9, 19)/Chapter 2). Iron(II) was determined using a modified 1,10-phenanthroline method (20). The initial pH (±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.

3.2.3 Kinetic experiments

All experiments were carried out in carbonate-buffered solutions, which were prepared by dissolving CaCO_3 in water supersaturated with CO_2 , in light with $\lambda > 550$ nm to avoid photochemical reactions, at 25°C and were shaken on a rotary shaker (125 rpm). Initial pH values of between 5.5 and 6.4 were obtained by outgassing of CO_2 , whereas all other pH values were obtained by addition of HCl or KOH. The parameters for all kinetic experiments are listed in Table S3.1 (Supporting Information).

For the oxidation experiments in the presence of Fe(II) or Fe(III) and O_2 , Fe(II) or Fe(III) was quickly mixed into 250 or 500 mL of the pH-adjusted air-saturated buffer solution, which already contained Sb(III) or As(III) and 2-propanol (an $\cdot\text{OH}$ radical scavenger), when appropriate. Samples (2 mL) for Sb(III), Sb_{tot} , As(III) and As_{tot} analysis were taken at appropriate time intervals and added into 0.1 M sodium oxalate solution at pH 2.2 (2 mL) in order to quench the reaction and dissolve the amorphous Fe hydroxides. For Sb(III) and As(III) analysis (dissolved plus adsorbed), 1 M di-sodium-hydrogen-citrate (10 mL) was added after ~ 90 min and samples were filled up to 20 mL with water. Samples for Sb_{tot} and As_{tot} analysis were stored in 3 M HCl. Both samples were kept at 4°C prior to analysis. Iron(II) and pH were measured at the beginning of experiments immediately after Fe addition and again at the end of the experiment. During the experiments, the pH increased by 0.1-0.3 pH units, most probably due to outgassing of CO_2 . The Sb_{tot} concentration remained constant except at pH values around pH 5 (with Fe(II)) and pH 5-6 (with Fe(III)), where reduced concentrations were measured as a result of Sb sorption to Fe colloids attached to the bottle walls. The Fe(II) co-oxidation experiments were repeated in 11 small tubes, each tube being extracted by addition of 7.5 mL of the oxalate

solution to the experimental solution (7.5 mL) in order to ensure that all Sb was obtained.

In the experiments with H_2O_2 , a pH-adjusted buffer solution containing twice the initial Sb(III) or As(III), H_2O_2 and 2-propanol concentration, and a pH-adjusted buffer solution containing twice the initial Fe(II) concentration were mixed rapidly in the ratio of 1:1 to avoid locally higher concentrations of reactants during initial mixing. Total concentration of Sb or As and pH were measured at the beginning and at the end of the experiments.

3.2.4 Reproducibility

Each experiment was repeated 2-3 times except the experiments with Fe(II) concentrations below 20 μM and 3 μM for the oxidation with O_2 and H_2O_2 , respectively, which were performed once. The average relative standard deviations of duplicate analyses of As and Sb are 7% and 3%, respectively. Duplicates were taken for sampling intervals greater than 30 s. For the Sb oxidation experiments with H_2O_2 and for all the As experiments, only single samples were taken. The reproducibility between different experiments was mostly limited by changes in pH due to loss of CO_2 from the solution and lack of buffering below pH 6. The relative standard deviations of rate coefficients obtained from repeated experiments were approximately 10%.

3.2.5 Kinetic Modeling

The experimental data were modeled with ACUCHEM (21) and with improved global fitting routines written in Matlab (The MathWorks Inc.) similar to those used in a previous study of As(III) oxidation in the presence of Fe(II) (15). The reactions listed in Table 3.1 were used as input for ACUCHEM. Equilibrium reactions were written as separate forward and backward reactions, with fast, nonrate-determining forward/back rate constants. Dissolved O_2 and pH were

Table 3.1: Kinetic Model and rate coefficients of the hypothetical reaction model

Kinetic Model ^a				Rate coefficients ^b log k _i (M ⁻¹ s ⁻¹)	
	reactions	rate coefficients (s ⁻¹) or (M ⁻¹ s ⁻¹)	ref	Model for Sb and As	Model for As (15)
Antimony Oxidations					
A1 _{Sb}	Sb(III) + •OH → Sb(IV)	8 x 10 ⁹ (estimated)			
A2 _{Sb}	Sb(IV) + O ₂ → Sb(V) + O ₂ • ⁻	1.1 x 10 ⁹ (estimated)			
Arsenic Oxidations					
A1 _{As}	As(III) + •OH → As(IV)	8 x 10 ⁹	(22)		
A2 _{As}	As(IV) + O ₂ → As(V) + O ₂ • ⁻	1.1 x 10 ⁹	(22)		
Fe^{II} Oxidations					
B1	Fe ²⁺ + O ₂ → O ₂ • ⁻ + Fe ³⁺	k ₁	(23)	calc. from (23)	calc. from (24)
B2	Fe ²⁺ + O ₂ • ⁻ + 2H ⁺ → Fe ³⁺ + H ₂ O ₂	1 x 10 ⁷	(25)		
B3	Fe ²⁺ + HO ₂ • + H ⁺ → Fe ³⁺ + H ₂ O ₂	1.2 x 10 ⁶	(25)		
B4	Fe ²⁺ + •OH → Fe ³⁺ + OH ⁻	3.2 x 10 ⁸	(26)		
Modified Fenton Reactions					
F1	Fe ²⁺ + H ₂ O ₂ → INT	k ₂	(27)	2.1 (27)	1.4
F2	Fe ^{II} OH ⁺ + H ₂ O ₂ → INT-OH	k ₃	(27)	7.2 (27)	7.1
I1	INT-OH + H ⁺ ↔ INT	K ₄		4.0	5.2

I2	$\text{INT} \rightarrow \text{Fe}^{\text{III}}(\text{OH})^{2+} + \bullet\text{OH}$	1×10^6 (estimated)
I3	$\text{INT-OH} \rightarrow \text{Fe(IV)}$	1×10^6 (estimated)

Fe(IV) Reactions

J1	$\text{Fe(IV)} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{3+}$	k_5	6.3	3.3
J2	$\text{Fe(IV)} + \text{Fe}^{\text{II}}\text{OH}^+ \rightarrow \text{Fe}^{3+} + \text{Fe}^{3+}$	k_6	9.3	8.1
J3 _{Sb}	$\text{Sb(III)} + \text{Fe(IV)} \rightarrow \text{Sb(IV)} + \text{Fe}^{3+}$	$k_{7\text{Sb}}$	7.8	-
J3 _{As}	$\text{As(III)} + \text{Fe(IV)} \rightarrow \text{As(IV)} + \text{Fe}^{3+}$	$k_{7\text{As}}$	6.2	5.6

Fe(III) Reductions

R1	$\text{Fe}^{3+} + \text{O}_2^{\bullet-} \rightarrow \text{Fe}^{2+} + \text{O}_2$	1.5×10^8	(25)
R2	$\text{Fe}^{\text{III}}\text{OH}^{2+} + \text{O}_2^{\bullet-} \rightarrow \text{Fe}^{2+} + \text{OH}^-$	1.5×10^8	(25)
R3	$\text{Fe}^{\text{III}}\text{OH}_2^+ + \text{O}_2^{\bullet-} \rightarrow \text{Fe}^{2+} + \text{O}_2 + 2\text{OH}^-$	1.5×10^8	(25)

Reactive Oxygen Radical Reactions

O1	$\text{HO}_2^{\bullet} + \text{O}_2^{\bullet-} + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	9.7×10^7	(25)
O2	$\text{HO}_2^{\bullet} + \text{HO}_2^{\bullet} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	8.3×10^5	(25)
O3	$\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{HO}_2^{\bullet} + \text{H}_2\text{O}$	3×10^7	(28)
Q1	$\bullet\text{OH} + 2\text{-prop} \rightarrow \text{O}_2^{\bullet-} + \text{acetone}$	1.9×10^9	(28)

Table 3.1 continued

	reactions	rate coefficients (s ⁻¹) or (M ⁻¹ s ⁻¹)	ref	Model for Sb and As	Model for As (15)
Fe(III) Equilibria					
E1	$\text{Fe}^{3+} \leftrightarrow \text{Fe}^{\text{III}}(\text{OH})^{2+} + \text{H}^+$	$4.57 \times 10^9 / 1 \times 10^{12}$ (pK ₁ 2.3)	(29)		
E2	$\text{Fe}^{\text{III}}(\text{OH})^{2+} \leftrightarrow \text{Fe}^{\text{III}}(\text{OH})_2^+ + \text{H}^+$	$2.51 \times 10^8 / 1 \times 10^{12}$ (pK ₂ 3.6)	(29)		
E3	$\text{Fe}^{\text{III}}(\text{OH})_2^+ \leftrightarrow \text{Fe}^{\text{III}}(\text{OH})_3 + \text{H}^+$	$1.17 \times 10^4 / 1 \times 10^{12}$ (pK ₃ 7.9)	(29)		
Fe(III) Precipitation					
P1	$\text{Fe}^{\text{III}}(\text{OH})_3 + \text{Fe}^{\text{III}}(\text{OH})_3 \rightarrow \text{precip}$	<i>k</i> ₈		4.7	8.3
P2	$\text{Fe}^{\text{III}}(\text{OH})_3 + \text{precip} \rightarrow \text{precip}$	<i>k</i> ₈		4.7	8.3
Sb(III) Oxidation by Fe(III)					
X0	$\text{Fe}^{3+} + \text{Sb(III)} \rightarrow \text{Fe(II)} + \text{Sb(IV)}$	<i>k</i> ₉		-3.1	-
X1	$\text{Fe}^{\text{III}}(\text{OH})^{2+} + \text{Sb(III)} \rightarrow \text{Fe(II)} + \text{Sb(IV)}$	<i>k</i> ₉		-3.1	-
X2	$\text{Fe}^{\text{III}}(\text{OH})_2^+ + \text{Sb(III)} \rightarrow \text{Fe(II)} + \text{Sb(IV)}$	<i>k</i> ₉		-3.1	-
X3	$\text{Fe}^{\text{III}}(\text{OH})_3 + \text{Sb(III)} \rightarrow \text{Fe(II)} + \text{Sb(IV)}$	<i>k</i> ₉		-3.1	-

Fe(II) Equilibria				
E4	$\text{Fe}^{2+} \leftrightarrow \text{Fe}^{\text{II}}\text{OH}^+ + H^+$	$3.09 \times 10^2 / 1 \times 10^{12}$ (pK_1 9.51)	(29)	
Superoxide Equilibria				
E5	$\text{O}_2^{\bullet-} + H^+ \leftrightarrow \text{HO}_2^{\bullet}$	$1 \times 10^{12} / 1.58 \times 10^7$ (pK_a 4.8)	(25)	
E6	$\text{air} \leftrightarrow \text{O}_2$	$1 \times 10^6 / 1 \times 10^{12}$ constant [O ₂] (250 M air reservoir)		
				SSD = 1.5 SSD = 1.5
<p>^a List of reactions used in the model. Italics marked species were not included in the model and are only written to keep equations balanced. Rate coefficients in bold were optimized by simultaneous fitting. Estimated rate coefficients are nonrate determining; all others were taken from the literature. The pH-dependent k_I was calculated for each pH from ref (23).</p> <p>^b Fitted rate coefficients and sum of squared differences (SSD) for this model and the model of Hug and Leupin (15). Numbers in italics were kept at fixed values, while the rate coefficients in bold were optimized by simultaneous fitting.</p>				

kept constant during the experiments by equilibrium with a large air reservoir and by formulating all equilibrium reactions as H^+ -preserving reactions. The adjustable rate constants were varied by the Matlab routine until the total sum of normalized squared differences between data and model for all experiments was minimized with the Nelder-Mead simplex routine.

3.3 RESULTS AND DISCUSSION

3.3.1 Oxidation of Sb(III) in the presence of Fe(III)

Since Fe(III) is formed during Fe(II)-mediated Sb(III) oxidation, the influence of Fe(III) on Sb(III) oxidation was investigated. At pH 2.2 (Fig. 3.1A) and 3.2 (data not shown), Fe(III) oxidized Sb(III) to Sb(V) with pseudo-first-order rate coefficients of $5.7 \times 10^{-8} \pm 3.8 \times 10^{-9} \text{ s}^{-1}$ and $1.1 \times 10^{-7} \pm 1.3 \times 10^{-8} \text{ s}^{-1}$, respectively, which are similar to the reaction in the presence of Fe(II). At pH 5.0 and 6.2, no Sb(V) was observed, but both the total dissolved Sb_{tot} concentrations decreased (Fig. 3.1B,C), most probably because some Sb(III) was sorbed to a fraction of Fe colloids that was sorbed to the bottle walls. In the same time span Fe(II) was able to oxidize a significant amount of Sb(III), indicating that at pH values around and above 5, the role of Fe(III) was insignificant.

Belzile et al. (12) observed a pH independent complete Sb(III) oxidation by freshly prepared Fe(III) oxyhydroxides within 6 d in a pH range of 5.0 to 10.2. Pseudo-first-order rate coefficients were $1.0 \times 10^{-5} \pm 1.9 \times 10^{-6} \text{ s}^{-1}$ at an Fe:Sb molar ratio of 4500 at 20°C. Recalculating this value for a Fe:Sb molar ratio of 90, a value for k_{obs} of $2.0 \times 10^{-7} \text{ s}^{-1}$ and a half-life of 40 d are estimated, which agrees well with our value at pH 3.2. Assuming that the reaction with Sb(III) and Fe(III) is pH independent as shown by Belzile et al. (12), the influence of

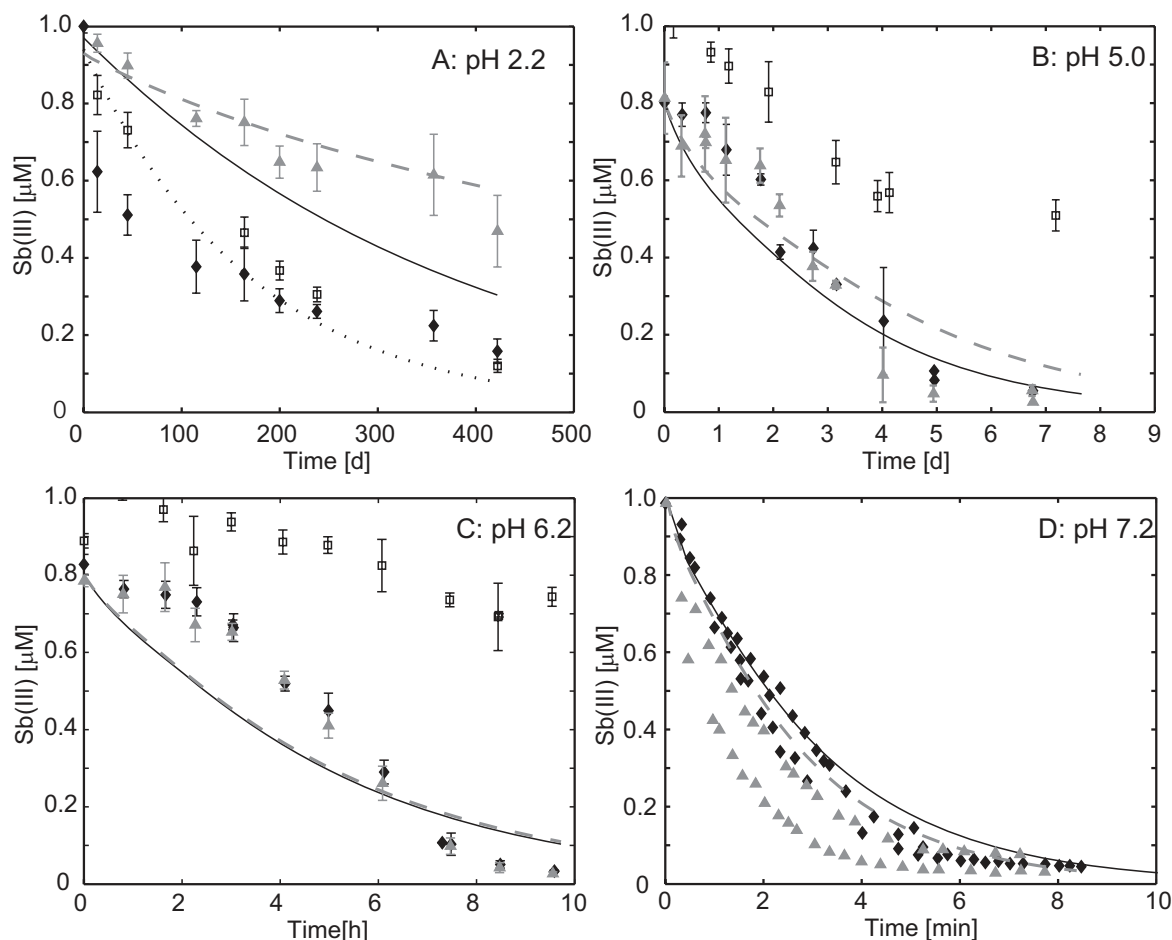


Fig. 3.1: pH-dependence of Sb(III) oxidation in the presence of Fe(II) (♦ -), Fe(II) + 2 propanol (▲ -) and Fe(III) (□ ...). The aerated solutions contain initial concentrations of $[\text{Sb(III)}]_0 = 1 \mu\text{M}$, $[\text{Fe}]_0 = 90 \mu\text{M}$, $[\text{2-prop.}]_0 = 14 \text{ mM}$. Lines represent the fit of the hypothetical reaction model. In B and C, Sb(III) concentrations in the presence of Fe(III) were not modeled. Error bars represent the standard deviation of triplicates. At pH 7.2 samples were not taken at the same time; therefore duplicates are shown.

