Cation exchange chemistry and the long-term effects of liming on acidic forest soils in the northeastern United States

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Abstract

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I collected samples from four previously established liming experiments in order to characterize the long-term effects of liming on cation exchange properties and test various proposed models for the relationships between pH, base saturation (BS), and cation exchange capacity (CEC). Limed sites generally had higher pH and BS in all horizons, and fewer E horizons; limed organic horizons had lower organic matter content, and limed mineral horizons had lower effective CEC, suggesting that podzolization processes may be disrupted in limed soils. Limed horizons generally had more organically bound Al and less bound hydrogen. Regression analyses testing models of charge development on OM suggest that sites binding OAl should be excluded from the pool of potentially dissociable functional groups. Results for models of exchangeable cation equilibria suggest that ExAl does not behave as a base cation, but rather is part of an equilibrium with OAl that is responsive to pH changes.

Keywords: NORTHERN HARDWOOD FOREST; ORGANIC MATTER; ALUMINUM; PH; HORIZONS; SPODOSOL; CATION EXCHANGE; BASE SATURATION

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Introduction

Agricultural liming has long been used to increase soil pH and improve nutrient status (Adams, 1984). Liming of forests has been undertaken to similar ends in northern Europe and Scandinavia to address soil acidification due to anthropogenic acid deposition (Lundstrom et al., 2003). In the northeastern United States, forest liming has not been widely used, although it has been considered as a management option to address anthropogenic acidification of lakes (Driscoll et al., 1996) and as a fertilizer for sugar maple (*Acer Saccharum)* (Long et al., 1997; Wilmot et al., 1996). There is strong evidence of soil acidification in the region, however (Bailey et al., 2005; Driscoll et al., 2003; Driscoll et al., 2001), with studies showing a loss of Ca and Mg from soils, an increase in exchangeable aluminum, and a lowering of soil pH. This has been suggested as a contributing factor in sugar maple decline (Bailey et al., 2004; Wilmot et al., 1995).

Here, I review evidence of the effects of liming in the short and long term, with particular focus on the implications for cation-exchange chemistry. Discussion in the literature of cation exchange properties in acid forest soils has yielded evolving theories of pH buffering, charge development and exchangeable cation equilibria that have implications for how we understand the effects of liming, especially in the context of historical acidification of soils in the region. First, I examine the effects of liming, including both European research and the few domestic examples. I then consider the cation exchange literature, looking at theories of charge development and exchangeable cation equilibria. Because aluminum plays a significant role in both phenomena, I end with a review of recent work on aluminum acid/base behavior.

Liming

Liming has been reported to increase root length and biomass in sessile oak (*Quercus patraea*) seedlings (Bakker et al., 1999) and mature sessile and red oak (*Quercus robur*) (Bakker, 1999). Analysis of soil carbohydrates suggests a greater input of soil C from roots in limed soils (Rosenberg et al., 2003). Liming has also been observed to increased height and diameter growth in mature sessile and red oak (Bakker et al., 1998) and in sitka spruce (*Picea sitchensis*) (Kakei and Clifford, 2002). Other investigators have reported that liming can have inhibitory growth effects on red spruce (Smallidge and Leopold, 1997)

Demchik and Sharpe (2001) report that liming had no effect on the diversity of undergrowth species after a partial cutting, although a few species occurred in greater numbers. However, Olsson and Kellner (2002) reported twenty new species in limed plots after a clearcut versus just five species on control plots, and Smallidge and Leopold (1995) report increased relative frequency of species in the understory in a limed subcatchment.

Liming has been reported to increase Ca and Mg content in the tissues of certain species. Long et al. (1997) report elevated Ca and Mg in sugar maple (*Acer saccharum*) foliage, but not American beech (*Fagus grandifolia)* or black cherry (*Prunus serotina*). Houle et al. (2002) report increased Ca and Mg in sugar maple bole tissue. Liming also increased Ca, Mg, and other nutrients in stems, leaves, and twigs of sessile oak seedlings (Bakker et al., 1999). Sikstrom (2001) reports no growth effect from liming, but higher Ca and Zn in needles of Norway spruce (*Picea abies)* seedlings.

Liming has been noted to increase nitrifying activity in soil (Persson et al., 1990) and ultimately to increase nitrate leaching from soil (Persson et al., 1995), (Vesterdal and Raulund-Rasmussen, 2002). Carnol et al. (2002) reported increased nitrifying activity after liming, but no change in bacterial community composition in soil cores under Norway spruce (*Picea abies*) and sessile oak (*Quercus patraea*) 18 months after treatment with 5 Mg/ha of dolomitic lime. Backman et al. (2003) found that liming had increased the diversity of ammonia-oxidizing bacteria in a Norway spruce stand 6 years after treatment. They noted a pH effect in the organic horizons but not in the mineral soil. A high (6 Mg/ha) and a low (3 Mg/ha) lime dose were tested; the effects were greater in the higher dose. Lundell et al. (2001) note that the presence of live roots mitigates nitrate leaching after lime application.

Bauhus et al. (2004) studied the effect of liming and gap creation on forest floor C and N pools in a European beech (*Fagus sylvatica*) forest. Gaps alone had no discernable effect, but liming caused loss of C and N in the L and F horizons and accumulation of C and N in the top of the mineral soil. Kreutzer (1995) also reports a significant loss of C and N from the organic horizons, as do Marschner and Wilczynski (1991). In a study on an ancient grassland, Staddon et al. (2003) measured faster carbon throughput and increased numbers of mycorrhizal fungi on limed sites.

One of the motivations for applying lime is to increase the amount of Ca and Mg in soils, and not surprisingly, many investigators have reported increased Ca and Mg in the organic horizons of limed soils (Johnson et al., 1995; Kakei and Clifford, 2002; Long et al., 1997; Meiwes et al., 2002; Moore et al., 2000; Nohrstedt, 2002). Many researchers have also considered the effects

of liming on cation exchange properties of soils. The most commonly reported results are increased pH, base saturation, and effective cation exchange capacity (Frank and Stuanes, 2003; Geissen et al., 2003; Houle et al., 2002; Kreutzer, 1995), especially in organic horizons. Exchangeable Al is less frequently measured, but researchers generally report a decrease after liming (Geissen et al., 2003; Long et al., 1997; Moore et al., 2000).

Cation Exchange Chemistry

Cation exchange properties of acid forest soils have been the subject of debate in the literature over the past several decades. There are well established relationships between pH and CEC in soils where charge is predominantly variable charge from organic matter – an increase in pH means an increase in CEC. Work by Ross and others (Ross and Bartlett, 1995; Ross et al., 1991; Ross et al., 1996) documents this phenomenon when soils are manipulated in a laboratory setting, but also documents a negative correlation between pH and CEC when soils are compared at native pH.

A similar situation exists with relationships between pH and base saturation of the exchange complex. Bloom and Grigal (1985) suggested a relationship between pH and BS according to the extended Henderson-Hasselbalch equation, with acid and base cations at equilibrium – as pH increases, BS should increase as well. Reuss et al. (1990) suggested Ca-Al exchange as described by the Gapon equation as theoretical justification for the Bloom & Grigal result when soil is manipulated. Giesler et al. (1998) offer empirical evidence for the relationship across samples. They measured soil acidity and exchange properties along a "short but extreme" forest productivity gradient, and found that pH in soil solution was strongly correlated with BS; the

observed variation in pH could not be explained by the quantity or strength of the acids present, nor by ionic strength of solution.

Other workers have observed either no correlation or a negative correlation between pH and BS. Magdoff et al. (1987), Skyllberg (1994), (1996), (1999), and Johnson (2002) all report either no correlation or a negative correlation, comparing samples from different sites at native pH. In each case, however, including Al as a base cation in the calculation gave a positive correlation between pH and BS. The solubility of monomeric Al is pH-dependent – it will not hydrolyze below ph 5.3 – and this has been offered as justification for the observed non-acidic behavior of Al. Wesselink et al. (1996) suggest that instead of Ca-Al exchange, Al-H exchange is more accurate; they present a model relating the ratios of organically-bound to exchangeable Al and H. Skyllberg (1999) presents a similar model, arguing that Al does not generally exchange with base cations and relating the ratio of organically bound and exchangeable Al to that of bound and exchangeable H.

The chemistry of aluminum in acid forest soils has a body of literature unto itself. With regards to the exchange behavior of Al: Dahlgren et al. (1989) used over- and undersaturated solutions to test for an Al equilibrium with $Al(OH)_3$, and found that such an equilibrium was achieved, and generally in under three hours. Hargrove and Thomas (1982) reported that the acidity of OM saturated with Al was significantly less than H-saturated OM. They noted that organically complexed Al (OAl) will hydrolyze just as hydroxy-interlayer Al will in clays. Unlike in clays, however, OAl does not appear to react with base and is not titratable, suggesting that Al complexing reduces the CEC of OM in addition to reducing total acidity. David and Driscoll

(1984) reported that the vast majority of soil solution Al was either organically complexed or complexed with fluorine; very little free monomeric Al was present, although the amount was higher in mineral horizons than in organic horizons. Driscoll et al. (1985) further noted that the amount of inorganic Al in soil solution increased exponentially as pH decreased, and observed that dissolved inorganic Al was leached from B horizons during spring snowmelt. Giesler et al. (2000) measured soil solution Al at different depths and report that the majority of the Al moving from the O horizon into the Bs originated in O horizons. Skyllberg and Magnusson (1995) saturated soils with different cations and measured dissolved OM in soil solution; they report much less DOM in solution in Al-saturated soils.

Manuscript

I. Introduction

Agricultural liming has long been used to increase soil pH and improve the nutrient status of soils (Adams, 1984). Liming of forests has been used to similar ends in northern Europe and Scandinavia to address soil acidification due to anthropogenic acid deposition (Lundstrom et al., 2003). In the northeastern United States, forest liming has not been widely used, although it has been considered as a management option to address anthropogenic acidification of lakes (Driscoll et al., 1996) and as a fertilizer for sugar maple (*Acer Saccharum)* (Wilmot et al., 1996). Commonly applied as $CaCO_3$, lime consumes acidity and evolves carbon dioxide during dissolution, leaving behind a calcium ion and water. The short-term result in soil is to increase pH, base saturation (BS), and cation exchange capacity (CEC) (e.g. Nilsson et al. (2001)). Movement of organic matter from the forest floor to the mineral soil has also been reported to result from liming; improved nutrition is hypothesized to enable a larger and more diverse microbial population that enhances decomposition (Bauhus et al., 2004). Long-term results of liming are less straightforward, with pH and BS increases generally persisting while CEC may decrease below the original level in mineral horizons (Lundstrom et al., 2003).

