The fate and mobility of boron in the environment is largely controlled by adsorption reactions with soil organic matter and soil minerals to form surface complexes (Soil Sci. Soc. Am. J. 1991, 55, 1582; Geochim. Cosmochim. Acta 2002, 67, 2551; Soil Sci. Soc. Am. J. 1995, 59, 405; Environ. Sci. Technol. 1995, 29, 302). In this study, boric acid adsorption on pure am-Al(OH)3 and 5% (w/w) humic acid (HA) coated am-Al(OH)3 were investigated both as a function of pH (4.5–11) and initial boric acid concentration (0–4.5 mmol L−1). Batch adsorption isotherm experiments were also conducted with samples exposed to atmospheric CO2 and anaerobic (N2) conditions to examine the effects of dissolved CO2 on boric acid adsorption. Boron (B) K-edge X-ray absorption near-edge structure (XANES) spectroscopy was used to investigate the coordination of boric acid adsorbed at mineral/water interfaces. The XANES spectra of boric acid adsorption samples showed that both trigonally and tetrahedrally coordinated B complexes were present on the mineral surface. Both macroscopic and spectroscopic experiments revealed that the combination of HA coating on am-Al(OH)3 and dissolved CO2 decreased boric acid adsorption compared to adsorption on pure am-Al(OH)3.

Introduction

Boron (B) is one of several essential micronutrients required by plants at low levels. Boron is thought to be important during the development of cell walls and for the structural integrity of dicotyledonous plant cell walls (5). Phototoxic species account for only 10% of the total soil B content (7). Su and Suarez (4) also studied boric acid adsorption on am-Al(OH)3 surfaces but were not able to detect any tetrahedral B(OH)4 complexes using ATR-FTIR spectroscopy due to the strong interference bands from Al–O vibrations.

Atmospheric CO2 can be readily dissolved in water to form CO32(aq), H2CO3, HCO3−, and CO32− species. Studies that have encompassed carbonate species in adsorption experiments showed that they either decreased the sorption of oxyanions on metal oxides (16–18) or they promoted the adsorption of oxyanions via the generation of extra protonated surface groups (19, 20). The impacts of dissolved CO2 and CO3 species have not been specifically examined in previous B adsorption studies.

X-ray absorption near-edge structure (XANES) is a molecular-scale spectroscopic technique that yields electronic and structural information on the element of interest. Each chemical species has its own unique characteristics and the spectrum of a mixture of two or more chemical species of an element will quantitatively reflect the amount of each species in the sample being measured, allowing the use of XANES spectroscopy to quantitatively determine different chemical forms present in the sample (21).

Boron K-edge XANES spectroscopy has been used to differentiate between trigonally and tetrahedrally coordinated B complexes in borate and borosilicate minerals (21–24). Fleet and Liu (21) found that B K-edge XANES spectra collected in total electron yield (TEY) mode, which probes to ~60 Å, were markedly different than spectra collected in fluorescence yield (FY) mode, which is a bulk structure technique.

The overall objective for this paper was to investigate the effects of HA coating and dissolved CO2 on the sorption of boric acid onto am-Al(OH)3. The experimental approach for the present study was to combine macroscopic adsorption experiments with molecular-scale spectroscopic techniques to investigate boric acid reactions in the presence or absence of natural surface constituents such as humic acid and carbonate. This study represents the first use of B K-edge XANES spectroscopy to study boric acid adsorption on mineral surfaces.

Materials and Methods

Mineral Synthesis and Characterization. am-Al(OH)3 was synthesized according to the method of Sims and Bingham (25), modified as follows. A total of 250 mL of 1.0 M NaOH was added at a rate of 50 mL min−1 to a stirred solution of 250 mL of 0.375 M AlCl3 inside an anaerobic chamber. The pH at the end of the titration was 4.6. The mixture was shaken for 5 min and then centrifuged at 4000g for 30 min. Supernatants were discarded and gel-like precipitates were transferred to Spectra/Por 8000 MWCO dialysis tubing (California) for dialysis, until the dialysis filtrate tested negative for chloride (~24 h).

Humic acid sodium salt (Aldrich, USA) was purified following the procedure of Lemarchand et al. (26), modified as follows. After the alkalization and acidification steps, the precipitated HAs were then washed three times with 0.1 M HCl and centrifuged again at 4000g for 30 min. The HA was then dialyzed (Spectra/Por 8000 MWCO) until chloride-free (~24 h). The final HA was freeze−dried prior to use.

