

Long-Term Effects of Forest Liming on Soil, Soil Leachate, and Foliage Chemistry in Northern Pennsylvania

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Sugar maple (*Acer saccharum* Marsh.) decline disease, decreased growth, and regeneration failure have been related to a low supply of Ca and Mg. There is increased interest in augmenting cation availability via liming, but there is little information on the amounts of lime required and the longevity of the lime treatment. A single application of 22.4 Mg ha⁻¹ of dolomitic limestone in 1985 at four forested sites in Potter County, PA has shown that soil, soil water, and sugar maple foliage chemistry are significantly altered by liming and the changes in soils and foliage persist as long as 21-yr post-treatment. By 2001, only 3 kg ha⁻¹ of lime remained undissolved while increases in exchangeable Ca and Mg, and pH continued through 2006 at depths up to 35 to 45 cm. Exchangeable Mn and Al concentrations were significantly reduced by lime application, though effects were slower to develop at deeper depths. Soil solution chemistry from 1996 was highly variable but reflected the changed soil nutrients. On limed plots, sugar maple foliage had elevated concentrations of Ca and Mg in 2006 samples, indicating the persistence of the lime treatment. Comparison of Ca/Al ratios in soil solution, soils, and foliage show inconsistencies from previous published risk thresholds. Species-specific thresholds of Ca and Mg availability in soil and foliage have better potential management application and should be more rigorously tested as stress indicators.

Abbreviations: AR(1), autoregressive order 1; ARH(1), autoregressive order 1 with heterogeneous variances structure; BDR, Black Diamond Road; CEC, cation-exchange capacity; CS, Cherry Springs.

Forest liming has been used to reduce acidic soil conditions and provide base cations necessary for species such as sugar maple to sustain crown health, basal area growth, and flower and seed production in several experimental applications (Wilmot et al., 1995; Long et al., 2011; Moore et al., 2012). Both the health and growth of sugar maple have been shown to be linked to deficiencies in Ca and Mg (Hallett et al., 2006; Long et al., 2009; Moore et al., 2012; Sullivan et al., 2013). In Pennsylvania and other parts of the northeastern USA and Canada, base cations have been depleted by long-term inputs of acidic deposition leaving sugar maple susceptible to crown dieback and decline when other stresses such as drought and defoliation occur (Horsley et al., 2000; Driscoll et al., 2003; Bailey et al., 2005).

Sugar maple regeneration has been poor for decades in Pennsylvania and persistently high densities of white-tailed deer (*Odocoileus virginianus*) and associated browsing have been implicated in regeneration failures (McWilliams et al., 2004). In the 1980s, debate ensued over whether deer or acidic deposition was responsible for regeneration failures in Pennsylvania (Frye 2006). Across a range of historical deer densities in Pennsylvania (4–25 deer km⁻²), a 10-yr study showed deer browsing adversely affected desirable woody species such as sugar maple and increased

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browse resilient vegetation and plants interfering with woody regeneration in Pennsylvania (Horsley et al., 2003).

The liming study reported here was initiated in 1985 in cooperation with the Pennsylvania Department of Conservation and Natural Resources, Bureau of Forestry, to determine whether deer or acid deposition was responsible for regeneration failures in north central Pennsylvania (Auchmoody 1985). Dolomitic lime was applied at the end of September and the beginning of October 1985, at a high rate (22.4 Mg ha^{-1}) to reduce potential Al toxicity associated with acidic deposition and promote diverse seedling regeneration in fenced and unfenced plots at four unglaciated locations (Long et al., 1997). Sugar maple seedling regeneration was only temporarily improved, but ultimately unaffected, by the lime application or fencing (Long et al., 1997). Concurrent with the initiation of this study was the widespread crown dieback and mortality of sugar maple in the unglaciated portions of northern Pennsylvania (Horsley et al., 2000). This event shifted the focus of the study to the overstory community (Long et al., 1997).

Twenty-three years after lime application sugar maple crown health, growth, survival, and flower and seed production were positively affected by lime application (Long et al., 2011). Plots that were untreated suffered severe decline and mortality associated with drought events (Palmer Drought Severity Index < -1 in 1988, 1991, 1995, 1999, 2001, and 2005) and defoliations from several native defoliators (Long et al., 1997, 2011). Liming was shown to have no effect on American beech (*Fagus grandifolia* Ehrh.) crown health, growth, or mortality despite the presence of beech bark disease at all four sites. However, black cherry (*Prunus serotina* Ehrh.) showed a significant negative growth response to liming starting in the late 1990s with decreased basal area increment and increased mortality in limed plots (Long et al., 2011). Foliar Ca and Mg remained significantly elevated in sugar maple foliage sampled 21 yr after lime application demonstrating the persistence of the lime treatment. Previous publications from this study have not reported long-term changes in forest soils due to lime treatment. The changes in soil chemistry through 2006 in response to liming are the focus of this report.

The critical importance of base cations for maintaining the health and growth of sugar maple on unglaciated upper slope sites in northern Pennsylvania and southern New York was demonstrated in related research in this region and extended into New England (Bailey et al., 2004; Hallett et al., 2006; Long et al., 2009). On unglaciated plateau top sites, depletion of exchangeable Ca and Mg and increases in Al through the soil profile were documented in a 30-yr (1967–1997) retrospective study at four forested sites on the Allegheny National Forest (Bailey et al., 2005). On unglaciated soils in upper landscape positions (plateau-top, shoulder, and upper backslopes), sugar maple remains vulnerable to decline when other stresses occur (Horsley et al., 2000; Hallett et al., 2006).

Forest managers with soils affected by long-term inputs of acidic deposition are using or considering the use of lime to remediate soil base cation deficiencies (Johnson 2011). However, there are few published guidelines about the amount of lime re-

quired and the longevity of any treatment effect in forest soils. Additionally, managers and researchers are seeking tools to assess stress conditions affecting their forests to determine when lime may be needed. Cronan and Grigal (1995) developed stress thresholds for Ca/Al ratios that are based mainly on controlled environment studies with little field validation. Our study allows for field validation of Ca/Al molar ratios. Field validation of Ca/Al molar ratios would allow managers to more rigorously assess stress conditions before deciding on management or treatment options.

The long-term impact of lime application on soil chemistry and its changes over periods >5 yr have rarely been assessed (Long et al., 1997; Moore et al., 2008; Melvin et al. 2013). Most liming and Ca addition studies lack a long-term series of measurements in soils to assess the persistence and timing of changes in soil chemical properties through the soil profile. Except for Melvin et al. (2013) and Moore et al. (2008), most studies report only on the upper mineral soil, usually the upper 10 cm. Since many trees, including sugar maple, commonly root deeper in the soil profile it is important to sample and assess changes in these deeper soils. Sugar maple crown health improved and seedling density increased in response to liming (Long et al., 1997; Moore et al., 2008) but it is unknown how long these effects will persist. Our study permits an assessment over 21 yr of soil chemistry changes through the soil profile to 45 cm.

Beginning in 1986 (1-yr post-treatment), soils in our study (Long et al., 1997) have been sampled using an established grid. The initial focus was on the upper 15 cm of mineral soil, but in 2001 and 2006 soils were sampled to a depth of 45 cm to evaluate potential changes at deeper depths. Here we report on changes in soil chemistry in limed plots compared with untreated plots from 1986 through 2006. Soils were sampled in 1986, 1989, 1993, 1996, 2001, and 2006. We also examine the relationships among soil chemistry and soil water chemistry, both of which were sampled in 1996, and sugar maple and black cherry foliage chemistry in sampled in 1995 and 2006. Our objectives are to (i) characterize the changes in soil chemistry resulting from liming during this period, (ii) to evaluate the inter-relationships among soil, soil water, foliar chemistry, and the usefulness of the Ca/Al molar ratio as a stress indicator, and (iii) to assess the persistence of these changes over 21 yr.

MATERIALS AND METHODS

Field Sites

Study sites are in the Susquehannock State Forest, Potter County, Pennsylvania, within the unglaciated Deep Valleys Section of the Appalachian Plateaus Province (Sevon, 2000). Black Diamond Road (BDR) with Blocks 1 and 2 (BDR1 and BDR2, respectively) is at about 682 m elevation and is 2 km southeast of Inez, PA. Cherry Springs with Blocks 3 and 4 (CS3 and CS4, respectively) is at 716-m elevation and is immediately southeast of Cherry Springs State Park. All four blocks are located on plateau top landscape positions. Annual precipitation averages 1125 mm and is evenly distributed through the year (Pennsylvania State Climatologist, 2013). The area has a humid

temperate climate with an average daily temperature of 8.2°C and a growing season ranging from 91 to 120 d (Pennsylvania State Climatologist, 2013).

Soils at all sites are residual, formed in material weathered from sandstone, siltstone, and shale (Goodman et al., 1958; Aguilar and Arnold, 1985). Two soil pits were described in each block (total = 8) at the initiation of the study (July 1985) by a USDA Natural Resources Conservation Service soil scientist. These descriptions indicated that the soils were mixtures of Cookport (Aquic Fragiudult), Hazleton (Typic Dystrodept), Calvin (Typic Dystrodept), Hartleton (Typic Hapludult), and Wharton (Aquic Hapludult) series (Goodman et al., 1958). These soils have a fine-loamy particle-size class and mineralogy dominated by illite and kaolinite. Original pit descriptions indicate roots were “many” to “common” to a depth of 30 cm and “common” to “few” from 30 to 50 cm. The pit descriptions indicated A horizons were about 5 cm thick. Organic horizons were not measured in this study, but based on our observations of the treatment plots and other work in northern hardwood soils in Pennsylvania (Bailey et al., 2004, 2005) Oi + Oe thickness averages <4 cm and Oa is very thin (<0.5 cm) or absent from soils in this area.

