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Can soil clay content predict ammonia volatilization losses from sub-surface banded urea in eastern Canadian soils?

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ABSTRACT

To determine how soil physical and chemical characteristics affect NH3 volatilization, we measured NH3 losses from 8 different eastern Canadian soils with varying soil clay contents and cation exchange capacities (CEC). Losses were measured from soil mesocosms banded (0.05 m depth) with urea (equivalent of 140 kg N ha⁻¹) in a dynamic chamber system fitted with an acid trap; with soil properties measured in parallel mesocosms. Regression analysis indicated a negative relationship between 28-d NH3 volatilization losses and soil clay content (P < 0.001; R² = 0.978), CEC (P < 0.001; R² = 0.941), and buffer capacity (P = 0.006; R² = 0.772), and positive relations with maximum change in soil pH (P = 0.015; R² = 0.670) and maximum water-extractable NH₄⁺ (P = 0.010; R² = 0.721). A 90% reduction in NH3 losses occurred when clay content increased from 10 to 20%. Also, the correlation between water-extractable NH₄⁺ and NH3 loss and a lack of correlation between salt-extractable (1M KCl) NH₄⁺ and NH3 loss indicates that NH₄⁺ bound to cation exchange sites does not contribute to rapid NH₃ volatilization. However, more research on soils of different mineralogy is required to ascertain whether this holds in other regions as well.
INTRODUCTION

In agricultural production systems, the quantity of N harvested in the grain typically accounts for about 33% of applied N for grain crops (Raun and Johnson 1999), with other crops and forages having similar N yields. Some of the applied N is lost and can represent a large economic inefficiency, while also causing environmental degradation such as eutrophication of surface and ground water, N enrichment and possible saturation of downwind natural areas, acid rain, and the production of aerosols and smog causing human respiratory illnesses (Vitousek et al. 1997). One of the major N loss pathways is NH$_3$ volatilization, which accounts for an average of 14% and 23% of applied synthetic fertilizer and animal manure N, respectively (Bouwman et al. 2002). Therefore, better understanding of how soil properties affect NH$_3$ volatilization is critical in order to devise strategies that improve N use efficiency in cropping systems and diminish the negative effects of N fertilizer application on the surrounding environment.

Urea is a commonly used N fertilizer in Canada, likely because it is easily and cheaply manufactured, stored, distributed and handled (Hauck 1984). However, upon application, urea is rapidly hydrolyzed, causing high soil NH$_4^+$ concentrations as well as increasing pH; providing optimal conditions for increased NH$_3$ volatilization. As a result, NH$_3$ losses can account for up to 60% of broadcasted urea N (Raun and Johnson 1999; Rochette et al. 2009b). To minimize these losses, soils are typically plowed immediately following broadcast application, or the urea is applied in bands and re-covered with soils. Incorporating or banding N fertilizers reduces the supply of NH$_3$ and NH$_4^+$ (i.e. total ammoniacal N or TAN) to the soil surface by increasing the path length required to reach the surface. Thus banding urea in a silt loam at a depth of 0.05 m was found to reduce NH$_3$ volatilization losses dramatically, with cumulative 25 d losses that were approximately 20% of the losses from surface applications (Rochette et al. 2013a).

