Calcium and Magnesium Effects on Ammonia Adsorption by Soil Clays

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ABSTRACT

Anhydrous ammonia is a widely used N fertilizer and its interactions with soils and soil clays play an important role in its environmental fate. This study was conducted to determine the quantity and forms of ammonia adsorbed by clay-sized fractions of soils as a function of water content, exchangeable cation, and organic matter (OM). Fourier transform infrared spectroscopy was used to evaluate in situ the mechanisms of interaction of H2O, NH3, and NH4+ with the clay-size fractions of a Blount loam (fine, illitic, mesic Aeric Epiaqualfs) and a Fayette silty clay loam (fine-silty, mixed, mesic, superactive Typic Hapludalfs). Due to NH4+ dissolution in adsorbed water more total N was sorbed at high (90%) than at low (2%) relative humidity (RH) despite decrease in the amount of NH4+ sorbed. At high RH, the amount of NH4+, NH3, and total N increased by 12 to 23% on the Mg-exchanged compared with the Ca-exchanged soil clays. Of the two soil clays, the smectitic sample (Fayette) sorbed more of both N species than the illitic sample (Blount). Samples with OM removed adsorbed significantly more ammonia than untreated samples. The mechanism suggested for ammonia sorption by soil clays is a combination of protonation on water associated with metal cations, coordination to the exchangeable cations and dissolution in pore water. Soil clays can retain significant amounts of ammonium in excess of the cation exchange capacity (CEC) and out of competition for exchange sites. Dissolved NH3 constituted the majority of N adsorbed by the sample at high RH, which is typical of field conditions.

Anhydrous ammonia is the single largest source of N in the USA (Terry and Kirby, 2002). In Illinois, for example, over 50% of the N applied in 2001 was in the form of anhydrous ammonia.

Anhydrous ammonia is injected into the soil as a liquid at depth of 10 to 15 cm (Sommer and Christensen, 1992). Upon decomposition in the soil it becomes a gas (Fig. 1). Essentially all of the ammonia in the soil air dissolves into the soil solution if sufficient moisture is present in the soil (Step 1). This is based on the high affinity of NH3 to water. Dissolved NH3 rehydrates to water to form NH4+ (pKb = 4.8) (Step 2), resulting in a sharp increase in pH, which leads to OM solubilization and temporary sterilization of the ammonia injection zone (Stehouwer et al., 1993). Dissolved NH3 can also undergo hydrolysis in the local coordination sphere of hydrated exchangeable cations (Mortland and Raman, 1968) (Step 3). The acidity (or ability to donate protons) of the waters of hydration is much greater than that of the bulk water (Mortland, 1968) due to polarization of water molecules by exchangeable cations (Touillaux et al., 1968). For Ca2+ and Mg2+, the two commonly occurring exchangeable cations in soils, a smaller Mg2+ ion is more electronegative and, therefore, causes a greater polarization of water and enhances protonation of bases, including ammonia (Mortland, 1968) (Table 1).

Ammonium ions in the soil solution can subsequently enter into cation-exchange reactions with the soil matrix (Mortland, 1966) (Step 4). Depending on the type of soil minerals present, some of this exchangeable NH4+ can become fixed by phyllosilicates (Step 5). The extent of fixation depends mainly on the mineralogy of the soils with vermiculite being the most likely mineral phase to fix NH4+ (Nommik and Vantras, 1982). Additional mechanisms of NH3 retention include fixation by soil organic compounds (Step 6), which for mineral soils does not exceed 5% of applied N (Nommik and Vantras, 1982); hydrogen bonding to oxide and hydroxyl ions on the clay surface (James and Harward, 1964); and formation of ammine complexes with the exchangeable cations (Step 7) (Russell, 1965). It is clear that, even without invoking the biological transformations of N, the interaction web of N resulting from injection of anhydrous ammonia in soils is complex.