The four blocks (replications) were established in summer 1985. Each block consists of eight 60 m × 60 m (0.36 ha) treatment plots; there is a 7.5-m buffer zone around each plot and data were collected from within the interior 45 m × 45 m (0.2 ha) measurement plot. The original study design was a split plot with fencing (whole plot treatment) around four plots to exclude deer and four plots unfenced to assess the impact of deer on tree seedlings. Four treatments were randomly assigned to the plots and consisted of a lime only, herbicide only [to control ferns, grass, beech brush, and striped maple (*A. pensylvanicum* L.) which interfere with tree seedling survival], lime + herbicide, and an untreated control. In limed plots, there was a single application of commercial pulverized dolomitic limestone (Ca = 21%, Mg = 12%, CaO equivalent = 58.8, calcium carbonate equivalent [CCE] = 105.6) at 22.4 Mg ha⁻¹ during autumn 1985. Lime was applied only to the interior 45 m by 45 m (0.2 ha) portion of the plot when the soils were dry using a tractor equipped with a conventional hopper spreader. Subsequent analyses of overstory tree health, growth, and soils (Long et al., 1997, 2011) have shown no effects related to fencing or herbicide on overstory species. For the purposes of this report only the limed (lime only and lime + herbicide) vs. no lime (control and herbicide only) plots were evaluated. All plots were thinned to 50% relative density in winter 1985–1986 with most of the removed trees from intermediate and suppressed crown positions (Long et al., 1997).

Soil Sampling and Analyses

Soils were sampled starting in fall of 1986 (1-yr post-treatment) and again in 1989, 1993, 1996, 2001, and 2006. Six permanently marked sample points are centered on a 22.5 × 11.3 m grid in the center of each plot. Sample location was varied around the marked sample points by distance and azimuth to ensure sampling an undisturbed area in each sample year. From 1985

through 1996, samples were taken from the top of the mineral soil (0 cm) to a depth of 15 cm by 2.5-cm increments. For data analyses, the results of the 2.5-cm increments were averaged to provide data for 5-cm increments (0–5, 5–10, and 10–15 cm). In 2001 and 2006, samples were taken in 5-cm increments from 0 to 15 cm and by 10-cm increments from 15 to 45 cm to assess the effects of liming on these additional depth increments. All samples were air dried and sieved through a 2-mm screen and sent to the University of Minnesota Research Analytical Laboratory for analyses (Munter, 1982). Soil pH was determined in a 1/1 (v/v) soil/deionized water mixture. Major cations K, Ca, Mg, and Mn were determined by inductively coupled plasma spectroscopy (ICP) after extraction with 1.0 M NH₄OAc buffered at pH 7. Concentrations of soil Al were determined by ICP after extraction with 1 M KCl.

In 2001 soil samples were analyzed to determine the amount of remaining lime expressed as the CCE. Air-dried and sieved soil samples from two limed plots in each block (total *n* = 8 plots), were used for analyses of the amount of lime (CaCO₃) remaining in the 0- to 5-, 5- to 10-, and 10- to 15-cm depths (total *n* = 24 samples). Mean bulk density was also determined for these layers by sampling with a small core sampler of known volume (Federer et al., 1993). Samples were oven-dried at 105°C and weighed. Bulk density was calculated after correction for coarse fragments present in the samples (Culley 1993). The concentration of undissolved lime was analyzed by the pressure calcimeter method (Sparks et al., 1996): soil samples were reacted with 6 M HCl, with 3% (w/w) ferric chloride added to limit the oxidation of organic matter, in a closed vessel. A gas sample was taken from the head space and analyzed for CO₂ in a Shimadzu GC-8A gas chromatograph (Shimadzu Scientific Instruments, Columbia, MD). Concentrations were compared with a calibration curve made by mixtures of carbonate-free soil samples and fresh dolomitic limestone. Concentrations were expressed as a weight percentage of CCE.

Soil Water Sampling and Analyses

Ceramic cup suction lysimeters were installed at a depth of 30 cm in a limed and a control plot in all four blocks (total of eight plots with lysimeters) on 1 May 1995 using a hand auger. Three lysimeters were positioned in a plot so that each lysimeter was near a mature tree, usually sugar maple, American beech, or black cherry (*n* = 24 lysimeters). The lysimeters were flushed for 2 wk and sampling began in mid-May 1995. Each lysimeter was evacuated to a 60 KPa (60-centibar) vacuum using a hand pump. Samples from the three lysimeters in a plot were composited and kept on ice before laboratory analysis. Because of the disturbance associated with the lysimeter installation, the 1995 soil water data were highly variable and are not presented here. Lysimeter sampling commenced on 8 Apr. 1996 and continued at 14-d intervals through 19 Nov. 1996. Samples were transported to the Water Laboratory, Environmental Resources Research Institute, at the Pennsylvania State University for analysis of pH, Ca, Mg, K, Al, and Mn using standard protocols (U.S. Environmental

Protection Agency, 1983). For data analysis, only the lysimetry data corresponding to the growing season from April 8 to October 22 were used.

Foliage Sampling and Analysis

In mid-August 1995, a subset of 54 overstory (dominant and codominant crown classes) sugar maples, 27 in limed plots and 27 in unlimed plots, were sampled by shooting mid-crown foliage with a shotgun. Trees were randomly selected for sampling in each replicate from those that had healthy crowns with <10% fine twig dieback. Foliage from 35 black cherry trees, 15 from limed plots, and 20 from unlimed plots, were also sampled. In mid-August 2006, 70 overstory sugar maple trees and 64 black cherry trees were similarly sampled in the plots. Because of mortality and the uneven distribution of species in the four blocks, black cherry samples were mainly obtained from BDR1 (block 1) and CS4 (block 4) while sugar maples were sampled from all four blocks.

The 1995 foliage samples were oven dried at 65°C and ground in a Tecator Cyclotec mill (FOSS, Eden Prairie, MN), and analyzed at the University of Minnesota Research Analytical Laboratory (Munter, 1982). Total Kjeldahl N was determined with a Lachat autoanalyzer (QuikChem method 13–107–06–2D, Lachat Instruments, Milwaukee, WI) at the Forest Service Laboratory in Delaware, OH. Foliage was dry ashed at 485°C and taken up in 10% HCl for analysis by ICP spectroscopy at the University of Minnesota Research Analytical Laboratory. Total amounts (mg kg⁻¹) of P, K, Ca, Mg, Al, and Mn were determined. Post dry-ash boiling was used to improve the recovery of Al. The 2006 foliage samples were similarly dried and ground, but were analyzed at the Forest Service Laboratory in Durham, NH. Ground foliage was digested using a microwave-assisted acid digestion procedure (USEPA Method 3052) and analyzed for P, K, Ca, Mg, Al, and Mn by ICP spectroscopy. Foliar N was determined by combustion with a PerkinElmer 2400 series II CHNS/O analyzer (PerkinElmer, Waltham, MA). National Institute of Standards and Technology pine needles were used as a reference standard. Percentage of element recovery ranged from 90% for Al to 108% for Ca for analytes with certified concentrations (Vogt et al., 1987). Repeatability of determinations for both standards and duplicate samples (maximum value minus minimum value expressed as a percentage of the mean) was typically <3%, expressed as the percentage relative difference.

Statistical Methods

The study design is a randomized complete block with repeated measures. Statistical analyses were conducted with SAS PROC GLIMMIX (SAS Institute Inc., 2008) using a restricted or pseudo maximum likelihood technique and the Kenward-Roger correction method for the denominator degrees of freedom (Littell et al., 2006). Normality of the data was tested using the Shapiro-Wilk test and alternative distributions including the lognormal (with the identity link function) and γ (with the log link function) were used when they best fit the data. Because of the number of soil depths measured (three), the frequency of

measurement (six sample years), and the two lime treatments (lime vs. no lime), soils data were analyzed in two different models. The first model (Model 1), with fixed effects of lime, year, and the lime $\times$ year interaction, was used to assess the impact of lime treatment over time on soil chemistry within each 5-cm layer analyzed separately (i.e., 0- to 5-, 5- to 10-, and 10- to 15-cm layers each analyzed in separate models). This approach assesses the changes induced by liming over the five time intervals (six sample years). Sampling intervals were 3 to 5 yr, but we assumed these to be approximately equal intervals. Covariance structures used for these models included mainly the autoregressive order 1 structure [AR (1)] and the AR (1) with heterogeneous variances structure [ARH(1)]. The second model (Model 2), with the fixed effects depth, year, and the interaction of depth $\times$ year, was used to assess the changes in soil chemistry by depth over the six sample years, but separate analyses were conducted with lime only plots and control only plots. The Model 2 analyses permit comparisons among the sampled depths to determine when changes in mean concentrations occurred relative to concentrations at other sampled depths. Depths are not explicitly compared in Model 1 which focuses on determining when the liming treatment differed from the control within a specific depth.