However, the strong effect of pH on the relative proportions of NH$_3$ versus NH$_4^+$, particularly between a pH of 6 and 9 (Bates and Pinching 1950), means that soil pH is known to be correlated with NH$_3$ volatilization losses. Concentrating urea in bands can lead to larger, localized increases in pH because the generation of NH$_4^+$ and OH$^-$ ions through urea hydrolysis enhances NH$_3$ volatilization (Rochette et al. 2013b; Sommer et al. 2004). Indeed, banding urea in a dry acidic silty clay loam resulted in a localized increase of pH from 6.0 to 8.7 causing greater NH$_3$ losses compared to broadcast urea (Rochette et al. 2009c). Increases in soil pH after urea hydrolysis however, will be limited if soils have a high titratable or exchangeable acidity, or a high buffer capacity, resulting in lower emissions (Ferguson et al. 1984; Izaurralde et al. 1987).
Soil NH$_3$ fluxes are also related to other soil properties though, such as cation exchange capacity (CEC) and N fixation capacity, likely because these soil properties control the amount of available TAN near the soil surface (Ferguson et al. 1984; Mortland et al. 1963; Sommer et al. 2004; Wang and Alva 2000). After addition of fertilizer, soil TAN can be rapidly fixed to the clay minerals. This fixation then, reduces the pool of easily available TAN, reducing NH$_3$ volatilization. However, the amount of NH$_4^+$ fixed to the soils is related to the clay content and the type of clay minerals with kaolinites having less NH$_4^+$ fixation capacity than vermiculites and montmorillonites (Blasco and Cornfield 1966). Soil CEC would have a similar effect in that it too reduces the amount of available NH$_4^+$; although NH$_4^+$ bound to the CEC sites would be more available than clay-fixed NH$_4^+$. With the fixed NH$_4^+$ essentially unavailable and the CEC-bound NH$_4^+$ only moderately available, most of the NH$_3$ lost via volatilization would derive from the active pool of TAN within the soil solution. Under baseline conditions (i.e. not immediately following fertilizer applications), the decrease in soil solution NH$_4^+$ concentration via NH$_3$ volatilization would be replenished by desorption of the NH$_4^+$ pool bound to the CEC. Immediately following urea application (i.e. 1 to 2 weeks after application) however, the dissolved NH$_4^+$ concentration would be high, reducing the importance of replacement of dissolved NH$_4^+$ by exchangeable NH$_4^+$. The most common method for determining soil NH$_4^+$ concentration relies on extracting the NH$_4^+$ from soils using a salt (typically 1M KCl), which extracts not only the NH$_4^+$ in solution, but also the exchangeable NH$_4^+$ (i.e. that which is attached to the CEC sites; Maynard et al. 2006). In recently fertilized soils, where soil solution NH$_4^+$ concentrations are already high, including this exchangeable NH$_4^+$ in the extract may over-estimate the amount of NH$_4^+$ available for NH$_3$ production and loss. In studies using soils with similar CEC, the ratio of KCl-extractable and water-extractable NH$_4^+$ is likely consistent, meaning that the two estimates of available NH$_4^+$ should result in similar correlations with NH$_3$ volatilization; however across soils with different CEC, this ratio may change. Therefore, across soils with varying CEC, water-extractable (e.g., 5 mM CaCl$_2$ extract) NH$_4^+$, which should provide a more accurate measure of the amount of NH$_4^+$ available for NH$_3$ production and loss, should better predict NH$_3$ volatilization losses than a traditional 1M KCl extraction.

Previous studies have found that soil clay content was negatively correlated with NH$_3$ volatilization losses after surface application or incorporation of an ammonium-based or urea-based fertilizer (e.g. Fenn and Kissel 1973; Stevens et al. 1989), however none have examined whether this is still the case when the urea is applied as a sub-surface band. Therefore the objective of this study was to use linear regression to examine the relationship of soil clay content, CEC, buffer capacity, KCl-extractable or water-extractable NH$_4^+$ concentrations, as well as other soil properties (e.g., SOC,
exchangeable acidity) on soil NH\textsubscript{3} volatilization in a way that could allow us to predict NH\textsubscript{3} losses from sub-surface banding of urea to soils in the region. To determine these effects, we measured NH\textsubscript{3} flux and changes after fertilization with banded urea from eight different soils with a wide range of soil physical and chemical properties. Our hypothesis was that soil clay content would be negatively correlated with NH\textsubscript{3} volatilization losses after sub-surface banding of urea. Correlations with other soil properties believed to drive this relationship will also be explored.

MATERIALS & METHODS

Soil Sampling:

Approximately 30 kg of soil was collected from the 0 to 0.15 m depth from eight agricultural fields near Quebec City, Canada between 30 October and 6 November 2008 (Table 1). The soils were selected specifically to provide a wide range of soil textures, carbon (C) contents and cation exchange capacities (CEC). However, although these soils did exhibit a wide range of clay concentrations, the mineralogy of the clays were all similar, primarily derived from quartzite and chlorite mica schists (Dekimpe and McKeague 1974; Kodama 1979; Kodama et al. 1993). We also selected soils that were similar in initial pH, with pH\textsubscript{CaCl\textsubscript{2}} values ranging from 4.75 to 5.73. Large plant materials were removed from the soils, which were then air-dried to a moisture content allowing for sieving to pass a 6 mm mesh. Soils were then stored for about 3 months before initiation of the study. During storage, the soils were covered and water was added periodically to prevent the soils from drying out to avoid a pulse of labile C and N when initiating the experiment, as is known to occur after soil re-wetting (Birch 1960).