A number of studies have examined the interaction of anhydrous ammonia with whole soils (Young, 1964; Norman and Gilmour, 1987; Stehouwer and Johnson, 1991; Sommer and Christensen, 1992; Stehouwer et al., 1993). Additional studies have examined the interaction of NH3 with specimen clay minerals (Mortland et al., 1963; Russell, 1965; Mortland and Raman, 1968; Petit et al., 1998).

However, no studies, except for Ashworth (1978), have explored the clay-sized fraction of the soil, which includes phyllosilicate clay minerals, Fe and Al oxides and hydroxides, and OM associated with clay. Using soil clays to study ammonia sorption focuses on the reactive fraction of the soil without sacrificing the inherent heterogeneity.

The protonated form of ammonia, ammonium, has characteristic infrared absorption bands at 1440, 3270, 3050, and 2855 cm⁻¹. Fourier transform infrared (FTIR) spectroscopy can, therefore, be used to study the quantity and environment of ammonium in specimen smectites (Mortland et al., 1963; Russell, 1965; Mortland and Raman, 1968; Chourabi and Fripiat, 1981; Xu, 1997; Petit et al., 1998; Petit et al., 1999) and vermiculites (Mortland et al., 1963; Alhrichs et al., 1972).

The distribution of N between NH3 and NH4+ in the soil solution and the attendant reactions of these solutes in soils are not fully understood and are the focus of

Abbreviations: CEC, cation-exchange capacity; FTIR, Fourier transform infrared; OM, organic matter; RH, relative humidity.

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this study. The objective of this study was to quantify effects of RH, exchangeable cations, and OM on adsorption and protonation of ammonia by soil clays.

**MATERIALS AND METHODS**

Samples from the Ap-horizons of two soils from the Midwest USA were used in this study: Blount loam and Fayette silty clay loam. Basic properties of these soils and their clay fractions are listed in Table 2. Soils varied in OM and clay content. Mineralogical composition was determined by X-ray diffraction and confirmed by FTIR spectroscopy. The clay fraction of the Blount soil was comprised of illite, hydroxy interlayered vermiculite, kaolinite, and quartz, while the Fayette soil was dominated by randomly interstratified illite-smectite referred to later in this text as smectite with lesser quantities of kaolinite, illite, vermiculite and quartz (Dontsova and Norton, 2002). The mineralogical composition of the clays was reflected in the larger surface area of the smectitic Fayette soil compared with the illitic Blount clay. The clay fraction (<2 μm) of the soils was separated by using dispersion in deionized water and sedimentation. For a Fayette soil without OM treatment, OM was destroyed by reaction with peroxide (Kunze and Dixon, 1986). Freeze-dried clay samples were exchanged with 0.50-mol L⁻¹ solutions of CaCl₂ and MgCl₂ and washed free of Cl⁻ ion by centrifugation. A 0.4-mL aliquot of a 10-mg mL⁻¹ suspension was used to prepare each self-supporting film in a 2.63-cm² wire loop (Dontsova et al., 2004). This resulted in a film density of about 1.5 mg cm⁻².

Fourier transform infrared spectra (PerkinElmer 1600 spectrometer with a DTGS detector and a KBr beamsplitter, PerkinElmer, Inc., Wellesley, MA) and gravimetric data (Cahn D-2000 microbalance) were obtained simultaneously in an environmental infrared cell with controlled RH (Johnston et al., 1992). In the cell clay films were suspended from the microbalance inside an FTIR, which allowed collection of gravimetric and spectroscopic data as the experiment progressed. The unapodized resolution of the FTIR spectra was 2 cm⁻¹ with a step of 1 cm⁻¹. The experiment was controlled by the LabView program version 5.1 (National Instruments Corporation, Austin, TX).