Humic acid coated am-Al(OH)3 samples containing 5% (w/w) HA were prepared by adding 0.0527 g of purified HA to 20 mL of N2 purged 0.1 M NaOH solution. This HA solution was then adjusted to pH 7.5 via the addition of 1.0 M NaOH. The completely dissolved HA solution was then mixed with 1.0 g of pure am-Al(OH)3 and shaken for 24 h.

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The synthesized am-Al(OH)₃ minerals, and 5% (w/w) HA coated am-Al(OH)₃ minerals were characterized by X-ray diffraction (XRD) on a Rigaku Rotaflex 200SU (Tokyo, Japan). Specific surface areas were determined using both single-point and multipoint BET N₂ adsorption isotherms acquired with a Quantachrome Autosorb 1 gas sorption system (Florida).

**Point of Zero Charge.** The Zetasizer Nano ZS and MPT-2 autotitrator (Malvern, U.K.) were used to determine the point of zero charge (PZC) through the measurement of \( \zeta \) potential as a function of pH. am-Al(OH)₃ or HA coated am-Al(OH)₃ at a solid density of 1.0 g L\(^{-1}\) was added to the folded capillary \( \zeta \) potential cell. The \( \zeta \) potential measurements were made from pH 5 to 10 on three replicate samples. The pH values of the samples were adjusted using the MPT-2 autotitrator via the addition of 1.0 M HCl or 1.0 M NaOH.

**Adsorption Envelopes.** Batch boric acid adsorption envelope experiments were conducted on am-Al(OH)₃ and 5% (w/w) HA coated am-Al(OH)₃ at 25 °C under anaerobic conditions. These experiments were conducted in 0.1 M NaCl as a function of pH. am-Al(OH)₃ (0.04 g) and 5% (w/w) HA coated am-Al(OH)₃ (0.04 g) were added to reaction vessels with 40 mL of 0.1 M NaCl containing [B(OH)₃]\(_{init}\) at either 0.3 or 1.5 mmol L\(^{-1}\). The suspensions were adjusted to their desired pH with 1.0 M HCl or 1.0 M NaOH inside an anaerobic chamber. The total amount of base added resulted in less than a 2.5% change in ionic strength. The pH of the system was measured after 24 h of equilibration. The supernatant was separated from the mineral by centrifugation at 4000 g for 30 min and then filtered through a 0.25 \( \mu \)m membrane (Millipore). Boron concentration was determined colorimetrically using the azomethine-H method described by Bingham (27). The amount of B adsorbed was calculated by subtracting the total boric acid equilibrium concentration from the initial boric acid concentration. The B loading rate is calculated on the basis of mineral weight, determined gravimetrically.

**Adsorption Isotherms.** Batch experiments were conducted for boric acid isotherm adsorption on am-Al(OH)₃ and 5% (w/w) HA coated am-Al(OH)₃ at 25 °C in either an anaerobic chamber or under atmospheric conditions to determine the amount of adsorbed B, as a function of initial boric acid concentration in 0.1 M NaCl at pH 5.9 or 9.2. am-Al(OH)₃ (0.04 g) and 5% (w/w) HA coated am-Al(OH)₃ (0.04 g) were added to the reaction vessel with 40 mL of 0.1 M NaCl containing a known concentration of boric acid. The suspensions were adjusted to their desired pH with 1.0 M HCl or 1.0 M NaOH inside an anaerobic chamber or under atmospheric conditions. For atmospheric experiments, the amount of dissolved CO₂ was controlled by exposure to the atmosphere during the pH adjustment period as well as the presence of atmospheric levels of CO₂ in the headspace (10 mL) during the equilibration period. The total amount of base added (100 \( \mu \)L maximum) resulted in less than a 2.5% change in ionic strength. The pH of the systems was measured after 24 h of equilibration. The supernatant was separated from the mineral by centrifugation at 4000g for 30 min and then filtered through 0.25 \( \mu \)m filters. Boron concentration and loading rates were determined colorimetrically using the azomethine-H method described in the previous section.