All model terms were assessed at the significance level $\alpha = 0.05$. Residuals from all models were assessed for normality by plotting and with the Shapiro-Wilk test, and residuals for fixed effects were evaluated for homogeneous variance using Levene's test. Where appropriate, Tukey-Kramer multiple comparison tests were used with $\alpha = 0.05$ to compare changes in soil chemistry (least squares means) with respect to lime (Model 1) and depth (Model 2) or the interaction of these with year, if significant. Block (replicate) was considered a random effect for both models. Similar models were used to analyze soils data from 2001 and 2006, when samples were obtained from the 15- to 25-, 25- to 35-, and 35- to 45-cm depths.

Soil water chemistry data were highly variable between the plots and across the sample year (1996) and could not be analyzed using parametric statistics. Boxplots of the data are used to graphically characterize the differences in soil water chemistry between limed and unlimed plots.

The 1995 sugar maple and black cherry foliage chemical constituents were compared using *t* tests for means from trees sampled in limed and unlimed plots in a replication ($n = 4$ for sugar maple; $n = 2$ for black cherry). Foliar nutrient data are also used here in Spearman rank correlation analyses to evaluate the strength of their relationship with soil chemical constituents (1996 samples) or soil water chemistry (1996), or both factors. Similarly, sugar maple and black cherry foliage chemistry determined from 2006 samples was used in Spearman rank correlation analyses with soil chemical constituents determined from the 2006 soil samples.

RESULTS

Soils—Lime Effects

The soils in this study show the prolonged impact from a single application of dolomitic limestone at 22.4 Mg ha⁻¹. The repeated measures analyses of liming effects over time showed

significant effects on exchangeable Ca, Mg, Mn, K, Al, and pH (Fig. 1). For the 0- to 5-cm layer, the lime $\times$ year interaction was significant ($P \leq 0.05$) for all chemical parameters except K (K data not shown). Because lime was applied to the surface organic layer, changes in the upper mineral soil, 0- to 5-cm sample depth,

occurred rapidly (Fig. 1). Liming significantly increased Ca, Mg, and pH starting in 1986 (1-yr post-treatment) and maintained this effect through 2006. Exchangeable Mn in the 0- to 5-cm layer decreased dramatically in response to liming in 1986 and this reduction was sustained through 2006. Similarly, Al decreased in

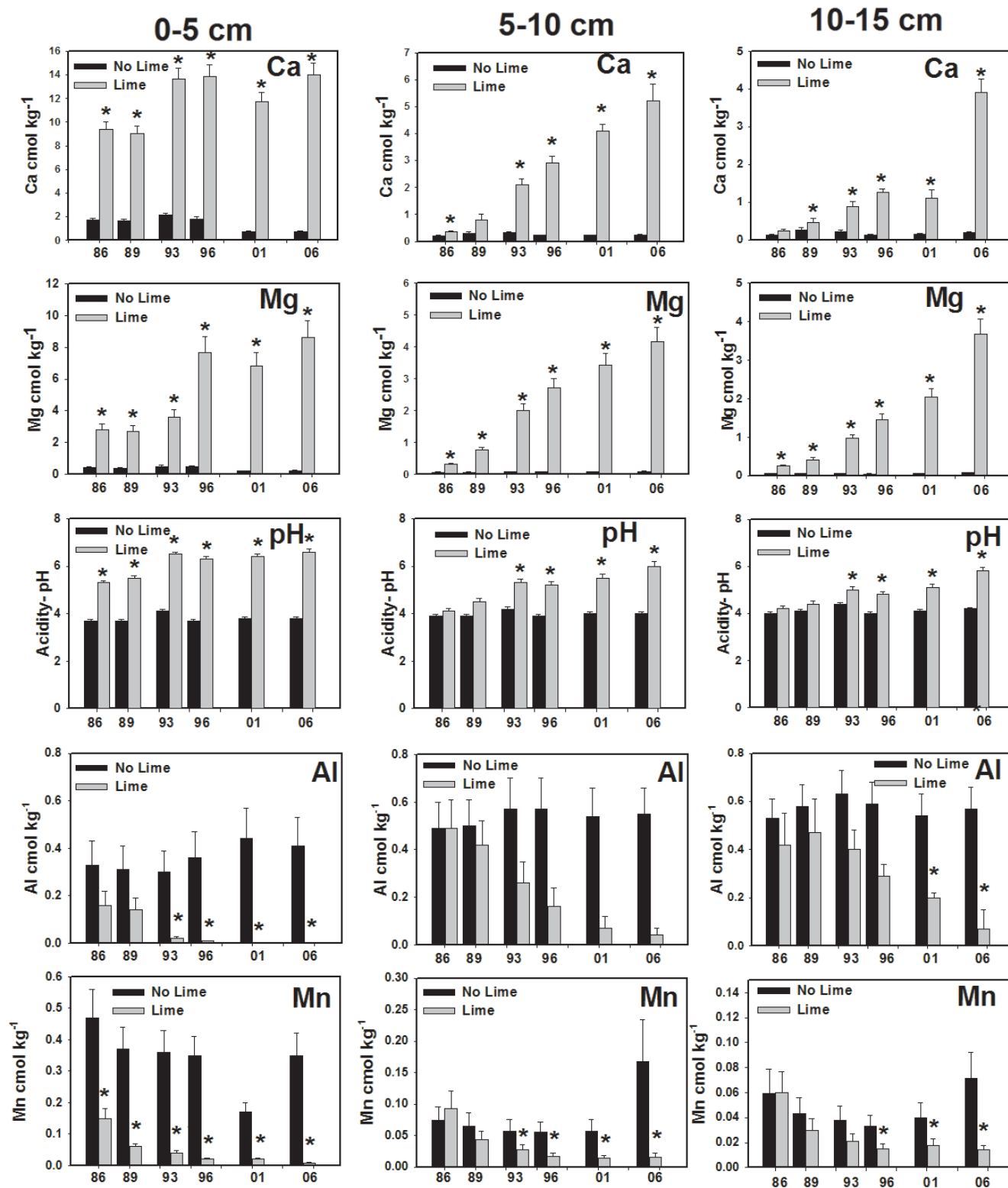


Fig. 1. Least squares means from repeated measures analysis of lime treatment effects on soil exchangeable Ca, Mg, Mn, Al, and pH in 1986, 1989, 1993, 1996, 2001, and 2006. Separate analyses were conducted for the 0- to 5-, 5- to 10-, and 10- to 15-cm depths. All elements and pH had significant ($\alpha \leq 0.05$) lime $\times$ year interactions and Tukey-Kramer pairwise comparisons with significant differences between lime and no lime treatments are noted by an asterisk (*).

response to lime treatment, but this change occurred more slowly and did not become significant in the 0- to 5-cm layer until 1993.

Liming increased exchangeable Ca and Mg in both the 5- to 10- and 10- to 15-cm layers from 1986 through 2006 (Fig. 1). For Ca and Mg at both of these depths the magnitude of difference between limed and control treatments increased through 2006, when exchangeable Ca at the 10- to 15-cm depth was almost 20 times greater and Mg was about 40 times greater in limed plots compared with untreated plots. Changes in soil pH and exchangeable Mn and Al were slower to occur at these depths. Soil pH increased significantly and exchangeable Mn decreased significantly at these deeper layers starting in 1993 and continuing through 2006. Changes in exchangeable Al were not as consistent at these deeper depths. The lime $\times$ year interaction was not significant ($P = 0.13$) nor was the year main effect ($P = 0.18$) for the 5- to 10-cm depth. However, the effect of lime, averaged over all time periods, was significant ($P = 0.04$). At the 10- to 15-cm layer exchangeable Al was significantly reduced in limed soils in the 2001 and 2006 samplings (Fig. 1).

Exchangeable K was affected by liming in the 0- to 5-cm layer, but the lime $\times$ year interaction was nonsignificant ($P = 0.53$). The least squares mean K concentration, averaged over all time periods, was $0.32 \pm 0.03 \text{ cmol}_c \text{ kg}^{-1}$ for unlimed plots and was significantly ($P < 0.01$) less, $0.22 \pm 0.02 \text{ cmol}_c \text{ kg}^{-1}$, in limed plots in the 0- to 5-cm layer. Exchangeable K was significantly reduced in the 5- to 10-cm layer and was reduced at the marginally significant (0.08) level at the 10- to 15-cm depth in limed plots.

The amount of lime remaining in the soil was evaluated in 2001 (16-yr post-treatment) by determining the amount of carbonates remaining in the 0- to 5-, 5- to 10-, and 10- to 15-cm layers in limed plots from all four blocks. Most of the applied lime dissolved by 2001. No lime was detected in the 10- to 15-cm layers and only three of the 5- to 10-cm sampled layers had a detectable amount of lime remaining. The CCE ranged from 0.3 to 7.2% in the 0- to 5-cm layer, and from 0 to 0.4% in the 5- to 10-cm layer. The mean amount of lime left on the plots in 2001 was 3 kg ha^{-1} (0.3 g m^{-2}) or about 0.01% of the original application.