Experimental design:

The soils were split into two parallel experiments run concurrently, with one following changes to soil pH, NH\textsubscript{4}\textsuperscript{+} concentration and NO\textsubscript{3} concentration, and the other experiment measuring the amount of N lost as NH\textsubscript{3}. For both experiments, the soils were incubated at a water content corresponding to a tension of 2 bars, as determined using pressure plates. For the study tracking changes to soil pH and inorganic N concentrations, we took 3.5 kg of each sieved soil and packed it into a plastic bin (0.40 x 0.80 m) at a bulk density of 1 g cm\textsuperscript{-3}. The bins were split into two sections, (Fig. 1), one with a width of 0.30 m and the other with a width of 0.10 m, using a plastic, polyethylene sheet to separate the two sections. Urea (12 g; equivalent to 140 kg N ha\textsuperscript{-1}) was banded into the wider section at 0.05 m depth, while the thinner section of the bin was left as a no-N control. After urea addition, the fertilizer pellets were recovered with soil and the overlying soil was packed to approximately 1 g cm\textsuperscript{-3}. These treatments were replicated for each soil 4 times, and the replicates were arranged into randomized complete blocks.
A schematic of the open chamber system for measuring NH$_3$ volatilization is provided in Rochette et al. (2009a). Briefly, the system consisted of a sealed PVC enclosure in which we placed a stainless steel cylinder (diameter = 0.19 m) containing 3.5 kg of air-dried, sieved soil re-packed to a bulk density of 1 g cm$^{-3}$. The cylinder was placed on a bed of silica sand, so that the cylinder was approximately 0.05 m below the top of the PVC enclosure. The enclosure was sealed with a 1.25-cm thick Plexiglass cover on a ring of closed-cell foam. Constant airflow was achieved by pulling air through the system using a dual vacuum pump (model 2107CA20, Thomas Pumps, Sheboygan, WI, USA). Air was first bubbled through a 0.05 M H$_3$PO$_4$ (100 mL) acid trap before entering the system to ensure that NH$_3$-free air entered the chamber. A second acid trap after the chamber was used to capture the ammonia emitted from the enclosure. Airflow was measured using a Gallus 2000-G4 flowmeter (Actaris Meterfabriek, Riems, France). Ammonia volatilization was calculated using Equation 1 from Rochette et al. (2009a). To measure background soil NH$_3$ emissions, we ran the chamber for 4 d prior to the banded (0.05 m depth) urea application on day 5 (2.85 g urea), similar to the application rate in the other mesocosms. We also added 5 mm of water on day 12. Acid traps were changed after 1, 2 and 4.5 d during the background check, every two hours on the day the urea was added, twice daily from day 6 – 8, daily from day 9 – 16, and every two days from day 17 – 29.

Soil Analyses:

Initial soils were analyzed for texture, CEC, base saturation, exchangeable acidity, soluble organic carbon (SOC) and total organic C (TOC). Soil particle size distribution was determined using the pipette method (Kroetsch and Wang 2008). Cation exchange capacity and base saturation were determined by BaCl$_2$ extraction (Hendershot et al. 2008b), while exchangeable acidity was determined using a 0.1M BaCl$_2$ extraction (Hendershot et al. 2008a). Soil soluble organic C (SOC) was measured by shaking fresh soil with 5 mM CaCl$_2$ (1:6 soil:extractant ratio) for 60 min. The slurry solutions were then centrifuged at 10 000 x g for 10 min and the supernatant filtered through a 0.45 µm nylon membrane (Millipore) using a suction funnel at -60 kPa. The filtered samples were refrigerated and analyzed within 3 d by injecting the sample in a TOC analyzer (Model Formacs, Skalar Analytical, Breda, the Netherlands). Total organic C was measured on dried (55°C for 3 d), finely ground soil samples using a dry combustion sampler (Leco CNS 1000, Leco Ltd, St. Joseph MI, USA). Soil physical and chemical properties are presented in Table 2.

