



## Surface complexation of antimony on kaolinite



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### HIGHLIGHTS

- Antimony adsorbs strongly onto kaolinite, a common soil clay mineral.
- Antimony adsorption on kaolinite is strongly dependent on solution pH.
- Component additivity modeling best fitted pH-envelope data at higher concentration.
- Modeling with general composite approach showed good fit at lower Sb concentration.
- Phosphate negatively influenced antimony sorption envelope on kaolinite.

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### ABSTRACT

Geochemical fate of antimony (Sb) – a similar oxyanion as arsenic (As) – in a variety of environment is largely unexplored. Kaolinite is an important, naturally occurring clay mineral in soils and aquifers and is known to control the fate of several contaminants via a multitude of geochemical processes, primarily adsorption. Here we report adsorption of antimony on kaolinite as a function of solution chemistry: initial antimony concentration, pH, ionic strength, and a competing anion. A surface complexation modeling (SCM) approach was undertaken to understand the potential mechanistic implications of sorption envelope data. In the SCM, a multicomponent additive approach, in which kaolinite is assumed to be a (1:1) mixture of quartz ( $\equiv\text{SiOH}$ ) and gibbsite ( $\equiv\text{AlOH}$ ), was tested. Results indicated that ionic strength has a minimal effect on antimony adsorption. For the lower initial antimony concentration (4.11  $\mu\text{M}$ ), the additive model with binuclear surface complexes on quartz and gibbsite showed a better fit at  $\text{pH} < 6$ , but somewhat under predicted the experimental data above  $\text{pH} 6$ . At the higher initial antimony concentration (41.1  $\mu\text{M}$ ), the sorption envelope was of different shape than the lower load. The additive model, which considered binuclear surface complexes for quartz and gibbsite, resulted in over prediction of the adsorption data at  $\text{pH} > 3.5$ . However, the additive model with binuclear surface complex on quartz and mononuclear surface complex on gibbsite showed an excellent fit of the data. Phosphate greatly influenced antimony adsorption on kaolinite at both low and high antimony loadings, indicating competition for available surface sites.

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### 1. Introduction

Antimony (Sb) is a contaminant of emerging concern and because of its reported toxicological effects, United States Environmental Protection Agency has set a maximum contaminant level (MCL) value of  $6 \mu\text{g L}^{-1}$  for drinking water (USEPA, 2009; Ilgen and Trainor, 2012). In addition, there are concerns over the suspected carcinogenic properties of Sb for humans (Gebel, 1997). Antimony (Sb) negatively influences the growths of roots and

sprout for rice plants as well (He and Yang, 1999). Phytotoxic effects of organic antimony compounds on floating water plants have also been reported (Duester et al., 2011).

The provenance of Sb in the environment is mainly from its various industrial uses such as storage batteries, flame retardants, and ammunitions (Filella et al., 2002a). Heavy accumulation of Sb has been reported in mining and smelting areas, roadsides, and shooting ranges (Mitsunobu et al., 2010). The reported range of background Sb concentration in soil is about  $0.05\text{--}22 \text{ mg kg}^{-1}$ , whereas the concentrations in soils contaminated by anthropogenic activities are as high as  $17500 \text{ mg kg}^{-1}$  (Wilson et al., 2010). For freshwater and seawater, dissolved Sb concentration

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has been found to be in the range of 0.1–2  $\mu\text{g L}^{-1}$  (Filella et al., 2002b).

In the environment, two major oxidation states of Sb, (III) and (V), have been reported (Leuz and Johnson, 2005). The expected dominance of Sb (III) in reducing environment and Sb (V) in oxidizing environment may not follow a similar trend as that of As. For As, although most common oxidation states in reducing and oxidizing environment are As (III) and As (V), respectively, existence of As (III) in oxidizing environment is possible due to microbial reduction of As (V) (Smedley and Kinniburgh, 2002). In contrast, for Sb, the reported prevalence of Sb (V) covers a wide redox range (360 to  $-140$  mV) (Mitsunobu et al., 2006). In fact, the mobility and solubility of Sb (V) is greater than Sb (III) (Mitsunobu et al., 2009, 2010).

The major mechanism of Sb retention in the environment is through adsorption to soil components (Leuz et al., 2006). Clay minerals are the essential reactive component of soil and can provide an important sink for Sb (Ilgen and Trainor, 2012). Kaolinite is a common variable charge clay mineral in the weathered soil and feldspathic aquifers (Sarkar et al., 2000). Adsorption of Sb (V) on kaolinite has been reported using macroscopic and spectroscopic studies; however, to date no surface complexation modeling approach of Sb (V) adsorption on kaolinite has been published (Xi et al., 2010, 2013; Ilgen and Trainor, 2012).

Surface complexation models (SCM) are based on the thermodynamic principles and provide marked advantages over empirical adsorption models such as Langmuir and Freundlich isotherms (Sposito, 1983; Goldberg et al., 2008; Schaller et al., 2009). Adsorption processes can be better defined by the SCM using specific surface complexes and charge and mass balanced chemical reactions (Goldberg et al., 2008). However, the applicability of SCM to the natural system such as soils, sediments, and aquifers in predicting adsorption of anions and cations has been faced with challenges (Davis et al., 1998). Two main SCM approaches, a general composite (GC) and a component additivity (CA), have been used to define adsorption in multicomponent systems (Davis et al., 1998). In the GC approach, it is assumed that the multicomponent system is too complex to predict sorption from summation of individual components. Therefore, a 'generic' surface functional group is assumed to describe sorption in the multicomponent system. In the CA approach, sorption on the multicomponent system is predicted based on the derived sorption constant of the individual components. Although, in their study, Davis et al. (1998) found better agreement of Zn (II) sorption on a natural sediment using GC than CA, other studies such as Sarkar et al. (1999, 2000), Landry et al. (2009), Alessi and Fein, (2010), Reich et al., (2010) found good agreement with the CA approach.

