



Antimony sorption at gibbsite–water interface

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ABSTRACT

Antimony (Sb) is extensively used in flame retardants, lead-acid batteries, solder, cable coverings, ammunition, fireworks, ceramic and porcelain glazes and semiconductors. However, the geochemical fate of antimony (Sb) remained largely unexplored. Among the different Sb species, Sb (V) is the dominant form in the soil environment in a very wide redox range. Although earlier studies have examined the fate of Sb in the presence of iron oxides such as goethite and hematite, few studies till date reported the interaction of Sb (V) with gibbsite, a common soil Al-oxide mineral. The objective of this study was to understand the sorption behavior of Sb (V) on gibbsite as a function of various solution properties such as pH, ionic strength (*I*), and initial Sb concentrations, and to interpret the sorption-edge data using a surface complexation model. A batch sorption study with 20 g L⁻¹ gibbsite was conducted using initial Sb concentrations range of 2.03–16.43 μM, pH values between 2 and 10, and ionic strengths (*I*) between 0.001 and 0.1 M. The results suggest that Sb (V) sorbs strongly to the gibbsite surface, possibly via inner-sphere type mechanism with the formation of a binuclear monodentate surface complex. Weak I effect was noticed in sorption-edge data or in the isotherm data at a low surface coverage. Sorption of Sb (V) on gibbsite was highest in the pH range of 2–4, and negligible at pH 10. Our results suggest that gibbsite will likely play an important role in immobilizing Sb (V) in the soil environment.

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1. Introduction

A large amount of antimony (Sb) (approximately 140 000 tons) is mined annually and used in various industrial products such as flame retardants, storage batteries, and ammunitions (Filella et al., 2002a; Leuz and Johnson, 2005). High Sb concentrations in soil have been found at shooting ranges, mining and smelting areas and road sides (Mitsunobu et al., 2010). United States Environmental Protection Agency (USEPA) and the Council of the European Communities have declared Sb and its compounds as pollutants of priority interest (USEPA, 1979; Council of the European Union, 1998; Filella et al., 2002a,b; Leuz and Johnson, 2005). However, little is known about the geochemical behavior of Sb in the environment. Antimony exists in the environment in mainly two oxidation states; Sb (III) and Sb (V) (Leuz and Johnson, 2005). While Sb (V) generally exists in oxidizing environments, Sb (III) dominates in reducing environments. However, owing to metastability and very slow rates of reduction, Sb (V) exists in a wide redox range (360 to –140 mV) (Mitsunobu et al., 2006).

Sorption to soil components is a major mechanism of Sb retention in the environment. A number of studies have investigated the sorption behavior of Sb (V) and Sb (III) on hydroxides of Fe, Mn, Al,

humic acids, and clay minerals (Thanabalsingham and Pickering, 1990; Xu et al., 2001; Tighe et al., 2005; Leuz et al., 2006; Xi et al., 2010). Researchers found that Sb (III) sorbs strongly to iron oxides, which shows no dependence on pH (Leuz et al., 2006). However, the authors indicated that at higher pH (~9.9), Sb (III) sorption on goethite decreased by 30% due to the oxidation of Sb (III) to Sb (V), and almost 77% solution Sb species existing as Sb (V). This trend is consistent with the pH-dependent sorption behavior of Sb (V) on goethite, where Sb (V) sorption decreased drastically above pH 6 (Leuz et al., 2006). Although Sb (III) compounds are 10 times more toxic than Sb (V) compounds, the mobility and solubility of Sb (V) is greater than Sb (III) (Mitsunobu et al., 2009, 2010). In a comparative study between As and Sb, Mitsunobu et al. (2006) found that Sb (V) can exist under reducing conditions (Eh = –180 mV, pH 8), compared to As (V) which is reduced to As(III) under the same conditions. Scheinost et al. (2006) reported the abundance of Sb (V) in shooting range soils under oxic conditions, but found no trace of Sb (III) in their investigation using EX-AFS. While there are many reports on the sorption of Sb (V) on iron oxides, few studies have reported the interaction mechanism of Sb (V) with Al-oxides (Xu et al., 2001; Kameda et al., 2009). Xu et al. (2001) reported that the sorption of Sb (V) on activated alumina was pH dependent, where maximum sorption was noticed within a pH range of 2.8–4.3. The mechanism of sorption was explained by a combination of electrostatic interactions and specific sorption