Soils were also sampled periodically for determination of the temporal dynamics of soil pH and NH$_4^+$ concentrations. For this periodic soil sampling, we collected samples from the control section and
directly on the band of the fertilized section of the plastic bins on days 1, 2, 4, 7, 10, 14, 21 and 25, using a stainless steel soil corer (0.025 m diameter). Soil pH_{CaCl\textsubscript{2}} was measured by mixing 5 g of fresh soil with 10 mL of 5 mM CaCl\textsubscript{2}, shaking for 30 min to create a slurry, letting the slurry settle for 1 h, and then measuring the pH of the slurry solution with a glass electrode pH meter. The highest measured soil pH for each mesocosm through time was noted and the original pH was subtracted from this maximum pH to determine a maximum change in pH (\Delta pH). Moisture content was measured by drying 30 g of fresh, sieved soil at 105°C for 24 h (until constant weight), with the gravimetric water content calculated as the difference in weight between wet and dried soil divided by the weight of the dried soil. Soil mineral N concentrations were determined using two different extractants; either 1 M KCl, or 5 mM CaCl\textsubscript{2} (For ease, this will be subsequently called the water-extractable NH\textsubscript{4}\textsuperscript{+}). For water extractable NH\textsubscript{4}\textsuperscript{+}, we mixed 5 g of fresh soil with 25 mL of 5 mM CaCl\textsubscript{2} in 50 mL centrifuge tubes and mixed thoroughly for 5 min. The slurry solutions were then centrifuged at 10 000 × g for 10 min. The supernatant was then poured through a pre-washed (5 mM CaCl\textsubscript{2}) Whatman #42 filter paper and the filtrate was analyzed for NH\textsubscript{4}\textsuperscript{+} concentrations using an automated continuous-flow injection colorimeter (QuickChem 8000 FIA+; Lachat Instruments, Loveland, CO). For the KCl extraction, we mixed 25 g of fresh soil with 125 mL of 1M KCl in 250 mL plastic jars and mixed on a reciprocal mixer for one hour. The slurry was then put into a centrifuge at 3 000 × g for 10 min, after which the supernatant was poured through a pre-washed (1 M KCl) Whatman #42 filter paper. The filtrate was then analyzed for NH\textsubscript{4}\textsuperscript{+} on the same colorimeter mentioned above. The NH\textsubscript{4}\textsuperscript{+} concentrations in the acid traps were also analyzed on the same colorimeter. Similar to pH, we noted the maximum value for salt and water extractable NH\textsubscript{4}\textsuperscript{+} to use in our regression and correlation analysis.

Calculations and Statistics:

Cumulative NH\textsubscript{3} volatilization was calculated by summing the amount of NH\textsubscript{3} volatilized in each sampling period. We used both linear and non-linear regression to measure the relationship between cumulative NH\textsubscript{3} volatilization and soil clay content, CEC, exchangeable acidity, organic C content, buffer capacity, the maximum change in pH (\Delta pH), and the maximum value for the KCl and water-extractable NH\textsubscript{4}\textsuperscript{+} concentrations. We also used multiple linear stepwise regression (bidirectional elimination) to determine if we could improve the predictive capacity of the models. All analyses were done using R v3.4.3 (R Core Team). Adherence to model assumptions was tested through examination of normal probability plots of the residuals.
Examination of various diagnostic plots indicated one soil (P1) that was continuously an outlier in the regression analyses. Further investigation indicated that, unlike all the other soils, this soil had recently been limed. As a result of the liming, we removed soil P1 from the analysis.

RESULTS

The cumulative 28-d NH$_3$ volatilization from the 7 different soils ranged from 0.005 to 2.42 g NH$_3$-N m$^{-2}$ (Fig. 2). The KCl-extractable NH$_4^+$ was consistently higher than the water-extractable NH$_4^+$, and while the KCl-extractable NH$_4^+$ was consistent across all soils (Fig. 2c), the water-extractable NH$_4^+$ was split between two groups (Fig. 2b). The first group, with clay contents greater than 200 g kg$^{-1}$ (soils G4, G5 and P4), had consistently lower water-extractable NH$_4^+$ concentrations than the soils with clay content less than 200 g kg$^{-1}$ (soils G2, G3, P2 and P3). These groupings were consistent with the patterns noted in the volatilization data where soils G2, P2 and P3 all have volatilization losses that exceeded 1 g NH$_3$-N m$^{-2}$, while soils G4, G5 and P4 have NH$_3$ volatilization losses that range from 0.005 to 0.039 g NH$_3$-N m$^{-2}$ (from 0.2 to 2.6% of volatilization losses of the low clay soils – see Fig. 2a). Soil G3 with a moderate amount of clay (Table 2) had NH$_3$ losses of about 0.197 g NH$_3$ m$^{-2}$, even though the water-extractable NH$_4^+$ concentrations were more similar to the low clay soils.