The short-term effects of liming are readily explained by current understanding of charge development and cation exchange – pH increases as acidity is consumed, BS increases as the added Ca^{2+} ions adsorb to the exchange surface, and exchange capacity increases as variable charge develops due to the increased pH. Long-term effects of liming are harder to explain.

Base saturation and CEC should both be positively correlated with pH; if pH remains elevated on limed sites, BS and CEC should as well. If CEC decreases while pH and BS do not, it suggests at the very least that the relationship between pH and CEC is not a necessary one.

Papers reporting on cation exchange chemistry in acid soils highlight further inconclusive results. Whereas manipulating soil pH yields a positive relationship between pH and BS, comparing unaltered samples from different sites suggests that pH and BS are either independent or have a negative relationship (Federer and Hornbeck, 1985; Johnson, 2002). A positive relationship can be found, however, when exchangeable aluminum (ExAl) is included as a base cation (Johnson, 2002; Skyllberg, 1994). The pH dependence of base saturation has traditionally been modeled as an equilibrium between exchange sites occupied by base cations and those occupied by acid cations; these data raise the question of how ExAl should be considered in the model – as acid cations (Bloom and Grigal, 1985) or as base cations (Johnson, 2002).

There have been similar reports about the pH – CEC relationship; manipulating pH will show a positive relationship between pH and CEC, but comparison of unaltered samples from different sites suggests independence (Ross and Bartlett, 1995). Organic matter is the primary source of charge in acid forest soils, and the pH-dependent development of variable charge in organic matter has traditionally been modeled as an equilibrium between dissociated organic acids and bound acidity (Johnson, 2002), which includes both undissociated acids and organically bound Al (OAl). Evidence that OAl is not readily titrateable (Hargrove and Thomas, 1982) suggests that it may not be appropriate to include OAl as bound acidity.

The first aim of this research is to characterize in detail the components of the exchange complex: the exchangeable acid and base cations occupying the available exchange surface, as well as the bound acidity (Al and H) occupying potential exchange sites. The second aim is to improve our understanding of cation exchange chemistry by testing different models for the pH dependence of base saturation and exchange capacity to see which, if any, can meaningfully explain the data.

II. Sites and Methods

Sites:

I revisited four previously established experiments in the northeastern US where lime had been applied to mature stands. Sampling was conducted during the summer and early fall of 2004. Figure 1 shows the locations of the four experiments; Table 1 gives summary information for the sites.

Bartlett: The Bartlett Experimental Forest is located in Bartlett, New Hampshire, USA, in the White Mountain National Forest (44°04'41" N and 71°17'00" W). Soils are moderately and well-drained aquic and typic Haplorthods, and parent material is glacial till derived from granite and gneiss (Safford and Czapowskyj, 1986). Forest cover is generally northern hardwoods. In 1963, lime was applied to a 2 ha area at a rate of 1.1 Mg/ha as part of a study testing for fertilization effects on root biomass (Safford, 1974). The treatment area and an adjacent control area were sampled in June of 2004.

Harvard: The Harvard Forest is located near Petersham in north central Massachusetts, USA (42°31'54" N and 72°11'22" W). Soils are entic Haplorthods, moderately to well-drained, and parent material is glacial till derived from granite, gneiss, and schist (Aber et al., 1993). Forest cover is transition hardwoods, with some areas in red pine plantations. Beginning in 1984, lime was applied to a 0.093 ha area in a hardwood stand as part of a study examining the effect of fertilization on mycorrhizal communities (Antibus and Linkins, 1992). Applications occurred every two to four weeks from April through October of 1984 and May through August of 1985; the cumulative treatment rate was 15.9 Mg/ha. The treatment area and an adjacent control area were sampled in November of 2004.

PMRC: The Proctor Maple Research Center is located near Underhill Center, Vermont, USA, on the western slopes of the Green Mountains (44°31'30" N and 72°51'58" W). Soils are oxyaquic Haplorthods, moderately to well drained, and parent material is glacial till derived from schist (Wilmot et al., 1995). In 1990, lime was applied at a rate of 3 Mg/ha to a 0.15 ha plot along with 400 kg/ha of a 10:5:1 K:Ca:Mg base cation fertilizer as part of a study on sugar maple response. An additional 2000 kg/ha of the base cation fertilizer was applied in 1991, for a cumulative rate of 2400 kg/ha (Wilmot et al., 1996). The treatment area and an adjacent control area were sampled in July of 2004. It should be noted, although the topic is not treated here, that the PMRC site is the only one at which earthworms were observed during sample collection. While earthworms affect the decomposition and distribution of organic matter in the soil profile, there is evidence that they do not affect soil chemistry after liming (Judas et al., 1997).

Woods Lake: Woods Lake is located in the west central portion of the Adirondack Park in NY, USA (43°52'13" N and 74°57'07" W). Soils are udic Haplorthods developed on glacial till derived from granite and gneiss (Blette and Newton, 1996). Forest cover is mixed hardwood. Two subcatchments of the Woods Lake watershed were treated with 6.9 Mg/ha of pelletized limestone in October of 1989 to test the influence of the resulting acid neutralization effects on the lake (Driscoll et al., 1996). A treatment area within one of the limed subcatchments and a control area within an adjacent untreated subcatchment were sampled in November of 2004.

Sampling methods

For treatment and control areas at the Bartlett, Harvard, and PMRC experiments, thirty small (~30cm diameter) soil pits were dug approximately every five meters along systematically located transects spaced to cover the site. Samples were collected from all horizons present down to and including the top of the B horizon, and horizon depths were measured twice, on opposite sides of each pit. Samples for a given horizon were randomly assigned to one of three groups, which were then combined, yielding three composite samples for each horizon from each treatment at each site.

At the Woods Lake experiment, we collected samples from three large pits (~1m diameter) in the limed subcatchment on the northeastern side of the lake and two large pits in the adjacent unlimed subcatchment to the south (see Smallidge (1993) for a map of the watershed). Horizon depths were measured at six locations around the perimeter of each soil pit.

Chemical Methods

Samples from all experiments were air dried and passed through a 2mm sieve before chemical analysis. Soil pH was measured in deionized water with a combination electrode (VWR SympHony, VWR International, Westchester PA); organic horizons (Oe, Oa, A) were measured at a 5:1 solution to soil ratio, mineral horizons (E, B) at 1:1. Organic matter content was measured by loss on ignition after combustion at 450 °C for 16-18 hours.

Following a similar approach to Skyllberg (1999), three separate extractions were performed to determine the makeup of the cations present on the exchange surface. For each, a mechanical extractor was used to draw approximately 60 mL of the extracting solution through 2.5 grams of soil over a period of 12-14 hours. The first extraction, using 1M KCl and followed by titration to pH 8.2 (after Thomas (1983)), was used to determine exchangeable acidity (EA). Inductively coupled plasma spectrometry (ICP) of the extract was used to determine exchangeable aluminum (ExAl). Exchangeable hydrogen (ExH) was then estimated as the difference between EA and ExAl. Extraction with 0.5M BaCl2- buffered at pH 8.2 with 0.2M triethanolamine (TEA), followed by back-titration (Thomas, 1983) was used to determine total acidity (TA). Extraction with 0.5M CuCl2 was used to determine exchangeable base cations and total aluminum; the concentrations of specific cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}). All ICP was conducted on a Perkin-Elmer OPTIMA 3300 DV (Perkin-Elmer, Wellesley, MA). Organically bound hydrogen (OH) was estimated as the difference between TA and the sum of total aluminum and ExH. Organically complexed aluminum (OAl) was estimated as the difference between total and exchangeable aluminum.

For this study, it was useful to distinguish between effective cation exchange capacity (CECe), interpreted as the amount of charge present at native pH, and total cation exchange capacity (CECt), interpreted as the total charge. CECe was estimated as the sum of base cations and exchangeable acidity. CECt was estimated as the sum of base cations and total acidity; the difference between CECe and CECt is accounted for by OAl and OH. A summary of abbreviations and definitions for all cation exchange components can be found in table 2.

Cation exchange equilibria

Exchange capacity in soil organic matter can be modeled as the dissociation of a weak acid using the extended Henderson-Hasselbalch equation,

$$pH = pK_a + n\log\frac{A^-}{HA} \qquad (1)$$

where pK_a is the effective dissociation constant and HA and A- are an acid and conjugate base representing the organic acids present in the soil which can contribute charge to the CEC. If the dissociated acids make up the CECe of the soil, the equation can be written (Johnson, 2002) as follows:

$$pH = pK_a + n\log\frac{CECe}{CECt - CECe} \qquad (2)$$

Since the difference between CECe and CECt consists of organically bound Al and H, the equation can be written more explicitly as:

$$pH = pK_a + n\log\frac{CECe}{OAl + OH} \qquad (3)$$

Under this model, pH is determined by the equilibrium between dissociated acids (which are neutralized by exchangeable cations) and bound acidity. However, since OAl is tightly bound and is not easily titrated or exchanged (Hargrove and Thomas, 1982), the bound acidity available to dissociate may be better represented by OH. With that in mind, an alternative model of charge development would be

$$pH = pK_a + n\log\frac{CECe}{OH}, \qquad (4)$$

where the pertinent equilibrium is between dissociated and undissociated functional groups.

The Henderson-Hasselbalch equation has also been used to model the base saturation of the CECe (Bloom and Grigal, 1985):

$$pH = pK_a + n\log\frac{BS}{1 - BS} \qquad (5)$$

To make the equilibrium suggested more explicit, the equation can be rewritten

$$pH = pK_a + n\log\frac{BC}{ExAl + ExH}, \qquad (6)$$

where BC is the sum of base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+). In this scenario, pH is determined by an equilibrium between base cations and "acid" cations. A number of investigators have suggested that exchangeable Al behaves as a base cation in acid soils (Johnson, 2002; Ross et al., 1996; Skyllberg, 1994); accordingly, base saturation has also been modeled including ExAl as a base cation:

$$pH = pK_a + n\log\frac{BC + ExAl}{ExH} \qquad (7)$$

Skyllberg et al. (2001) present data that suggest little interaction between ExAl and other exchangeable cations; with that in mind, a third variation on this model would exclude Al from the equilibrium altogether. In that case, the model would be:

$$pH = pK_a + n\log\frac{BC}{ExH}, \qquad (8)$$

and the equilibrium would exist between exchangeable base cations and exchangeable H.