Fe(III) on the Fe(II)-mediated oxidation of Sb(III) is negligible at pH values above 5.

For As, the literature is contradictory on the oxidation of As(III) to As(V) with Fe(III) (hydr)oxides. No As(III) oxidation was observed within 3 d at pH 7.5 in the presence of Fe(III) (hydr)oxides prepared from Fe(III) salts with an Fe:As molar ratio of 12 (14). Using Fe oxides produced by slow oxidation of Fe(II), 50-75% of As(III) is oxidized within 2 d with an Fe:As molar ratio of 3400 in a pH range from 4.7 to 10.2, and no trend with pH was observed (13). It

appears that both the ratio of Fe:As and the preparation of Fe oxides have a significant influence on the oxidation process.

3.3.2 Iron(II)-mediated oxidation of Sb(III) with O₂ in the pH range of 2.2-7.6

The oxidation rate coefficients for Sb(III) to Sb(V) followed a trend similar to those of the Fe(II) oxidation and were strongly pH dependent (Fig. 3.2). The pseudo-first-order oxidation rate coefficients, k_{obs} , increased by a factor of almost 100 with each pH unit between pH 6.2 ($k_{\text{obs}} = 1.4 \times 10^{-4} \pm 4.6 \times 10^{-6} \text{ s}^{-1}$) and 7.1 ($k_{\text{obs}} = 7.1 \times 10^{-3} \pm 7.2 \times 10^{-4} \text{ s}^{-1}$), while between pH 2.2 and 3.6, the rate coefficients were slow and almost pH independent ($4.2 \times 10^{-8} \pm 3.2 \times 10^{-9} \text{ s}^{-1}$ and $8.1 \times 10^{-8} \pm 2.0 \times 10^{-9} \text{ s}^{-1}$). The same pH dependence was reported for Fe(II) oxidation with O₂ (24, 30-32). The pH dependence of the Fe(II) oxidation is explained by the speciation of Fe(II). Either the formation of FeCO₃ or Fe(OH)₂ can increase the reaction rates by activating the Fe(II) (23).

Between pH 5 and 7, the Sb(III) concentration decreased very slowly at the beginning (“lag time”) (examples Fig. 3.1B,C). The “lag time” was below 15% of the total oxidation time, except at pH 6.2 and 6.4, where it was 30%. In pseudo-first-order plots the curve of the Sb(III) concentration is initially nonlinear. Pseudo-first-order rate coefficients were only calculated from the linear part, thus generally overestimating the oxidation rate. At pH values between 2.2 and 3.6 and above pH 7, it was not possible to observe this “lag time” because under both conditions the sampling intervals were too large. One explanation for this “lag time” is the autocatalytic oxidation of Fe(II) oxidation, which was reported to occur with initial Fe(II) concentrations above 54 μM in 0.1 M [NaClO₄⁻] and 0.01 M [NaHCO₃] in a pH range from 6 to 7 (33, 34). Considering the fast oxidation rates for Sb(III) in the presence of Fe(II) oxidation at neutral pH values, and the low Fe(II) concentrations in natural

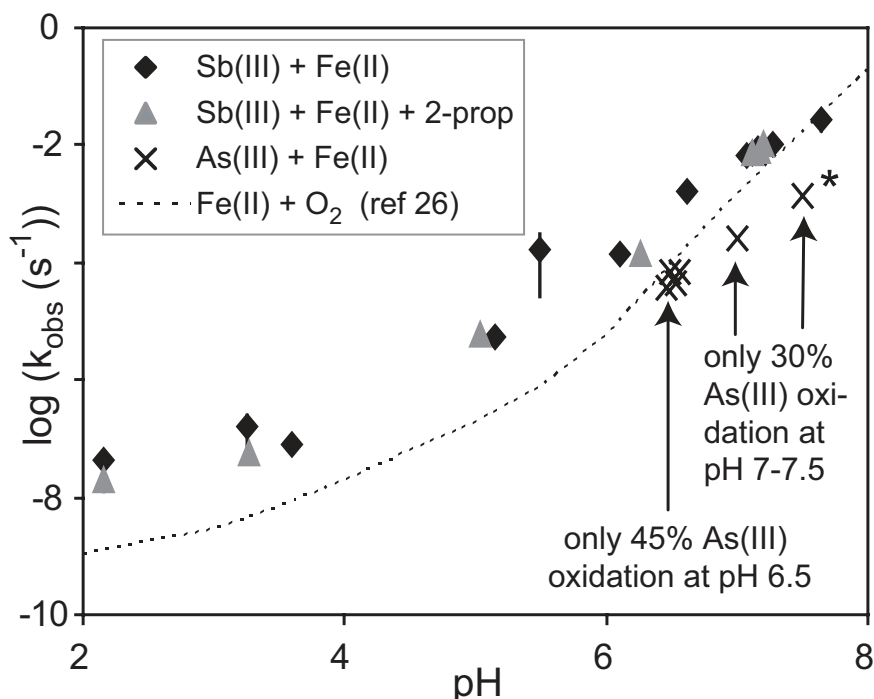


Fig. 3.2: Log values of the pseudo first order rate coefficients of 1 μM Sb(III) and 1/6.6 μM As(III) oxidation in the presence of 90 μM Fe(II) in aerated solutions as a function of pH. Error bars of the rate coefficients are within the size of the symbols in most of the data points. For a comparison, the dotted lines shows the Fe(II) oxidation rate coefficients as calculated from ref (23). This data point marked with an asterisk (*) was taken from the study of Hug and Leupin (2003) (15).

systems, this “lag time” does not appear to be environmentally relevant and was not investigated further.

Additionally, initial Fe(II) concentrations were varied between 0.1 and 200 μM at pH values between 6.4 and 7.5 (Fig. 3.3). Oxidation rates increased with increasing Fe:Sb ratio. At Fe:Sb ratios of 0.1, no significant oxidation of Sb(III) occurred, but 45% of the initial Sb(III) concentration was oxidized at a ratio of 1. The Sb(III) oxidation reaction stopped when all Fe(II) had been oxidized to Fe(III). At a ratio of 3, all Sb(III) was oxidized. At higher Fe:Sb ratios in the range of 20 to 200, the slope decreased in a $\log k_{\text{obs}} \log [\text{Fe(II)}]_0$ plot, which is ascribed to Fe(II) competing with Sb(III) for reaction intermediates.

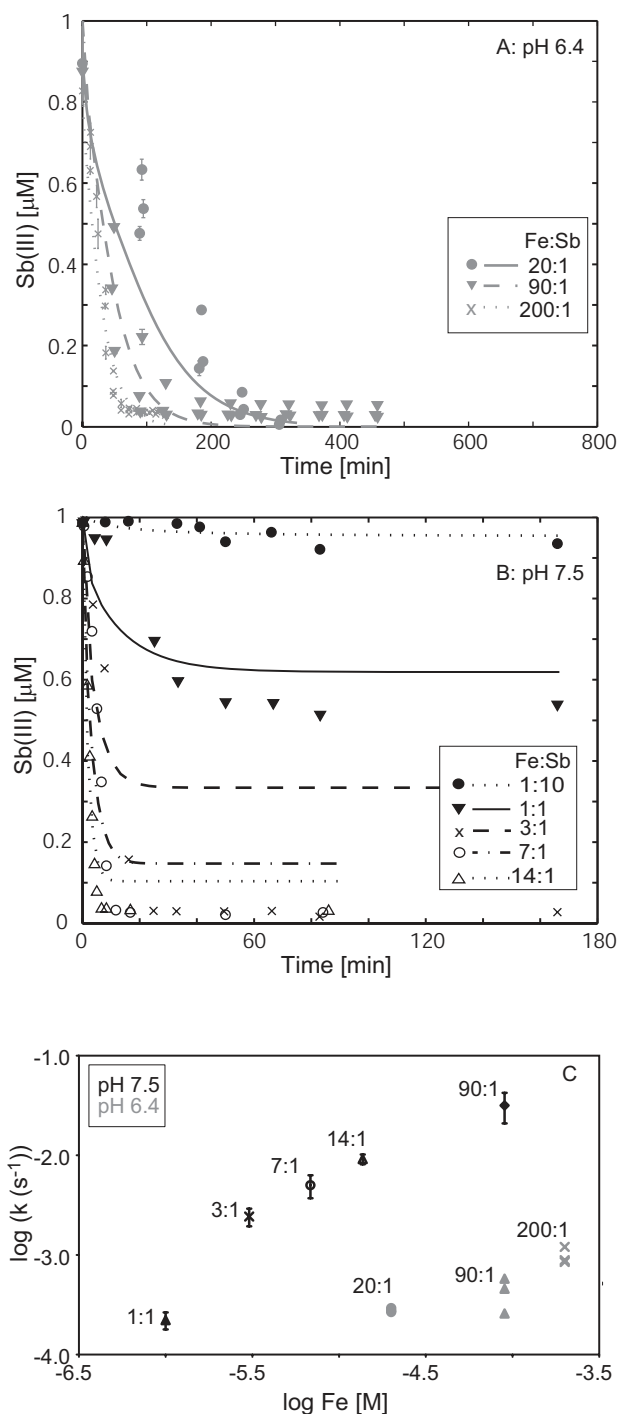


Fig. 3.3: Sb(III) concentrations as a function of time with different initial Fe(II) concentrations at pH 6.4 (A, gray symbols) and pH 7.5 (B, black symbols). Lines represent the fit of the hypothetical reaction model. (C) shows the dependence of pseudo-first-order rate coefficients for Sb(III) oxidation on Fe(II) concentrations. Numbers represents the Fe:Sb ratios; error bars are the 2-fold error of the slope of the linear regressions.

Reactive oxygen species ($\text{O}_2^{\bullet-}$, H_2O_2 , $\bullet\text{OH}$) and other reactive intermediates are formed during the reduction of O_2 by Fe(II) . At pH 2.2 (Fig. 3.1A) and at pH 3.2 (data not shown), the reaction with Sb(III) , Fe(II) , and 2-propanol, an $\bullet\text{OH}$ scavenger, is 2-3 times slower than the reaction without 2-propanol. However, 2-propanol cannot quench the reaction completely. At pH 5.0, 6.2 and 7.2, 2-propanol has no significant effect on the oxidation rate of Sb(III) (Fig. 3.1B-D). This indicates that at pH 2 and 3, $\bullet\text{OH}$ are partly involved in the reaction but at neutral pH values, other intermediates must react with Sb(III) . To investigate this mechanism further, we carried out the experiments, described in the next section, where Sb(III) was oxidized in the presence of Fe(II) and H_2O_2 .

3.3.3 Oxidation of Fe(II) and Sb(III) with added H_2O_2

Antimony(III) oxidation in the presence of Fe(II) and H_2O_2 was very fast (>95% within 20 s at pH 6.8 and 1 h at pH 2.9) compared to that in the presence of Fe(II) and O_2 (Fig. 3.4 A-C). This reaction was also pH dependent, and the rates increased with increasing pH. Additional experiments with initial Fe(II) concentrations from 0.01 to 3 μM and an initial H_2O_2 concentration of 3 μM at pH ~ 7.2 are shown in Fig. 3.4 D. Traces of Fe(II) , such as in the Fe:Sb ratio of 0.01 can oxidize 45% of Sb(III) in the presence of 3 μM H_2O_2 . Above a ratio of 0.1 Sb(III) was completely oxidized. Small Fe(II) concentrations are thus sufficient to start a chain reaction. First, Fe(II) reacts with H_2O_2 to form Fe(III) and $\bullet\text{OH}$ or a reactive intermediate, suggested to be Fe(IV) by Hug and Leupin (Table 3.1: F1/F2 (15)). Then, Sb(III) is oxidized to Sb(IV) by $\bullet\text{OH}$ or Fe(IV) (Table 3.1: A1_{Sb}/J3_{Sb}). Antimony(IV) reacts with O_2 to give Sb(V) and $\text{O}_2^{\bullet-}$ (Table 3.1: A2_{Sb}). The chain is propagated by the reduction of Fe(III) with $\text{O}_2^{\bullet-}$ to Fe(II) (Table 3.1: R1-R3).