Soils—Changes with Depth

Changes in soil chemical parameters with depth over the 21-yr study period were evaluated using a repeated measures model with separate analyses of limed and unlimed plots. In unlimed plots, the exchangeable cations, Ca, Mg, and K, all showed a general trend of decreasing cation concentrations with increasing depth (Fig. 2). Concentrations of exchangeable Ca and K were greatest over the course of the study in the 0- to 5-cm layer in 1993 while the exchangeable Mg concentration was greatest in 1996, and was significantly less in 2001 and 2006 (Fig. 2). Exchangeable Ca, Mg, and K have remained at low concentrations in the 5- to 10- and 10- to 15-cm layers throughout the study with Ca concentrations $< 0.5 \text{ cmol}_c \text{ kg}^{-1}$, Mg concentrations $< 0.1 \text{ cmol}_c \text{ kg}^{-1}$, and K concentrations $< 0.2 \text{ cmol}_c \text{ kg}^{-1}$ in the unlimed plots.

In unlimed plots, only Al showed no significant effect of sample year and no significant depth $\times$ year interaction (Fig. 2). Exchangeable Al has remained relatively stable at all three depths in the unlimed plots, but with a significant ($P = 0.004$) trend of increasing concentrations with increasing depth. Manganese concentration in the upper 5 cm of mineral soil averaged $0.36 \pm 0.04 \text{ cmol}_c \text{ kg}^{-1}$ and was highly variable, but significantly ($P \leq 0.002$) greater than concentrations observed in the 5- to 10- and 10- to 15-cm layers; there were no depth $\times$ year interactions (Fig. 2). Soil pH in unlimed plots remained relatively stable over time at all depths, but with a significant ($P \leq 0.001$) depth trend from pH 3.8 ± 0.06 in the 0- to 5-cm layer to pH 4.1 ± 0.06 in the 10- to 15-cm layer (Fig. 2).

Lime treatment significantly increased the concentration and changed the distribution of exchangeable Ca and Mg in the soil profile (Fig. 2; note the different X-axis scales on these graphs). Exchangeable Ca in the upper 0 to 5 cm of mineral soil increased to $14.0 \pm 0.93 \text{ cmol}_c \text{ kg}^{-1}$ by 2006 compared with $9.4 \pm 0.62 \text{ cmol}_c \text{ kg}^{-1}$ in 1986. A similar trend of increasing exchangeable Ca concentrations over time was also pronounced in the 5- to 10- and 10- to 15-cm depths, with Ca concentrations greatest in 2006 at $5.2 \pm 0.55 \text{ cmol}_c \text{ kg}^{-1}$ in the 5- to 10-cm layer and $3.9 \pm 0.50 \text{ cmol}_c \text{ kg}^{-1}$ in the 10- to 15-cm layer (Fig. 2). Similarly, exchangeable Mg concentrations were highest, $8.6 \pm 1.20 \text{ cmol}_c \text{ kg}^{-1}$, in the upper 5 cm of the mineral soil in 2006, while exchangeable Mg concentrations were greatest in 2006 for the 5- to 10- and 10- to 15-cm sample depths. Both Ca and Mg continued to increase significantly at these depths through 2006, 21 yr after the initial application.

Potassium chloride-extractable Al decreased significantly by 2006 in limed plots to almost undetectable levels, $< 0.1 \text{ cmol}_c \text{ kg}^{-1}$ in the upper 5 cm, and $< 1.0 \text{ cmol}_c \text{ kg}^{-1}$ in the 5- to 10- and 10- to 15-cm layers. Similarly, exchangeable Mn was reduced substantially at all three depths in limed plots (Fig. 2). Manganese concentrations in 2006 were $< 0.025 \text{ cmol}_c \text{ kg}^{-1}$ at all three sampled depths. Exchangeable K concentrations varied significantly by depth and year in limed plots with most of the changes in the 0- to 5-cm layer and only minor changes at the 5- to 10- and 10- to 15-cm sample depths (Fig. 2). Soil pH increased significantly in limed plots starting in 1986 and continued to increase at all three sample depths through 2006. Soil pH in 2006 was 6.6 ± 0.18 in the upper 5 cm, 5.9 ± 0.16 at the 5- to 10-cm depth and 5.8 ± 0.15 at the 10- to 15-cm depth (Fig. 2).

Soil Changes at Deeper Depths in 2001 and 2006

In 2001 and 2006 soils were sampled at 15- to 25-, 25- to 35-, and 35- to 45-cm depths to determine whether changes due to liming were detectable deeper in the mineral soil. Statistical analyses were conducted as described by Model 1 for each 10-cm depth sampled to evaluate lime treatment effects (Fig. 3). In the 15- to 25-cm layer, both Ca and Mg were highest in mean exchangeable concentrations in 2006 and there were significant lime $\times$ year interactions thus requiring Tukey-Kramer multiple comparisons. Aluminum and pH had no significant lime $\times$ year

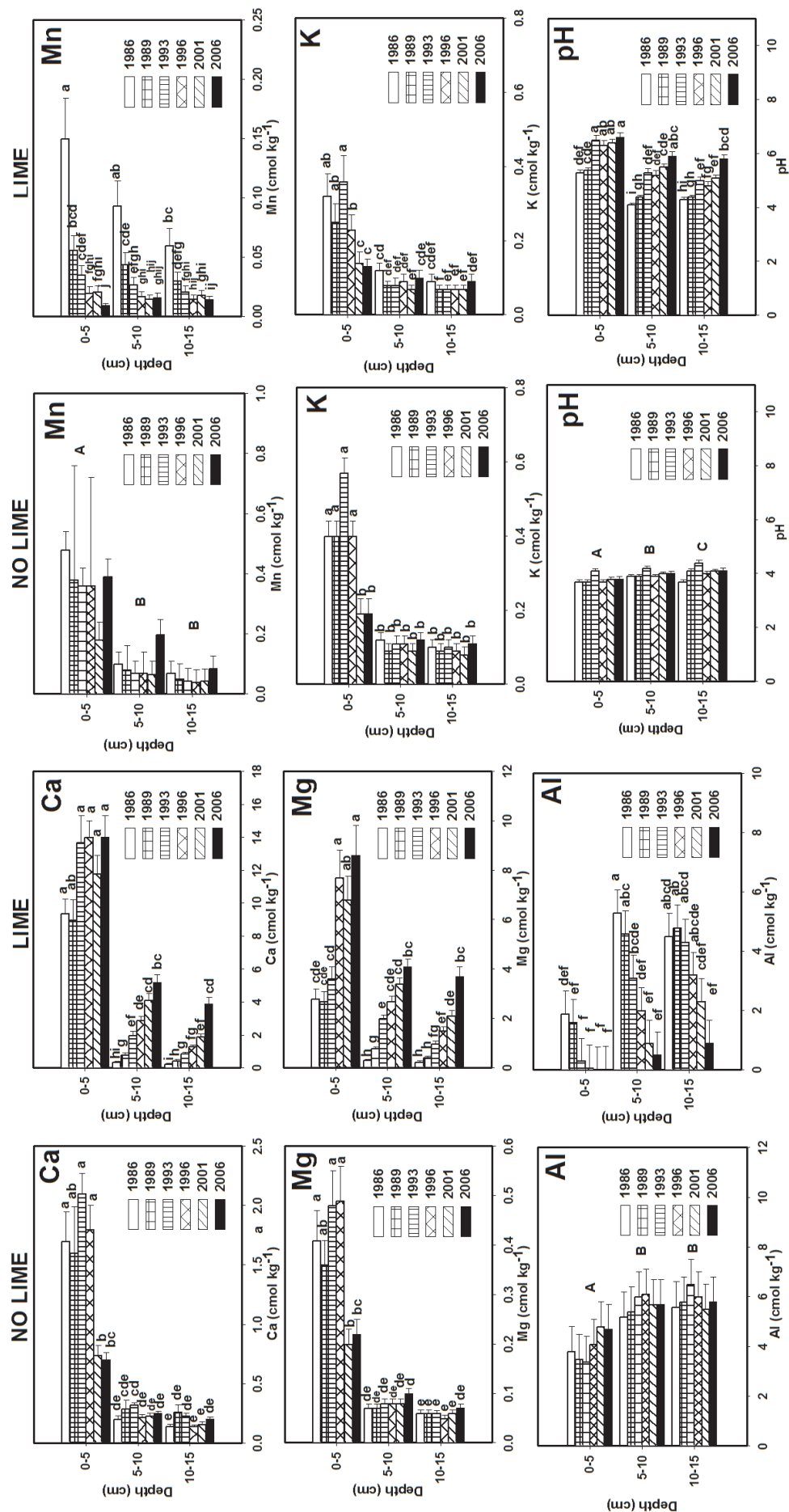


Fig. 2. Least squares means for repeated measures analysis of depth effects on soil exchangeable Ca, Mg, Al, Mn, K, and pH in 1986, 1989, 1993, 1996, 2001, and 2006. Separate analyses were conducted for control plots with no lime treatment and for lime treated plots. Elements with significant ($\alpha \leq 0.05$) depth $\times$ year interactions show Tukey-Kramer multiple comparisons with lowercase letters. Chemical constituents with no significant depth $\times$ year interaction (Al, Mn, and pH) but with significant main effects for depth have uppercase (A, B, C) letters indicating significant differences between depths, but show interaction least squares means. Means with the same letter are not significantly different. Note: the X-axis scales are not the same for no lime and lime graphs.

interactions or year effects at the 15- to 25-cm depth, but both had significant lime effects averaged over the sampling times with pH increasing and Al decreasing in response to lime. K and Mn were not significantly affected by lime treatment at the 15- to 25-cm depth (Fig. 3).