Skyllberg's work supports a strong role for Al in buffering pH changes, so it seems reasonable to think that there might be a pH-dependent Al equilibrium at work in these soils. If Al does not interact with other cations (as in equation 8), a possible model for that equilibrium would be:

$$pH = pK_a + n\log\frac{ExAl}{OAl}, \qquad (9)$$

where exchangeable Al is at equilibrium with organically complexed Al. Support for this model comes from the work of Gillman and Sumpter, who noted that below pH 5, a certain portion of the CECe continued to be re-occupied by Al, despite repeated washings and attempts to saturate it with Ca (Gillman and Sumpter, 1986). The only available source of Al is the Al already the on the soil – the organically complexed Al that was not removed by compulsive exchange – which implies that conversion from OAl to ExAl can occur. Since Al is known to be less soluble at higher pH, we would expect this model to show a negative relation – the logarithmic term decreasing as pH increases.

I tested two models for charge development (equations 3 and 4), three models for base saturation (equations 6, 7, and 8), and the Al equilibrium model (equation 9) by performing a simple linear regression of pH against the various logarithmic terms (see table 3). The equation for the resulting regression line takes the same form as the extended Henderson-Hasselbalch equation (equation 1), with slope equal to n and intercept equal to pK_a. Regressions were tested for significance ($p \leq 0.05$) and explanatory power (adjusted r^2).

Regressions were first performed using data from all samples. To allow for consideration of a treatment effect, the regressions were repeated using the control and lime data separately. To examine the behavior of individual horizons, the regressions were repeated again using data (control and lime together) from each horizon separately.

Statistical Methods

For each experiment, means and variances for treatment and control horizon properties were calculated according to the method for composite samples with unequal-sized units described in (Gilbert, 1987). Treatment and control means were tested for differences using two-sample t-tests in SAS (v. 9.1, SAS Inc., Cary, NC). Because there was only one composite for Woods Lake control E and B horizons, equal variances were assumed for the Woods Lake t-tests. Horizon presence/absence was compared using a two-tailed test of two proportions in Minitab (release 14.20, Mintab Inc., State College, PA). Relationships between pH, LOI, and CECe, were analyzed using simple least-squares linear regression in Minitab. To test for cation exchange equilibria, I performed linear regression analysis using Minitab. Regression relationships were deemed significant if $p \leq 0.05$.

III. Results

Bartlett Experimental Forest

Forty years after application of lime at 1 Mg/ha, pH was significantly higher in limed E (p=0.05) and B horizons (p=0.06) than in control horizons (figure 2). Limed Oe and Oa horizons had higher pH as well, but the differences were not significant (p>0.20). There were no significant differences in OM content (figure 3) or horizon thickness between the limed and treated soils, but significantly fewer (p<0.001) E horizons were encountered at the limed site. Only limed E horizons showed any difference in CECe – it was was significantly smaller (p=0.04) in E horizons – and there were no detectable differences in CEC per unit OM in any horizon (figure 4). Total base cations were higher in the limed Oe (p=0.06), Oa (p=0.04), and A (p=0.01) horizons due to more Ca^{2+} and Mg^{2+}, but were lower in limed E (p=0.02) and B horizons

(p=0.001), where there was less Ca^{2+} than in control soils. The higher level of base cations was sufficient to give limed Oa (p=0.05) and A horizons (p=0.01) a greater base saturation. Limed Oe (p=0.05) and Oa horizons (p=0.06) had less EA, but neither ExAl nor ExH were significantly different in any horizon. Limed E horizons had less TA (p=0.02); while OAl was not significantly different, OH was lower (p=0.001).

Harvard Forest

Twenty years after application of lime at 16 Mg/ha, there was still a strong pH signal in all horizons (figure 2). Organic matter content was significantly lower in the Oe horizon, but showed no difference in the A or B horizons (figure 3). The Oe horizon was significantly thinner in the limed site, and the A horizon was significantly thicker (p < 0.001); there was no difference in the overall depth to the B horizon. All horizons on the limed site had significantly higher CECe (figure 4; all p<0.03) and CECe per unit OM (all p<0.02). There were no significant differences in CECt or CECt per unit OM, although the limed site had higher values in the Oe and A horizons and lower values in the B horizon. All limed horizons had dramatically more total base cations, due to higher levels of Ca^{2+} and Mg^{2+}. Base saturation was significantly higher in all limed horizons, with values over 95%. Accordingly, EA was significantly lower. There was minimal ExAl in all limed horizons; ExH was lower in limed Oe and A horizons, but higher in the B horizon. Limed soils also had significantly lower TA, with less OAl in Oe and A horizons, and less OH in all horizons.

Proctor Maple Research Center

Fourteen years after application of lime at 3 Mg/ha, pH was significantly higher in all horizons on the limed site (figure 2). Limed Oe horizons had lower OM content (p=0.002), but there was no significant difference in other horizons (figure 3). Individual horizon thicknesses were not significantly different between the control and limed sites, but total depth to the B horizon was significantly less on the limed site (p = 0.03). Additionally, significantly fewer A (p = 0.02) and E horizons (p = 0.03) were encountered on the limed site. Limed B horizons had lower CECe (p=0.08); limed Oe horizons showed no difference in CECe (figure 4), but due to the lower OM content had more CECe per unit OM (figure 4; p=0.006). Limed A horizons had more CECt (p=0.04), and both Oe (p=0.01) and A horizons (p=0.005) had more CECt per unit OM. Total base cations were higher in limed A (p=0.09) and B horizons (p=0.04), due to higher Ca in the A and higher Ca^{2+} and Mg^{2+} in B horizons. Limed Oe horizons had lower K^+ and higher Na^+. With the higher levels of base cations, base saturation was higher in limed A (p=0.03) and B horizons (p<0.001). All limed horizons had less EA (all p<0.05); ExH was lower in Oe horizons (p=0.04), ExAl was lower in A horizons (p=0.04), and neither component alone was lower in B horizons. Limed A horizons had more TA (p=0.10); OAl was not significantly different, but OH was higher (p=0.03).

Woods Lake

Fifteen years after application of lime at 7 Mg/ha, pH was higher in all horizons of the limed watershed (figure 2), but at this site, where only 2 control and 3 lime pits were excavated, the statistical power was too low the detect any difference. Organic matter content was lower in all limed horizons, but again, no differences were significant (figure 3). Because samples at Woods Lake were collected from large soil pits, horizon thicknesses and frequencies could not be

compared as at other sites, but it is worth noting that no A horizons were seen in either control pit, but were present in all three of the pits dug in the limed watershed. Limed E (p=0.04) and B horizons (p=0.004) had lower CECe (figure 4), and CECe per unit OM was lower in the limed E horizons as well (p=0.04). Although the differences were not significant, CECt was lower in all limed horizons; no differences were observed in CECt per unit OM. Total base cations were significantly higher in limed B horizons (p=0.002), due to higher levels of Ca^{2+}. Limed horizons had less Mg^{2+} in the Oe, E, and B, less K^+ in the Oa and E, and less Na^+ in the E. Limed B horizons had greater base saturation (due to the higher levels of Ca^{2+}; p=0.02) and accordingly, less EA (p=0.006). Despite having less EA, limed B horizons had more ExH (p=0.02); levels of ExAl were so much lower (p=0.008) that the sum was less. Only limed E horizons had significantly lower TA (p=0.07); OAl was not significantly different in any horizon, but all limed horizons had significantly less OH (all p<0.07; E and B p<0.01).

Cation Exchange Properties and Equilibria

There were significant positive relationships between LOI and CECe on both limed and control sites, although the relationship was stronger and the slope of the regression line was shallower (m = 0.38 vs. 0.64 cmol$_c$/kg OM) on control sites (figure 5). There were also significant positive relationships between pH and CECe on both limed and control sites, although there was a large amount of scatter in the data and the explanatory power of the regression was poor (lime adjusted r2 = 0.33, control = 0.10) (figure 6). There was no significant relationship between LOI and pH on either limed or control sites (figure 7).

Regression analyses were carried out to test the different equilibrium models (table 4). For the most part, all models showed significant linear relationships, notable exceptions occurring when regressions included only control samples and when they included only E horizon samples. When pH was regressed over all samples (limed and control samples from all four experiments), all variables showed significant linear relationships. Among the base saturation models, the strongest regression (adj. $r2 = 0.55$) was for equation 8, the model with Al excluded (figure 8). Equation 4 was the stronger of the CEC models – again, the model with Al excluded – but it had relatively weak explanatory power (adj. $r2 = 0.32$) (figure 9). Equation 9, the Al equilibrium model, had the strongest relationship (adj. $r2 = 0.76$) of any tested (figure 10).

When the regressions were performed using data from only the limed samples, once again all models showed significant relationships. As with the combined data, equation 8 had the strongest regression of base saturation models (adj. $r2 = 0.56$) (figure 8), equation 4 was the stronger of the CEC models (figure 9), and equation 9 (the Al equilibrium) had the tightest fit (adj. $r2 = 0.80$) of any tested (figure 10). When the regressions were performed using data from only the control samples, the results were different: Equation 7 (where Al is considered a base cation) had the strongest regression out of the base saturation models (adj. $r2 = 0.52$), neither of the CEC models had significant relationships, and equation 9, while significant, had weak explanatory power (adj. $r2 = 0.38$).

When the regressions were performed using data from only the Oe horizons, all models had significant relationships and high adjusted r^2 values (>0.7). Equation 6 (where Al is considered an acid cation) had the strongest relationship out of the base saturation models (adj. $r^2 = 0.81$),

equation 4 was the better of the CEC models (adj. $r^2 = 0.88$), and equation 9 had high explanatory power (adj. $r^2 = 0.83$). For Oa horizons, all models again showed significant relationships, although the explanatory power was not as strong as in the Oe. Equation 8 was the best of the base saturation models (adj. $r^2 = 0.69$), equation 4 the better of the CEC models (adj. $r^2 = 0.77$), and equation 9 had reasonable explanatory power (adj. $r^2 = 0.68$). For A horizons, all models once again showed significant relationships and high adjusted r^2. Similar to the Oe horizon, equation 6 was the best of the base saturation models (adj. $r^2 = 0.87$), equation 4 was the better CEC model (adj. $r^2 = 0.88$), and equation 9 had particularly strong explanatory power (adj. $r^2 = 0.98$). In E horizons, only equation 8 – the base saturation model with Al excluded – yielded a significant relationship, and that relationship was not particularly strong (adj. $r^2 = 0.44$). Neither CEC model showed a significant relationship, nor did the Al model. In B horizons, like in the Oe and A horizons, equation 6 was the best of the base saturation models (adj. $r^2 = 0.84$), equation 4 was the better CEC model (adj. $r^2 = 0.51$), and equation 9 once again had strong explanatory power (adj. $r^2 = 0.93$).