At pH 2.9, 2-propanol inhibited the Sb(III) oxidation completely, while at pH 4.2 the inhibition was less marked, and at pH 6.8 there was no significant

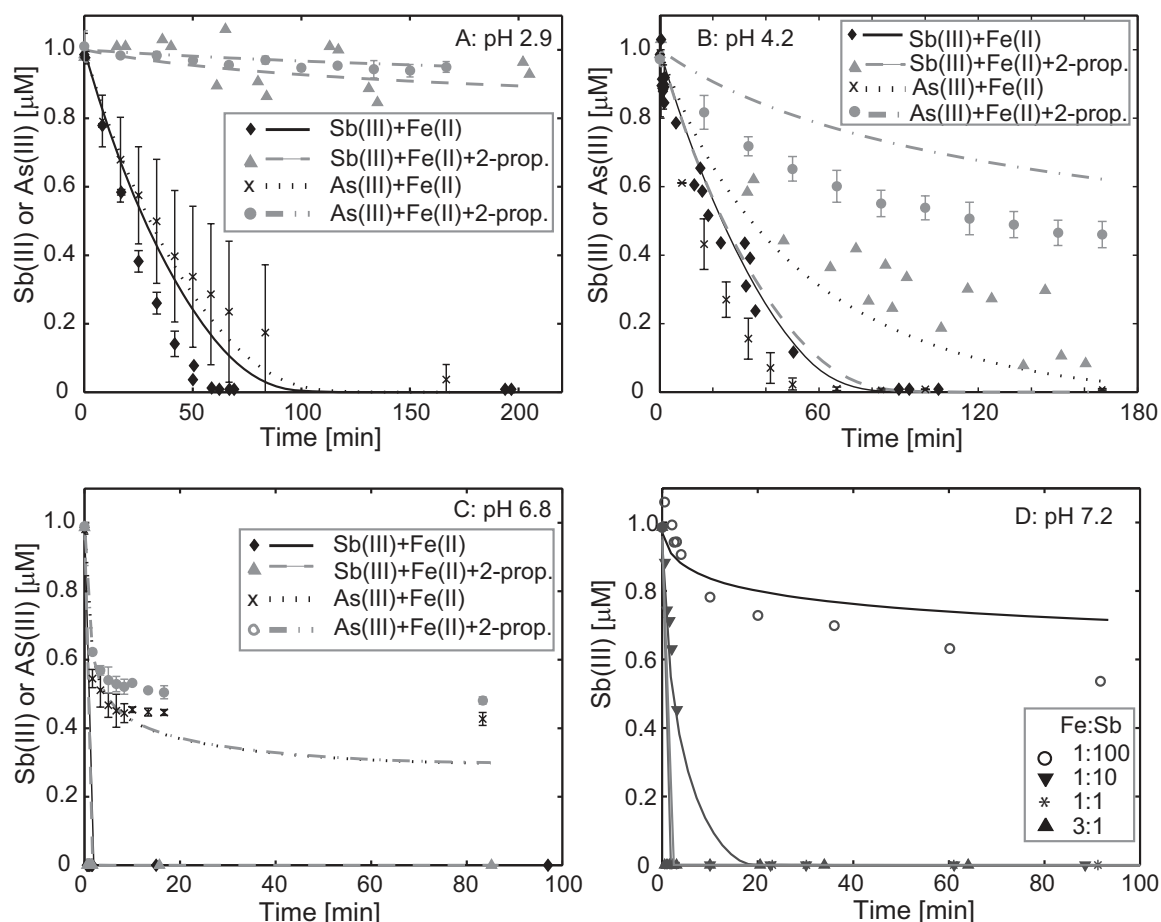


Fig. 3.4 A-C: pH-dependence of 1 μM Sb(III) and 1 μM As(III) oxidation in the presence of 3 μM Fe(II) and 3 μM H_2O_2 in aerated solutions. Lines represent the fit of the hypothetical reaction model. Error bars represent the standard deviation of duplicates when sampling was at the same time; otherwise duplicates are shown. **D:** Sb(III) concentrations as a function of time with different initial Fe(II) concentrations and an initial H_2O_2 concentration of 3 μM at pH ~ 7.2 . Lines represent the fit of the hypothetical reaction model.

difference between the reaction rates with and without 2-propanol. Again, $\bullet\text{OH}$ radicals might be the oxidant for Sb(III) at pH values below 3, where the reaction is quenched with 2-propanol. However, with increasing pH, an additional oxidant must be formed. In agreement with other studies ((9, 10)/ Chapter 2), H_2O_2 alone did not oxidize Sb(III) on a time scale of hours at pH values below 7, so it cannot be responsible for the fast Sb(III) oxidation.

Superoxide and HO_2^\bullet ($\text{p}K_a = 4.8$) (35) are weaker oxidants than H_2O_2 and $^\bullet\text{OH}$ from a thermodynamic point of view (16) and do not appear to play a role in this system. At low pH values $^\bullet\text{OH}$ reacts mainly with 2-propanol to produce acetone and HO_2^\bullet . If HO_2^\bullet were to be important, no quenching with 2-propanol at pH 2.9 would be observed. Consequently, additional oxidants are formed in the Fenton reaction ($\text{Fe(II)} + \text{H}_2\text{O}_2$) at higher pH values. One possibility is Fe(IV) (15).

3.3.4 Comparison of As and Sb oxidation in the presence of Fe(II) or Fe(II) and H_2O_2

The main difference between As(III) and Sb(III) oxidation is that Sb(III) oxidation by Fe(II) and O_2 was approximately an order of magnitude faster and that at least 95% Sb(III) was oxidized, while only 45% of As(III) was oxidized at pH 6.5. No significant As(III) oxidation occurred at pH 5 within 4 days (Fig. 3.2).

In the experiments with Fe(II) and H_2O_2 , the Sb(III) oxidation rate appeared to be faster than that of As(III) at pH 2.9 (Fig. 3.4 A-C). At pH 6.8, > 95% of Sb(III) was oxidized, whereas 50% of As(III) remained in solution after the Fe(II) oxidation was completed. At pH 4.2, Sb(III) oxidation is faster in the experiments with 2-propanol. The difference in reactivity between Sb and As could be related to electronegativity, that of As(III) being slightly higher (As: 2.18, Sb: 2.05 (36))

3.3.5 Hypothetical Reaction Model

The hypothetical model described by Leupin and Hug ((15), Table 3.1) appears to apply to the Sb(III) oxidation curves. A key role is played by the Fenton reaction, in which differently protonated Fe(II) species exchange H_2O with H_2O_2 (24, 32) via an inner-sphere electron-transfer (37-39), and two intermediates ($[(\text{H}_2\text{O})_5\text{Fe}^{\text{II}}-\text{O}_2\text{H}_2]^{2+} \rightarrow \text{INT} \rightarrow ^\bullet\text{OH}$ or $[(\text{H}_2\text{O})_4(\text{OH})\text{Fe}^{\text{II}}-\text{O}_2\text{H}_2]^+ \rightarrow \text{INT-OH} \rightarrow$

possibly Fe(IV)) are formed. It is difficult to directly detect these intermediates, which probably form at nanomolar steady-state concentrations. However, Fe(IV) or other higher-valent Fe species have been suggested in several more recent studies (38, 40-42).

For the modeling, all known rate coefficients were taken from the literature apart from reactions involving Fe(IV), the oxidation of Sb(III) by Fe(III) and the polymerization of Fe(III), and its removal from the reactive system (Table 3.1). The effect of carbonate on the Fe(II) oxidation was included in the calculated rate coefficients for the Fe(II) oxidation by O₂ since carbonate can increase the oxidation rate (23, 43). The reactions of Sb(III) with the reactive intermediates and the Sb(III) oxidation by Fe(III), which is not significant at pH values above 5, were added to the model of Hug and Leupin (15). Most of the optimized rate coefficients in the adopted model are in the same order of magnitude as the optimized rate coefficients used in the previous model for As(III) oxidation (Table 3.1, (15)). One of the most critical factors in both models is the pK_4 value of INT (I1). The pK_4 value between INT-OH and INT of our model is one pH unit lower than of the previous model. However, in both models only a few experiments in the pH range of 3.5-5.5 were carried out, thus it was not possible to determine this value precisely. Another critical factor is the reaction of the intermediate with Fe²⁺ (k_5 , J1), which in the previous study was 200 times smaller than fitted by this model. Our value is probably more accurate because experiments were carried out where Fe²⁺ was the predominant species in solution. The rate coefficient for the Fe(III) precipitation (k_8 , P1-P2) also differs. This is ascribed to the following reasons: the use of lower Fe concentrations in most of the experiments, and the reactions of polynuclear Fe(III) or Fe(III)-Fe(II) species are not considered in the model, which might explain discrepancies in the fitted rate coefficients. However, the reactions J1, J2, P1 and P2 all effectively reduce the concentrations of the intermediates and slow the oxidation of As(III) and Sb(III) down. With this data set it is not possible to eliminate

covariance. This covariance was probably responsible for the failure of our attempts to model the “lag time” in terms of Fe(II) adsorption to Fe(III)(hydr)oxides (after (33)), which would then react more quickly with O₂ than free Fe(II). At low pH values (<3) for the reaction with Fe(II) and O₂, the model predicts a slower reaction than the Sb(III) oxidation was. This is probably because not all reactions relevant at low pH were considered.

Despite the uncertainties of the rate coefficients, our results show that the model developed for As(III) can also be applied to the oxidation of Sb(III) using established Fe redox reactions over a wide pH range (Fig. 3.1, 3.3A, 3.3B and 3.4). It explains the pH-dependent partitioning of the reactions by using 2 different intermediates [•]OH at low pH and an intermediate such as Fe(IV) at neutral pH. According to the model, the oxidation rate coefficient for Sb(III) with Fe(IV) (k_{7Sb}) is estimated to be 40 times faster than for As(III) (k_{7As}). Differences in electronegativity resulting from the greater polarizability of the Sb atom, may, as mentioned before, provide an explanation for the differences in oxidation rates.

3.3.6 Empirical Model for Sb(III) oxidation in the presence of Fe(II)

The Sb(III) concentrations as a function of time in the presence of Fe(II) and O₂ were calculated by an empirical model based on the equation for the autocatalysis of Fe(II) (33, 34). This model successfully reproduced the initial “lag phase” and is a simple tool for users. The model and the fits are given in the Supporting Information (Fig. S3.1).

3.4 ENVIRONMENTAL SIGNIFICANCE

The Fe(II)-mediated oxidation of Sb(III) is faster than the oxidation with O₂ or H₂O₂ as sole oxidants at pH values below 8. This reaction may occur at the

oxidizing end of redox gradients, such as lake sediments, stratified lakes and saturated soils, where redox reactions involving Fe(II) and O₂ are present. In the freshwater lake, Baldegger (Switzerland), an enrichment of Sb(V) with respect to lake water content and a minimum Sb(III) content was observed at the sediment-water interface (44). The pore water profiles suggest that Sb is released by oxidation processes either catalyzed by Fe(II) oxidation or by Mn oxides.

The Fenton reaction can be relevant in sunlit surface waters and rainwater. In sunlit surface waters, H₂O₂ concentrations vary from 10 nM to 1 μM and dissolved Fe(II) is in the low nM range (0.1-10 nM) (45-47). Total Sb concentrations in surface water range from about 1 to 5 nM (1). Since an Fe:Sb ratio > 0.1 is obtained, Sb(III) may be completely oxidized by the Fenton reaction. This may explain the generally low Sb(III) concentrations (<10% of Sb_{tot}) in natural waters (1).

Acknowledgements. The authors thank the Swiss National Science Foundation for funding and H. Mönch and Thomas Ruettimann for their advice and support in the laboratory.

Supporting Information Available

Details of the reagent and materials and the experimental parameters (Table S3.1) and the empirical model description and the fits of the empirical model for the Sb(III) oxidation in the presence of Fe(II) and O₂ (Fig. S3.1)

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3.6 SUPPORTING INFORMATION

3.6.1 Reagents and materials.

All chemicals were of at least pro analysi (p.a.) grade and used as received. CaCO_3 , $\text{Fe(II)SO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe(III)Cl}_3 \cdot 6\text{H}_2\text{O}$, HCl (30 % Suprapur), H_2O_2 (30 %), KOH solution (1 M, Titrisol), pH-buffer solutions (2-9), 1,10-phenanthroline chloride monohydrate and the Sb(III) standard solution (1002 ± 0.002 mg/L Sb_2O_3 , CertiPUR) in 2 M HCl were purchased from Merck. Aminoacetic acid, ascorbic acid (puriss p.a.), citric acid anhydrous (Ultra), KI (puriss p.a.), NaAsO_2 , NaBH_4 (puriss p.a.), NaOH (Ultra), nitrilotriacetic acid, oxalic acid anhydrous (purum) and 2-propanol (puriss p.a.) were bought from Fluka. Deionized water, treated with a Milli-Q water purification device (resistivity $> 18 \text{ M}\Omega\cdot\text{cm}$, Millipore), was used for the preparation of solutions and rinsing processes. All glassware, polyethylene bottles and sample vessels used for the experiments and analyses were leached in acid solutions (0.3 M HCl, Merck) over night and rinsed 3 times with water prior to use.

Stock solutions of Fe(II) (90 mM), Fe(III) (90 mM), Sb(III) (10 mg/L), As(III) (1 mg/L) and H_2O_2 (10 mM) were always freshly prepared prior to each set of experiments. The Fe(II) and Fe(III) solutions were obtained by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1 mM HCl, respectively. A 1 g/L As(III) solution was prepared by dissolving 0.1734 g of NaAsO_2 in 100 mL water, this solution was used for further dilutions. The Sb(III) standard solution and H_2O_2 solution were diluted in water.

3.6.2 Empirical Model for Sb(III) oxidation in the presence of Fe(II)

The data of Sb(III) oxidation in the presence of Fe(II) and O_2 were also fitted by an empirical model in order to simulate the lag time and to provide a simple empirical model for users (Fig. S3.1). Antimony(III) concentrations as a

Table S3.1: Experimental parameters (initial concentrations after mixing)

species (conc.)	pH variation			Fe(II) variation	
	Fe(II)+O ₂ ^a	Fe(III)+O ₂ ^a	Fe(II)+H ₂ O ₂ ^b	Fe(II)+O ₂ ^a	Fe(II)+H ₂ O ₂ ^b
<i>Sb(III) experiments</i>					
Sb(III)^c (μM)	1	1	1	1	
Fe(II)^d (μM)	90	0	3.0	20 ^e , 90 ^e , 200 ^e , 6.8 ^f , 13.7 ^f , 90 ^f , 0.1 ^g , 1.0 ^g 3.0 ^g , 6.8 ^g , 13.7 ^g , 90 ^g	0.01, 0.1, 1.0 and 3.0
Fe(III)^d (μM)	0	90	0	0	0
H₂O₂ (μM)	0	0	3.0	0	3.0
initial pH^h	2.2-7.5	2.2; 3.2; 5.0 and 6.2	2.9; 4.2 and 6.8	see suffixes	7.2
2-propanol (mM)	0, 14	0	0, 14	0	0
<i>As(III) experiments</i>					
As(III) (μM)	1, 6.6		1		
Fe(II)^d (μM)	90		3.0		
H₂O₂ (μM)	0		3.0		
initial pH^h	5.0, 6.5		2.8; 4.1 and 6.8		
2-propanol (mM)	0		0, 14		

Temperature was 25°C. ^a Ca²⁺ and HCO₃⁻ concentrations were 2.5 mM and 5 mM. ^b Ca²⁺ and HCO₃⁻ concentrations were 1.25 mM and 2.5 mM. ^c Due to the acidic Sb(III) solution each Sb(III) experiment contains 0.2 mM Cl⁻. ^d SO₄²⁻ and Cl⁻ concentrations were the same as Fe(II) and 3 times the Fe(III) concentrations, respectively. ^e at pH 6.4, ^f at pH 7.1, ^g at pH 7.5. ^h Experiments at low pH values also contain Cl⁻.

function of time were calculated using the equation for the autocatalysis of Fe(II) given elsewhere (33, 34).

$$[Fe(II)](t) = \frac{[Fe(II)]_0 \cdot (k_{hom} + k_{ads})}{k_{ads} + (k_{hom} \cdot \exp(t \cdot (k_{hom} + k_{ads})))} \quad (1)$$

where $[Fe(II)]_0$ is the initial Fe(II) concentration, k_{ads} and k_{hom} are pH-dependent rate coefficients for the Fe(II) oxidation of adsorbed Fe(II) and free Fe(II), respectively. Equations for k_{ads} and k_{hom} are described by Tamura et al. (33) and King (23), respectively:

$$k_{ads} = \frac{k_s [O_2] K}{[H^+]} \quad (2)$$

where k_s is the surface rate in $M^{-1} \text{ min}^{-1}$, $[O_2]$ is the oxygen concentration in solution and K is the adsorption constant of Fe(II) on Fe(III) (hydr)oxides, whose numerical value was determined to be $10^{-9.6} \text{ mol mg}^{-1}$ for amorphous Fe (hydr)oxides (33).

$$k_{hom} = 4 \left(k_1 \alpha_{Fe^{2+}} + k_2 \alpha_{Fe(OH)^+} + k_3 \alpha_{Fe(OH)_2} + k_4 \alpha_{Fe(CO_3)_2^{2-}} \right) \cdot [O_2] \quad (3)$$

where $k_1 = 10^{-4.26} \text{ M}^{-1} \text{ min}^{-1}$, $k_2 = 10^{2.62} \text{ M}^{-1} \text{ min}^{-1}$, $k_3 = 10^{7.72} \text{ M}^{-1} \text{ min}^{-1}$ and $k_4 = 10^{5.82} \text{ M}^{-1} \text{ min}^{-1}$ at $I = 0$ and alphas are the molar fractions of the species (23).