Cumulative NH$_3$ volatilization losses were negatively correlated with soil clay content (Fig. 3a). A regression using the power function: cumul NH$_3$-N = 145.7 * Clay$^{-2.446}$ explained 98% of the variability in the model ($P < 0.001$). Cumulative NH$_3$ volatilization losses were also negatively correlated with the soil CEC (Fig. 3b). A similar power function (cumul NH$_3$-N = 10$^{6.92 * CEC^{-5.913}}$) explained 94% of the variability in the model ($P < 0.001$). The maximum concentration of KCl-extractable NH$_4^+$ was not correlated with the cumulative NH$_3$ flux ($P = 0.4662$), however the maximum concentration of water-extractable NH$_4^+$ was positively correlated with the cumulative NH$_3$ volatilization, with the exponential model (cumul NH$_3$-N = 10$^{(-4.61+WEN*0.0072)}$, where WEN = maximum water-extractable NH$_4^+$ [mg N kg$^{-1}$]), explaining 72% of the model variability ($P = 0.010$, Fig. 3d). The cumulative NH$_3$ volatilization was also negatively correlated with the soil pH buffer capacity (cumul NH$_3$-N = 4.042 – 1.802*buffer capacity), which explained 77% of variability ($P < 0.006$, Fig. 3e) and positively correlated with the maximum change in soil pH during the incubation ($Y = e^{(3.396x\Delta pH-10.475)}$), explaining 67% of variability ($P < 0.015$, Fig. 3f). However exchangeable acidity was not correlated with the cumulative NH$_3$ losses ($P = 0.495$).

Along with the single regressions, we also looked at a multiple linear regression. However none of the multiple linear regressions could predict the cumulative NH$_3$ flux as well as the clay content or CEC alone. The stepwise selection method selected buffer capacity and ΔpH; with only a slight...
improvement on the model that only used buffer capacity (addition of ΔpH increased the adjusted $R^2$ from 0.772 to 0.802). Within the soil properties, Pearson correlations showed strong relations between clay content and CEC, water extractable NH$_4^+$ and ΔpH, and a weak relation between buffer capacity and both CEC and clay content (Table 3). Water extractable NH$_4^+$ was also strongly correlated with ΔpH, while the salt extractable NH$_4^+$ was correlated with initial pH, while ΔpH and exchangeable acidity were weakly correlated (Table 3).

**DISCUSSION**

The NH$_3$ emissions were generally low (losses ranged from 0.04 to 17.3% of applied N) when compared to North America field studies where the mean emissions were 17.5% (Pan et al. 2016). However, this was likely due to the differences in solar radiation and turbulent airflow in a field versus a laboratory setting (Miola et al. 2015) and therefore the results from this study should not be used to estimate field flux rates. Indeed, Rochette et al. (2013a) conducted a field study using one of the soils used in this study and measured fluxes that were approximately eight-times greater (1.614 g NH$_3$-N m$^{-2}$) than the fluxes in this study for the same soil (0.197 g NH$_3$-N m$^{-2}$). However, the purpose of this study was to compare NH$_3$ volatilization from soils with very different physical and chemical properties and these comparisons should still be valid.

Urea hydrolysis increases soil pH through the production of NH$_4^+$ and OH$^-$ ions (Court et al. 1964), which strongly affects the relative proportions of NH$_4^+$ and NH$_3$ in aqueous solutions, particularly in the range from 7 to 10 (Bates and Pinching 1950). This greater proportion of gaseous phase NH$_3$ therefore causes greater NH$_3$ losses as soil pH increases (Ernst and Massey 1960). The maximum pH a soil will reach is a function of its initial pH and the change in pH from the urea addition (du Plessis and Kroontje 1964), which will be related to the pH buffering capacity and the amount of urea added. As expected, the maximum changes in pH for the soils in this study were correlated with soil buffer capacity (Table 3), and both factors were strongly correlated with NH$_3$ volatilization loss (Fig. 3e, f); consistent with previous studies (Ferguson et al. 1984; Rochette et al. 2013a; Rochette et al. 2009b). One soil (G3) had NH$_3$ losses that were approximately 20% of what was predicted by the regression with water extractable NH$_4^+$ and the ΔpH (Fig. 3d, f). This soil is high in silt content (Table 2) and susceptible to surface crusting (N'Dayegamiye and Angers 1990) so the re-packing and watering of the sieved soil over the banded urea may have formed a barrier to gas diffusion. This potential for crusting could explain why emissions in this incubation study were much lower than field studies using the same soil (Rochette et al. 2013a; Rochette et al. 2009c), suggesting that even though NH$_3$ production may be primarily
related to soil chemical properties, the physical properties of soils can also influence NH$_3$ volatilization losses.

The cumulative NH$_3$ flux was not affected by initial pH ($P = 0.491, R^2 = -0.081$), likely because we purposely limited the range in pH values (Table 2). However, the lack of correlation between exchangeable acidity and NH$_3$ volatilization losses was unexpected because cumulative volatilization and titratable acidity were correlated in previous studies (Ferguson et al. 1984; Izaurralde et al. 1987). The positive correlation between exchangeable acidity and ΔpH and the negative correlation between exchangeable acidity and buffer capacity were also contrary to what we expected as soil acidity generally increases the buffer capacity and reduces ΔpH (Ferguson et al. 1984). However exchangeable acidity is not equal to titratable acidity (e.g. does not include acidity generated from the dissociation of weak acid groups of soil organic matter or the disruption of the edge surfaces of clay particles). The discrepancy between this study, which used exchangeable acidity, and previous studies that used titratable acidity suggest that much of the soil buffer capacity against increased pH from urea hydrolysis is derived from dissociation of weak acid groups of soil organic matter or the clay particle surface disruption.