Very few studies to date have reported surface complexation of Sb (V) on kaolinite using the above SCM approaches. Consequently, the main objectives of this study are to (i) investigate Sb (V) adsorption on kaolinite as a function of pH, ionic strength, initial Sb concentration, and competing anion such as phosphate, (ii) model Sb (V) adsorption envelope on kaolinite and evaluate the model to predict Sb (V) adsorption by assuming the kaolinite surface to be a 1:1 mixture of silanol ( $\equiv\text{SiOH}$ ) and aluminol ( $\equiv\text{AlOH}$ ) groups, and (iii) model Sb (V) adsorption envelope on kaolinite using generic surface of either quartz (i.e.  $\equiv\text{SiOH}$ ) or gibbsite ( $\equiv\text{AlOH}$ ).

## 2. Materials and methods

### 2.1. Reagent and materials

Kaolinite (KGa-1b) was purchased from the Source Clays Repository of the Clay Minerals Society. Gibbsite was collected from

Almatis Inc., PA, USA. Natural, ground  $\alpha$ -quartz (MIN-U-SIL5) was received from U.S. Silica, Berkeley Springs, WV. Potassium-hexahydroxyantimonate [ $\text{KSb}(\text{OH})_6$ ], Potassium Chloride and PIPES (1,4-piperazinebis (ethane sulfonic acid) were purchased from Sigma-Aldrich (St. Louis, MO).

### 2.2. Preparation of the solids

Kaolinite, gibbsite, and quartz were prepared following the procedure of Sarkar et al. (1999, 2000) and Chorover et al. (2003). Briefly, for kaolinite, a  $< 2$   $\mu\text{m}$  size fraction of the clay was collected by suspension and centrifugation. In a large beaker (2 L), 200 g of kaolinite was weighed and 1000 mL of ultrapure (Milli-Q) water was added. The clay was then dispersed by adding small quantities of 0.01 M NaOH to the suspension until a pH value of 9.5 was obtained. The suspension was thoroughly mixed and transferred to 50 mL centrifuge bottles and size fractionated by centrifugation (5 min at 119g) to collect  $< 2$   $\mu\text{m}$  size fraction. Resuspension at pH 9.5 and centrifugation were repeated several times to obtain a clear supernatant. The clay was then washed repeatedly using 0.01 M KCl until the pH value of the supernatant reached 5.5. The samples were air-dried and stored. For gibbsite, the solid was dispersed with 0.01 M NaOH by shaking for 30 min. After centrifuging the suspension to remove NaOH, the solid was washed with 1 M KCl solution repeatedly until the pH value of the supernatant became  $\sim 7$ . The suspension was air-dried and stored for further use. Quartz was heated at 500  $^{\circ}\text{C}$  for 24 h for oxidizing organic matter. After cooling to room temperature, quartz was refluxed with 4 M  $\text{HNO}_3$  for 4 h to remove iron oxide impurities. Quartz suspension was then repeatedly washed with ultrapure (Milli-Q) water until a supernatant pH  $\sim 6$  was attained. The solid was dried at 75  $^{\circ}\text{C}$  in an oven and stored for further use.

### 2.3. Antimony sorption experiments

Antimony adsorption envelopes for kaolinite, gibbsite, and quartz were determined in batch systems. Surface characteristics and the amount of kaolinite, gibbsite, and quartz used for sorption experiments were listed in Table S1 (supporting documents). Initial concentrations of Sb (V) were 4.11 (500  $\mu\text{g L}^{-1}$ ) and 41.1  $\mu\text{M}$  (5000  $\mu\text{g L}^{-1}$ ). It is noted by other researchers that at low Sb concentrations ( $< 5$   $\mu\text{M}$ ) sorption-edge data is scarce (Leuz et al., 2006). A ten times higher Sb (V) concentration than 4.11  $\mu\text{M}$  was also used to understand the surface complexation behavior at a greater surface saturation.

Appropriate amount of substrate (kaolinite, gibbsite or quartz) was weighed in 15 mL polypropylene centrifuge tubes and equilibrated with 0.001, 0.01, or 0.1 M KCl solution made with 0.1 M PIPES buffer. Desired pH values (range 2–11) for sorption envelope were achieved by adding appropriate amounts of 1 M HCl or NaOH. Sorption experiments were initiated by adding calculated amount of Sb(V) stock solution to the suspension in 15 mL polypropylene centrifuge tubes to get a final volume of 10 mL. Centrifuge tubes containing the reaction mixture were shaken at room temperature ( $\sim 25$   $^{\circ}\text{C}$ ) in an end-to-end shaker at 300 rpm for 7 d. The equilibrium times chosen for gibbsite, quartz, and kaolinite were based on our earlier work, preliminary experiments (Fig. S1), and literature, respectively (Xi et al., 2010; Rakshit et al., 2011; Ilgen and Trainor, 2012). After the equilibration time, the final pH values of the suspension were measured and the suspension was filtered through 0.2  $\mu\text{m}$  syringe filter (Fisher Scientific, 09-730-19). The filtrates were analyzed for total Sb concentration in ICP-MS (Thermo X-series II, Thermo Electron, San Jose, CA). The amount of Sb (V) adsorbed was calculated by the difference between the initial Sb (V) concentration and the Sb (V) concentration measured in the filtrate. A control experiment was carried out under the same

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