The partial pressure of water, monitored by a Vaisala model HMP35A humidity probe (Vaisala Oyj, Helsinki, Finland), was varied by mixing a stream of dry N₂ gas with N₂ gas saturated with water vapor. Total flow was 100 std cm³ min⁻¹ (sccm). Initially, samples were equilibrated for 3 h at 100% RH and then RH was decreased in the following steps: 60, 30, 25, 20, 15, 10, 5, and 0% (Fig. 2). At each RH step, samples were allowed to equilibrate for 2 h. After this, for high RH treatment, RH was raised back to 100%. Fourier transform infrared spectra were obtained every hour, and gravimetric and RH measurements were taken every minute. Dry weight of the sample was estimated by extrapolating a regression between the absorbance of the 1640 cm⁻¹ water band and weight of the sample to zero absorbance (Johnston et al., 1992).

After target RH was reached, 36 cm³ of N₂ gas at atmospheric pressure was introduced into the system while a flow of N₂ gas at a set RH continued. Injections were repeated several times until a sample reached equilibrium, as evidenced by stable weight and 1440 cm⁻¹ band intensity. For a quantitative determination of water and ammonium contents, the position, area, and height of the ~1640 and ~1440 cm⁻¹ bands were determined using curve-fitting of the Gaussian–Lorentzian lineshape to spectra in the 1800 to 1330 cm⁻¹ region. Spectra were analyzed using the GRAMS/32 software, version 5.2 (Thermo Electron Corporation, Walther, MA). The study focused on the ν₃ NH₄⁺ band because the intensity of this band is linked quantitatively to the N content of the analyzed samples. Unlike NH₄⁺-stretching vibrations, which overlap with the OH-stretching vibrations of water, the NH₄⁺–deformation region is relatively free of other absorptions (Petit et al., 1999).

The amount of ammonium sorbed on the clay (cmol kg⁻¹), Q, was calculated from the integrated absorbance of the 1440 cm⁻¹ band using following formula based on the Beer–Lambert law (Atkins, 1998, p.458):

**Table 1. Reported values for ammonia sorption on clay minerals.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Cation</th>
<th>Conditions</th>
<th>NH₄⁺</th>
<th>NH₃</th>
<th>NH₄⁺ + NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>Ca</td>
<td>evacuated</td>
<td>65</td>
<td>78</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>evacuated</td>
<td>80</td>
<td>22</td>
<td>102</td>
</tr>
<tr>
<td>Bentonite</td>
<td>Ca</td>
<td>evacuated</td>
<td>80</td>
<td>163</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>evacuated</td>
<td>101</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wyoming bentonite</td>
<td>Ca</td>
<td>RH = 20%</td>
<td>80</td>
<td>42</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>RH = 20%</td>
<td>101</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SWy-1 montmorillonite</td>
<td>Ca</td>
<td>RH = 2%</td>
<td>16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>RH = 2%</td>
<td>16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SAz-1 montmorillonite</td>
<td>Ca</td>
<td>RH = 2%</td>
<td>69</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>RH = 2%</td>
<td>48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Loch Scye vermiculite</td>
<td>Ca</td>
<td>RH = 2%</td>
<td>24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>RH = 2%</td>
<td>52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Llano vermiculite</td>
<td>Ca</td>
<td>RH = 2%</td>
<td>91</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>RH = 2%</td>
<td>83</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

† RH = relative humidity.
‡ (van Olphen and Fripiat, 1979).
Table 2. Selected mineralogical, physical, and chemical properties of the soils and their clay fractions (CF). †

<table>
<thead>
<tr>
<th>Soil</th>
<th>Dominant clay minerals‡</th>
<th>CEC</th>
<th>OM</th>
<th>EGME SA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>soil</td>
<td>CF</td>
<td>Clay</td>
<td>soil</td>
</tr>
<tr>
<td></td>
<td>cmol kg⁻¹</td>
<td>mg kg⁻¹</td>
<td>m² g⁻¹</td>
<td>cmol kg⁻¹</td>
</tr>
<tr>
<td>Blount loam</td>
<td>I(3), K (2), HIV(2)</td>
<td>21.7</td>
<td>28.2</td>
<td>254</td>
</tr>
<tr>
<td>Fayette silty clay loam</td>
<td>S(4), K(3), I(3), V(2)</td>
<td>22.7</td>
<td>38.9</td>
<td>291</td>
</tr>
</tbody>
</table>