The reduction in volatilization losses with increased clay content (from 2.40 to 0.20 g NH$_3$-N m$^{-2}$ when clay content increased from 4.2% to 16.5%; Fig. 3a) could be because soil clay content was positively correlated with soil CEC and buffer capacity and negatively correlated with water-extractable NH$_4^+$ and the change in pH (Table 3), all of which were correlated with NH$_3$ volatilization loss. Also, clay particles, particularly those of young soils (e.g. chlorites, illites and vermiculites) are known to rapidly fix NH$_4^+$ (Cavalli et al. 2015; Chantigny et al. 2004; Mortland et al. 1963; Mortland 1955; Nieder et al. 2011), which further reduces the availability of NH$_4^+$/NH$_3$. Finally, higher clay content changes soil pore size distribution; lengthening the diffusion path, which further reduces NH$_3$ volatilization losses (Van der Molen et al. 1990). Soil clay content therefore, is an integrated measure of several soil properties that all strongly affect soil NH$_3$ volatilization rates (Fig. 3a).

This correlation between soil clay content and NH$_3$ volatilization suggests that banding urea at 0.05 m depth in Eastern Canadian soils with a clay content of >20% should minimize NH$_3$ volatilization losses. This is slightly shallower than a previous study that measured volatilization losses of 8.6% of applied N when urea was banded (160 kg N ha$^{-1}$) at 0.05 m in a soil with a clay content of 19%, instead suggesting incorporation depths of 0.075 m (Rochette et al. 2013a). However, although the soils used in this study did exhibit a wide range of clay concentrations, the mineralogy of the clays were all similar,
primarily derived from quartzite and chlorite mica schists (Dekimpe and McKeague 1974; Kodama 1979; Kodama et al. 1993). Clay mineralogy is known to affect NH$_3$ volatilization (Dontsova et al. 2005; du Plessis and Kroontje 1966; Mortland 1955) likely due to differences in NH$_3$/NH$_4^+$ fixation capacity as well as differences in initial soil pH, so it is unclear whether other clay minerals would exhibit a similarly strong negative correlation with NH$_3$ flux. Also, the proportion of Ca$^{2+}$ and Mg$^{2+}$ in soils can also affect NH$_3$/NH$_4^+$ fixation (Dontsova et al. 2005), which may further alter NH$_3$ volatilization rates. Therefore, further studies are required to determine whether this relationship is consistent across other soil classes with different mineralogy. Given the strong correlation between clay content and NH$_3$ losses though, we believe that NH$_3$-N losses from banding urea at a depth > 0.05 m in soils with more than 20% clay content will be less than 1/10th of the emissions when the soil clay content is less than 10%, as long as the soils contain similar mineralogy.

The amount of available NH$_4^+$ in surface soils may be used to predict potential NH$_3$ volatilization losses. However the method of determining available NH$_4^+$ could be critical. Ammonium concentrations are often measured using a salt solution that may also extract NH$_4^+$ that would be bound to the cation exchange sites within the soils (e.g., Martins et al. 2015; Rochette et al. 2013a). According to Sommer et al. (2004), soils with a CEC of more than 25 cmol$_c$ kg$^{-1}$ have sufficient capacity for NH$_4^+$ exchange that minimizes NH$_3$ emissions, similar to the current study that found minimal NH$_3$ losses from soils with a CEC of 20 cmol$_c$ kg$^{-1}$ or more (Fig 3b). This negative correlation between CEC and NH$_3$ losses in this study (Fig. 3b) and in previous studies (Fenn and Kissel 1976), indicates that using salt solutions to extract NH$_4^+$ from soils could overestimate the amount of NH$_4^+$ that actively contributes to the NH$_3$ volatilization. This would not be a problem in many of these previous studies since only one or two soils were used, and the proportion of NH$_4^+$ on the cation exchange sites and in solution would likely remain consistent. However, in the current study using 7 different soils with CEC ranging from 12 to 37 cmol$_c$ kg$^{-1}$, the maximum KCl-extractable NH$_4^+$ was not correlated with the NH$_3$ flux (Fig. 3c). Due to the differences in CEC, the proportion of NH$_4^+$ from the free (in solution) and bound (attached to the CEC) pools could differ. The maximum water-extractable NH$_4^+$ though, was correlated with the NH$_3$ flux ($P = 0.010$, $R^2 = 0.721$, Fig. 3d), likely because it does not include ions attached to the CEC sites and therefore would provide a more accurate estimate of the pool size of NH$_4^+$ susceptible to volatilization as NH$_3$. As a result, we suggest that for studies examining NH$_3$ volatilization from soils, that a dilute solution (e.g. 5 mM CaCl$_2$), rather than a strong salt solution, be used to extract NH$_4^+$ concentrations.