There were similar trends of increasing concentrations of Ca, Mg, and pH in limed plots at the 25- to 35- and 35- to 45-cm sample depths. Concentrations of exchangeable K, Al, and Mn, averaged over the two sample times, decreased significantly in the 25- to 35-cm depth in response to liming (Fig. 3).

At the deepest sampled depth, 35 to 45 cm, Ca, Mg, and pH all had the same general trends. Ca and Mg were significantly higher in limed plots compared with unlimed plots, and 2006

levels were higher than 2001 levels in the limed plots. Both K and Mn were unaffected by lime treatment at this depth while Al in limed plots showed a significantly reduced concentration, $2.2 \pm 0.37 \text{ cmol}_c \text{ kg}^{-1}$ by 2006. Soil pH at this deepest sampled depth in limed plots reached 5.1 ± 0.06 in 2006, significantly greater ($P < 0.001$) than $\text{pH } 4.6 \pm 0.04$ in 2001 (Fig. 3).

Analyses of changes with depth were conducted separately using Model 2 on limed and unlimed plots as was done at the upper three depths (Fig. 4). For unlimed plots, Ca, Mg, Al, Mn, and K all showed a trend of decreasing concentration with increasing depth (Fig. 4). Only Al had a significant depth $\times$ year interaction, but the same trend of decreasing concentration with depth was evident. Soil pH was the only parameter that showed

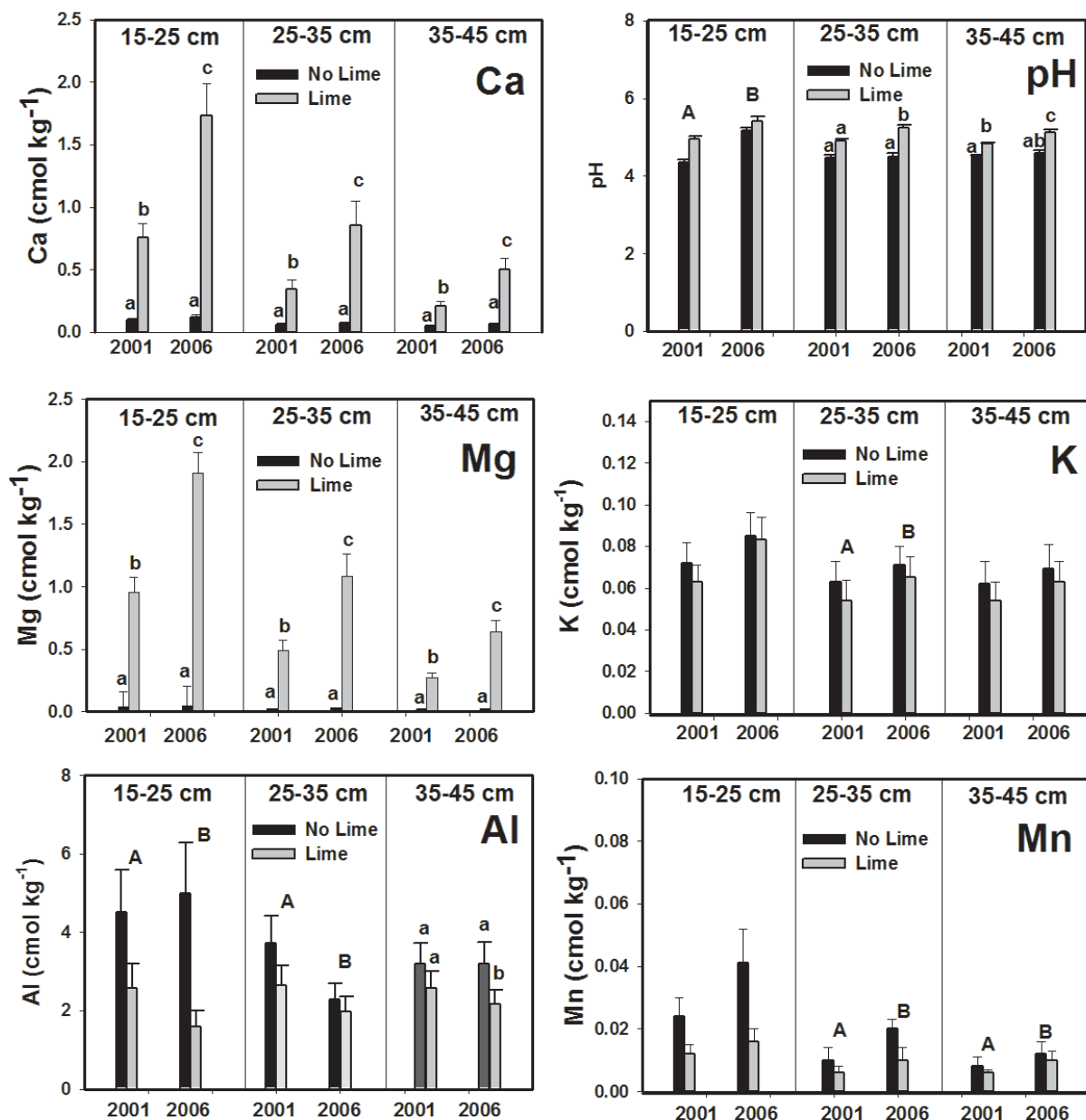


Fig. 3. Least squares means for repeated measures analysis of lime treatment effects on soil exchangeable Ca, Mg, Al, K, Mn and soil pH in 2001 and 2006. Separate analyses were conducted for the 15- to 25-, 25- to 35-, and 35- to 45-cm depths. Elements with significant ($\alpha \leq 0.05$) lime $\times$ year interactions show Tukey-Kramer multiple comparisons with lowercase letters (a, b, c), and means with the same letter are not significantly different. Chemical constituents with no significant lime $\times$ year interaction show uppercase letters (A, B) if the overall lime main effect was significant. Those means with no letters indicate no significant differences.

an increasing trend with depth; it increased from 4.3 ± 0.03 in the 15- to 25-cm layer to 4.6 ± 0.03 in the 35- to 45-cm layer.

In limed plots only Mn had a significant depth $\times$ year interaction, and exchangeable Mn was greatest, $0.015 \pm 0.004 \text{ cmol}_c \text{ kg}^{-1}$, in the 15- to 25-cm layer in 2006 (Fig. 4). Calcium, Mg, and K all had significant main effects for depth and year with a general trend of decreasing exchangeable quantities with increasing depth and greater concentrations of these elements in 2006 than 2001. Soil pH was significantly higher and Al was lower in 2006 compared with 2001 and depth differences were not significant for either of these parameters (Fig. 4).

Soil Water Chemistry in 1996

Soil lysimeter samples from 1996 revealed that liming increased solution Ca, Mg, and pH, and decreased K, Mn and Al (Al data not shown) (Fig. 5). The high degree of variability in these data is notable (Fig. 5). Median Ca concentration across the 16 sample periods in unlimed plots was 0.64 mg L^{-1} (range 0.22 to 3.42 mg L^{-1}), and in limed plots 3.0 mg L^{-1} (range 0.38 to 15.1 mg L^{-1}). In unlimed plots, soil solution median pH was 4.8 (range 4.5 to 5.5) and 6.2 (range 5.7 to 7.5) in limed plots. The median Ca/Al molar ratio, a key stress indicator, was 0.72 (range 0.15 to 5.43) in unlimed plots, and in limed plots, 7.53 (range 0.42 to 509.70). Figure 5 shows the outliers common in these data, but despite the considerable variability both between plots and through the sampled growing season, the soil solution chemistry shows the same trends as were observed in concentrations of exchangeable cations and pH in soils.