IV. Discussion

Long-term effects of liming

Limed organic horizons (Oe, Oa) generally were thinner and had lower OM content (figure 3) than controls, corroborating previous reports that liming can reduce OM content of the forest floor (Bauhus et al., 2004; Kreutzer, 1995; Marschner and Wilczynski, 1991). Loss of OM is hypothesized to be the result of more rapid decomposition (Bauhus et al., 2004); an additional consequence may be disruption of podzolization processes. Limed sites had significantly fewer

E horizons than controls at three of the four experiments. Formation of an E horizon requires a thick organic layer acting as a source of organic acids, so it seems reasonable that more rapid decomposition of organic matter could interfere with that process. Decreases in CECe and BS in limed E and B horizons at Bartlett and Woods Lake (figure 4) also support the idea that podzolization is being disrupted – the top of the B horizon in a Spodosol should be a zone of accumulation for leached base cations and organic matter.

Most organic horizons on limed sites had lower K than the corresponding control horizons, which supports other reports that liming can reduce K in organic horizons (Kakei & Clifford 2002). Low pH and high Al saturation increase K selectivity relative to Ca (Delvaux et al 1989), so it is plausible that liming (which raises pH and should reduce Al saturation) would mobilize K from organic horizons. At Harvard Forest and PMRC, limed B horizons had higher K than controls, suggesting that K lost from the organic horizons might accumulate in the mineral soil. Since B horizons tend to be more Al saturated than organic horizons, conditions would favor K adsorption.

Base saturation (and Ca saturation in particular) was generally higher and EA was generally lower in limed horizons (figure 4), as would be expected - liming should provide Ca to the exchange complex and reduce soil acidity. With pH generally higher in limed horizons, this apparently supports a positive relationship between pH and BS. Theoretical justification for the pH-BS relationship rests on Ca-Al exchange, however (Reuss et al. 1990), and despite lower EA in most limed horizons, there was no general trend for ExAl. While a general relationship between pH and BS may exist, this suggests that a Ca-Al equilibrium does not explain it.

The total amount of bound acidity (OAl + OH) was generally lower in limed horizons, despite generally higher levels of OAl. While the source of additional Al is not obvious, this squares with reports (Hargrove & Thomas 1982) that OAl does not exchange easily and binds more tightly with OM at higher pH. It also suggests that OH is the reservoir of bound acidity for charge development   It may be inappropriate, then, to model charge development in OM as an equilibrium between CECe and bound acidity; a better equilibrium might be between CECe and OH.

Cation exchange equilibria

Because the various equilibria tested share many of the same components, we would expect them to behave similarly; considering relative performance should provide information about the contribution of the components that differ. Equation 8 is the simplest of the base saturation models – it includes only BC and ExH. Equation 6 adds ExAl in the denominator; equation 7 puts ExAl in the numerator. For a given regression, if equation 8 has the most explanatory power, it suggests that the acid/base cation equilibrium can be better described without including ExAl. If equation 7 has the most explanatory power, it suggests that the equilibrium is better described when ExAl is included as a base cation; if equation 6 has the most explanatory power, ExAl should be included as an acid cation.

When the regressions are performed using data from all samples, equation 8 has the best fit of the base saturation models, suggesting that ExAl is not part of the equilibrium among exchangeable cations. The same is true when the regressions are performed over just limed

samples; however, with just control samples, equation 7 has the most explanatory power, suggesting that ExAl is acting as a base cation. I would explain this by suggesting that exchangeable cation equilibria reflect several processes: an equilibrium between BC and ExH where BC increases with pH, an equilibrium between ExAl and OAl where ExAl decreases with pH, and a tendency for samples with higher pH to have more total Al (adj. r2 = 0.61 for control samples; see figure 11). This tendency (total Al increasing with pH) makes ExAl appear to act as a base cation, since it would otherwise decrease as pH increases (see figure 10). This gives equation 7 (which includes Al as a base cation) the strongest explanatory power for the control sample data.

The difference between the CEC models is fairly straightforward – equation 3 includes OAl in the denominator of the logarithmic term, while equation 4 does not. If equation 3 has more explanatory power, it suggests that hydrolysis of OAl at higher pH (Hargrove and Thomas, 1982) makes more exchange sites available (see Johnson (2002)), much as dissociation of OH does. If Equaton 4 gives a better fit, it suggests that exchange sites made available by hydrolysis of OAl are not properly considered part of the CECe.

When the regressions are performed using data from all samples, equation 4 has the better fit, suggesting that charge development is best modeled excluding OAl. While significant, both models have low adjusted r^2 (equation 3 = 0.12, equation 4 = 0.32), indicating that there are other factors influencing the relationship between pH and charge development. Neither model gives a significant relationship when only control sample data are used, supporting reports of pH independence of charge when samples from different sites are compared (Ross & Bartlett 1995).

With data from limed samples, both models give significant relationships, and equation 4 has greater explanatory power. The pH dependence of CECe when soil pH is manipulated is well documented (Gillman and Sumpter, 1986), so we would expect both models to do better with the limed sample data. The behavior of OAl – increasing with pH - hampers the explanatory power of equation 3.

Equation 9, the Al equilibrium model, is included to test the hypothesis suggested by the work of Skyllberg, who suggests that Al plays a role in pH buffering that does not involve exchange with Ca, and of Gillman & Sumpter, who imply that OAl can convert to ExAl. When regressions are performed using data from all samples, equation 9 yields a significant regression with high explanatory power (adj. r2 = 0.76). With just control sample data, the Al equilibrium is significant, but has a much lower adjusted r^2 (0.375); with just limed sample data, it is again significant, and the explanatory power is high (adj. r^2 = 0.80). The high explanatory power with the lime data suggests that the equilibrium described by the model may well exist, and is very sensitive to pH. The low explanatory power with control data suggests that under natural conditions, there are other factors influencing the amounts of ExAl and OAl present in the soil. The dramatic difference between the control and lime results supports suggestions by (Skyllberg, 1999) that Al equilibria are the major pH buffering processes in acid forest soils.

When regressions were performed over data from individual horizons, there was remarkable consistency, with the exception of the E horizon, where only equation 8 gave a significant result. Either equation 6 or 8 were the best of the base saturation models – never equation 7 (which includes Al as a base cation). This suggests that despite the strong performance of equation 7

with the control data, ExAl is not behaving as a base cation in any horizon. It also supports the model described in equation 9, where ExAl would be expected to behave as an acid cation. Equation 4 was the best CEC model in every horizon except the E, where neither CEC model gave a significant result. This supports the idea that sites binding OAl do not readily take part in the development of variable charge. Equation 9 had very strong explanatory power in every horizon except the E, suggesting that an ExAl-OAl equilibrium may well exist.

Taken together, the regression analyses seem to support the hypothesis that cation exchange chemistry involves three interrelated but operationally separate equilibria that all exhibit a degree of pH-dependence: one between dissociated organic acids, neutralized by exchangeable cations, and undissociated functional groups; a second between base cations and exchangeable hydrogen on the available exchange surface; and a third between exchangeable Al and organically-complexed Al, that plays a major role in pH buffering.

V. Conclusions

Corroborating previous reports (Lundstrom et al., 2003), the long-term effects of liming appear to include a decrease in organic matter content of organic horizons, and an increase in pH and base saturation throughout the upper soil profile. These combined effects appear to be reducing podzolization processes, since limed sites had fewer E horizons. While other investigators have reported increased CECe in limed soils in the short term (Blette and Newton, 1996; Geary and Driscoll, 1996), there was no evidence to that effect here, with the exception of Harvard forest, where the highest dose of lime was applied. To the contrary, and supporting results reported by Kreutzer (1995), CECe was lower in most limed mineral horizons. Limed horizons also generally saw an increase in OAl and a decrease in OH.

Regression analyses testing models of charge development on OM suggest that sites binding OAl should be excluded from the pool of potentially dissociable functional groups. Results for models of exchangeable cation equilibria suggest that ExAl does not behave as a base cation, but rather is part of an equilibrium with OAl that is responsive to pH changes.

Figures and Tables

Figure 1. Site map

Location	Forest Type	Treatment	Years since treatment
Bartlett	Northern Hardwood	1 Mg/ha dolomite	41
Harvard	Northern Hardwood	16 Mg/ha limestone	20
PMRC	>85% Sugar Maple	1) 3 Mg/ha lime 2) 2400kg/ha 10:5:1 K-Ca-Mg	14
Woods Lake	Mixed Hardwood	7 Mg/ha CaCO3	15

Table 1. Site description

Directly measured components	Abbreviation	Extraction	Method
Ca^{2+}	Ca	$CuCl_2$	ICP
Mg^{2+}	Mg	$CuCl_2$	ICP
K^+	K	$CuCl_2$	ICP
Na^+	Na	$CuCl_2$	ICP
total Al	total Al	$CuCl_2$	ICP
exchangeable Al	ExAl	KCl	ICP
total acidity	TA	$BaCl_2$-TEA	titration
exchangeable acidity	EA	KCl	titration

Estimated components	Abbreviation	Definition	
organically bound Al	OAl	total Al - ExAl	
exchangeable H	ExH	EA - ExAl	
organically bound H	OH	total H - ExH	
exchangeable base cations	EBC	Ca + Mg + K + Na	
effective cation exchange capacity	CECe	Ca + Mg + K + Na + EA	
total cation exchange capacity	CECt	Ca + Mg + K + Na + TA	
base saturation	BS	(Ca + Mg + K + Na)/CECe	
base saturation (including ExAl)	BS*	(Ca + Mg + K + Na + ExAl)/CECe	

Table 2. Definitions and abbreviations of exchange surface components.