**X-ray Absorption Near-Edge Structure Spectroscopy.** Samples for XANES spectroscopy were made up of crystalline boric acid, various borate mineral standards, and B adsorption samples. Boron adsorption samples were freeze-dried powders obtained via centrifugation of equilibrated mineral-solution suspensions prepared by the method described in the previous section. The mineral pastes were rinsed with 120 mL of 18 MΩ water, following centrifugation to remove any B in the entrained solution, and then freeze-dried. The freeze-drying process is required to run adsorption samples at the B K-edge energy. While we recognize that freeze-drying has the potential to change surface complexes due to removal of some surface waters, it is a much less destructive method than oven-drying. Boron K-edge XANES spectra were recorded at the Canadian Light Source (Saskatoon, SK) on the Variable Line Spacing Planar Grating Monochromator beamline. This beamline is monochromatized by three variable line spaced gratings over the photon region of 5–250 eV and yields a photon resolution >10 000 eV/ΔeV in the B K-edge region (~193.6 eV) (28). The vacuum at the sample is between 10⁻⁸ and 10⁻⁹ Torr. A microchannel-plate detector was used to record the FY-XANES spectrum; detailed information on the detection system is described in the literature (29). The TEY-XANES spectrum was obtained by measuring the sample current as the result of the photoabsorption.

All XANES spectra were obtained in the same experimental session. Data from the TEY and FY detectors were collected simultaneously. Mineral samples were analyzed as fragments, with adsorption samples reconstituted in specific surface area mortars and pestles before mounting on carbon tape for analyses. Data reduction and analyses were performed using WinXAS version 3.1 software (Berlin, Germany). The individual spectra were first averaged, a linear baseline correction was performed between 190 and 192 eV, and finally the spectra were all normalized to an edge step of 1 from 190 to 212.2 eV. Difficulties in normalization of the sorption samples were sometimes observed in the postedge region (between 210 and 215 eV), which do not overlap exactly. However, only quantitative analyses were made in the absorption edge region (from 193 to 195 eV), where normalization was done correctly and the spectra overlapped. For other energies, the discussion will be limited to qualitative observations only.

**Results and Discussion**

The surface area for am-Al(OH)₃ was 263.3 ± 5.9 m² g⁻¹. However, drying samples such as amorphous metal oxide and humic substances can change their structure and strongly affect the adsorption of Na⁺(aq). For this reason, it is difficult to exclusively monitor changes in specific surface area or humic acid coating of our samples. The PZC values of am-Al(OH)₃ and 5% (w/w) HA coated am-Al(OH)₃ were 8.45 and 7.86, respectively; these values are in agreement with reported values for similar phases (30). A decrease in PZC was observed in 5% (w/w) HA coated am-Al(OH)₃ compared to pure am-

![FIGURE 1. Boric acid pH envelopes from batch adsorption experiments.](image-url)
the presence of dissolved CO2 decreased boric acid adsorption occurred at pH 9.2 relative to pH 5.9. At both pH 5.9 and 9.2, increases. Greater boric acid adsorption on both surfaces and greater affinity for adsorption as solution concentration acid adsorption at low boric acid solution concentrations, and greater affinity for adsorption as solution concentration increases. Greater boric acid adsorption on both surfaces occurred at pH 9.2 relative to pH 5.9. At both pH 5.9 and 9.2, the presence of dissolved CO2 decreased boric acid adsorption on both pure and HA coated minerals. Despite the change in surface charge associated with HA sorption, HA coating did not affect boric acid adsorption in systems under N2. Boric acid adsorption was most strongly affected by the combination of HA coating and the presence of dissolved CO2. This decrease in boric acid adsorption may be a consequence of (1) carbonate and bicarbonate adsorption, leading to the formation of protonated surface groups, and (2) the change in surface charge due to HA sorption.

**Boron K-Edge XANES Spectroscopy.** Polynuclear B species are not known to form at boric acid concentrations under 25 mmol L\(^{-1}\) (33). Even at boric acid concentrations of 100 mmol L\(^{-1}\), less than 5% (w/w) polynuclear species are present (8). In the present study, it was assumed that the XANES spectra of boric acid adsorption samples at pH 7.0 and 9.2 were dictated predominantly by mononuclear species.