Foliar Nutrients

Sugar maple and black cherry foliar nutrients were affected by liming in both 1995 and 2006 sample years (Table 1). For sugar maple, foliar Ca in limed plots sampled in 2006

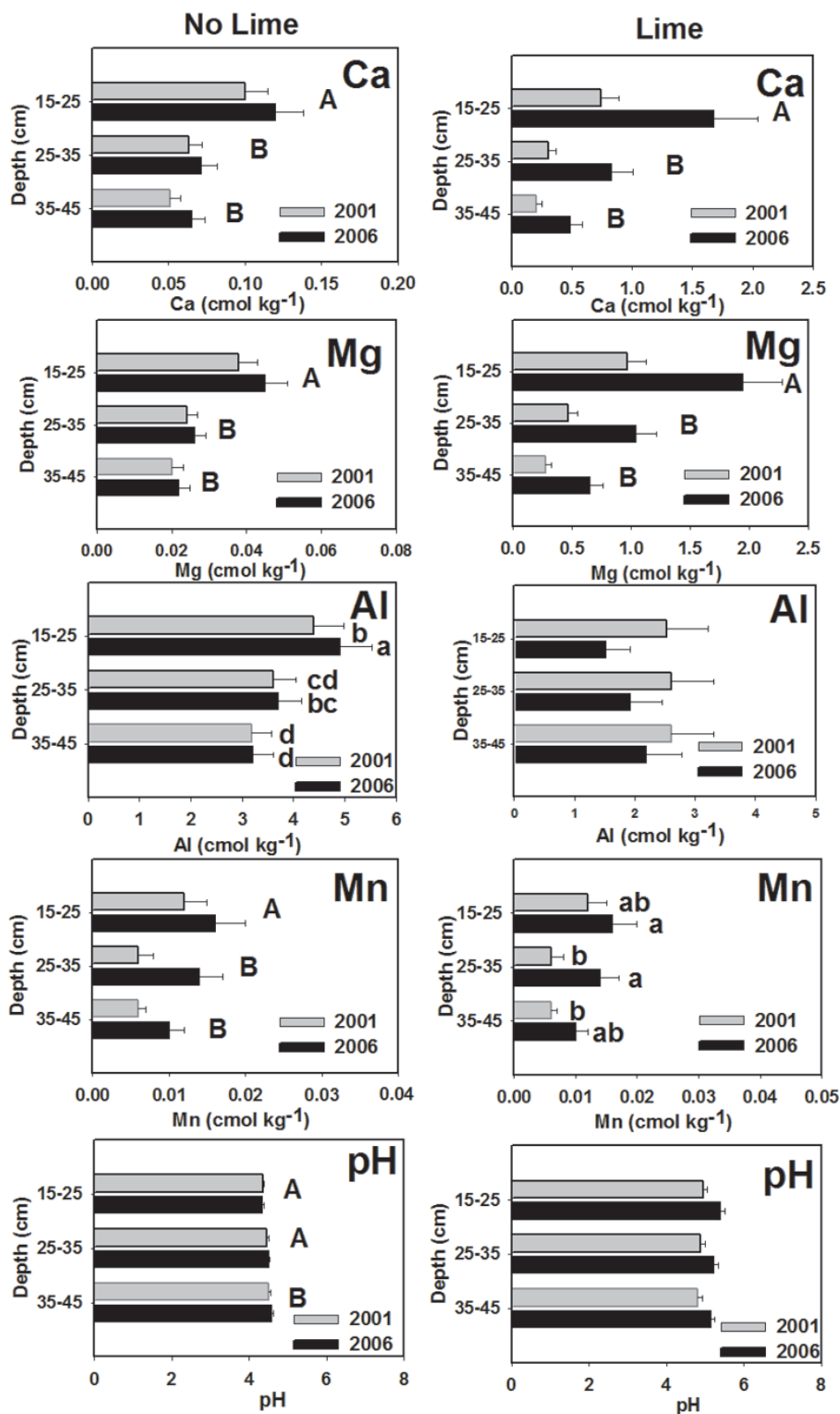


Fig. 4. Least squares means for repeated measures analysis of depth effects on soil exchangeable Ca, Mg, Al, Mn, K, and pH in 2001 and 2006. Separate analyses were performed for control plots with no lime treatment and for lime treated plots. Tukey-Kramer mean comparisons are shown with lowercase letters (a, b, c) when depth $\times$ year interactions were significant ($\alpha \leq 0.05$). Uppercase letters (A, B) indicate significant differences between mean concentrations at the three sampled depths. Year was the only significant main effect for Al (lower concentrations in 2006 compared with 2001) and pH (greater value in 2006 compared with 2001). Means with the same letter are not significantly different.

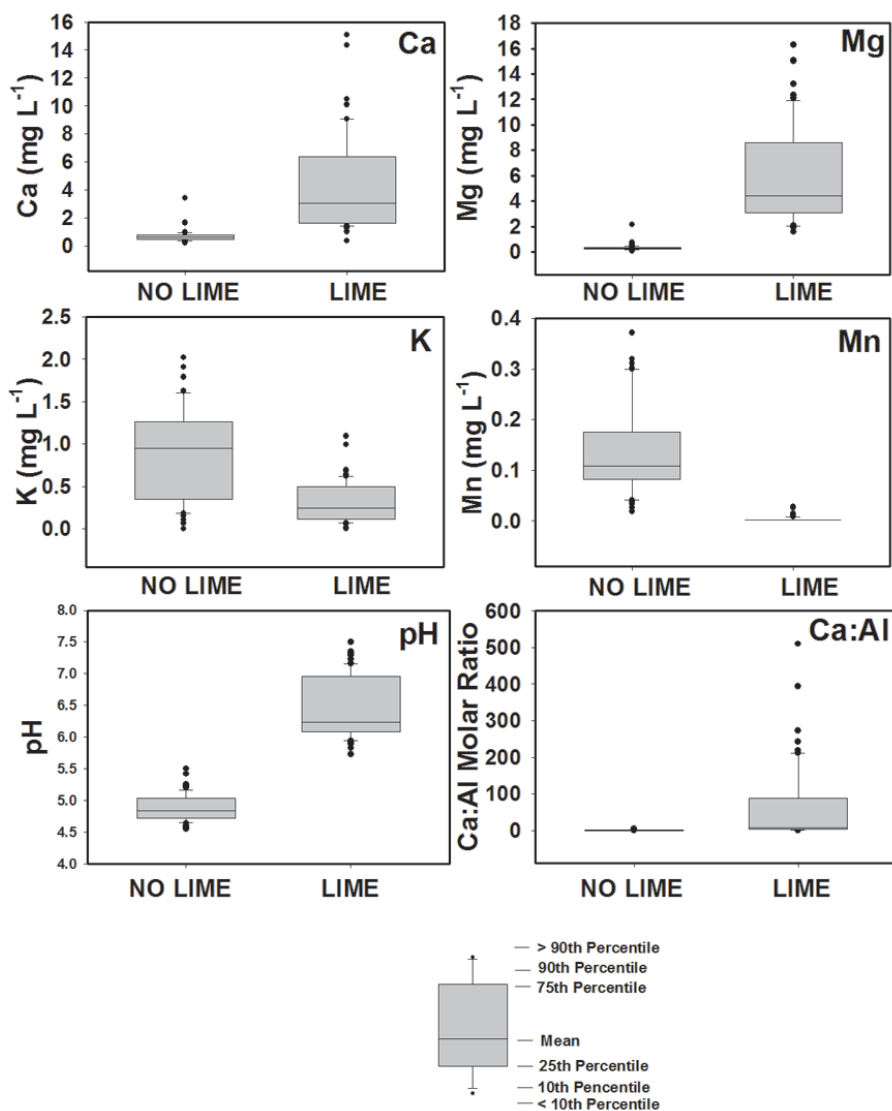


Fig. 5. Box plots of soil water chemistry data from 16 sample periods in 1996. Each dot represents the mean of four plots.

was $9519 \pm 549 \text{ mg kg}^{-1}$, more than double the amount from trees in unlimed plots, $3913 \pm 191 \text{ mg kg}^{-1}$. Foliar Mg was more than four times greater in sugar maple foliage from limed plots than from unlimed plots ($2855 \pm 113 \text{ mg kg}^{-1}$ compared with $646 \pm 39 \text{ mg kg}^{-1}$). Only foliar P and N were unaffected by liming for sugar maples sampled in 2006. Foliar K, Al, Mn, and Fe were all significantly less in plots originally limed in 1985 compared with control plots. Foliar N levels were unaffected. Similar results were observed for the 1995 sugar maple foliar analyses; however, foliar Mn in limed plots was much higher, $1083 \pm 144 \text{ mg kg}^{-1}$, in 1995 compared with 2006, $426 \pm 76 \text{ mg kg}^{-1}$.

Black cherry foliar analyses were similar in both 1995 and 2006 on limed and unlimed plots (Table 1). Foliar P, K, Al, Fe, and N concentrations were not significantly affected by liming in either time period. Foliar Ca and Mg were both elevated by liming in 1995, but the difference was not significant for Mg in 2006, despite having a greater concentration, $4688 \pm 359 \text{ mg kg}^{-1}$, in 2006 than in 1995, $3873 \pm 307 \text{ mg kg}^{-1}$. Foliar Mn was reduced by liming in 1995 and 2006, but only the 2006 difference

was significantly different from unlimed sample trees.

Relationships among Water, Soil, and Foliage Chemistry

Soil water nutrient data from lysimeter samples were averaged across the growing season (16 sample dates) from each of the 8 sampled plots (4 limed, 4 unlimed). Spearman rank correlations between soil water chemical constituents and soil exchangeable nutrients from the 1996 sample period showed the highest and most consistent correlations with soil chemistry at the 10- to 15-cm depth, and all chemical parameters had significant correlations except K, Al and the Ca/Al molar ratio (Table 2). Only at the 10- to 15-cm sample depth were both exchangeable Ca and Mg positively correlated with soil solution chemistry.

Spearman rank correlations of 1996 soil water chemistry with 1995 sugar maple foliar nutrients showed positive and significant correlations between soil solution concentrations and foliar concentrations of Ca, Mg, and Mn and the Ca:Al molar ratio (Table 3). Correlations for K (data not shown) and Al in soil water and foliage were all positive but not significant ($P > 0.05$). The Ca/Al molar ratio is a key stress indicator. For black cherry, only the foliar Ca/Al molar ratio was significantly correlated with the soil solution Ca/Al molar ratio (Table 3).