Equation	logarithmic component	Description
6	EBC/(ExAl+ExH)	Base cations at equilibrium with acid cations, ExAl as an acid cation
7	(EBC+ExAl)/ExH	Base cations at equilibrium with acid cations, ExAl as a base cation
8	(EBC)/(ExH)	Base cations at equilibrium with ExH, no Al included
3	(EBC+ExAl+ExH)/(OAl+OH)	CECe at equilibrium with bound acidity
4	(EBC+ExAl+ExH)/(OH)	CECe at equilibrium with bound acidity, no OAl included
9	ExAl/OAl	ExAl at equilibrium with OAl

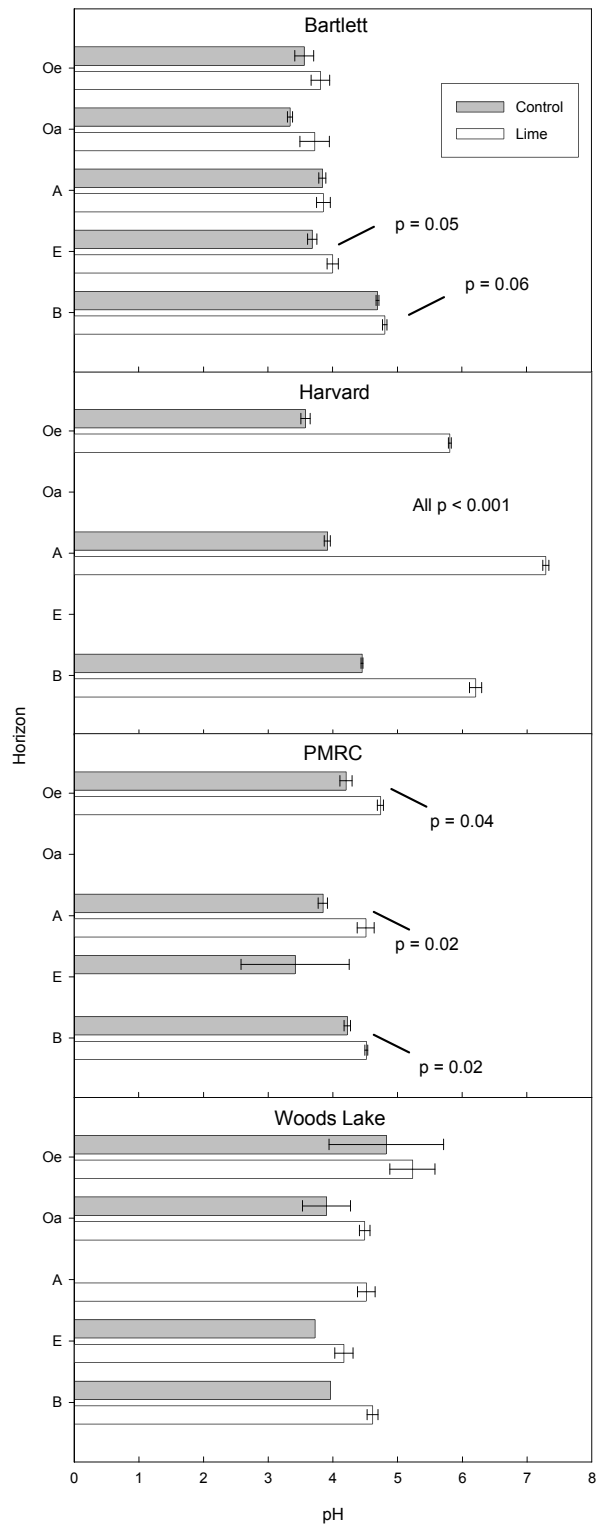Table 3. Description of exchangeable cation and charge equilibrium variables.
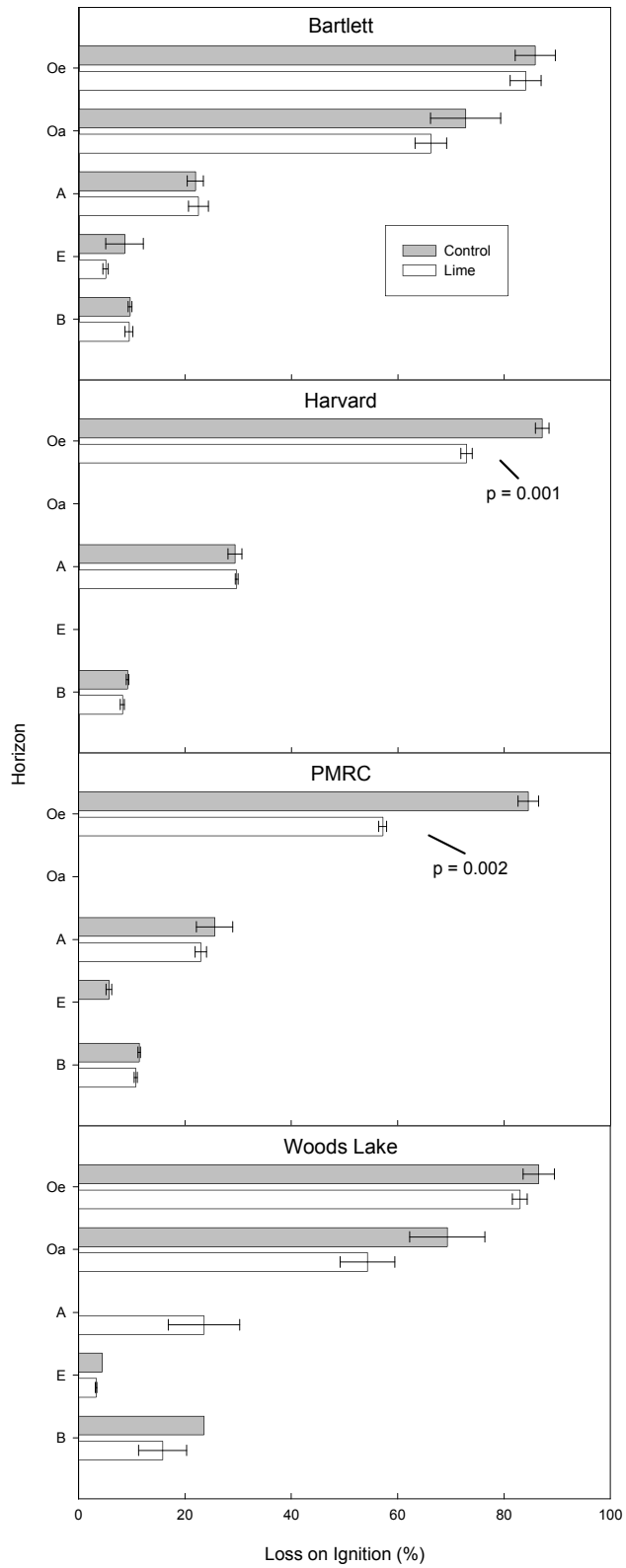
Figure 2. pH by horizon at the four experiments.

Figure 3. Loss on ignition by horizon at the four experiments.
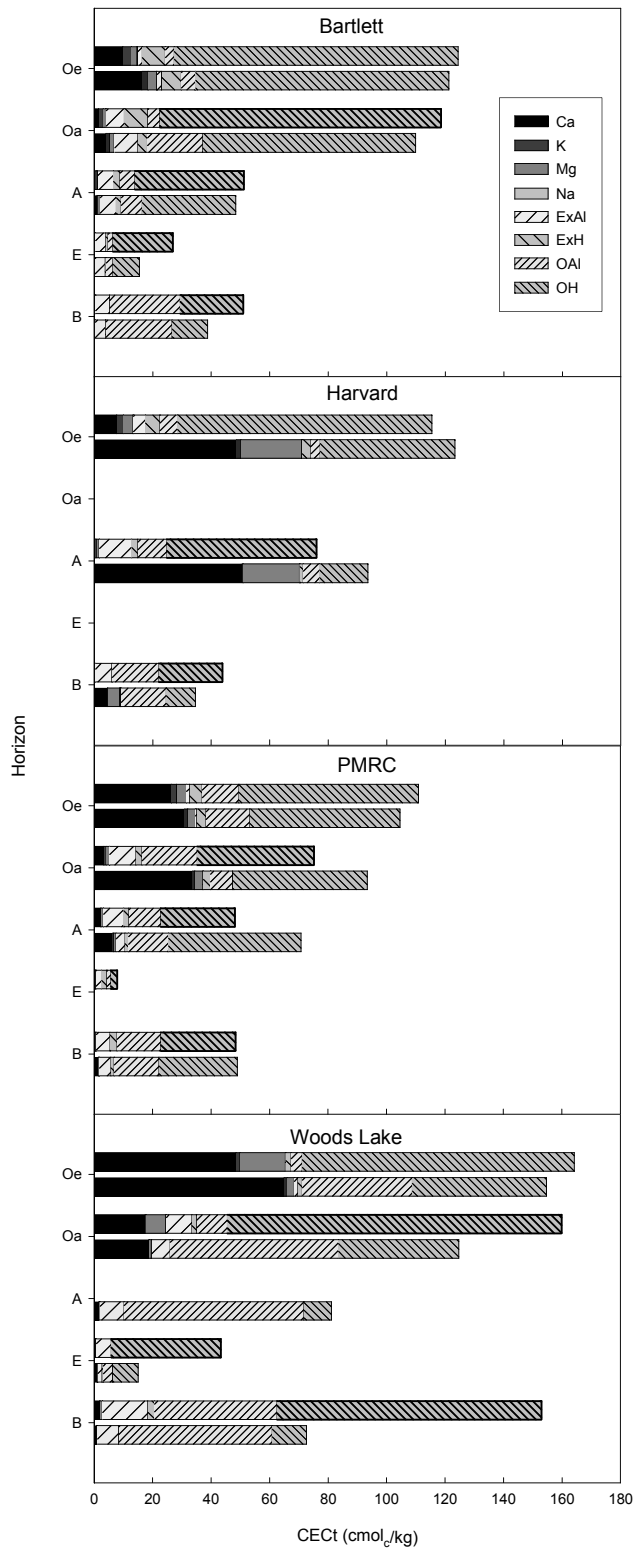
Figure 4. Occupants of the exchange surface. The top bar in each pair represents the control site, the bottom the limed site.
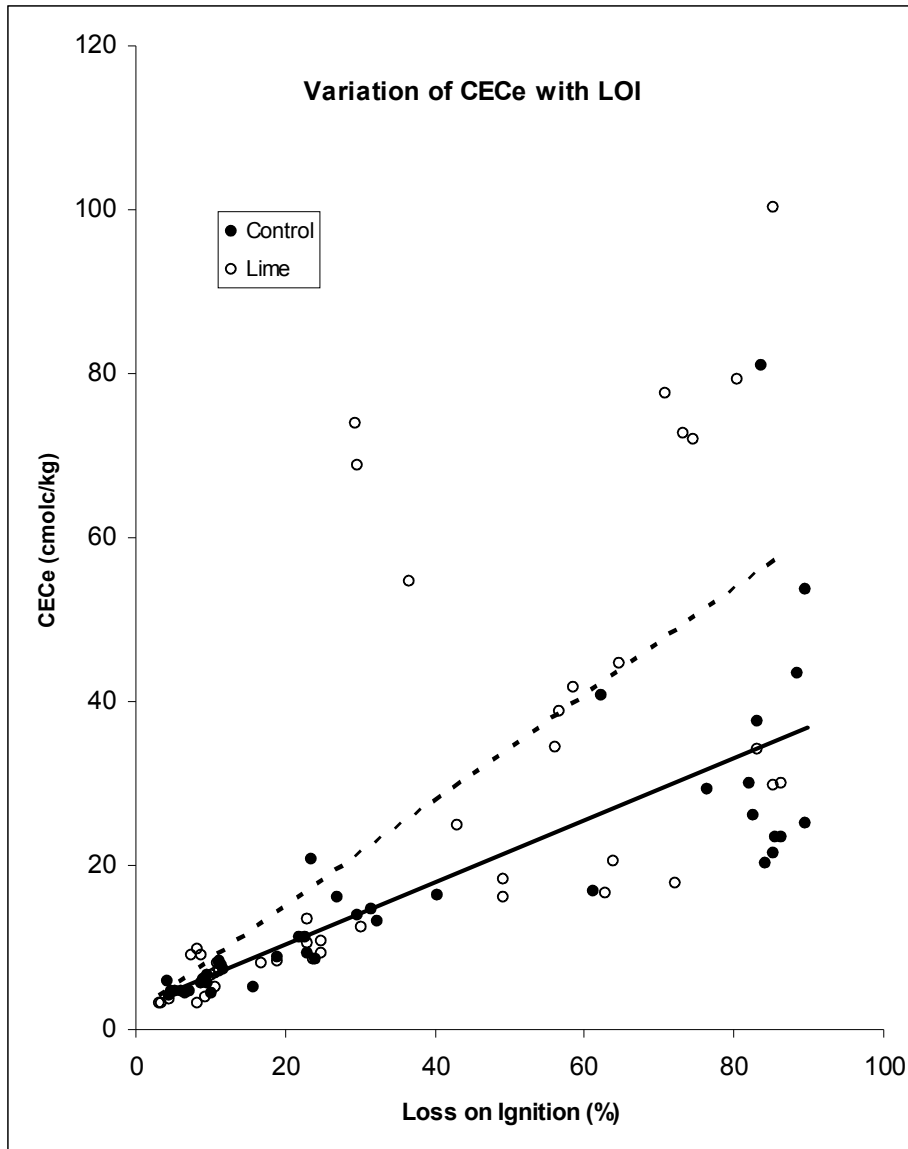
Figure 5. Exchange capacity also increased with the amount of organic matter present in the soil; the increase was steeper in limed soils than in controls. The regression line for the control samples is solid (p<0.01, adj. r^2 = 0.61); that for the limed samples is dashed (p<0.01, adj. r^2 = 0.47).