CONCLUSION
The strong relation between soil clay content and NH$_3$ volatilization indicates that soil clay content, an easily attainable metric, can be used to predict a percent reduction for NH$_3$ volatilization losses when urea is banded at 0.05 m depth. Also, the data suggests that banding urea at 0.05 m depth should be deep enough to minimize NH$_3$ volatilization losses from Eastern Canadian soils containing more than 20% clay. However, as this was a laboratory study, field studies are still required to verify that these findings are still valid under field conditions. Finally, we suggest that subsequent studies examining NH$_3$ volatilization losses from soils use 5 mM CaCl$_2$ extracts to determine available NH$_4^+$ and predict NH$_3$ volatilization, rather than extractions using stronger salt solutions.

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REFERENCES


TABLES

Table 1: Farm location and crop history for the 8 soils collected near Quebec City in eastern Canada used in this study.

Table 2: Physical and chemical properties of the 8 soils collected near Quebec City in eastern Canada used in this study.

Table 3: Pearson correlations between various soil physical and chemical properties for 7 soils of varying clay contents collected near Quebec City, in eastern Canada.
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<td>P2</td>
<td>Podzol</td>
<td>Beaurivage (var. skeletal)</td>
<td>Loamy sand</td>
<td>St. Narcisse de Beaurivage</td>
<td>Maize</td>
<td>46°29.4'N</td>
<td>71°12.2'W</td>
</tr>
<tr>
<td>P3</td>
<td>Podzol</td>
<td>Woodbridge</td>
<td>Sandy loam</td>
<td>St. Elzear de Beauce</td>
<td>Maize</td>
<td>46°24.3'N</td>
<td>71°07.8'W</td>
</tr>
<tr>
<td>P4</td>
<td>Podzol</td>
<td>Tilly</td>
<td>Clay loam</td>
<td>St. Nicolas</td>
<td>Maize</td>
<td>46°41.5'N</td>
<td>71°27.5'W</td>
</tr>
<tr>
<td>G2</td>
<td>Gleysol</td>
<td>Le Bras (var. loamy substratum)</td>
<td>Sandy loam</td>
<td>St. Narcisse de Beaurivage</td>
<td>Oats</td>
<td>46°29.4'N</td>
<td>71°12.2'W</td>
</tr>
<tr>
<td>G3</td>
<td>Gleysol</td>
<td>Le Bras</td>
<td>Silt loam</td>
<td>St. Lambert de Lauzon</td>
<td>Oats</td>
<td>46°05'N</td>
<td>71°02'W</td>
</tr>
<tr>
<td>G4</td>
<td>Gleysol</td>
<td>Kamouraska (var. transition to La Pocatière)</td>
<td>Clay loam</td>
<td>Harlaka</td>
<td>Maize</td>
<td>46°48'N</td>
<td>71°23'W</td>
</tr>
<tr>
<td>G5</td>
<td>Gleysol</td>
<td>Kamouraska</td>
<td>Clay</td>
<td>Harlaka</td>
<td>Barley</td>
<td>46°48'N</td>
<td>71°23'W</td>
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</tbody>
</table>

<sup>a</sup> Canadian soil classification (Soil Classification Working Group 1998)
Table 2