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using $\text{Sb}(\text{OH})_6^-$ as the reactive species (Xu et al., 2001). In another report, Kameda et al. (2009) examined the efficiency of Fe–Al layered double hydroxide (Fe–Al LDH) in removing Sb (V) from solution. The authors found about 40 mg L^{-1} Sb (V) was sorbed on Fe–Al LDH within a period of 2 h.

However, there are no reports on the sorption behavior of Sb (V) on gibbsite, a common soil mineral. Gibbsite has been shown to sorb metal oxyanions such as molybdate and arsenite (Weerasooriya et al., 2003; Goldberg, 2010). Filella et al. (2002a,b) indicated that fate of Sb in the soil is most likely a key factor in Sb cycling in the environment. Therefore, knowledge of the Sb (V) sorption behavior on gibbsite will isolate novel pathways of Sb (V) immobilization in soil. The main objective of this research was to study the sorption behavior of Sb (V) at the gibbsite–water interface as a function of solution properties: pH, ionic strength and initial Sb (V) concentrations. A surface complexation modeling tool such as FITEQL 2.0 (Herbelin and Westall, 1999) was used to model the pH-dependence of the sorption behavior.

2. Materials and methods

2.1. Reagents and materials

Gibbsite (Almatis Inc., PA, USA) was provided by Dr. Christopher Matocha, Department of Plant and Soil Science, University of Kentucky. The measured N_2 BET surface area of the gibbsite was $2.63 \text{ m}^2 \text{ g}^{-1}$. Potassium hexahydroxyantimonate [$\text{KSb}(\text{OH})_6$] was purchased from Sigma–Aldrich (St. Louis, MO). Potassium chloride, and PIPES (1,4-piperazinebis(ethane sulfonic acid) were purchased from Sigma–Aldrich (St. Louis, MO).

2.2. Gibbsite Pretreatment

Powdered gibbsite was cleaned using the procedure of Sarkar et al. (1999). Briefly, the solid was shaken (Orbital Shaker 57018–754, VWR Scientific) at 200 rpm with 0.01 M NaOH (Fisher) for 30 min and centrifuged (2000 rpm, 5 min) to remove NaOH. Subsequently, the solid was washed repeatedly using 1 M KCl solution until the pH value of supernatant was ~ 7 . The suspension was air-dried and stored for further use.

2.3. Antimony sorption experiments

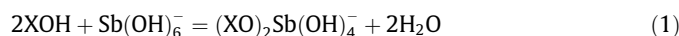
All experiments were carried out using a background electrolyte KCl at various concentrations appropriate for the experiments. Sorption isotherms were created using a range of initial Sb (V) concentrations (2.03–16.43 μM) relevant to the soil environment (Filella et al., 2002b). The concentration of gibbsite was 20 g L^{-1} . The pH of the solution was maintained at 6.1 using a non-interfering buffer such as PIPES at 0.1 M concentration. A preliminary experiment was conducted to verify if PIPES had any effect on the sorption of Sb (V) on gibbsite. The data indicated negligible influence of PIPES on sorption (data not shown). Batch experiments for sorption isotherm were conducted at three different ionic strengths (I) by addition of 0.001, 0.01, and 0.1 M KCl with an equilibration time of 7 d. The samples were centrifuged at 1000 rpm and filtered through 0.2 μm syringe filters (Fisher Scientific, 09-730-19). The filtrates were analyzed for Sb (V) concentrations using ICP-MS (Thermo X-series II, Thermo Electron, San Jose, CA). The Sb sorption on gibbsite was calculated by difference.