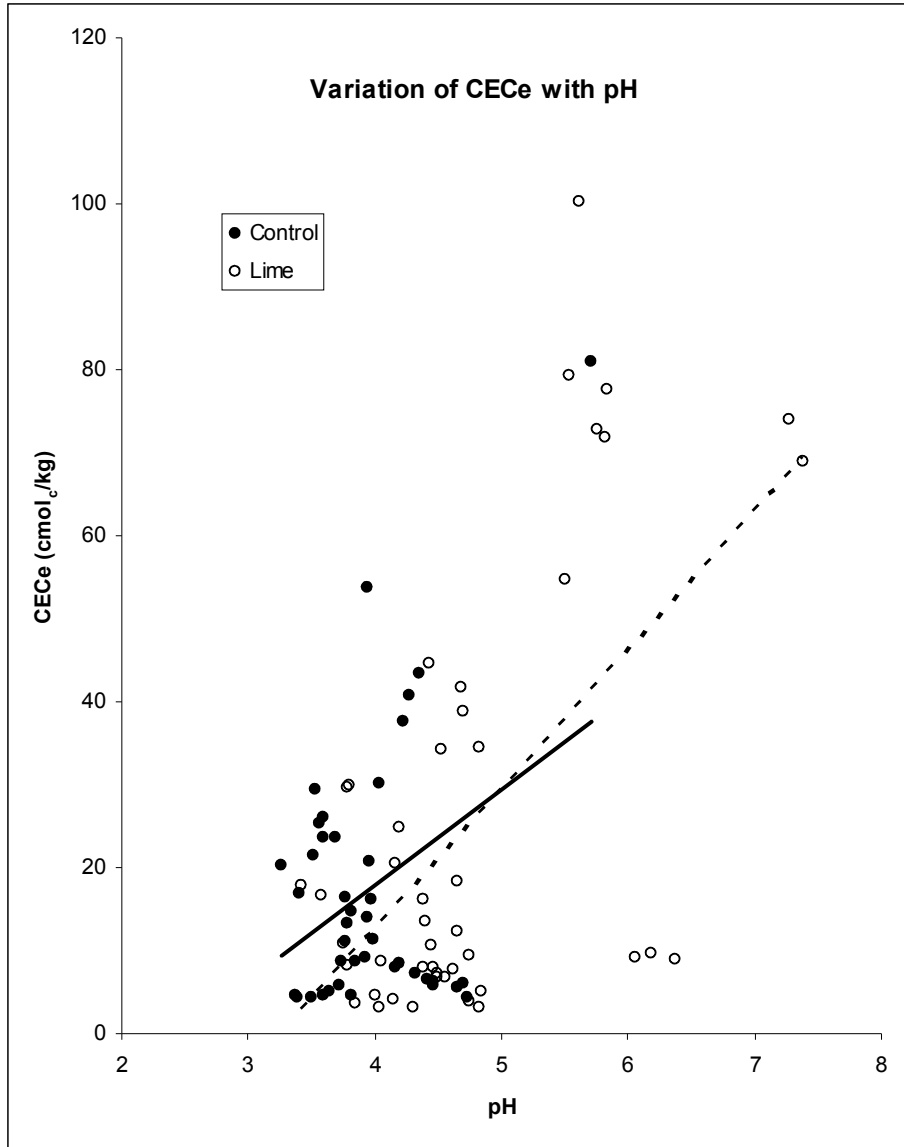Figure 6. Exchange capacity increased with pH in both control and limed soils, although there was a large amount of scatter in both cases. The regression line for the control samples is solid (p=0.03, adj. $r^2 = 0.10$); that for the limed samples is dashed (p<0.01, adj. $r^2 = 0.33$).
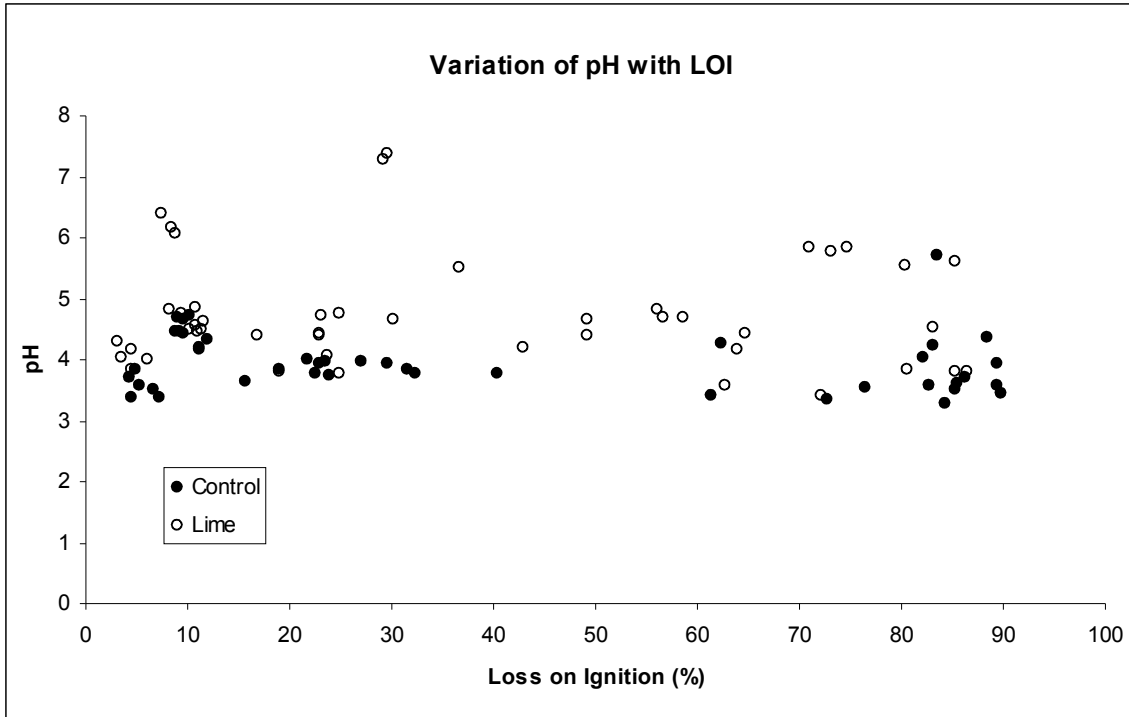
Figure 7. There was no significant relationship between pH and organic matter content in either control or limed soils.