† CEC = cation exchange capacity by summation of natural exchangeable cations for whole soil and by exchange of Mg for Ca in CF; OM = organic matter; EGME SA = surface area by ethylene glycol monoethyl ether method, soil ground to < 0.25 mm, CF exchanged with Mg.
‡ HIV = hydroxy-interlayered vermiculite; I = illite; K = kaolinite; S = randomly interstratified illite-smectite; V = vermiculite; (1) through (5) = relative abundance with (1) = least abundant and (5) = most abundant.

where \( A \), cm⁻¹, is the integral absorbance of the 1440 cm⁻¹ band; \( \varepsilon \) is the extinction coefficient of \( \text{NH}_4^+ \), equal to 13 cm µmol⁻¹ cm⁻¹; \( m_c \) is dry weight of the sample in milligrams; \( a_c \), cm², is area of clay film; and 100 cmol g mmol⁻¹ kg⁻¹ is a correction coefficient. The extinction coefficient value was obtained from Bortovskly et al. (2001) and verified by comparing with the value obtained from the intensity of the \( \text{NH}_4^+ \) band in an \( \text{NH}_4^+ \) exchanged Blount and Fayette clays with a known CEC. Good agreement was found between the two extinction coefficient values.

The following equation from Mortland and Raman (1968) was used to calculate the equilibrium constant (\( K_e \)) value of ammonia protonation.

\[
K_e = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{H}_2\text{O}][\text{NH}_3]} [2]
\]

In this equation, \( \text{H}_2\text{O} \) and \( \text{NH}_4^+ \) contents were determined respectively from the intensity of the HOH bending band at 1640 cm⁻¹ and the absorbance of the 1440-cm⁻¹ band. The amount of \( \text{NH}_3 \) was determined by difference from the total mass of the sample (clay, adsorbed \( \text{H}_2\text{O} \), \( \text{NH}_4^+ \), and \( \text{NH}_3 \)).

The experimental design was a randomized block, with clay extraction as the block. The experiment was repeated over time. As a result, each treatment was replicated four times. Organic matter effect on ammonia adsorption by Fayette clay was studied only in the second repeat of the experiment; therefore, it was replicated twice. Combined statistical analyses of two repeats were performed using SAS GLM procedure, Type III Sums of Squares (SAS Institute, 1990). Error terms were pooled, whenever possible (\( P > 0.25 \)).

RESULTS AND DISCUSSION

A survey FTIR spectrum of the Fayette soil clay is shown in Fig. 3a. Of importance in this study is the \( \text{H}–\text{O}–\text{H} \) bending band of water in the 1590- to 1700-cm⁻¹ region. This band increased in intensity with an increase in sample water content. The spectrum also shows water-stretching modes at 3580, 3420, and 3250 cm⁻¹. Where the IR-active band of ammonium appears at 1430 cm⁻¹ these samples show evidence for the presence of carbonate.

When ammonia was injected into the environmental cell at low RH, the weight of the sample increased sharply due to adsorption of \( \text{NH}_3 \) (Fig. 2). Within minutes, as \( \text{NH}_3 \) gas was gradually removed from the environmental cell by the flow of \( \text{N}_2 \) gas, the weight started to decrease. The weight at equilibrium was less than the weight before ammonia injection for all studied clays and treatments. A decrease in weight of the sample was explained by loss of water, confirmed by a decrease in absorbance of water stretching and bending bands. Consecutive injections resulted in an analogous pattern. Xu (1997) also observed that the weight of Ca-montmo-
Ammonium

When ammonia was introduced, the type of saturating cation, RH and clay mineralogy affected its interaction with the clay (Fig. 5). Under wet conditions, the Mg-exchanged soil clays retained 23 and 22% (for Blount and Fayette clays, respectively) more NH$_4^+$ than the Ca-exchanged clays. Differences were significant at 90%. The same trend was reported in earlier work of Mortland and Raman (1968).