If the ratio of $[Fe(II)](t) / [Sb(III)]_0 > 0.2$, the Sb(III) concentration at time t , $[Sb(III)](t)$, can be calculated as follows:

$$[Sb(III)](t) = \frac{[Sb(III)]_0 \cdot (k_{hom} + k_{ads})}{k_{ads} + (k_{hom} \cdot \exp(t \cdot (k_{hom} + k_{ads}) \cdot A))} \quad (4)$$

where $[Sb(III)]_0$ is the initial Sb(III) concentration, k_{ads} and k_{hom} are the rate coefficients for the Fe(II) oxidation (Eqs. 2-3) and $A = 4.98$, a fitted parameter. It is necessary to define this ratio since Sb(III) is only oxidized if sufficient Fe(II) is in solution. The ratio cannot be determined precisely, because the fits do not change as long as the ratio is between 0.16 and 0.80.

The fits of Sb(III) oxidation in the presence of Fe(II) and O_2 reproduce the experimental data. The lag time is well simulated using this equation indicating that the autocatalysis can describe the initially curves for the experiments

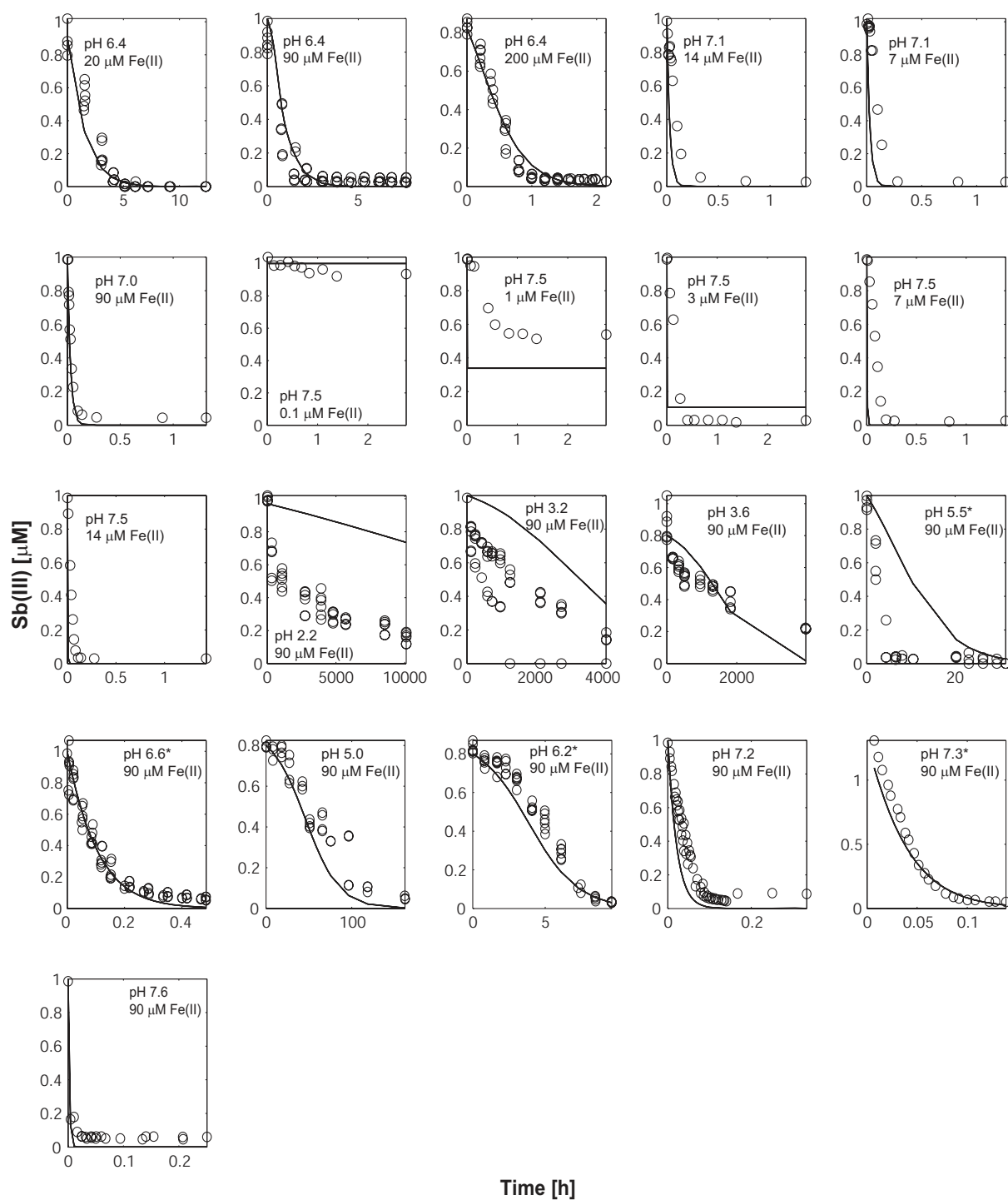


Fig. S3.1: Fits of the Sb(III) oxidation in the presence of Fe(II) and O₂ with the empirical model. Lines represent the fit and circles are the experimental data. * For these experiments, rate coefficients were adjusted to improve the fit (maximum 0.3 pH units).

between pH 5 and 7. Only at low pH values (<3), the model predicts slower oxidation rates than observed experimentally (see Hypothetical Reaction Model).

Sorption of Sb(III) and Sb(V) to goethite: Influence on Sb(III) oxidation and mobilization

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Abstract. 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 (hydr)oxides appear to be important sorbents for Sb in soils and sediments, but mineral surfaces can also catalyze oxidation processes and thus may mobilize Sb. The aim of this study was to investigate whether goethite immobilizes Sb by sorption or whether Sb(III) is oxidized and released.

Therefore, 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 Sb(V) adsorption occurs below pH 7 and desorption of Sb(V) rapidly increases above this pH. At higher ionic strength, desorption of Sb(V) is shifted to lower pH values, most likely due to formation of ion pairs K₂Sb(OH)₆⁺. 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 oxidation of adsorbed Sb(III) on Fe (hydr)oxides over a wide pH range explains why mainly Sb(V) is measured in natural waters and soils.

4.1 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 ((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). 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, 6), which forms oxides (Sb_2O_5) that are more soluble than oxides of Sb(III) (Sb_2O_3) (3). Antimony(III) occurs as Sb(OH)_3 in aqueous solutions and is more stable under anoxic conditions (6). Sorption processes to mineral phases can control the mobility of Sb.

Only very few sorption studies of Sb on natural sorbents have been reported to date ((7) and reference therein). Both Sb(III) and Sb(V) appear to bind strongly to oxides of Fe and Mn and only weakly to clay minerals (8). EXAFS measurements of soils from shooting ranges provide evidence for a strong preference of Sb binding to Fe (hydr)oxides (9). However, the binding mechanism is still unclear. From the 5 studies, dealing with Sb sorption to Fe (hydr)oxides, known to the authors, both surface coverage and pH have a strong influence on Sb(III) and Sb(V) the sorption process (8, 10-13). The sorption maxima of Sb(V) on Fe (hydr)oxides was generally reported at low pH values and extended up to pH 7 at low surface coverage (8, 10, 11, 13). Only a single study investigated the pH-dependence of Sb(III) adsorption on amorphous Fe oxides in the absence of organic ligands, namely tartrate and acetate, indicating that Sb(III) sorbs strongly in the pH range 6 to 10 (10). However, in that study high Sb(III) concentrations were used. In order to assess the binding potential of

Fe (hydr)oxides for Sb, both Sb(III) and Sb(V) sorption data at low Sb concentrations over a wide pH range is needed but is not available in literature.

Aqueous mineral surfaces not only bind metal ions, but also can accelerate redox reactions, such as the oxygenation of Fe(II), Mn(II) and VO^{2+} (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, $\text{Sb}(\text{OH})_4^-$ is the reactive species for the Sb(III) oxidation by O_2 and H_2O_2 ((18, 19)/Chapter 2), it is expected that adsorption of Sb(III) on Fe (hydr)oxides accelerates the oxidation of Sb(III). There is a study, showing that Sb(III) is oxidized in the presence of amorphous Fe oxides 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 is to determine whether Fe (hydr)oxides 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 oxide in natural soils, as a function of ionic strength and pH, is investigated. Oxidation processes of Sb(III) and the release of Sb(V) is monitored by distinguishing redox species in solution and the solid phase.

4.2 EXPERIMENTAL SECTION

4.2.1 Reagents and Materials

All chemicals were used as received and of at least pro analysi (p.a.) grade. For solutions and rinsing processes Milli-Q (18 $\text{M}\Omega\text{-cm}$) water was used. All glassware, reactions and sample vessels (Polypropylen) were leached in 0.3 M HCl (Merck) overnight and rinsed 3 times with water prior to use. The Sb(V)-

stock solution was prepared from KSb(OH)_6 (Riedel-de-Haën, puriss p.a.) in water and the Sb(III) stock solution from Sb_2O_3 (Fluka, puriss p.a.) in 2 M HCl (Merck, Suprapur).

4.2.2 Mineral Sorbent

Sorption experiments were carried out with goethite, which was prepared by mixing 180 mL of 5 M KOH (Riedel-de-Haën, puriss. p.a.) with 100 mL of 1 M $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Riedel-de-Haën) while stirring continuously. The suspension was diluted to 2 L and aged for 60 h at 70°C (21). After being centrifuged and washed repeatedly with water the suspension was freeze-dried and ground with a mortar. The specific surface area of the goethite is $33.7 \text{ m}^2 \text{ g}^{-1}$, which was determined by N_2 BET using a Carlo Erba Sorptomatic 1900 instrument. The identity of the goethite was confirmed by X-ray powder diffraction (Scintag XDS 2000 diffractometer using a copper x-ray source).

4.2.3 Antimony Sorption Experiments

All experiments were carried out with a background electrolyte of 0.01 or 0.1 M KClO_4 (Fluka, puriss p.a.) at 25 °C and in light $\lambda > 550 \text{ nm}$ to avoid photochemical reactions. All experiments were performed as triplicates in a glove box (Mecaplex) equipped with a CO_2 -scrubber ($p_{\text{CO}_2} < 2 \text{ ppm}$, DMP) to avoid pH drifts around neutral conditions due to CO_2 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 HClO_4 (Merck) or KOH (Merck, Titrisol). The final solid concentration was 0.5 g L^{-1} . Suspensions were shaken on a rotary shaker (125 rpm). Suspensions of Sb(III) and Sb(V) were equilibrated for 2 and 7 days, respectively. The shorter equilibration time for Sb(III) was chosen to minimize oxidation reactions of Sb(III). After the desired reaction time, suspensions were centrifuged and the supernatant filtered through $0.45 \text{ }\mu\text{m}$ (Titan2, nylon). 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. 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 N_2 in an anaerobic chamber (VAC). Glass bottles for batches were sealed in order to shake them outside of the glove box. These experiments were compared with similar experiments under oxic conditions. Since Sb was only measured in solution in the oxidation experiments, 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 $KClO_4$ 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, 7.2 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 NH_4 -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 reproducibility of the adsorbed Sb concentration on goethite or in solution between triplicate or duplicate experiments was 8% on average.

4.2.4 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)/Chapter 2). 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).

4.2.5 Surface Complexation Model

The modified triple-layer model, 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 4.1). Surface complexes used for fitting sorption data are given in Table 4.1. The program Fit 2.5 was used to obtain the intrinsic Sb(V) surface complexation constants, while forward calculations were carried out with the chemical speciation program ECOSAT 4.7 (24). Solution speciation was taken into account, adopting stability constants from ref (6, 25). The surface site density was set to 2.4 sites nm⁻², which was obtained from Sb(V) sorption isotherm experiments. Activity coefficients of aqueous species were calculated using the Davies equation.

Table 4.1. Aqueous and Intrinsic Surface Complexation Constants^a

Reactions	log K or β
Antimonate Protonation Constants	
$\text{Sb(OH)}_5 + \text{H}_2\text{O} = \text{Sb(OH)}_6^- + \text{H}^+$	-2.47 ^b
$\text{Sb(OH)}_6^- + \text{K}^+ = \text{KSb(OH)}_6^\circ$	2.0
Antimonite Protonation Constants	
$\text{Sb(OH)}_3 + \text{H}_2\text{O} = \text{Sb(OH)}_4^- + \text{H}^+$	-11.82 ^b
$\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3 + \text{H}^+$	-1.42 ^b
Intrinsic Surface Complexation Constants	
$\equiv\text{FeOH}^{\text{d}} + \text{H}^+ = \equiv\text{FeOH}_2^+$	6.09 ^e
$\equiv\text{FeOH}^{\text{d}} = \equiv\text{FeO}^- + \text{H}^+$	-11.71 ^e
Antimonate Adsorption Constants	
$\equiv\text{Fe(OH)}_2 + \text{Sb(OH)}_6^- = \equiv\text{FeO}_2\text{Sb(OH)}_4^- + 2\text{H}_2\text{O}$	5.21 ± 0.05
Background Electrolyte Adsorption Constants	
$\equiv\text{FeOH} + \text{H}^+ + \text{ClO}_4^- = \equiv\text{FeOH}_2^+ - \text{ClO}_4^-$	7.8 ^e
$\equiv\text{FeOH} + \text{K}^+ = \equiv\text{FeO}^- - \text{K}^+ + \text{H}^+$	-9.5 ^e
^a I= 0 M; ^b ref (6); ^c model parameters: C ₁ = 1.45 F m ⁻² C ₂ = 0.2 F m ⁻² , 2.4 sites nm ⁻² , specific surface area 33.7 m ² g ⁻¹ ; ^d a simplification summing all surface hydroxyl groups, ^e ref (26). Equilibrium constant in bold was optimized.	