Horizon	Treatment	equation number	equation	n	T-statistic	p-value	r^2	adj. r^2
All	Both	6	4.40 + 0.559	90	7.27	0.000	0.395	0.387
All	Both	7	3.29 + 1.13x	90	8.01	0.000	0.475	0.467
All	Both	8	3.85 + 0.937	90	9.37	0.000	0.553	0.546
All	Both	3	5.18 + 1.25x	90	3.54	0.001	0.130	0.119
All	Both	4	4.97 + 0.850	90	6.41	0.000	0.326	0.318
All	Both	9	3.73 - 0.873x	90	-16.23	0.000	0.760	0.758
All	Control	6	4.01 + 0.123	43	1.30	0.203	0.042	0.017
All	Control	7	3.43 + 0.638	43	6.34	0.000	0.534	0.521
All	Control	8	3.82 + 0.424	43	4.21	0.000	0.336	0.317
All	Control	3	3.71 - 0.376x	43	-1.10	0.278	0.030	0.005
All	Control	4	3.88 - 0.073x	43	-0.46	0.647	0.005	0.000
All	Control	9	3.75 - 0.482x	43	-5.00	0.000	0.391	0.375
All	Lime	6	4.57 + 0.685	47	6.58	0.000	0.513	0.501
All	Lime	7	3.36 + 1.28x	47	5.02	0.000	0.426	0.409
All	Lime	8	3.79 + 1.17x	47	6.76	0.000	0.573	0.561
All	Lime	3	6.05 + 2.07x	47	4.77	0.000	0.346	0.331
All	Lime	4	5.35 + 1.16x	47	6.97	0.000	0.531	0.520
All	Lime	9	3.77 - 0.916x	47	-12.96	0.000	0.800	0.795
Oe	Both	6	3.32 + 1.38x	23	9.36	0.000	0.822	0.813
Oe	Both	7	3.02 + 1.49x	23	7.69	0.000	0.757	0.744
Oe	Both	8	3.10 + 1.44x	23	8.11	0.000	0.776	0.764
Oe	Both	3	6.59 + 4.46	23	10.65	0.000	0.856	0.849
Oe	Both	4	5.05 + 2.29x	23	12.76	0.000	0.886	0.880
Oe	Both	9	3.31 - 0.971x	23	-9.80	0.000	0.835	0.826
Oa	Both	6	3.93 + 0.514	14	3.35	0.007	0.504	0.459
Oa	Both	7	3.16 + 0.877	14	4.02	0.003	0.643	0.603
Oa	Both	8	3.47 + 0.742	14	4.77	0.001	0.717	0.685
Oa	Both	3	5.60 + 2.31x	14	3.07	0.011	0.461	0.412
Oa	Both	4	4.89 + 1.34x	14	6.58	0.000	0.783	0.765
Oa	Both	9	3.60 - 0.514x	14	-5.19	0.000	0.710	0.684
A	Both	6	4.74 + 1.23x	19	10.53	0.000	0.874	0.866
A	Both	7	2.15 + 2.54x	19	9.08	0.000	0.855	0.844
A	Both	8	3.82 + 1.57x	19	8.25	0.000	0.829	0.817
A	Both	3	7.08 + 4.15x	19	5.54	0.000	0.657	0.636
A	Both	4	5.81 + 1.94x	19	10.66	0.000	0.883	0.876
A	Both	9	3.79 - 1.16x	19	-26.66	0.000	0.978	0.977
E	Both	6	3.96 + 0.274	12	0.96	0.367	0.103	0.000
E	Both	7	3.58 + 0.233	12	1.98	0.083	0.329	0.245
E	Both	8	3.75 + .349x	12	2.86	0.021	0.505	0.443
E	Both	3	3.47 - 0.577x	12	-2.03	0.070	0.291	0.220
E	Both	4	3.60 - 0.211x	12	-1.27	0.236	0.152	0.058
E	Both	9	3.83 -0.399x	12	-1.18	0.267	0.134	0.038
B	Both	6	5.12 + 0.696	22	10.20	0.000	0.846	0.837
B	Both	7	4.02 + 0.702	22	2.03	0.063	0.240	0.182
B	Both	8	4.49 + 0.968	22	6.39	0.000	0.758	0.740
B	Both	3	6.82 + 2.46x	22	3.14	0.005	0.330	0.296
B	Both	4	5.65 + 0.853	22	4.74	0.000	0.529	0.506
B	Both	9	3.92 - 0.942x	22	-16.94	0.000	0.935	0.932

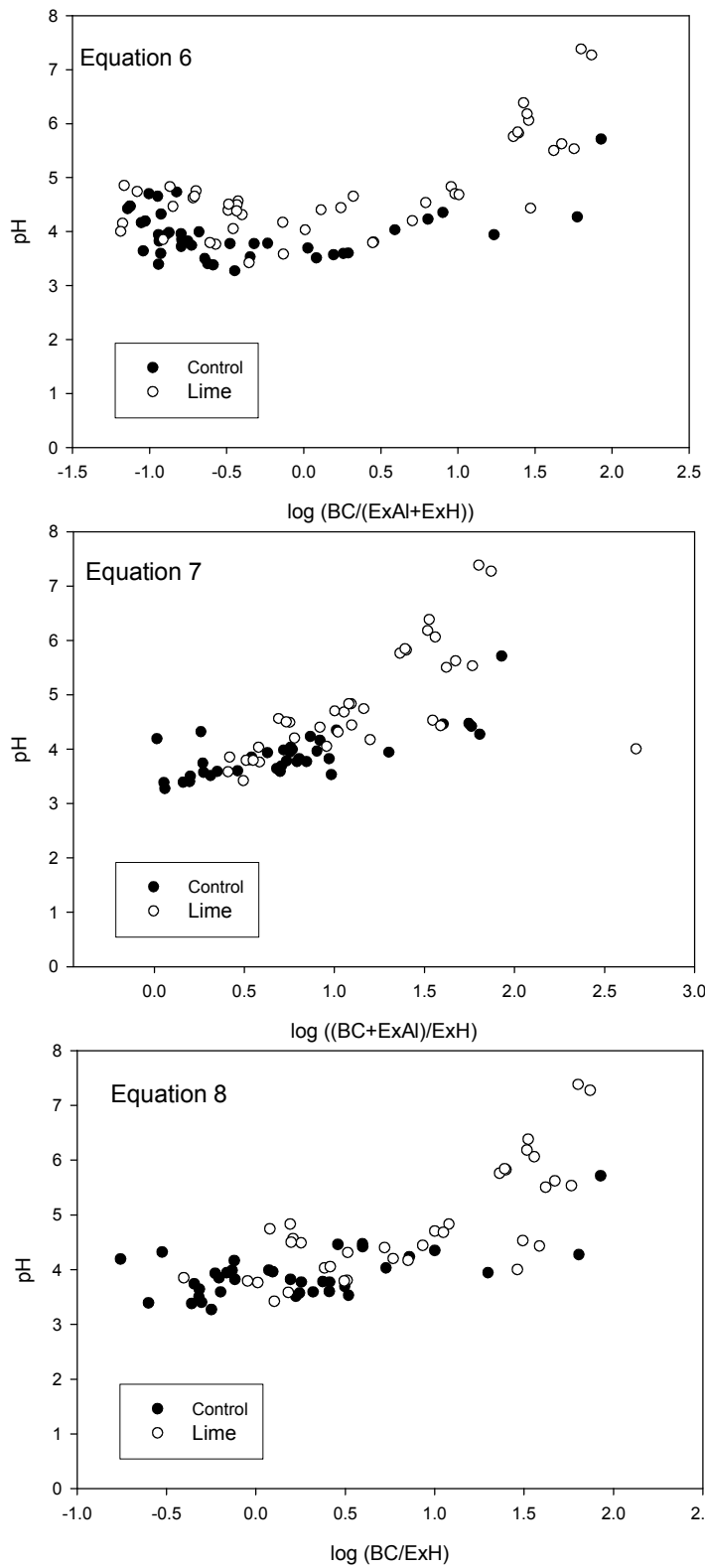Table 4. Regression results for the six equilibrium variables

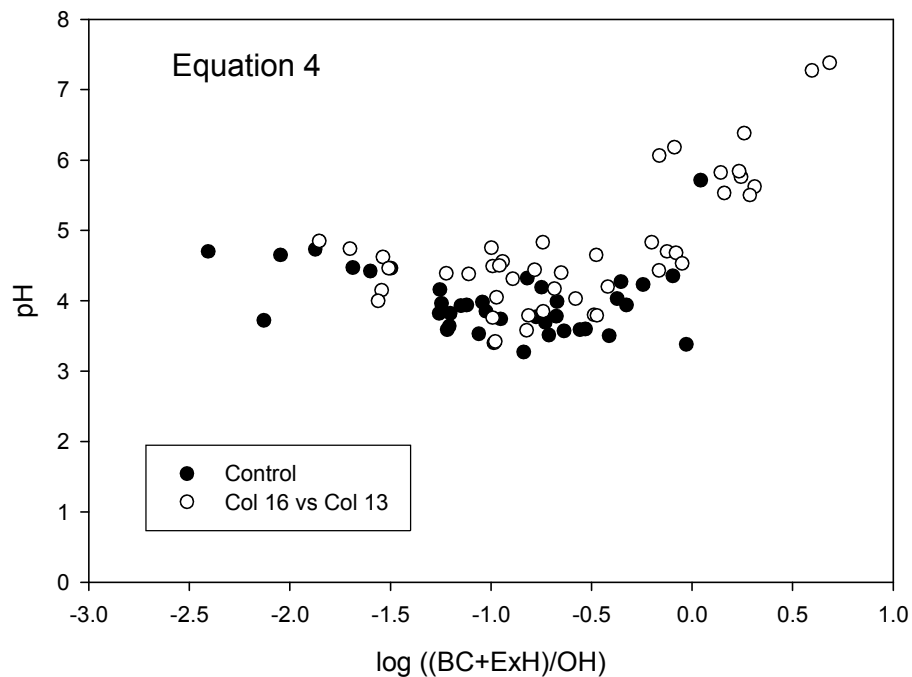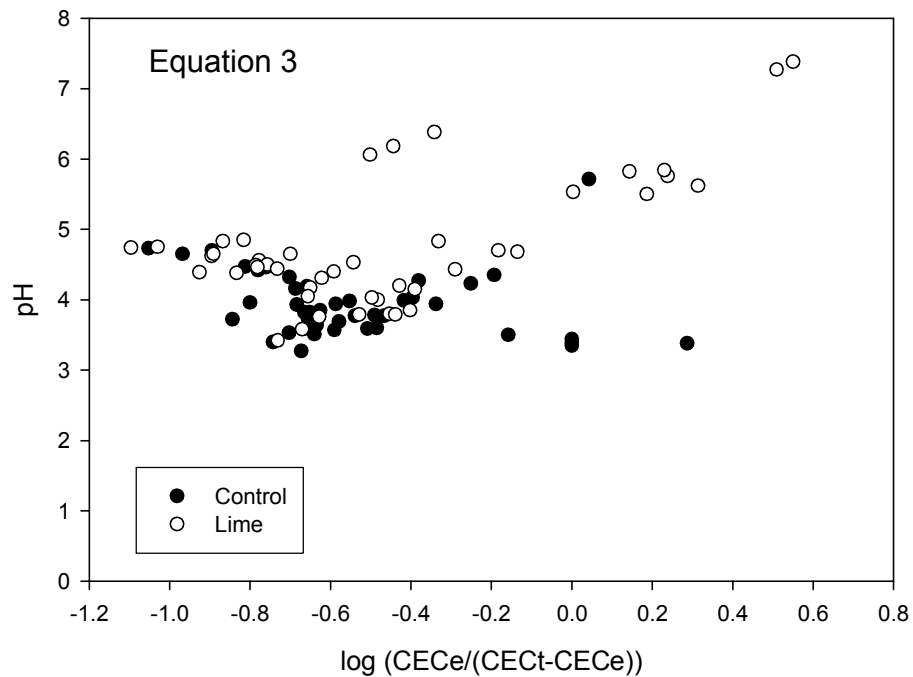Figure 8. Scatterplots for the exchangeable cation models.