Under dry conditions, the amount of NH$_4^+$ adsorbed was similar for Ca- and Mg-exchanged Blount clay (dominated by illite). For smectitic Fayette clay, significantly more ammonium was sorbed on Ca-exchanged than on Mg-exchanged samples. While contradicting Mortland and Raman (1968), this result agreed with findings of Xu (1997) for SWy-1 and SAz-1 montmorillonites (van Olphen and Fripiat, 1979). If the amount of ammonia protonation is related to electronegativity (Mortland, 1968), then more water should be protonated on Mg clay. However, electronegativity of exchangeable cations also enhances water sorption of soil clays (Dontsova et al., 2004). This results in competition...
between water and ammonia for coordination spheres of cations.

Observations in this study agreed with those of Mortland and Raman (1968), who found that more ammonia was sorbed on dry clays than on wet ones. Fayette Ca wet clay sorbed only half as much as dry clay. At low (2%) RH a highly significant negative linear relationship \((P > F = 0.0001)\) was observed between the amount of ammonium adsorbed on the clay and the total water content of the clay (Fig. 6). This relationship was independent of clay mineralogy or exchangeable cation. At high RH, ammonium protonation was independent of water content, probably due to the overwhelming amount of water. Mortland et al. (1963) also observed the negative relationship between water and ammonium absorbance and concluded that adsorbed water serves as a proton donor for ammonia. The inverse relationship between water content and ammonium protonation also supports the notion that ammonia protonation in bulk water is less likely than protonation by coordinated water.

In agreement with earlier works (Brown and Bartholomew, 1962; Mortland et al., 1963; Young and McNeal, 1964; Ahlrichs et al., 1972) the absolute amounts of adsorbed ammonia varied between the materials in accordance with their CEC. Differences were significant at low RH, but not significant at high RH. The NH\(_4^+\) sorption values obtained at high RH were close to the CEC of the samples (28.2 and 38.9 cmol kg\(^{-1}\) for Blount and Fayette, respectively). Ahlrichs et al. (1972) have also shown that the amount of NH\(_4^+\) adsorbed is similar to the CEC of the material. The relationship between CEC and ammonia protonation confirms that cations play a major role in the process. Contrary to the expectation, soil OM had no effect on ammonia protonation (Fig. 7).

### Ammonia

The amount of ammonia adsorbed by the clays displayed a highly significant linear relationship with the water content of the sample (Fig. 8) \((P > F = 0.0001)\). Unlike NH\(_4^+\), the ammonia content increased with increase in water content. An intercept with the \(x\)-axis occurred at 152 cmol kg\(^{-1}\) of clay, or 27 mg of water per gram of clay. No free water was expected to be present in a sample at this water content. A positive correlation between water content and aqueous ammonia retention was explained by the very high solubility of ammonia in water: 89.9 g per 100 cm\(^3\) (Weast, 1988). Exchangeable cations did not affect this relationship.
This supports the theory that NH₃ is mostly dissolved in adsorbed and bulk pore water, rather than, as suggested by Young and McNeal (1964), associated with metal cations.

This dependence of ammonia on water content was reflected in the highly significant effect of RH on ammonia sorption (Fig. 5). Both Blount and Fayette clays sorbed more ammonia at high RH than at low RH. The difference was 5 to 9 times for Blount clay and 3.4 times for Fayette clay. The trend toward an increase in ammonia adsorption at high RH contradicted previous studies. Mortland and Raman (1968) observed a negative relationship between water and NH₃ content. The method used in this experiment possibly has an advantage over previous studies due to measurement of NH₃ content in situ. The relationship between ammonia sorption and water content of the sample is complex. Mortland et al. (1963) suggested that ammonia sorption is influenced by the competition between water and ammonia for the polarization spheres of exchangeable cations, the relative affinity of water and ammonia for complexing these cations, and the proton affinity for NH₃ molecules.