4.3 RESULTS AND DISCUSSION

4.3.1 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 (Fig. 4.1A). 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 Extended x-ray

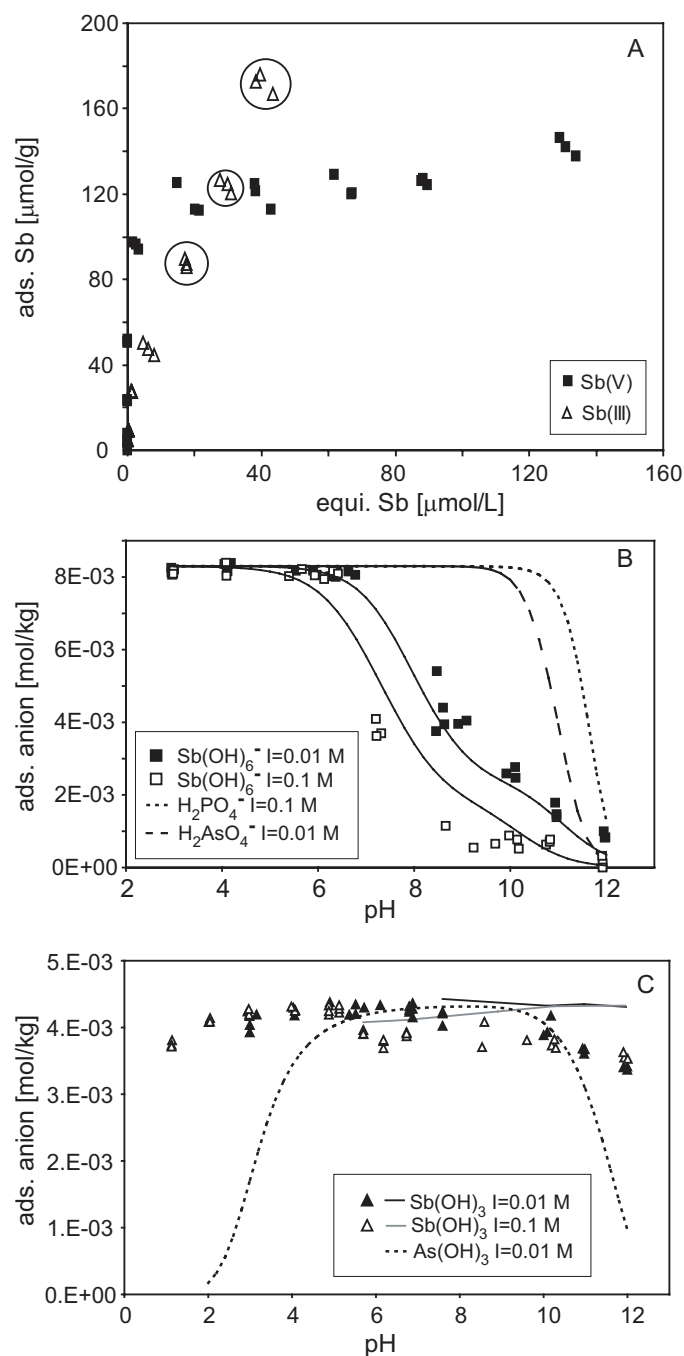


Fig. 4.1A: Sorption isotherms of Sb(III) (triangles) and Sb(V) (squares). Experimental conditions for Sb(V): 0.5 g/L goethite, I=0.01 M pH 3.0 and for Sb(III): 0.5 g/L goethite, I=0.1 M pH 4-3. For the data points in circles, initial Sb(III) concentrations were critical with regard to the solubility product of Sb₂O₃ (6). 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 4.1). Dashed lines show predicted adsorbed phosphate, arsenate and arsenite concentrations for the same initial concentrations of anions and goethite calculated from ref (27, 28). C: Solid lines show corrections for Sb(III) oxidation.

adsorption fine structure (EXAFS) measurements for the same goethite (9). Edge linkage sites are considered to be high energy sites, which are preferentially occupied at low surface coverage (29).

The Sb(III) isotherm is linear for low surface coverage (Fig. 4.1A). No maximum sorption density can be determined since precipitation of Sb_2O_3 occurs at initial Sb(III) concentrations above $63\ \mu\text{M}$ (6).

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 (8). Blay (2000) also found a linear sorption isotherm for Sb(III) for initial concentrations below $25\ \mu\text{M}$ (8).

For both As(V) and As(III), similar maximum sorption site densities on goethite of 2.0 sites nm^{-2} were found (28).

4.3.2 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, Fig. 4.1B). 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 (9). 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 Triple Layer Model 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 KSb(OH)_6° in solution is assumed. The KSb(OH)_6° ion pairs reduce the activity of Sb(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 ($\log K \approx -0.2$ - -0.5 (31)).

A simultaneous fit of the surface complexation constant of Sb(V), $\log K_{\text{adsSb}}$, and the stability constant of KSb(OH)_6° , $\log K_{\text{KSb(OH)}_6^\circ}$, for both ionic strengths yielded a $\log K_{\text{adsSb}}$ of 6.7 and a questionably high value for $\log K_{\text{KSb(OH)}_6^\circ}$ 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 to 1 at $I = 0$ M for ion pairs with opposite charge of 1 (32). Therefore, the surface complexation constant was estimated in a fit for the data of both ionic strength with a fixed \log value of 1 for the stability constant of KSb(OH)_6° . 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 (Fig. S4.1). Assuming a fixed \log value of 2 for the stability constant of KSb(OH)_6° and a fit for the data of both ionic strength yield a \log value of 5.21 for the surface complexation constant of Sb(V) (Table 4.1, Fig. 4.1B). With this data set, the influence of ionic strength on Sb(V) sorption is better reproduced than with the lower stability constant of KSb(OH)_6° . This indicates that 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 (33).

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 Triple Layer Model, were obtained assuming a combination of an outer-sphere ($\text{FeOH}_2^+ \text{-Sb(OH)}_6^-$) and an inner-sphere surface complex (Fe-OSb(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 expected to 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 (8). However, at this high surface coverage either surface precipitation or polymerization of Sb(V) may occur (6).

Compared to antimonate, phosphate and arsenate are also bound inner-spherically to the goethite surface ((29) and references therein). However, the adsorption of arsenate and phosphate on goethite are less pH-dependent and occur over a wide pH range of 3-10 (Fig. 4.1B, (27, 28)). The stronger adsorption of phosphate and arsenate above the point of zero charge (PZC) of goethite can be ascribed to the fact that phosphoric acid and arsenic acid are triprotic acids with high pK_a values for the second and third deprotonation reaction, whereas antimononic acid is a monoprotic acid (6). The main mechanism for inner-spheric 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 (34). Since arsenate and phosphate occur as HAsO_4^{2-} and HPO_4^{2-} at pH values greater than 7, surface hydroxyl groups can 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 (6), and thus binds only below the PZC.

4.3.3 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 (Fig. 4.1C). At low pH values, adsorption of Sb(III) decreased with increasing concentrations of Sb(OH)_2^+ (Table 4.1), 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 (Fig. 4.1C solid lines). 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. According to EXAFS spectra Sb(III) forms a bidentate, corner-sharing inner-sphere complex at the goethite surface (9). 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 oxides 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 (Fig. 4.1C (28)). Antimonite is a stronger Lewis base than arsenite and 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 As(OH)_4^- , which is a stronger Lewis base than As(OH)_3 . In analogy, As(III)

binds more weakly to humic acids than Sb(III) (35, 36), where binding sites are also oxygen bridges of carboxylic or phenolic functional groups (36).

4.3.4 Influence of O₂ on Oxidation of Adsorbed Sb(III) at pH 12

At pH 12 oxidized Sb should be released according to the sorption experiments (Fig. 4.1B). Within 23 days, a release of 26% total Sb was observed in the absence of measurable O₂ (< 1 mg/L), while 58% was released in the presence of approximately 6.6 mg/L O₂ (Fig. 4.2A). At 23 days, the fraction of Sb(III) in solution was smaller than 1% in the presence of O₂, while Sb(III) concentrations varied in the duplicates between 9 and 39% in the absence of measurable O₂. The results indicate that the oxidation rate of adsorbed Sb(III) on goethite at pH 12 was 4 times faster in the presence of O₂. The question arises as to why Sb(III) is oxidized in the absence of measurable oxygen since Fe(III) as α -FeOOH has a lower redox potential than Sb(III) as Sb(OH)_4^- at pH 12 and no other oxidant is present in the system. The only explanations are that either traces of O₂ diffused into the bottles for the experiments without O₂ or O₂ was sorbed to the surface particles and are responsible for the Sb(III) oxidation in the presence of goethite.

Without goethite and O₂, Sb(III) remained constant for 23 days (data not shown). In the presence of O₂, the oxidation rate for dissolved Sb(III) was similar to that of adsorbed Sb(III) ((18)/Chapter 2). Either Sb(III) is oxidized in solution and released from the surface by re-equilibration, or, and this is probably, that the environment around the Sb(III) atom is similar in solution as sorbed to the goethite surface. In aqueous solution at pH 12, Sb(OH)_4^- predominates, while Sb(III) bound inner-spherically to goethite receives an increase in electron density as surface oxide ions act as σ -donor ligand (34).

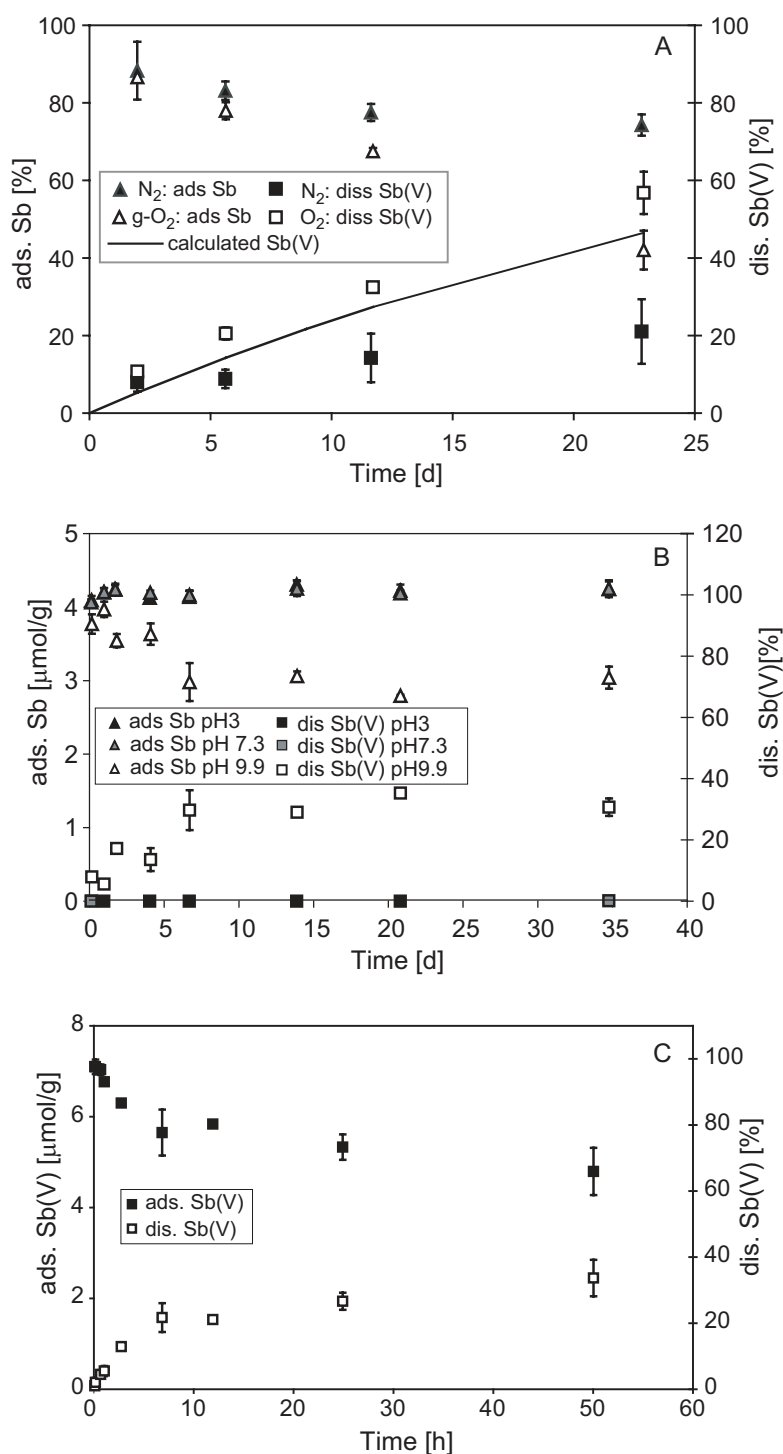


Fig. 4.2A: Oxidation of adsorbed Sb(III) on goethite at pH 12.0 in the presence (O_2) and absence (N_2) of measurable oxygen. Homogeneous oxidation of Sb(III) at pH 12, calculated from ref (18) is represented by the line. **B:** Adsorption of Sb(III) on goethite as a function of time in the pH range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

4.3.5 Influence of Adsorption on Sb(III) Oxidation in the pH range 3-10

The concentrations of adsorbed Sb(III) on goethite remained constant for 35 days at pH 3.0 and 7.3 (Fig. 4.2B). During this time period, no significant amount of Sb(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 Sb(V) and after 2 days no significant amounts of Sb(III) were measured in solution. This indicates that adsorbed Sb(III) on goethite was oxidized at pH 9.9 and then Sb(V) was released into solution. At pH 3.0 and 7.3, either no Sb(III) oxidation occurred within 35 days or the Sb(V) was still adsorbed on the surface and could not be measured.

Results of the desorption experiments (sorption at pH 6.7 for 7 days) are shown in Fig. 4.2C to aid interpretation. Within 7 hours, 22% of Sb(V) was desorbed, but subsequently desorption began to slow down and within 2 days only 34% of adsorbed Sb(V) had been released. 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 Sb(V) was found in the solid phase at pH 3.0 and 5.9 (Fig. 4.3A-C). The amount of total Sb(V) appears to be pH-dependent: 35, 50 and 90% of Sb(III) were oxidized within 7 days at pH 3, 5.9 and 9.7, respectively. After 7 days no significant amount of Sb(III) was further oxidized. This could be explained if only a small percentage of the goethite surface sites were reactive for Sb(III) oxidation. At pH 9.7, Sb(V) desorption occurs and reaction sites can be recycled, whereas sites remain occupied at pH 3 and 5.9 due to strong adsorption of Sb(V). The pseudo-first-order rate coefficients for the total Sb(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. Were Fe(III) to be the oxidant, a different relationship between pH

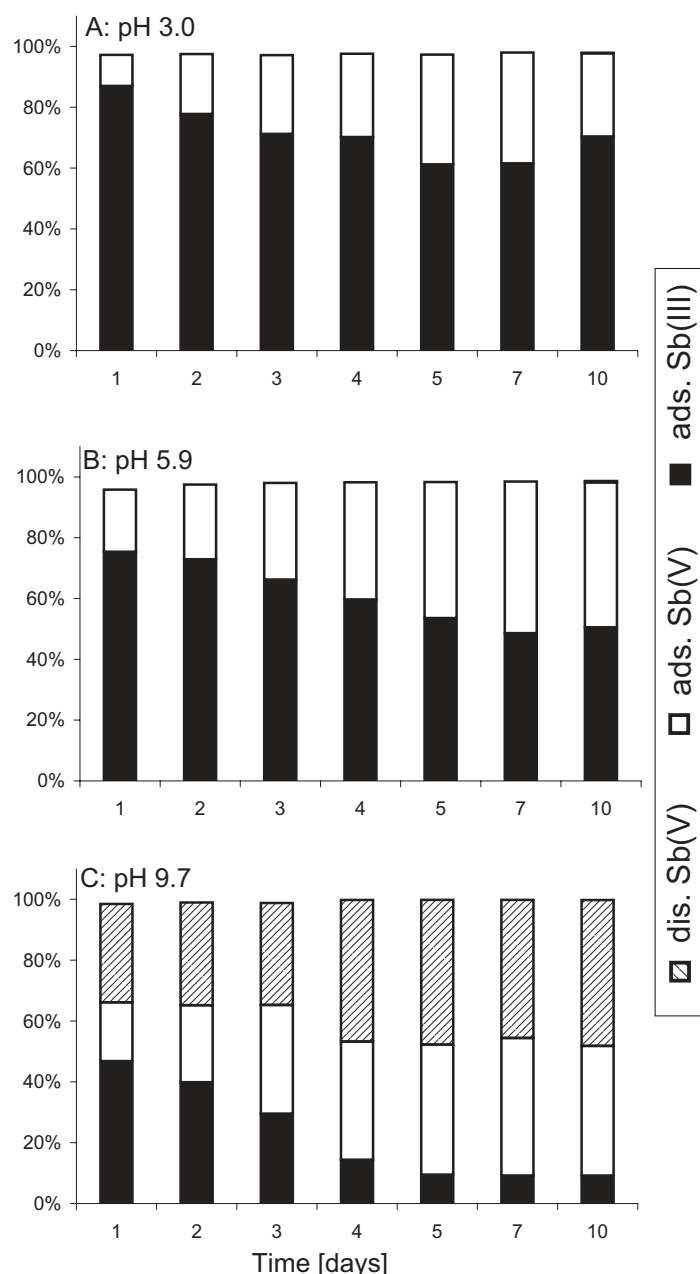


Fig. 4.3: Distribution of adsorbed Sb(III), adsorbed Sb(V) and dissolved Sb(V) as a function of time during oxidation. Initial Sb(III) concentration was 2.2 μM , 0.5 g/L goethite at different pH values at 25 $^{\circ}\text{C}$ and $I = 0.01 \text{ M KClO}_4$. Dissolved Sb(III) concentrations were $< 5\%$ of the total Sb concentration and are not shown.

and oxidation rate coefficient would be expected, since Fe(III) has a higher redox potential than Sb(III) only below pH 7.5 and would only be able to oxidize Sb(III) in acidic solutions. Instead the weak pH-dependence of the rate coefficients could be related to the pH-independent similarity of the environment around the Sb(III) atom when sorbed to goethite.