Various borate standard minerals were analyzed with B K-edge XANES spectroscopy to identify peaks attributed to trigonally and tetrahedrally coordinated B (Figure 3). Results in this study were very similar to Fleet and Muthupari’s B K-edge study on borate minerals (22). Specifically, diagnostic peaks “a” and “c” (Figure 3) for trigonal B(OH)\(_3\) were present for all boric acid crystals and borate mineral standards known to contain trigonal B(OH)\(_3\) species. Peak “b,” characteristic of tetrahedrally coordinated B, was present in danburite, a mineral known to contain 100% tetrahedral B(OH)\(_4\), and other borate minerals that contain over 50% tetrahedral B(OH)\(_4\) proportionally (Figure 3). Peak “a” in mineral ludwigite (Mg2-Fe3BO5) was shifted to a lower energy (Figure 3) as a result of complexation of trigonal B(OH)\(_3\) with a 3d transition metal. Previous studies have also reported a downshift in energy for the white line (peak “a”) resulting from interactions between the 2p state of the binding atom and the 3p and 3d states of metal cations (34, 35). Differences seen in TEY- and FY-XANES spectra (Figure 3) of the borate minerals indicate that the chemical compositions of the surface and bulk sample were different. The dissimilarities between the TEY- and FY-XANES spectra can be attributed to mechanical damage and/or hydration (23). Self-absorption was evident in the FY-XANES spectra of the boric acid as the height of peak “a” is dampened compared to its corresponding TEY-XANES spectra (Figure 3).

Parts A and B of Figure 4 show TEY-XANES spectra for the boric acid adsorption on am-Al(OH)\(_3\), and 5% (w/w) HA am-Al(OH)\(_3\) under both anaerobic and atmospheric conditions at pH 7.0 and 9.2, respectively. Parts A and B of Figure 5 show the corresponding FY-XANES spectra for the above-men-
tioned samples at pH 7.0 and 9.2, respectively. Generally, the shape and peak positions for the samples are similar, and the major difference between the TEY- and FY-XANES data is the dampening of the peak “a” intensity that can be attributed to self-absorption effects. A detailed discussion and evidence of self-absorption effect present in the FY-XANES spectra of high B adsorption samples is provided in the Supporting Information.

**FIGURE 4.** B K-edge TEY-XANES spectra of boric acid adsorption isotherm samples: (A) conducted at pH 7.0 and expanded view of peak a; (B) conducted at pH 9.2 and expanded view of peak a. Detailed sample information and loading rate are provided in Table 1.

**FIGURE 5.** B K-edge FY-XANES spectra of boric acid adsorption isotherm samples: (A) conducted at pH 7.0 and expanded view of peak a; (B) conducted at pH 9.2 and expanded view of peak a. Detailed sample information and loading rate are provided in Table 1.

**TABLE 1.** Boric Acid Adsorption Isotherm Freeze-Dried Paste Samples Analyzed by B K-Edge XANES (X-ray Absorption Near-Edge Structure) Spectroscopy

<table>
<thead>
<tr>
<th>sample</th>
<th>pH</th>
<th>loading rate (mmol kg⁻¹)</th>
<th>decrease in loading rate (%)</th>
<th>peak a (FY)</th>
<th>decrease in peak a (FY) (%)</th>
<th>position (eV)</th>
<th>height</th>
<th>decrease in peak a (TEY) (%)</th>
<th>position (eV)</th>
<th>height</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂−Al(OH)₃</td>
<td>9.2</td>
<td>2782.1</td>
<td>N/A</td>
<td>7.72</td>
<td>194.04</td>
<td>N/A</td>
<td>14.53</td>
<td>193.99</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>N₂−5% (w/w) Al(OH)₃</td>
<td>9.2</td>
<td>2442.4</td>
<td>12.21</td>
<td>7.16</td>
<td>194.04</td>
<td>7.25</td>
<td>12.55</td>
<td>193.96</td>
<td>13.63</td>
<td></td>
</tr>
<tr>
<td>CO₃−Al(OH)₃</td>
<td>9.2</td>
<td>2745.8</td>
<td>1.30</td>
<td>7.67</td>
<td>193.99</td>
<td>0.64</td>
<td>14.34</td>
<td>193.96</td>
<td>13.63</td>
<td></td>
</tr>
<tr>
<td>N₂−Al(OH)₃</td>
<td>7.0</td>
<td>1654.2</td>
<td>N/A</td>
<td>7.78</td>
<td>193.99</td>
<td>N/A</td>
<td>9.23</td>
<td>193.99</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>N₂−5% (w/w) Al(OH)₃</td>
<td>7.0</td>
<td>1585.5</td>
<td>4.14</td>
<td>7.58</td>
<td>194.04</td>
<td>1.67</td>
<td>9.08</td>
<td>193.99</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>CO₃−Al(OH)₃</td>
<td>7.0</td>
<td>1633.2</td>
<td>1.27</td>
<td>7.70</td>
<td>193.99</td>
<td>1.03</td>
<td>8.70</td>
<td>193.99</td>
<td>5.74</td>
<td></td>
</tr>
<tr>
<td>CO₂−Al(OH)₃</td>
<td>7.0</td>
<td>1231.1</td>
<td>25.58</td>
<td>6.42</td>
<td>193.99</td>
<td>17.48</td>
<td>8.13</td>
<td>193.99</td>
<td>11.92</td>
<td></td>
</tr>
<tr>
<td>boric acid</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>6.87</td>
<td>194.07</td>
<td>N/A</td>
<td>10.90</td>
<td>194.07</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>danburite</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.035</td>
<td>194.08</td>
<td>N/A</td>
<td>0.16</td>
<td>194.08</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