Considering that the Mg clays adsorbed more water (Dontsova et al., 2004) than Ca clays, and that a positive relationship was observed between water and ammonia sorption, Mg clays can be expected to retain more NH₃ than Ca clays. This study, in fact, showed that Mg clays sorbed consistently more NH₃ than Ca clays. However, the differences were significant only for Fayette samples with OM removed at low RH.

At a low RH, ammonia sorption increased 1.8 to 2.8 fold from Blount to Fayette soil, while at a high RH, the differences were smaller. None of the differences were significant. This contradicted the findings of Ahlrichs et al. (1972), who reported an inverse relationship between quantity of NH₃ sorbed and CEC. Differences in ammonia sorption between the clay materials can be explained by differences in their water sorption, which increased with CEC.

Organic matter removal increased ammonia sorption on Fayette clay by a factor of 2 to 3.5 for dry samples and 1.4 to 1.7 for wet samples (Fig. 7) probably due to nonrestrictive adsorption in the interlayer and stripping of the clay surfaces. Interlayer adsorption of ammonia by clays is supported by the results of Mortland et al. (1963), who observed swelling of montmorillonite and vermiculite in an ammonia environment. While in bulk soils OM was shown to be one of the sinks of anhydrous ammonia (Young, 1964), OM can also interfere with ammonia sorption by the clays due to the competition between OM and adsorbates, including ammonia, for the reaction sites on the clay (Mortland, 1970; Voudrias and Reinhard, 1986; Bhatti et al., 1998).

### Equilibrium Constant

The equilibrium constant (Kₑ) for ammonia protonation is expressed by Eq. [2]. Concentrations were used in calculations instead of the activities because the latter were not available. In Table 3, the equilibrium constant is expressed as its negative logarithm, pKₑ, and smaller values of pKₑ indicate greater acidity.

If the pKₑ values calculated for solution were compared with the measured values for the clay (Table 3), the water associated with the clay possessed a greater ability to donate protons than bulk water. This was especially true for the Ca treatment. This result confirmed that findings of Mortland et al. (1963) who reported that adsorbed water on montmorillonites exhibits greater acidity than bulk water are also valid for the soil clays used in this study.

The values of pKₑ were always significantly smaller at low humidity indicating higher acidity of clay surfaces. Mortland (1968) and Mortland and Raman (1968) also reported an increase in acidity of the sorbed water when clay was dried. The polarizing influence of the cations was concentrated on fewer molecules, with a resulting increase in water molecule dissociation and acidity. Mortland and Raman (1968) even suggested the existence of two Kₑ values—one for low RH when only the inner sphere coordinated water was present, and another when both inner and outer sphere coordinated water was present.

When pKₑ values for solutions of Ca²⁺ and Mg²⁺ in water in the presence of ammonia were compared, water in the Mg system exhibited a greater acidity. The same trend was observed for soil clays at high RH conditions: pKₑ values were smaller for Mg treatment, but the differences were not significant. For low RH conditions, the opposite trend was observed, which was significant only for Fayette soil with OM removed. While reported pKₑ values were not the same, the same relationship between the treatments was observed by Xu (1997) for SWy-1 montmorillonite.

The Kₑ values were sensitive to water content. Ammonia sorption increased with increased water content of the sample. Concentrations of both ammonia and water are in the denominator of Eq. [5]. An increase in water, therefore, would decrease the calculated values of Kₑ.

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Table 3. Negative logarithm of equilibrium constants for ammonia protonation on the surface of the clay.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>low RH †</td>
<td>high RH</td>
</tr>
<tr>
<td>Blount</td>
<td>0.632 Ab‡</td>
<td>2.080 Aa</td>
</tr>
<tr>
<td>Fayette</td>
<td>0.466 Ab‡</td>
<td>2.041 Aa</td>
</tr>
<tr>
<td>Fayette without OM</td>
<td>0.322 Ac‡</td>
<td>2.308 Aa</td>
</tr>
<tr>
<td>Solution</td>
<td>3.456</td>
<td></td>
</tr>
</tbody>
</table>

† Relative humidity.  
‡ Values followed by the same letter are not different at 0.05 probability level. Capital letter across clays (LSD = 0.402), lowercase letter across treatments within clay material (LSD Dönso = 0.362, LSD Fayette = 0.442, LSD Fayette w/Om = 0.536).
and increase pKc. For example, high values of pKc for Fayette Mg clay with OM removed at low RH compared with Fayette clay with OM are likely high due to high water and ammonia content. Ammonium protonation in this treatment was not significantly different from the sample with OM.