Similar experiments were carried out with adsorbed Sb(III) on amorphous Fe(III) (hydr)oxides at an Fe:Sb ratio of 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 1×10^{-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 (hydr)oxides.

For As(III), the oxidation of adsorbed As(III) on Fe (hydr)oxides, ferrihydrite and goethite was also observed (37-39). Between 50 and 75% of adsorbed As(III) on amorphous Fe (hydr)oxides 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 (37). At an Fe:As ratio of 75:1, 10-20% of adsorbed As(III) on goethite was oxidized at pH 5 within 4 days (39).

For As(III) oxidation processes in the presence of Fe (hydr)oxides, the effect of preparation of Fe (hydr)oxides from Fe(II) or Fe(III) salts is discussed in literature (37, 40). The experiments of the present study show clearly that goethite prepared from Fe(III) salts in order to avoid traces of Fe(II) also oxidize Sb(III) to Sb(V), however oxidation rate coefficients are approximately 6 and 8000 times slower at pH 5 and 7, respectively ((41)/Chapter 3).

4.5 Environmental Significance

Analyses of Sb in aquatic systems have usually shown that Sb(V) predominates and Sb(III) is only found at low concentrations (4). The reason for this may be that Sb(III) sorbs strongly to Fe (hydr)oxides, 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 Sb(III) thus becomes an insignificant redox species. 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 oxides, occur. The EXAFS spectra of the Sb(V) species were similar to the spectra of adsorbed Sb(V) on goethite (9). Investigations of soils, contaminated by Sb and Sb₂O₃ smelter emissions also found that Sb(V) is the predominant species and that oxidation processes must occur in the soil environment (42).

Acknowledgments. The authors 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.

Supporting Information Available

Sorption edges of Sb(V) on goethite with the fits of the modified TLM model with $\log K_{\text{KSb(OH)}_6^{\circ}} = 1$ and $\log K_{\text{ads.Sb}} = 4.8$ (Fig. S4.1).

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4.7 SUPPORTING INFORMATION

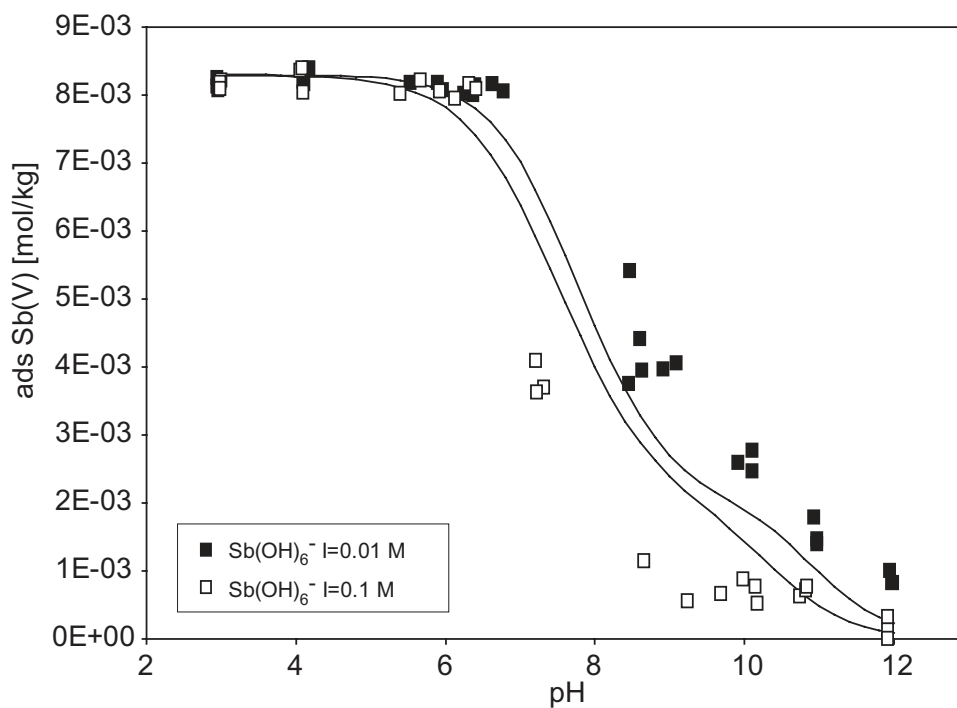


Fig. S4.1: Sorption edges of Sb(V) on goethite at $I=0.01$ M (solid symbols) and $I=0.1$ M (open symbols). Experimental conditions: $[\text{Sb(V)}]_0=4.15$ μM , 0.5 g/L goethite, 25 $^\circ\text{C}$. Solid lines represent fits of the modified TLM model with $\log K_{\text{KSb(OH)}_6^-} = 1$ and $\log K_{\text{ads,Sb}^+} = 4.8$.

Development of extraction methods for Sb species in soils

Ann-Kathrin Leuz, Alexander Englert, Martin Schneider and C. Annette Johnson

Abstract: In Switzerland, main emissions of the toxic metalloid antimony (Sb) to the soil environment occur along road sides due to abrasion of car brake pads and tires (28 t/a) as well as at shooting ranges due to shooting activity (10-25 t/a). In bullets, Sb is used as a hardening agent in Pb alloys. As the bullets corrode, Pb and Sb are released to the soil. It appears that Pb, as a cation, is strongly retarded in the top soils, while Sb, as an oxyanion, can be transferred to lower soil horizons. This has caused concern regarding possible groundwater contamination by Sb. To assess this risk, it is necessary to understand how Sb is bound in soils.

The aim of this study was to investigate and evaluate common extraction agents with different Sb compounds and with soils from shooting ranges. An appropriate extraction agent should provide information regarding the association of Sb with particular mineral fractions and should distinguish between species of Sb (Sb(III) and Sb(V)).

Therefore, deionized water, oxalate and oxalate-ascorbic acid were tested as extraction agents for elemental Sb, Sb_2O_3 , $\text{KSb}(\text{OH})_6$ and for goethite to which Sb(III) or Sb(V) had been adsorbed. In addition, 4 soils with different Sb concentration, soil pH and organic matter were air-dried, sieved < 2 mm and ground to < 0.5 mm and used for the development of the method.

Leaching experiments with water showed that a liquid to solid ratio of 100:1 is appropriate to avoid precipitation of Sb phases in the extract solution. Up to 15% of total Sb was dissolved by deionized water. This fraction presents the mobile Sb content in soils. Oxalate extractions led to oxidation of elemental Sb and desorption of Sb from crystalline Fe (hydr)oxides. Therefore, the oxalate extraction does not specifically determine the fraction of Sb associated with amorphous Fe (hydr)oxides. Only a small percentage (<10%) of elemental Sb was extracted by oxalate-ascorbic acid. During the extraction by oxalate-ascorbic acid, Sb speciation remained constant and goethite was completely dissolved. From contaminated soil samples, between 74% and 85% of total Sb was extracted with the oxalate-ascorbic acid, indicating that the main fraction of Sb is bound to amorphous and crystalline Fe (hydr)oxides.

5.1 INTRODUCTION

Antimony (Sb) is a toxic metalloid with increasing industrial significance. In the year 2000, when 140'000 tons were mined worldwide, Sb was the 9th most consumed metal in the USA (1). Major industrial applications employ Sb(III) compounds, mainly for flame retardants in plastics and textiles or as elemental Sb as a hardening agent in lead alloys. One important example is the use of lead-antimony alloys in bullets. In Switzerland, it is estimated that between 400 to 500 t of Pb and between 10 to 25 t of Sb enter the soil environment annually as a result of shooting practice at over 2000 shooting ranges (2, 3). Soils at shooting ranges are highly contaminated with Pb and Sb, primarily in the top soil of embankments, which act as stop butts behind the target. Lead and Sb are released from the bullets due to corrosion processes. It appears that Pb, as a cation, is strongly retarded in the top soils, while Sb, as an oxyanion, can be transferred to lower soil horizons. This has given rise to fears that Sb may contaminate surface waters and ground waters. To assess this risk, it is necessary to understand the geochemistry of Sb and how Sb is bound in soils. To date, the mobility of Sb in soils has been investigated in few studies. At clay pigeon shooting ranges with neutral soils, the soil water concentrations of Sb were higher than those of Pb, despite the higher solid-phase content of Pb, while the opposite situation occurs in acidic soil water (4).

Antimony exists either as Sb(III) or as Sb(V) in natural systems. In the aqueous phase, Sb is strongly hydrolyzed and occurs as $\text{Sb}(\text{OH})_3$ or as $\text{Sb}(\text{OH})_6^-$. However, $\text{Sb}(\text{OH})_6^-$ is the predominant species in oxic waters (5, 6). The oxide Sb_2O_5 is more soluble than Sb_2O_3 (7). Sorption isotherms of Sb(III) and Sb(V) on components of the soil matrix, including goethite, hematite, kaolinite, montmorillonite and illite, suggest that sorption of both Sb(III) and Sb(V) is stronger to Fe (hydr)oxides than to clay minerals at pH 7 (8). At low surface

coverage, both Sb(III) and Sb(V) form inner-sphere complexes at the goethite surface ((9, 10)/Chapter 4). However, adsorption of Sb(V) on goethite is pH-dependent. In the pH-range 3-7, Sb(V) sorbs strongly to goethite at an ionic strength of 0.01 M KClO₄. Above pH 7, adsorption decreases rapidly ((9)/Chapter 4). In the same medium, Sb(III) strongly adsorbs on goethite over the pH range 3-12. Above pH 7, weak desorption of Sb has been observed, which was explained by Sb(III) oxidation and desorption of Sb(V) ((9)/Chapter 4). Thus, oxidation processes are critical with regard to the mobility of Sb.

Since Sb(III) oxidation by O₂ requires centuries under ambient conditions ((11)/Chapter 2), other soil parameters may play a role. The Fe (hydr)oxides and Mn oxides are potential oxidants with average pseudo-first-order rate coefficients of 2.35 d⁻¹ and 0.887 d⁻¹, respectively, between pH 5 and 10 (12). The sorption study on goethite showed that Sb(III) is oxidized at pH 3 and pH 5.9, though no significant amount of Sb(V) was released into the solution. At pH 9.7 Sb(III) is oxidized to Sb(V), which desorbs from the surface. Another potential oxidation process for Sb(III) is the co-oxidation with Fe(II) and O₂. During the Fe(II) oxidation, reactive intermediates are produced that quickly oxidized Sb(III) around neutral pH values ((13)/Chapter 3). Since the bullets have a steel mantle, and the Fe(0) oxidizes via Fe(II) to Fe(III) during corrosion, this pathway may play a major role in soils from shooting ranges.

In a previous study, Scheinost et al. (2005) found only two main components of Sb in nine different soil samples. One species was still metallic and the second species was Sb(V), associated to Fe (14). No Sb(III) species could be identified. In an acidic (pH 3), organic rich soil, the metallic Sb species appeared to dominate, while the Fe-Sb(V) species dominated in neutral calcareous soils. Electron probe microanalyses have shown that bullets consist of a Pb matrix with embedded Sb grains (15). Only if the mantle and core of a bullet have been damaged upon impact, other Sb phases are formed. In the same acidic soil, Sb prevails in its elemental form, whereas in a neutral soil Sb was present as Sb(V)

in Fe- and Pb-rich crusts around soil-building materials. Both studies indicate that Sb is oxidized during weathering of the bullets and that oxidation processes are favored in neutral soils.

Since the two methods described above involve sophisticated measurements and are limited to high concentrations, a method that is more easily accessible and that has lower detection limits would be very useful. Therefore, the goal of this study is to develop an extraction method able to distinguish between elemental Sb(0) and Fe-Sb(V) species. It would then be possible to apply this method to soils with lower Sb concentration and depth profiles of the soils. The analysis of depth profiles of the soils will show whether Sb is transferred to lower soil horizons.

Many sequential extractions with various solvents are known (16, 17). Unfortunately, most methods are suitable for cations, only few for anions and even fewer specifically for Sb. Additionally, most sequential extractions only represent an operational distinction based on extraction techniques.

The aim of this study is to test common extraction agents, such as water, oxalate and oxalate-ascorbic acid on Sb standards in order to develop an appropriate extraction procedure for Sb in soils, which provides information on the association of Sb with particular Fe fractions and may distinguish between species of Sb (Sb(III) and Sb(V)). The extraction method was applied on 4 soils with different soil properties, such as pH, organic matter and Fe content.

5.2 EXPERIMENTAL PROCEDURES

5.2.1 Materials

Chemicals used as Sb standards. To evaluate the extraction methods elemental Sb (Fluka), Sb₂O₃ (Fluka) and KSb(OH)₆ (Riedel-de-Haën) were used as

received. Sorption samples were prepared by equilibrating 9 mg Sb with 3 g /L goethite at pH 3.5 for 1 day. Goethite was prepared as described in Chapter 4. Adsorbed Sb(III) was prepared from a standard solution (1000 mg/L Sb_2O_3 in 2 M HCl and CertiPUR, Merck) and adsorbed Sb(V) from $\text{KSb}(\text{OH})_6$. The suspensions were filtered through $< 0.45 \mu\text{m}$ (Nylon, Whatman) and washed with deionized water.

Sampling. Samples were taken at 4 different 300 m rifle shooting ranges in Switzerland. The samples from Tägerwilen, Davos and Eschenbach are embankment material, whereas the samples of Losone were taken behind the stop butts in the forest. Samples from Davos and Tägerwilen were taken by shovels and soil cores samples (Humax) from Losone and Eschenbach. At each sampling site, approximately 5 kg of soils were sampled at 10 different locations for each sample site and mixed in the laboratory. The soils were dried to constant weight at room temperature within 5 days and afterwards sieved into 2 fractions: $< 2 \text{ mm}$ and $> 2 \text{ mm}$. Visible fragments of the bullets were removed by hand and weighed separately.

In preliminary leaching experiments with water, 0.5 g soil of the fraction $< 2 \text{ mm}$ was used. The standard deviations of triplicates were very high ($> 15\text{-}33\%$). One explanation is that the sieved soil fraction $< 2 \text{ mm}$ is still very heterogeneous and 0.5 g is too small to provide a representative sub-sample. In order to homogenize the soil samples, the fraction of $< 2 \text{ mm}$ was ground to $< 0.5 \text{ mm}$. This fraction was used in the extraction experiments.