Spearman correlations based on mean foliar nutrients (samples from 1995) and soil chemistry (samples from 1996) for both sugar maple and black cherry are shown in Table 3. For sugar maple, foliar Ca, Mg, and Mn, were positively and significantly correlated with exchangeable Ca, Mg, and Mn in the 0- to 5-cm sample layer. Only exchangeable Mn was significantly and positively correlated at all three sampled depths. For black cherry, only foliar Mg and foliar Mn concentrations were positively correlated with exchangeable levels of these respective elements in soils. None of the correlations between the foliar Ca/Al molar ratio and the soil solution Ca/Al molar ratio was significant for either sugar maple or black cherry (Table 3). Correlations among foliar P, K, and Al and soil exchangeable concentrations of these elements (data not shown) were nonsignificant ($P > 0.05$).

Spearman correlations among soils and foliage nutrients, both sampled in 2006, for sugar maple and black cherry showed different results (Table 3). For sugar maple, the Ca/Al molar ratio in foliage was significantly and positively correlated with exchangeable soil concentrations at all six sampled depths. Foliar

Ca was positively correlated with soil exchangeable Ca at the 0- to 5-cm depth and at the 15- to 25-cm depth. Foliar Mg was positively correlated with soil exchangeable Mg starting in the 10- to 15-cm layer and continuing through the profile to the 35- to 45-cm depth. Foliar Mn was positively correlated with soil exchangeable Mn at the upper three sampled depths. Black cherry showed no significant Ca/Al molar ratio correlations with soil Ca/Al molar ratios (Table 3). Foliar quantities of Ca, Mg, and Mn were positively correlated with soil exchangeable quantities of these nutrients, but only in the upper 5 cm of mineral soil.

These results allow comparisons among soil water and foliar Ca/Al molar ratios, and provide field data to permit assessment of whether indicators provide consistent information. In our study 72% of the soil solution samples from unlimed plots collected during the 1996 growing season had Ca/Al ratios <1.0, and 29% had ratios <0.5. These levels indicate stress and correlate well with crown condition and growth observed during this period (Long et al., 1997, 2011). However, sugar maple foliar Ca/Al ratios from our 1995 foliar samples taken in unlimed plots far exceeded the 12.5 threshold value proposed by Cronan and Grigal (1995). On an individual tree basis, rather than a plot average, foliar Ca/Al ratios averaged 75 ± 6 and ranged from 26 to 148 for unlimed trees ($n = 27$), while Ca/Al ratios averaged 221 ± 11 , and ranged from, 26 to 334 for limed trees ($n = 27$). By 2006, when stress conditions had abated considerably, and with a slightly larger sample size, sugar maple foliar Ca/Al ratios for unlimed trees ($n = 33$) averaged 68 ± 3 and ranged from 42 to 126, while for limed trees ($n = 37$) the ratio averaged 213 ± 7 and ranged from 1190 to 316. Likewise, black cherry Ca/Al molar ratios far exceeded the 12.5 value and the Ca/Al ratio in foliage was not significantly correlated with the soil solution Ca/Al molar ratio.

DISCUSSION

The critical importance of base cation nutrition for maintaining sugar maple health and growth has been shown in other studies (Horsley et al., 2000; Long et al., 2011; Moore et al., 2012). Managers seeking to remediate base poor soils with lime amendments will need to know how much lime to apply and how long an application will be efficacious. The results from our liming study on unglaciated, base poor, soils show that undissolved lime from a one-time application of 22.4 Mg ha^{-1} will persist for more than 15 yr, with beneficial changes in soil chemistry still increasing for 20 yr and as deep as 45 cm in the mineral soil. Since

Table 1. Sugar maple (*Acer saccharum* Marsh.) and black cherry (*Prunus serotina* Ehrh.) mean foliage element concentrations (mg kg^{-1} ; standard error in parentheses) and Ca/Al molar ratio and t test probability levels for comparisons based on means from each replication in limed and unlimed plots in 2006 and 1995.

Element	Sugar maple†			Black cherry‡		
	No lime	Lime	t test Prob. level	No lime	Lime	t test Prob. level
2006§						
Ca	3913 (191)	9519 (549)	<0.001	4952 (72.7)	8485 (354)	0.010
Mg	646 (39)	2855 (113)	<0.001	2279 (1.7)	4688 (359)	0.094
P	1140 (61)	1268 (119)	0.373	1380 (19)	1420 (27)	0.343
K	7657 (204)	6133 (93)	<0.001	11821(1038)	8226 (753)	0.107
Al	38.3 (1.2)	29.7 (1.1)	0.002	26.6 (3.0)	30.2 (4.1)	0.560
Mn	2946 (221)	426 (76)	< 0.001	2160 (70)	627 (77)	0.005
Fe	58.6 (3.6)	43.8 (1.0)	0.008	53.4 (0.9)	50.9 (0.8)	0.175
N	19329 (356)	18906 (172)	0.326	23979 (585)	21972 (372)	0.101
Ca/Al	65 (0.5)	206 (13)	0.008	130 (13)	195 (36)	0.228
1995¶						
Ca	3930 (245)	9074 (290)	< 0.001	5734 (78)	8768 (256)	0.008
Mg	584 (52)	2435 (133)	< 0.001	1924 (38)	3873 (307)	0.024
P	1067 (108)	1378 (90)	0.070	1453 (42)	1414 (79)	0.706
K	7336 (521)	5366 (279)	0.016	13759 (877)	10186 (692)	0.086
Al	38.0 (3.6)	27.6 (0.8)	0.058	28.1 (3.1)	27.3 (1.0)	0.815
Mn	2399 (164)	1083 (144)	< 0.001	2100 (334)	629 (208)	0.065
Fe	62.3 (5.7)	53.1 (0.8)	0.207	60.6 (0.9)	55.6 (1.6)	0.113
N	16020 (600)	17253 (765)	0.134	25260(1020)	21421 (179)	0.066
Ca/Al	74 (5)	221 (4)	< 0.001	141 (17)	217 (15)	0.081

† $n = 4$ for all sugar maple t tests.

‡ $n = 2$ for all black cherry t tests.

§ For sugar maple, 33 trees were sampled in unlimed plots, 37 in limed plots; for black cherry, 33 trees were sampled in unlimed plots and 31 in limed plots.

¶ For sugar maple, 27 trees were sampled in unlimed and limed plots for a total of 54 trees; for black cherry, 20 trees were sampled in unlimed plots and 15 in limed plots.

1996, 11 yr after lime application, exchangeable Ca and Mg have increased in limed plots to more than six times the amounts in unlimed soils, $\approx 2 \text{ cmol}_c \text{ Ca kg}^{-1}$ and $\approx 1 \text{ cmol}_c \text{ Mg kg}^{-1}$, in the upper 5 cm of soil and this increase has been sustained through 2006. This is the first study to report multi-decadal persistence of a lime treatment effect on forest soils in North America.

In the 21-yr period since a 22.4-Mg ha^{-1} dolomitic lime application, a wave of chemical changes has moved through the soil profile at least as deep as 35 to 45 cm. During this time nearly all

Table 2. Spearman correlation coefficients ($n = 8$) of 1996 seasonally averaged soil solution chemical constituents each paired with 1996 plot means of soil exchangeable amounts of Ca, Mg, Mn, and Al, and soil pH and the Ca/Al molar ratio.

Parameter	Sampled soil depths, cm		
	0–5	5–10	10–15
pH	0.79*	0.87**	0.88**
Ca	0.59	0.76*	0.86**
Mg	0.67	0.64	0.76*
Mn	1.00***	1.00***	0.86**
K	0.95***	0.24	0.48
Al	0.57	0.19	0.05
Ca/Al	0.76*	0.76*	0.69

* $P \leq 0.05$.

** $P \leq 0.01$.

*** $P \leq 0.001$.

Table 3. Spearman correlations among foliar concentrations of Ca, Mg, Mn, and Ca/Al molar ratio and soil exchangeable quantities of the same cations and the correlation of 1995 foliar nutrients and 1996 soil solution chemistry from lysimeters. Correlations shown are for foliage sampled in 1995 and lysimeter data from 1996, for foliage sampled in 1995 compared with soils sampled in 1996, and soils and foliage both sampled in 2006.

	Al	Ca	Mg	Mn	Ca/Al
<u>1995 foliage/1996 soil solution</u>					
Sugar maple (<i>Acer saccharum</i> Marsh.) <i>n</i> = 8	0.62	0.86**	0.74*	0.83**	0.79*
Black cherry (<i>Prunus serotina</i> Ehrh.) <i>n</i> = 4	0.40	0.80	0.60	0.80	1.00***
<u>1995 foliage/1996 soils</u>					
	Depth (cm)	Ca	Mg	Mn	Ca/Al
Sugar maple <i>n</i> = 8	0–5	0.90**	0.90**	0.83**	0.57
	5–10	0.69	0.83**	0.83**	0.57
	10–15	0.64	0.57	0.83**	0.62
Black cherry <i>n</i> = 4	0–5	0.80	1.00***	0.80	0.80
	5–10	0.80	0.80	0.80	0.80
	10–15	0.80	0.60	1.00***	0.80
<u>2006 foliage/2006 soils</u>					
Sugar maple <i>n</i> = 8	0–5	0.79*	0.67	0.81*	0.88**
	5–10	0.57	0.69	0.79*	0.81*
	10–15	0.64	0.71*	0.76*	0.83**
	15–25	0.76*	0.74*	0.38	0.83**
	25–35	0.62	0.74*	0.24	0.79*
	35–45	0.59	0.71*	0.19	0.76*
Black cherry <i>n</i> = 4	0–5	1.00***	1.00***	1.00***	0.60
	5–10	0.60	1.00***	0.80	0.60
	10–15	0.60	1.00***	0.80	0.60
	15–25	0.80	0.80	0.40	0.60
	25–35	0.60	0.80	0.80	0.80
	35–45	0.60	0.80	0.80	0.60

* $P \leq 0.05$.