This leads to a conclusion that for processes on clay surfaces, Kc values, while useful for studying general trends, should be viewed with caution. Reported values for the equilibrium constant for ammonia protonation reaction do not follow a consistent pattern. Unlike the liquid systems, where, with time, all the molecules have a chance to participate in the reaction, part of the water present on the clay surface might not be participating in the reaction as shown on Fig. 1, thus affecting the equilibrium constants (Mortland and Raman, 1968). Other reactions can also be taking place on the clay surface. For example, solvation of exchangeable cations in ammonia could occur, in which case not all ammonia would be participating in protonation reactions. Between the clay materials, there were no significant differences.

Total Nitrogen

The total N amount (NH₃ + NH₄⁺) retained by the soil clays (Fig. 5) generally followed the same trend in the effect of humidity, cations, clay mineralogy and OM, as NH₃ because at high RH greater amounts of ammonia were sorbed in unprotonated form than in protonated form. Total N was significantly affected by the RH (P > F = 0.001 for Blount and 0.002 for Fayette). Total N sorption was increased 1.9 to 3.5 times by increasing RH from 2 to 90% in samples with OM and 1.2 to 1.8 in Fayette samples with OM removed. Magnesium-saturated clays, which before ammonia injection contained more water at all humidities, retained 12 to 23% more total N than Ca clays (not significant at 95%) (Fig. 5). This agrees with results of Brown and Bartholomew (1962), who for dry bentonite and halloysite found that total ammonia sorption was increased in the following order: K⁺ < Na⁺ < Ca²⁺ < Al³⁺.

Smectitic Fayette clay sorbed more ammonia in both NH₄⁺ and NH₃ forms than Blount clay, dominated by illite and vermiculite (Fig. 5). A number of researchers observed the effect of mineralogy on ammonia sorption by clay minerals (Brown and Bartholomew, 1962; Mortland et al., 1963; Young and McNeal, 1964; Mortland and Raman, 1968; Ahlrichs et al., 1972; Xu, 1997). In addition to CEC effects quoted by the authors, Mortland and Raman (1968) also observed a decrease in the quantity of ammonia sorbed when the location of the charge was in the tetrahedral layer. Xu (1997) explained the difference by H-bonding of the surface oxygens of the tetrahedral layer with the water that forms a bridge between cation and clay surface, thus diminishing the ability of water to protonate NH₃. This can partially explain greater N sorption by smectitic Fayette than illitic Blount soil clays.

Fayette clay treated with peroxide adsorbed more total N than untreated clay (Fig. 7). These differences were significant at α = 0.05 for Mg at low RH and Ca at high RH. Total amount of N retained by clays (55–248 cmol kg⁻¹) was in general agreement with amounts reported for soils, taking into account clay content and fraction of total area affected by ammonia injection. The practical importance of sorption values for total N lies in the fact that retained ammonia is temporarily protected from loss after the injection of anhydrous ammonia into the soil.

CONCLUSIONS

In this study, adsorption of ammonia by soil clays was quantitatively determined in situ. The mechanisms suggested for ammonia sorption by soil clays are protonation on water associated with metal cations, dissolution in pore water and coordination to the exchangeable cations.

This work generally confirmed an increase in ammonia retention in Mg-saturated soil clays, compared with Ca-clays. Furthermore, soil clays can retain significant amounts of ammonium in excess of the CEC and out of competition for exchange sites. Even after removal of NH₃ gas from the environment, adsorbed NH₃ was an important pool of N in the sample. Availability of both forms of nitrogen to plants is unknown, but easy desorption by water indicated that both forms are likely to be easily available.

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