The sorption-edge experiments were carried out at three different I by adding 0.001, 0.01, and 0.1 M KCl to the reaction mixture. The initial concentration of Sb (V) was chosen at a value $< 5 \mu\text{M}$ because at low Sb concentrations sorption-edge data is scarce (Leuz et al., 2006); $4.11 \mu\text{M}$ Sb (V) was added to a suspension of

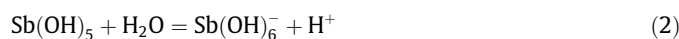
20 g L^{-1} gibbsite. The pH was controlled within a range of 2–11 using PIPES buffer and additions of small quantities of 1 M HCl and NaOH. Previously, PIPES buffer was used at these pH ranges by Figueroa and Mackay (2005), and Yu et al. (1997). Final pH was measured after 7 d equilibration time and used for plotting pH vs. % Sb (V) sorption. Dissolved Al was also monitored using ICP-MS. A control experiment was conducted without the addition of gibbsite to the reaction mixture to monitor for any loss of Sb (V) at a pH range of 2–11. All experiments were carried out in duplicates.

2.4. FITEQL modeling of Sb sorption on gibbsite

The pH dependence of Sb (V) sorption to gibbsite was modeled using FITEQL (Herbelin and Westall, 1999) to predict possible surface complexation reactions. A diffuse layer model with least number of input parameters was used. Protonation constants for surface hydroxyl groups were taken from the literature (Table 1). The surface complexation reaction used for modeling the sorption-edge of Sb (V) sorption on gibbsite is:



Solution speciation of Sb (V) was also considered following the reaction below:



The log K ($= -2.47$) value of reaction (2) was obtained from Leuz et al. (2006). In our model no ionpair with K^+ and $\text{Sb}(\text{OH})_6^-$ was considered as in Leuz et al. (2006).

3. Results and discussion

3.1. Sorption isotherm

Preliminary data suggested that Sb (V) sorption on gibbsite was nearly complete within 2 d, however, an equilibration time of 7 d was used to confirm the plateau value. Leuz et al. (2006) reported an equilibration time of 7 d for Sb (V) sorption on goethite. The sorption isotherm was fitted with Langmuir model at all the three different I s assuming only one type of surface site. The Langmuir parameters are listed in Table 2. Maximum sorption capacity varied between 0.26 and $0.52 \mu\text{mol g}^{-1}$ for different I s. The differences between sorption capacities at three I s were negligible at low surface coverage. The very low values of maximum sorption capacities are most likely related to low surface area of gibbsite (Table 1). However, the amount of Sb (V) sorption is relevant to environmentally available Sb (V) concentrations in soil pore water (Filella et al., 2002a,b). The sorption isotherm indicated very weak I dependence at lower surface coverage (Fig. 1). Only at the highest surface coverage some I-effect was noticeable. However, this type of minor I dependence is most likely not related to outer-sphere sorption. Further mechanistic speculations are not justified in absence of spectroscopic results.

Table 1
Surface properties of gibbsite.

Specific surface area ($\text{m}^2 \text{ g}^{-1}$)	2.63 ^a
Concentration of surface sites (Sites nm^{-2})	8.5 ^b
pK_a_1 ($\text{XOH}_2^+ = \text{XOH} + \text{H}^+$)	4.7 ^c
pK_a_2 ($\text{XOH} = \text{XO}^- + \text{H}^+$)	8.7 ^c
Total surface sites in reaction mixture (mol L^{-1})	0.000742 ^d

XOH refers to a general surface of gibbsite as ($>\text{AlOH}$).

^a Determined from BET surface area analysis.

^b Using the value from Weerasooriya et al. (2003).

^c Using the pK_a values from Sarkar et al. (1999).

^d Calculated using a suspension density of 20 g L^{-1} in reaction mixture.

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