5.2.2 Analytical Methods

Cation and Sb analysis. Total concentrations of Ca, Al and Fe were measured in 3% HCl by inductively coupled plasma optical emission spectrometry (ICP-OES) (Ciros CCP, SPECTRO Analytical Instruments) using the method adapted from Ciros CCP, SPECTRO. Total Sb and Sb(III) concentrations were

determined by ICP-OES coupled with a hydride generator as described for the AFS ((11), Chapter 2). Antimony(III) was analyzed in 0.5 M disodium hydrogen citrate. Antimony(III) was converted to SbH_3 by mixing with 0.19 M NaBH_4 (dissolved in 0.1 M NaOH). Total Sb was measured by reducing Sb(V) to Sb(III) with KI-ascorbic acid solution (0.06 M KI, 0.01 M ascorbic acid) in 3 M HCl prior to analysis.

Characterization of the soils. Soil pH was determined potentiometrically 0.01 M CaCl_2 . Grain size distribution was determined using the pipette method (18). The organic matter of the soil was destroyed with 35% H_2O_2 , and the fraction was determined by weight difference (18). The carbonate content was analyzed by dissolving the carbonate with 10% hydrochloric acid and the formed amount of CO_2 was measured (19). In the soil samples, the total concentrations of different elements were measured by X-ray fluorescence (X-Lab2000; SPECTRO Analytical Instruments, Kleve, Germany). The soil properties and the elemental content are given in Tables 5.1 and 5.2.

5.2.3 Extraction methods

General procedure. To avoid photochemical reactions the whole extraction procedure was always carried out in light at wavelengths > 550 nm, henceforth referred to as red light conditions. The suspensions were shaken on a rotary shaker (175 rpm). Afterwards, samples were centrifuged for 20 min (4000 rpm) at 10°C . The supernatant was filtered through $< 0.45\ \mu\text{m}$ (Titan2, nylon). Samples for total Sb (Sb_{tot}) and cations determinations were stored in 3 % HCl (Merck, Suprapur) and Sb(III) in 0.5 M disodium hydrogen citrate (Fluka, Ultra) at 4°C prior to analysis. The amount of Sb(V) was calculated by difference.

Deionized water. In order to assess the equilibration time for the water extraction, samples of 0.5 g soil was extracted in 50 mL water as a function of

Table 5.1: Soil parameters of the four different soils from shooting ranges.

soils:	depth	pH	CaCO ₃	org. C ^a	Fe ox. ^b	sand	silt	clay	>2mm	metal
	[cm]		[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%] ^c
Tägerwilen	0-20 ^d	7.4	5.5	3.5	2.5	73.0	18.9	8.2	26	2
Losone	0-12.5	3.7	0.3	27.9	2.8	45.5	35.8	18.8	8	2
Davos	0-20 ^d	7.3	13.4	0.5	2.5	82.0	12.5	5.6	24	6
Eschenbach	0-12.5	6.6	12.0	4.7	6.3	76.7	16.3	7.1	32	14

^a organic matter^b amorphous and crystalline oxides calculated from oxalate-ascorbic acid extraction^c Parts of the bullets > 2 mm^d Samples from Tägerwilen and Davos were taken by a shovel and the depth was ~20 cm.**Table 5.2: Total concentrations for different elements of the soils measured by XRF.**

soils	depth	Sb	Al	Ca	Fe	Pb
	[cm]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
Tägerwilen	0-20 ^a	34	38000	27000	25000	860
Losone	0-12.5	97	41000	7500	28000	2900
Davos	0-20 ^a	1100	44000	63000	25000	23000
Eschenbach	0-12.5	5800	35000	62000	63000	129000

^a Samples from Tägerwilen and Davos were taken by a shovel and the depth was ~20 cm.

time. Within 56 days equilibrium in the solution was not reached. In the Losone samples, the fraction of dissolved Sb(III) decreased from 8% to <0.5% within 96 hours (data not shown). This indicates that oxidation processes occur during extraction by water, which leads to continuous release of Sb from the solid phase into the solution. We thus required a short time as possible for equilibration, whilst trying to take into account that antimonate phases appear to dissolve quite slowly (own observations). For these preliminary experiments we therefore chose a 48-hour equilibration time.

For the leaching experiments as a function of water to solid ratio, the soil samples were equilibrated at different liquid to solid ratios (1 - 100) for 48 hours. In general, the solid to water ratio of 100 appears to be appropriate in order to avoid effects due to saturation. This ratio was chosen for all soil extraction experiments.

Ammonium-oxalate extraction. A 0.2 M ammonium-oxalate extraction solution at pH 3.25 was prepared as described elsewhere (16, 20). The Sb standards were extracted with a solid to liquid ratio of 1:1000, i.e. 0.05 g were weighed in a 50 mL centrifuge tube and 50 mL of oxalate were added. The suspensions were shaken for 4 h.

Ammonium-oxalate-ascorbic acid extraction. The preparation of the 0.2 M ammonium-oxalate/ 0.1 M ascorbic acid solution is described elsewhere (16, 20). Extraction for Sb standards was carried out in centrifuge tubes: 50 mL extraction agent was added to 0.05 g of the Sb standards. The suspensions were heated in a water bath at 96 °C for 30 min. In 5 min intervals, the samples were shaken by hand. The extraction procedure for the soils was the same as for Sb standards except the solid to liquid ratio, which was 1:100.

5.3 RESULTS AND DISCUSSION

5.3.1 Extraction in water

Deionized water as extraction agent was used in order to determine the fraction of total Sb that is easily available in contaminated soils.

Antimony standards. Approximately 3.8% of the elemental Sb was dissolved in water (Table 5.3). Either a small percentage of the elemental Sb powder was oxidized before or elemental Sb oxidizes during the extraction procedure in water. Only < 1% of Sb was extracted from the samples of adsorbed Sb (Sb(III) and Sb(V)) of goethite (Table 5.3).

Soils. Concentrations of leached Sb as a function of water to solid ratio are shown in Fig. 5.1. For the sample from Losone, the dissolved Sb concentrations

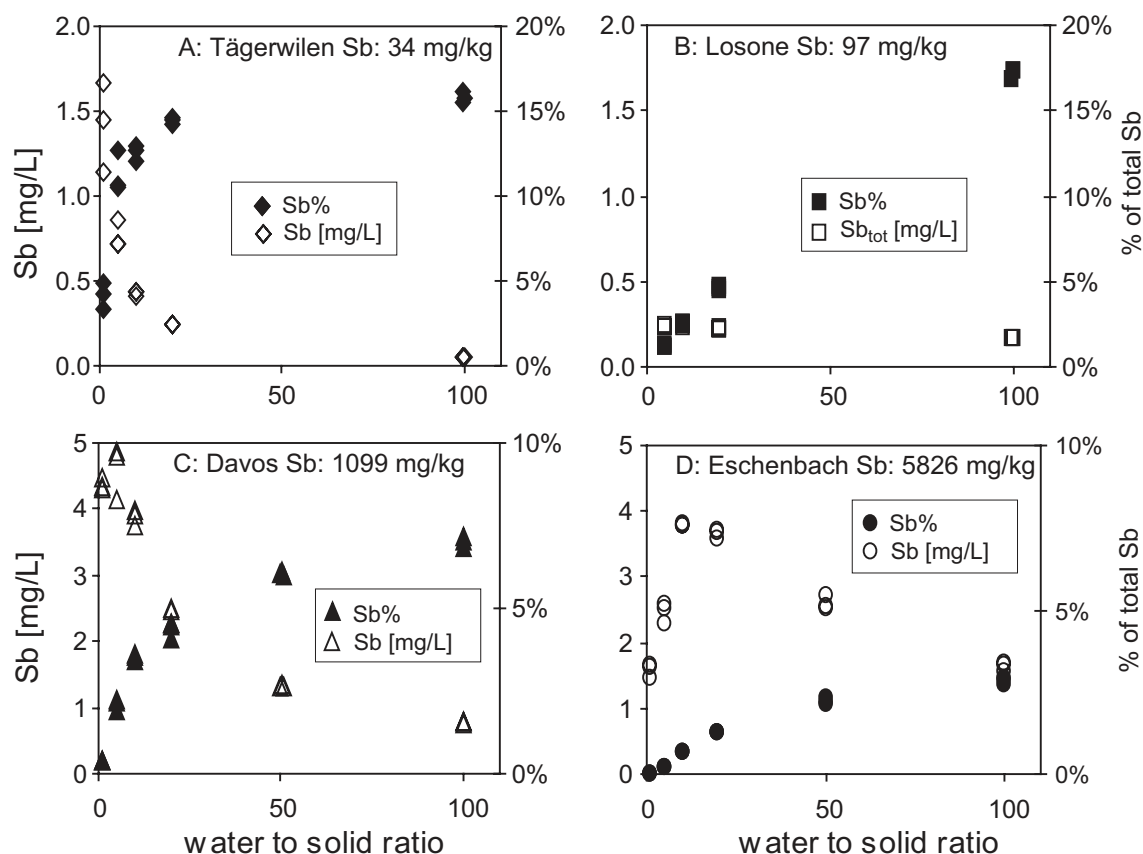


Fig. 5.1: Leached total Sb concentration as a function of water to solid ratio. Open symbols (left y-axis) show the concentrations in solution. Solid symbols (right y-axis) represent the dissolved Sb fraction of the total Sb concentrations in soils. Soils were extracted in deionized water for 48 h at 25°C under red light conditions.

were ~0.2 mg/L and were relatively independent of the water to solid ratio. For the samples of Tägerwilen and Davos, the concentrations in solution decreased with increasing water to solid ratio. The Sb concentrations of the sample from Eschenbach increased to 4 mg/L at low water to solid ratio and then decreased slightly with higher water to solid ratios. This indicates that the solubility of Sb can be limiting at small water to solid ratios. For the soil samples Tägerwilen and Losone up to 15% of Sb relative to the total Sb concentration was dissolved in water (Fig. 5.1A, B), whereas only a small percentage of Sb (3-7%) was dissolved from the highly contaminated soils (Fig. 5.1C, D). It appears that the maximum possible soluble Sb content in water is dissolved at a water to solid, ratio of 100:1 for Tägerwilen, Davos and Eschenbach. For the sample of Losone

Table 5.3: Single extractions with water, oxalate and oxalate-ascorbic acid of Sb standards and soils, including speciation of Sb(III) and Sb(V).

Sample	Total Sb [g/kg]	H ₂ O	0.2 M ammonium-oxalate			0.2 M ammonium-oxalate 0.2 M ascorbic acid		
		Sb _{tot} [g/kg]	Sb(III) [g/kg]	Sb(V) [g/kg]	Sb _{tot} [g/kg]	Sb(III) [g/kg]	Sb(V) [g/kg]	Sb _{tot} [g/kg]
Sb standards:								
Sb(0)	1000	38 ± 2	950	47	997	97 ± 9	-2.0	95 ± 10
Sb ₂ O ₃	835.3	--	859 ± 29	-30	829 ± 18	858 ± 13	-37.0	821 ± 13
Sb(III) goethite	3.0	0.05 ± 0.001	2.2 ± 0.01	0	2.2 ± 0.1	2.8 ± 0.01	0.1	2.9 ± 0.07
KSb(OH) ₆	463.1	--	< 0.01	241	241 ± 1	3.7 ± 0.07	463	467 ± 6.4
Sb(V) goethite	2.8	< 0.01	< 0.01	1	1 ± 0.02	< 0.01	2.8	2.8 ± 0.03
Soils:								
Losone	0.097	0.0166 ± 0.0003	--	--	--	--	--	0.07 ± 0.004
Tägerwilen	0.034	0.0054 ± 0.0001	--	--	--	--	--	0.03 ± 0.001
Davos	1.1	0.0769 ± 0.002	--	--	--	--	--	0.8 ± 0.02
Eschenbach	5.8	0.163 ± 0.006	--	--	--	--	--	5.8 ± 0.2

the relative concentration of Sb increased with increasing water to solid ratios, indicating that Sb is mobilized during the extraction due to oxidation processes.

5.3.2 Ammonium-oxalate

The oxalate extraction of the Sb standards is shown in Fig. 5.2 and the results of the Sb(III) and total Sb measurements in the extraction solution are given in Table 5.3. Elemental Sb is partly dissolved (~25%) at the same solid to liquid ratio (1: 1000), which was used for the other standards. However using a solid to liquid ratio of 1: 10'000, elemental Sb is completely soluble in oxalate. Speciation measurements yielded that 95% of total Sb is Sb(III), indicating that Sb(0) is oxidized to Sb(III) in the presence of oxalate. Approximately 4.7% of the dissolved concentration was Sb(V). Thus, the question arises as to whether elemental Sb is further oxidized to Sb(V) in the presence of oxalate or whether the surface of the elemental Sb was oxidized before extraction. Comparing these results to those of the water extraction, in which ~4% was dissolved in water, it appears that the elemental Sb contained a small percentage of oxide.

The salt Sb_2O_3 was completely dissolved in oxalate and in the extraction solution only Sb(III) was measured. Around 54% of total Sb was extracted from $\text{KSb}(\text{OH})_6$ and no Sb(III) was measured in solution. In general, oxalate extractions are used to extract amorphous Fe, Mn and Al oxides. The Fe concentrations of the extracted goethite samples were below the detection limit (<0.01 g/kg), confirming that the goethite was not dissolved in oxalate. However, in the extraction agent 73% and 36% of adsorbed Sb(III) and Sb(V) on goethite, respectively, were extracted. These results show that Sb probably desorbs in the presence of oxalate. The higher Sb concentration of the Sb(III) samples indicates that Sb(III) is stronger complexed by oxalate than Sb(V). For adsorbed Sb(III) on goethite, only Sb(III) was detected in the extraction solution and for adsorbed Sb(V) only Sb(V) was found. It appears that the speciation of Sb(III) and Sb(V) did not change during extraction procedure.

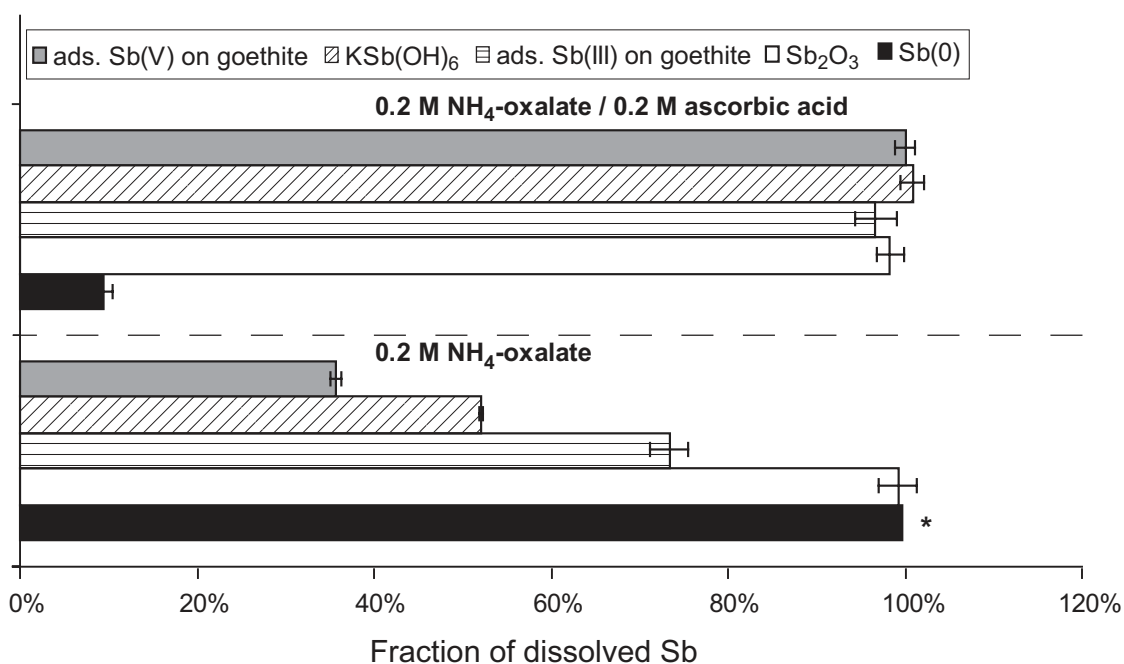


Fig. 5.2: Extracted Sb of the Sb standards (elemental Sb, Sb₂O₃, KSb(OH)₆, adsorbed Sb(III) and adsorbed Sb(V) on goethite) in 0.2 M ammonium-oxalate and in 0.2 M ammonium-oxalate / 0.2 M ascorbic acid at 25°C under red light conditions. The solid to liquid ratio was 1000 except for the bar marked with an asterisk (*). There the ratio was 10000.