Figure 9. Scatterplots for the charge development models. In each case, the x-axis variable represents an interpretation of the ratio of available charge to bound charge. Removing Al from the model (the bottom graph) reduces scatter. There appears to be an inflection point in the graph at approximately -0.3 on the x-axis; this is partially due to different behavior in mineral (E, B) and organic (Oe, Oa, A) horizons.
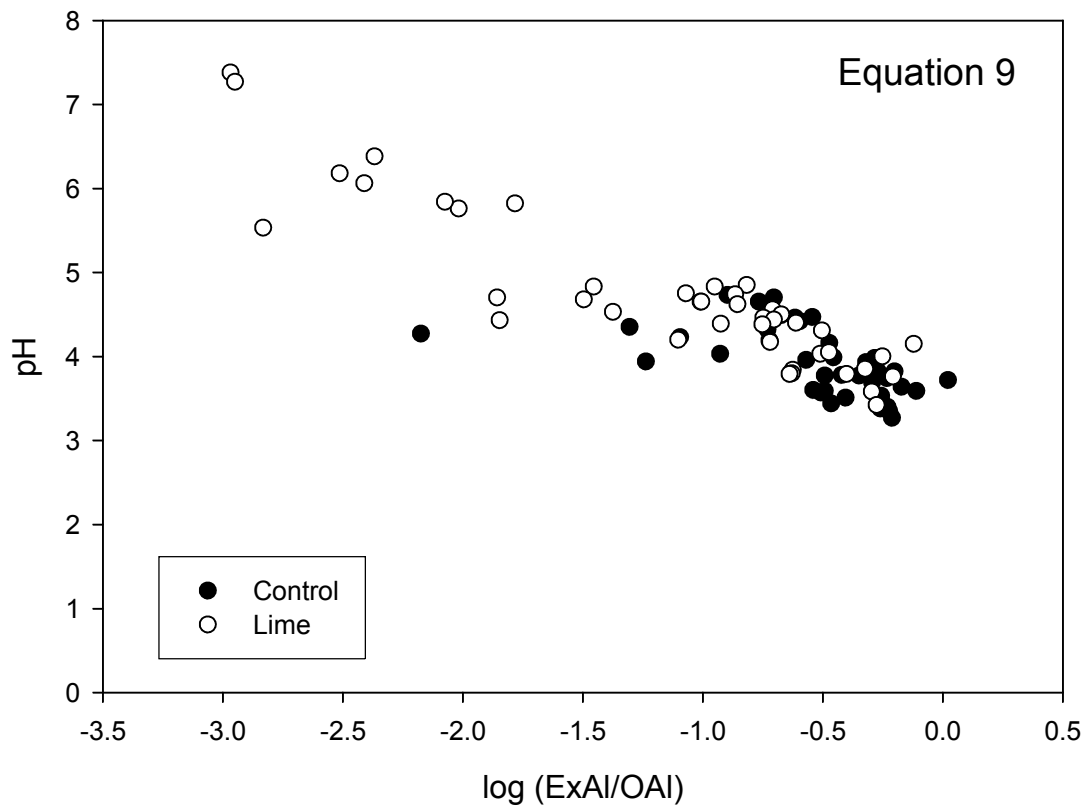
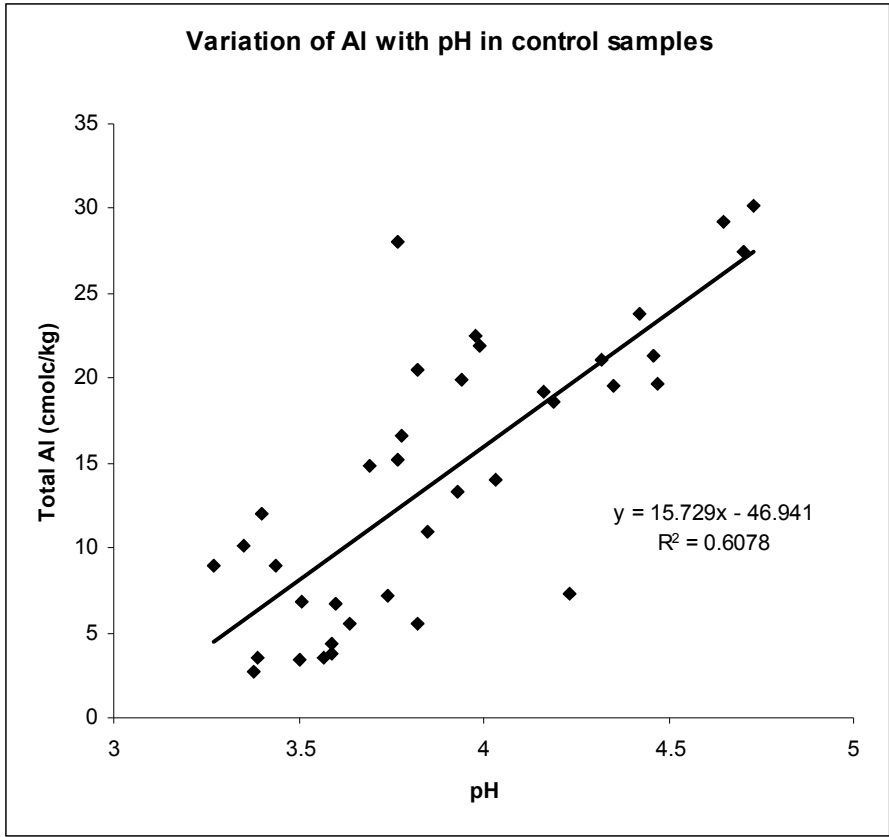Figure 10. Scatterplot for the Al model.

Figure 11. Control samples with higher pH had more total Al.

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Education

Ph.D. (in progress) Natural Resouces (Certificate in Ecological Economics), University of
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    Advisor: Jennifer C. Jenkins

M.S. 2006 Forest and Natural Resource Management, SUNY College of Environmental Science
and Forestry - Syracuse, NY
*Thesis: Cation exchange chemistry and the long-term effects of liming on acidic forest
soils in the northeastern United States*
    Advisor: Ruth D. Yanai
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                    Chris E. Johnson, Syracuse University
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1999   B.A. Philosopy, Yale University

Employment History and Research Experience

2005-Present: University of Vermont, Burlington VT – Research Assistant
- Research on carbon dynamics in residential vegetation, as part of the Baltimore Ecosystem Study LTER

2003-2005: SUNY ESF – Research Project Assistant.
Liming and cation exchange chemistry
- Conducted study of long-term effects of liming on cation exchange chemistry: identified previously established liming experiments; secured permissions to revisit sites; developed sampling design and protocol; collected and processed samples; analyzed samples for organic matter content, pH, cation exchange capacity, total and exchangeable acidity, exchangeable base cations, total and exchangeable acidity; statistically analyzed results and prepared manuscript

Urban Forest Effects species selection module
- Built a companion database to the USFS Urban Forest Effects (UFORE) model that allows urban resource managers to select appropriate tree species based on input criteria including local climate, site conditions, tree characteristics, and desired tree functionality.

Calcium cycling with stand age and species succession
- Surveyed vegetation, dug quantitative soil pits, and sampled forest floors as part of a large, multi-year calcium cycling project in the White Mountains, NH, involving principle investigators and field crews from four universities.

2002-2003: UC Berkeley – Lab Assistant
Sudden Oak Death projects
- Measured, felled, and bucked trees, prepared and analyzed tree cores and cookies, and entered data for a stand reconstruction project examining the effect of Sudden Oak Death on stand dynamics in Marin and Mendocino counties, CA.
- Mapped stem positions and surveyed plots for a project analyzing spatial patterns in the development and spread of Sudden Oak Death.

Multiple species stocking model
- Mapped, measured, and characterized trees for a project modeling light conditions in multi-age, multi-species stands in montane forests in the Sierra Nevada. Forest managers will be able to use the finished model to allocate growing space appropriately in stands with multiple cohorts and multiple species.

2001: Appalachian Trail – Thru-hike
- Walked from Springer Mountain, GA to Mt. Katahdin, ME

1999-2001: i-drive.com – Marketing Assistant/Account Manager
- Developed standardized marketing program for online storage start-up; worked with design firm to develop campaign elements; sourced and distributed marketing materials to target audiences; given additional duties as account manager for University clients.

1999: Hallormsstaður, Iceland – Research Assistant
Influence of dominant species on carbon sequestration
- Sampled for leaf area analysis, development of allometric equations, and rootball analysis, measured soil respiration, and collected and analyzed soil and water samples for a project investigating carbon sequestration rates in different forest types in Hallormsstaður, Iceland. Coordinated the sampling schedule to meet deadlines and oversaw operation of the project while senior researcher attended meetings and conferences.

1998: Copper River Delta, Alaska – Field Assistant
Forest health and response to human impacts
- Collected litterfall, surveyed understory vegetation, measured and cored trees, and collected decomposition data for a study measuring upland and wetland community response to natural and anthropogenic disturbances on the Copper River delta, near Cordova, AK. Trained and supervised four other field assistants, led site tours, and explained methodology to major donors

Spruce bark beetle management
- Established plots and sampled to detect treatment effects for a project investigating management strategies for areas with extensive spruce bark beetle damage on Weyerhauser lands on the Kenai Peninsula, AK.

Publications and Presentations

Lilly, P.J. Cation exchange chemistry and the long-term effects of liming on acidic forest soils in the northeastern United States. (in prep)

Myeong, S.J., P.J. Lilly, B.B. Park, R.D. Yanai, D.J. Nowak, and R.B. Platt. Contributions of trees, grass, and maintenance to the carbon balance of an urban residential plot. Landscape and Urban Planning (in prep)

Lilly, P.J. and R.D. Yanai. "Long-term effects of liming on acid forest soils". Ecological Society of America annual meeting, Montreal, QC, August 2005

Lilly, P.J. "Long-term effects of liming on acid forest soils". Society of American Foresters New England meeting, Portland, ME, April 2005

Lilly, P.J. "Characterizing soil acidity and the long-term effects of liming". Hubbard Brook Experimental Forest annual meeting, July 2004.

Myeong, S.J., P.J. Lilly, B.B. Park, R.D. Yanai, D.J. Nowak, and R.B. Platt. "Contrasting tree- and lawn-dominated residential lots in Syracuse, NY: Pollutant loads, energy balance, and carbon sequestration. Syracuse Symposium on Environmental and Energy Systems, October, 2003.

Awards/Scholarships
Edna Bailey Sussman Foundation Internship, Summer 2004
Finalist, Chase Coggins Memorial Scholarship, 1998

Personal/Professional Affiliations
Society of American Foresters; Ecological Society of America; St. Anthony Hall