** $P \leq 0.01$.

*** $P \leq 0.001$.

of the originally applied lime has dissolved and is now incorporated into the soil exchange system and vegetation, or leached out of the solum. Exchangeable Ca and Mg have increased and remained elevated at all depths sampled over a 21-yr sampling period. More importantly, the effects of this single lime treatment in 1985, based on samples taken in 2001 and 2006, show both Ca and Mg significantly elevated as deep as 35 to 45 cm in soils from limed plots. Similar increases in exchangeable Ca and Mg were observed 15 yr after dolomitic lime application at the Duchesnay Experimental Forest in Quebec (Moore et al., 2012) where a long-term dose–response liming study showed more modest changes in the upper 10 cm of soil with a 20-Mg ha⁻¹ lime treatment. The differences between these two studies may be related to a slightly higher lime treatment rate in Pennsylvania, differences in organic matter and parent materials, and the difference in application methods. In our study lime was applied across an entire 0.2 ha plot while at Duchesnay individual trees were treated in a 5-m radius around the bole of individual trees.

Other long-term liming studies (Moore et al., 2012; Melvin et al., 2013) have not reported changes in exchangeable Al or Mn, both of which are potentially toxic to trees (Hallett et al., 2006). In our study there were reductions in exchangeable Al and Mn as the soil chemistry changed in response to the 1985 lime applica-

tion. Al concentrations in the upper 5 cm did not decrease significantly until 1993, and by 2001 in the 10- to 15-cm depths and deeper layers, exchangeable Al was significantly reduced in limed plots compared with unlimed plots. At Hubbard Brook Experimental Forest (New Hampshire) a Ca addition using wollastonite (CaSiO₃) significantly reduced exchangeable Al only in the Oa horizon; exchangeable Al in the upper 10 cm of mineral soil was not affected by the Ca addition through 2010, 11-yr post-treatment (Johnson et al., 2014). Reductions in exchangeable Mn concentrations in our study developed more rapidly in the upper 5 cm of mineral soil than did the changes in Al concentrations, but reductions in exchangeable Mn did occur more slowly in the deeper sampled layers and did not become significant until 1993 (5- to 10-cm depth) or 1996 (10- to 15-cm depth).

Unlimed plots showed continued decreases in concentrations of Ca and Mg in the 0- to 5-cm layer, particularly in the 2001 and 2006 samplings, while base cations in the 5- to 10-cm and 10- to 15-cm layers showed little variation over the span of the study. Acidic deposition inputs may continue to deplete base cations in some soils and thus further reduce the capacity of these sites to support base cation

demanding species such as sugar maple. Wet sulfate (SO₄) and nitrate (NO₃) have decreased substantially since the mid-1980s (National Atmospheric Deposition Program, 2015); however, total inorganic N wet+dry deposition remains high at about 10.1 kg ha⁻¹ based on the Community Multiscale Air Quality (CMAQ) model (Butler et al., 2015). On-site factors that may have contributed to temporal dynamics in the unlimed plots include thinning stands to 50% relative density (*sensu* Stout, 1983) in winter 1985–1986 by cutting mainly from below the canopy. As maple decline accelerated in the late 1980s and abated by the mid to late 1990s, dead trees were left on site to decay and decompose. Beech bark disease mortality was evident by 1988, adding fine and coarse woody debris to the forest floor. Other disturbances associated with defoliating insects may also have affected soil nutrients. There were notable defoliations in 1993 and 1994 from elm spanworm (*Ennomous subsignaria* [Hübner]), fall cankerworm (*Alsophila pometaria* [Harris]), and forest tent caterpillar (*Malacosoma disstria* [Hübner]). A very wet 1994 growing season caused an extended outbreak of anthracnose fungi that mainly affected sugar maple (Hall et al., 1999), which may account for additional crown dieback that was observed (Long et al., 2011). This was followed by a major defoliation of black cherry caused by cherry scallop shell moth, *Hydria prunivore*

(Ferguson), in 1995 and 1996. These disturbances all contributed organic materials to the forest floor which decomposed and added nutrients to the mineral soil. Organic matter is a significant source of CEC in forest soils and these additions likely caused a transient increase in the nutrient holding capacity in the soils. Yet, despite these disturbances, temporal trends in soil chemistry on the unlimed plots suggests no sign of recovery from the effects of atmospheric acid deposition.

To decide whether ecosystems are at risk due to depleted base cations or acidified soils, managers and researchers may evaluate soil base cation status or use the Ca/Al molar ratio found in soil solution, foliage, or fine roots (Cronan and Grigal, 1995). Soil solution chemistry, especially the Ca/Al molar ratio, has been a key focus for studies examining the impact of acidic deposition on both aquatic and terrestrial ecosystems (David and Lawrence, 1996; Lawrence et al., 2000). Stress responses of red spruce (*Picea rubens* Sarg.) in the northeastern U.S. during the 1980s and 1990s were linked to soil acidification and mobilization of Ca and Al in the soil solution (Shortle et al., 1997). The use of Ca/Al ratios as an indicator of ecosystem stress has been widely applied based on thresholds established in a comprehensive review of the existing literature (Cronan and Grigal 1995). Soil solution, foliage, and fine root Ca/Al molar ratio thresholds were proposed as indicators of the probability of suffering Al stress (Cronan and Grigal 1995). However, this review relied on published studies where seedlings were grown with hydroponic or artificial media. The authors found that foliar Ca/Al ratios ≤ 12.5 were associated with soil solution Ca/Al molar ratios ≤ 1.0 and both measures were considered to indicate a 50% risk of injury from Al-related toxicity or stress. Foliar Ca/Al ratios of ≈ 6.2 or less and soil solution ratios ≤ 0.5 correspond to a 75% risk of injury from Al-related stresses. Cronan and Grigal (1995) suggest that foliar Ca/Al ratios should not be used as independent indicators of Al stress, but should be assessed in combination with soil solution chemistry.

Our field results do not support the co-occurrence of soil solution Ca/Al ratios ≤ 1.0 and foliar ratios ≤ 12.5 as an indicator of stress for mature sugar maple. While soil solution ratios measured in 1996 in unlimed plots were ≤ 1.0 , indicating a 50% probability of Al stress, foliar Ca/Al ratios were much greater than the 12.5 threshold for a 50% probability of Al stress. A much greater foliar Ca/Al threshold may be a more realistic indicator of stress or sugar maple foliar Ca/Al ratios may not be reliable stress indicators for mature trees. While the assumptions associated with the Cronan and Grigal (1995) foliar threshold guidelines were clearly stated, our data show that it is problematic, at least for mature sugar maple foliage, to extrapolate controlled environment seedling studies to mature trees growing under field conditions. Additionally, black cherry trees growing in these same plots did not have foliar Ca/Al ratios near the 12.5 threshold. We suggest that additional field data are needed to refine the relationship between soil nutrition and foliar Ca/Al ratios, and that this relationship varies by species.

Our data indicate that soil solution chemistry is highly variable both at the site level and through the growing season. Because of this, other more robust indicators should be considered. Bailey et al. (2004) proposed a threshold for healthy sugar maple based on upper B horizon Ca saturation $\geq 2\%$ and Mg saturation $\geq 0.5\%$. In northern Pennsylvania and southern New York, foliar Mg concentrations $< 700 \text{ mg kg}^{-1}$ and two or more moderate to severe defoliations in the preceding 10 yr were associated with moderately to severely declining sugar maple stands (Horsley et al., 2000). Other work in New York, Massachusetts, and Vermont found similar relationships with defoliation and low soil base cation status (Pitel and Yanai, 2014), and stands with above average mortality had low concentrations of Ca ($0.31\text{--}0.46 \text{ cmol}_c \text{ kg}^{-1}$), Mg ($0.06\text{--}0.10 \text{ cmol}_c \text{ kg}^{-1}$), and K ($0.03\text{--}0.05 \text{ cmol}_c \text{ kg}^{-1}$). Other soil thresholds based on 246 sugar maple stands have been developed for diagnosing foliar Ca, K, and P deficiency in Quebec (Quimet et al., 2013). More work is needed to reconcile these different measures with consideration for ease of measurement, repeatability of the analytical methods, and fitting thresholds to different levels of impact, for example, reduction in growth, crown dieback, or excessive mortality.

This liming study provides key insights into the role of base cations in maintaining sugar maple health despite defoliation and drought stressors which induced severe sugar maple crown dieback and mortality in unlimed plots. Beneficial effects from liming on sugar maple crown health and flower and seed production have been documented through 2008 (Long et al., 2011). The impact of the single lime application at a rate of 22.4 Mg ha^{-1} on soil chemistry has persisted for 21 yr and now extends through the soil profile to at least 35 to 45 cm.

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