For Sb, this method appears to be inadequate to distinguish between amorphous Fe oxides and crystalline Fe oxides, because Sb is desorbed from goethite in the presence of oxalate. In soils, in which Sb(0) is the contamination source, oxalate extractions leads to misinterpretation, since oxalate favors oxidation and dissolution of elemental Sb. This extraction method was not considered further.

5.3.3 Ammonium-oxalate-ascorbic acid

This method is usually applied to soils in order to estimate the fraction associated to crystalline Fe oxides, such as goethite. Around 9.5% of elemental Sb is dissolved during the oxalate-ascorbic acid extraction (Fig. 5.2 and Table 5.3). The salts Sb₂O₃ and KSb(OH)₆ were completely dissolved in oxalate-ascorbic acid extraction and speciation remained constant during the extraction

procedure. The goethite samples with adsorbed Sb(III) and Sb(V) were totally extracted. Extraction of adsorbed Sb(III) on goethite yielded 97% of Sb(III) and 3% of Sb(V) in the extraction solution. Compared to oxidation reactions of adsorbed Sb(III) on goethite, it is possible that within 1 day's equilibration time a small percentage of Sb(III) is oxidized on the goethite surface ((9)/Chapter 4). In the extract for the adsorbed Sb(V) on goethite, Sb(III) concentrations were lower than the detection limit (< 0.01 g/kg), indicating that Sb(V) speciation remained constant.

For all Sb standards the speciation of Sb(III) and Sb(V) was not changed. Only a small percentage of elemental Sb was dissolved ($< 10\%$). This extract dissolved crystalline Fe oxides. This indicates that this method can provide valuable information on Sb bound to amorphous and crystalline Fe oxides and on speciation of Sb(III) and Sb(V). Thus, oxidation processes may be investigated with this method.

In Table 5.3, the Sb concentrations of the extraction in oxalate-ascorbic acid are given. The concentrations in the extract were $\sim 75\%$ of total Sb for Losone, Tägerwilen and Davos and $\sim 86\%$ for Eschenbach. This indicates that oxalate-ascorbic acid is an important extraction for Sb, and Sb is strongly associated with amorphous and crystalline Fe oxides, irrespective of pH and organic matter (Table 5.1-5.3). The Fe oxide content of the soils Losone, Tägerwilen and Davos was around 2.6% and for Eschenbach 6.3%. Adopting the Sb sorption maximum on goethite of $4.04 \mu\text{mol}/\text{m}^2$, (determined by sorption isotherms ((9)/Chapter 4)), and assuming a specific surface area for amorphous Fe oxides of $600 \text{ m}^2/\text{g}$ (21), a sorption capacity of $63 \mu\text{mol Sb}/\text{g soil}$ (or $7.37 \text{ g Sb}/\text{kg soil}$) was estimated for Losone, Tägerwilen and Davos and $153 \mu\text{mol Sb}/\text{g soil}$ (or $18.6 \text{ g Sb}/\text{kg soil}$) for Eschenbach. For the less contaminated soils the surface coverage is $< 1\%$ and for Davos and Eschenbach 11% and 27%, respectively. Thus, the surface area of Fe oxide is not saturated with respect to Sb sorption complexes in the four soils.

EXAFS spectra of soil samples from shooting ranges showed that the Sb(V) species associated with Fe are similar to those of adsorbed Sb(V) on goethite. The difference in the spectra is explained by Sb being sorbed to amorphous Fe oxides and not to crystalline Fe oxides in soils (14). A comparison of the oxalate-ascorbic acid extraction and EXAFS measurements of the same samples resulted in a promising correlation between the values of total Sb content (XRF) minus total Sb in the oxalate-ascorbic acid and the metallic Sb species, determined by EXAFS. A similar correlation was found between the species Sb(V)-EXAFS and Sb(V) extracted by oxalate-ascorbic acid (14, 20). Applying this to the four samples in this study, 14% of Sb was elemental Sb in the soil Eschenbach and in the other soils 25% was estimated. It appears that a main fraction of Sb(0) is oxidized via Sb(III) to Sb(V) in the soils. Oxidation processes of Sb(0) to Sb(III) were observed during extraction by water and oxalate. The Sb(III) oxidation most likely occur by adsorption on Fe (hydr)oxides or Fe(II) co-oxidation as described elsewhere ((9, 13)/Chapter 4, 3).

5.4 CONCLUSIONS

Sequential extractions are not applicable for the determination of the association of Sb in soils since extractions by water and ammonium-oxalate change the speciation of Sb in the sample due to oxidation processes. The combination of different single extractions of soil samples most probably provide better information on the speciation of Sb in soils.

Extraction by deionized water yields the mobile fraction of Sb in soils, whereas the extraction of oxalate-ascorbic acid is a suitable method for the determination of the association between Sb and Fe. The oxidation state of Sb is mainly retained during the oxalate-ascorbic acid extraction, which facilitates the investigation of the oxidation processes of Sb in soils. This provides valuable

information, which can be used in combination with other factors such as soil pH and distance to groundwater to asses the risk that Sb enters the groundwater below contaminated soils.

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Chapter 6

Conclusions and outlook

Of the many factors influencing the mobility of Sb in the environment, oxidation reactions are of key importance since Sb(V) is more soluble than Sb(III). The principle aim of this work was to increase the knowledge of Sb(III) oxidation processes caused by naturally occurring oxidants. The oxidation of Sb(III) was investigated over a wide pH range in the presence of O_2 , H_2O_2 , Fe(II) and O_2 , Fe(II) and H_2O_2 , and goethite. In addition, the sorption capacity of goethite for Sb(III) and Sb(V) was determined as a function of pH. A secondary objective was to develop an extraction method for the speciation of Sb in contaminated soils from shooting ranges in order to assess the binding of Sb and oxidation processes in soils. The main results and general conclusions are summarized in the following paragraphs:

- The oxidation of Sb(III) by O_2 as the sole oxidant is extremely slow and pseudo-first-order rate coefficients can only be measured above pH 10.9. Half-lives range from 3 days at pH 12.9 to 230 days at pH 10.9. Therefore, this reaction plays a minor role under environmental conditions.
- Hydrogen peroxide, a more powerful oxidant than O_2 , oxidizes Sb(III) and pseudo-first-order rate coefficients were measured in the pH-range 8-13. Increasing the pH yields higher concentrations of the negatively charged complex, $Sb(OH)_4^-$, (and of the deprotonated species of H_2O_2 , HO_2^-) and Sb(III) is oxidized more quickly. This indicates that hydrolysis of Sb(III) most probably accelerates the oxidation. This reaction is relevant in sunlit surface waters and cloud waters, where H_2O_2 concentrations vary in the range of 10^{-8} - 10^{-6} M and 10^{-7} - 10^{-5} M, respectively.
- Antimony(III) is co-oxidized very quickly in the presence of Fe(II) at pH values between 6 and 8. During the Fe(II) oxidation by O_2 , reactive intermediates, such as $\cdot OH$ radicals and possibly Fe(IV) are produced,

which also reacts with Sb(III). Quenching experiments showed that $\cdot\text{OH}$ radicals are involved in the Sb(III) oxidation at low pH values, whereas other oxidants, such as possibly Fe(IV) play a role around neutral pH values. The Fe(II)-mediated Sb(III) oxidation occurs in the upper region of redox gradients between oxic and anoxic conditions, where Fe(II) diffuses into the oxic zones. This reaction can also take place in anthropogenic environments with high Sb concentrations such as bullet rims and car brake pads. The steel in the mantle of the bullet or in the brake pad corrodes and Fe(0) is oxidized via Fe(II) to Fe(III). Thus, bullets and car brake pads not only contaminate the environment with Sb but also increase the oxidation and thus mobilization potential for Sb since Fe and Sb are released together.

- Over a wide pH range of 3-10, Sb(III) adsorbed on goethite is oxidized by O_2 with pH-independent pseudo-first-order oxidation rate coefficients. Coordination of Sb(III) at the goethite surface increases the electron density at the Sb(III) atom and Sb(III) is more quickly oxidized by O_2 than in homogeneous solutions. The percentage of Sb(V) formed increases with increasing pH. This indicates that the availability of reactive sites at the goethite surface is limiting Sb(III) oxidation. Since Sb(V) desorption occurs above pH 7, reactive sites may be recycled and allow more Sb(III) to be oxidized. It appears that increasing the surface area of Fe (hydr)oxides improves oxidation conditions for Sb(III).
- Both Sb(III) and Sb(V) form inner-sphere surface complexes at the goethite surface. However, the sorption of Sb(V) is strongly pH-dependent, whereas Sb(III) sorbs strongly throughout the pH range 3-12. Adsorption of Sb(V) occurs in the pH range 3-7 while desorption of Sb(V) occurs above. Thus, whether oxidation processes of Sb(III) lead to mobilization of Sb(V) depends on pH.

- Up to 15% and 3% of the total Sb concentration was extracted in water for low and high contaminated soils, respectively, representing the mobile fraction of Sb in soils. In average 75% of the total Sb concentration was associated with amorphous and crystalline Fe oxides, most likely sorbed to Fe oxides. Since it is unlikely for elemental Sb to be bound to Fe oxides, oxidation processes of Sb must occur in soils.

In Fig. 6.1 the oxidation rate coefficients for Sb(III) are shown as a function of pH. The oxidation rates increase with increasing pH in the presence of O_2 , H_2O_2 and Fe(II). The figure also indicates that in the presence of Fe, and irrespectively of the Fe oxidation state, oxidation of Sb(III) is favored over the whole pH range under oxic conditions. Since Fe is widespread in soils and is released together with Sb into the environment, it becomes clear why Sb(III) is not stable in soils and thus mainly Sb(V) is found in soils from shooting ranges and smelter areas. Iron oxides immobilize Sb by sorption at low pH values and low Sb concentrations, whereas above pH 7, desorption of Sb(V) is observed. In addition, Fe oxides increase the mobilization potential of Sb, because they promote oxidation processes. Zero valent iron barriers, which are used as in situ immobilization for other oxyanions such as chromate are not applicable for Sb contaminated sites because they lead to oxidation of Sb to the more soluble species Sb(V). In addition, this work indicates that oxidation and sorption of As and Sb are not as similar as was assumed. Compared to As(III), Sb(III) is more easily and often completely oxidized due to its stronger cationic character. The sorption of As(V) and Sb(V) on Fe (hydr)oxides is very different, which is explained by arsenate occurring as a tetrahedral triprotic acid, whereas Sb(V) is an octahedral monoprotic acid.

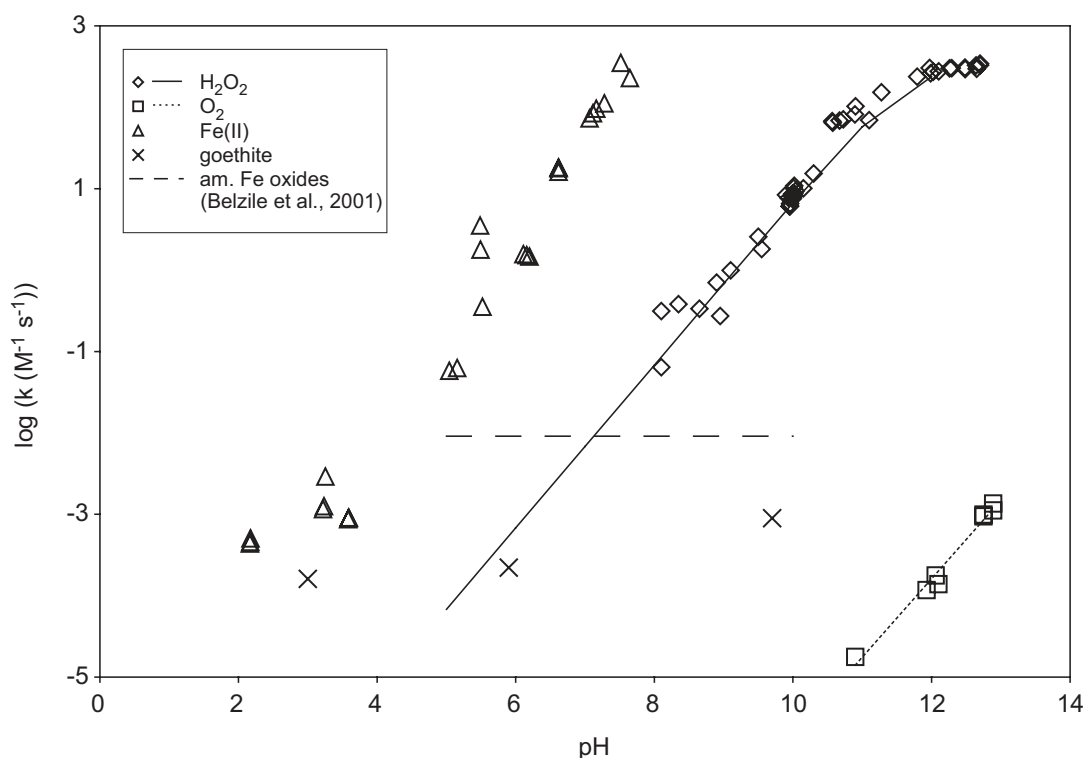


Fig. 6.1: Log values of the Sb(III) oxidation rate coefficients, $k \text{ M}^{-1} \text{ s}^{-1}$ in the presence of O_2 , H_2O_2 , Fe(II) and goethite as a function of pH. The dotted line represents linear regression between log values of k and pH. The solid line shows rate coefficients calculated from Leuz et al., 2006. For comparison oxidation rate coefficients of adsorbed Sb(III) on amorphous Fe (hydr)oxides, investigated by Belzile et al., 2001 are shown (dashed line). The Sb(III) rate coefficients in the presence of Fe are divided by the Fe concentration rather than the oxidant concentration.

Based on the results from this study, it would be of interest to investigate the following additional aspects regarding the mobility of Sb in soils:

- Factors controlling the adsorption of Sb(V) on Fe (hydr)oxides are very important: The presence of other competitive ions adsorbing on Fe (hydr)oxides, such as phosphate or organic ligands may remove Sb from the surface or hinder adsorption of Sb, because adsorption of ions, which form negative charges on the surface and adsorb over a wider pH range than Sb(V) may significantly decrease Sb(V) adsorption or favor

desorption. Formation of ion pairs between Sb(OH)_6^- and K^+ or Na^+ can also reduce the adsorption of Sb(V) on Fe (hydr)oxides.

- The influence of natural organic ligands on the oxidation of Sb(III) is still unclear, since citrate stabilizes Sb(III) and hinders further oxidation, whereas binding to humic acids favors oxidation processes.
- Information on factors controlling the oxidation processes of Sb(0) to Sb(III) are needed. The extraction methods have shown that Sb(0) is completely dissolved in the presence of oxalate and that Sb(III) is the dominant oxidation state in the resulting extractant. Thus, the presence of organic ligands may mobilize Sb(0).
- Development of a method to quantitatively separate elemental Sb from other Sb species in soils would improve the extraction methods used to characterize the binding of Sb to soils.

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