<table>
<thead>
<tr>
<th>Soil ID</th>
<th>Clay (g kg(^{-1}))</th>
<th>Sand (g kg(^{-1}))</th>
<th>pH(_{\text{CaCl}_2})</th>
<th>Soluble C (g kg(^{-1}))</th>
<th>Total C (g kg(^{-1}))</th>
<th>Total N (g kg(^{-1}))</th>
<th>CEC (mEq 100 g(^{-1}))</th>
<th>Exchangeable acidity (cmol kg(^{-1}))</th>
<th>Buffer capacity (pH units)Log [H(^+)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>29.8</td>
<td>811.3</td>
<td>5.73</td>
<td>1.87</td>
<td>20.3</td>
<td>1.0</td>
<td>8.06</td>
<td>0.00</td>
<td>3.58(^a)</td>
</tr>
<tr>
<td>P2</td>
<td>42.3</td>
<td>874.0</td>
<td>4.87</td>
<td>1.02</td>
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<td>0.9</td>
<td>2.24</td>
<td>0.44</td>
<td>1.05</td>
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<tr>
<td>P3</td>
<td>76.0</td>
<td>569.0</td>
<td>4.96</td>
<td>1.90</td>
<td>19.4</td>
<td>1.9</td>
<td>4.18</td>
<td>0.24</td>
<td>1.21</td>
</tr>
<tr>
<td>P4</td>
<td>283.0</td>
<td>238.0</td>
<td>5.66</td>
<td>1.62</td>
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<td>2.1</td>
<td>12.75</td>
<td>0.02</td>
<td>1.90</td>
</tr>
<tr>
<td>G2</td>
<td>69.5</td>
<td>559.3</td>
<td>5.52</td>
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<td>6.16</td>
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<tr>
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<td>287.0</td>
<td>4.75</td>
<td>2.10</td>
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<td>1.7</td>
<td>4.44</td>
<td>0.57</td>
<td>2.27</td>
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<tr>
<td>G4</td>
<td>322.8</td>
<td>319.0</td>
<td>5.27</td>
<td>2.57</td>
<td>26.4</td>
<td>2.5</td>
<td>14.91</td>
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<tr>
<td>G5</td>
<td>621.0</td>
<td>68.3</td>
<td>5.19</td>
<td>3.08</td>
<td>31.4</td>
<td>2.7</td>
<td>23.05</td>
<td>0.15</td>
<td>2.31</td>
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</tbody>
</table>

\(^{a}\) After the analysis we learned that this plot had been recently limed. As such, we decided to remove this soil from the analysis.
### Table 3.

<table>
<thead>
<tr>
<th></th>
<th>Clay</th>
<th>CEC</th>
<th>NH$_4^+$ (CaCl$_2$)</th>
<th>NH$_4^+$ (KCl)</th>
<th>Exchang. Acidity</th>
<th>pH</th>
<th>Buffer capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEC</td>
<td></td>
<td>0.986***</td>
<td></td>
<td></td>
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<tr>
<td>NH$_4^+$ (CaCl$_2$)</td>
<td>-0.832**</td>
<td>-0.891***</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NH$_4^+$ (KCl)</td>
<td>0.560</td>
<td>0.464</td>
<td>-0.015</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exchang. Acidity</td>
<td>-0.391</td>
<td>-0.501</td>
<td>0.717*</td>
<td>0.36</td>
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<tr>
<td>pH</td>
<td>-0.391</td>
<td>-0.346</td>
<td>-0.035</td>
<td>-0.835**</td>
<td>-0.456</td>
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<tr>
<td>Buffer capacity</td>
<td>0.729*</td>
<td>0.734*</td>
<td>-0.562</td>
<td>0.495</td>
<td>-0.150</td>
<td>-0.42</td>
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</tr>
<tr>
<td>Δ pH</td>
<td>-0.775**</td>
<td>-0.838**</td>
<td>0.959***</td>
<td>0.046</td>
<td>0.790*</td>
<td>-0.163</td>
<td>-0.622</td>
</tr>
</tbody>
</table>

**Note:** * = significant at $P=0.10$; ** = significant at $P=0.05$; *** = significant at $P=0.01$
FIGURES

Figure 1: Experimental set-up for measuring changes to soil pH and NH\textsubscript{4}\textsuperscript{+} concentrations after banding urea (equivalent to 140 kg N ha\textsuperscript{-1}) at 0.05 m depth. Soils were sampled within the band (treatment) and within the separate control section (control).

Figure 2: Ammonia volatilization (a), water and salt extractable NH\textsubscript{4}\textsuperscript{+} concentrations (KCl [b] and CaCl\textsubscript{2} [c]) in and pH (d) after banding urea (equivalent to 140 kg N ha\textsuperscript{-1}) at 0.05 m depth in mesocosms from 7 agricultural soils collected near Quebec City, Canada.

Figure 3: Cumulative NH\textsubscript{3} volatilization from 7 agricultural soils collected near Quebec City, Canada plotted against (a) soil clay content, (b) cation exchange capacity, (c) maximum KCl-extractable NH\textsubscript{4}\textsuperscript{+}, (d) maximum CaCl\textsubscript{2}-extractable NH\textsubscript{4}\textsuperscript{+}, (e) soil buffer capacity, and (f) maximum change in soil pH. Error bars are 1 SE. The point that is circled is a soil (G3) that is prone to surface crusting. Only significant regressions (P < 0.05) show trend lines.
Figure 1:
Figure 2:
Figure 3.