a All samples contain [B(OH)₃]tot = 50 mmol L⁻¹ and ionic strength = 0.1 M NaCl. b FY (fluorescence yield). c TEY (total electron yield). d Calculated with respected to the N₂−Al(OH)₃ sample at the corresponding pH. e Height of peak a in TEY-XANES spectra linearly correlated with B loading rate with a R² value of 0.9256.
Data for the adsorption samples, including the B loading rate, position and height of peak “a” are listed in Table 1. The height of peak “a” from the TEY-XANES spectra was found to be linearly correlated to the B loading rate ($R^2$ value of 0.9256); furthermore the percent decrease in the height of peak “a” corresponded to the percent decrease in the B loading rate (Table 1). The combined effects of HA complexation with am-Al(OH)$_3$ and dissolved CO$_2$ resulted in the largest reduction in the proportion of trigonally coordinated B complexes (the height of peak “a”) at both pH 7.0 and 9.2 (see insets, Figures 4 and 5).

In both TEY- and FY-XANES spectra, a slight downshift in the energy of peak “a” was observed in all of the adsorption samples compared to standards (Table 1). The shift of energy in peak “a” can be attributed to inner-sphere complexation between boric acid with pure and coated mineral. The presence of peak “b” in the adsorption samples showed that tetrahedrally coordinated B complexes were present (Figures 4 and 5). Most of the tetrahedral B(OH)$_4$ complexes are assumed to be inner-sphere, because outer-sphere interactions (hydrogen bonding, long-range electrostatic) are unlikely when the pH is above the PZC of the mineral.

On the basis of the results from macroscopic adsorption studies and BK-edge XANES spectroscopy, we conclude that boric acid forms inner-sphere trigonal B(OH)$_3$ complexes with am-Al(OH)$_3$ and HA coated am-Al(OH)$_3$ at neutral and alkaline pH values. Inner-sphere tetrahedral B(OH)$_4$ species are present; however the proportion of these species remains relatively low compared to trigonal B(OH)$_3$.

Although not explicitly considered in the analysis, it is unlikely that boric acid or a borate group could interact with dissolved CO$_2$ to form B(OH)$_2$CO$_3$ in the am-Al(OH)$_3$ system. However, the occurrences of these boric acid–carboxyl complexes might be possible in the HA system, as fewer OH sites from the mineral would be available for binding. Regardless of these possible complexes, the primary effects of inorganic and organic carbon are yielding significant decrease in boric acid adsorption in systems combining dissolved CO$_2$ and HA.

Much research emphasis has been placed on the study of boric acid–organic acid (i.e., HA) complexation (26, 38). The results from this study suggest that future HA complexation studies may be different if one considers a ternary boric acid–humic acid–mineral system. These aggregate surfaces are extremely common in soils, as HAs are naturally found adsorbed to soil mineral aggregated surfaces (37, 38). Additionally, since the soil gas phase has a markedly higher CO$_2$ content relative to the atmosphere (39), the results from this study, as well as studies conducted by Wijnja and Schulthess (19, 20), suggest the inclusion of dissolved CO$_2$ species in future oxyanion sorption studies.

**Acknowledgments**

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**Supporting Information Available**

Self-absorption discussed in further detail in the FY-XANES spectra of boric acid adsorption on am-Al(OH)$_3$ at pH 7 and pH 9.2. This material is available free of charge via the Internet at http://pubs.acs.org.

**Literature Cited**


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