

# Early Indications of Soil Recovery from Acidic Deposition in U.S. Red Spruce Forests

## Gregory B. Lawrence\*

U.S. Geological Survey  
New York Water Science Center  
425 Jordan Rd.  
Troy, NY 12180

## Walter C. Shortle

USDA Forest Service  
Northern Research Station  
271 Mast Rd.  
Durham, NH 03824

## Mark B. David

Univ. of Illinois  
Dep. of Natural Resources and  
Environmental Sciences  
W-503 Turner Hall  
1102 South Goodwin Ave.  
Urbana, IL 61801

## Kevin T. Smith

USDA Forest Service  
Northern Research Station  
271 Mast Rd.  
Durham, NH 03824

## Richard A. F. Warby

Arkansas State Univ.  
118 South Caraway Rd.  
PO Box 419  
State University, AR 72467

## Andrei G. Lapenis

Univ. at Albany  
Dep. of Geography and Planning  
1400 Washington Ave.  
Albany, NY 12222

Forty to fifty percent decreases in acidic deposition through the 1980s and 1990s led to partial recovery of acidified surface waters in the northeastern United States; however, the limited number of studies that have assessed soil change found increased soil acidification during this period. From existing data, it's not clear whether soils continued to worsen in the 1990s or if recovery had begun. To evaluate possible changes in soils through the 1990s, soils in six red spruce (*Picea rubens* Sarg.) stands in New York, Vermont, New Hampshire, and Maine, first sampled in 1992 to 1993, were resampled in 2003 to 2004. The Oa-horizon pH increased ( $P < 0.01$ ) at three sites, was marginally higher ( $P < 0.1$ ) at one site, and lower ( $P < 0.05$ ) at the New York site. Total C concentrations in Oa horizons decreased ( $P < 0.05$ ) at sites where the pH increased, but the cause is uncertain. Exchangeable Al concentrations in Oa horizons decreased ( $P < 0.05$ ) 20 to 40% at all sites except New York, which showed no change. The Al decrease can be attributed to decreased deposition of  $\text{SO}_4^{2-}$ , which decreased the mobility of Al throughout the upper soil profile. Results indicate a nascent recovery driven largely by vegetation processes.

**Abbreviations:** CEC, cation exchange capacity.

Widespread decline of red spruce trees was well documented in the northeastern United States during the 1970s and 1980s (LeBlanc, 1992), and widespread decline symptoms such as winter injury have been observed as recently as 2003 (Lazarus et al., 2004). The primary causal factor in this decline was determined to be depletion of soil Ca from acidic deposition that resulted in a reduction in cold tolerance, as well as an increase in general tree stress (Halman et al., 2008; Hawley et al., 2006; Minocha et al., 1997; Shortle et al., 1997). Loss of soil Ca did not emerge as the key factor in this problem, however, until confirmation that acidic deposition had in fact decreased the availability of soil Ca, a finding that was not well established until the 21st century. Soil acidification caused by acidic deposition is now recognized as a widespread problem in the northern hemisphere (Rice and Herman, 2012).

Efforts to determine the effects of acidic deposition on soils were hindered by the lack of chemical data on soils that predated 1980; however, soils collected during the earlier phases of acid rain research have led to a growing number of soil resampling studies. In some cases, these studies did not detect changes (Hazlett et al., 2011; Yanai et al., 2000, 2005), but other studies have detected decreases in exchangeable base concentrations over several decades (Bailey et al., 2005; Johnson et al., 2008a; Lawrence et al., 2005), and in some soils, changes were apparent during a single decade (Courchesne et al., 2005; Johnson et al., 2008b).

An opportunity for evaluating acidic deposition effects on soils of red spruce stands in the northeastern United States was provided by soil collections

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\*Corresponding author (glawrenc@usgs.gov)

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made in 1992 and 1993 as part of an investigation to identify the physiological responses of red spruce to changes in soil-Ca availability (Shortle et al., 1997). In the ensuing decade, acidic deposition continued a decreasing trend that dated back to the 1970s, and partial recovery of acidified surface waters became apparent in the region (Kahl et al., 2004). Decreased acidic deposition and less acidic surface waters suggested that recovery in soils would also be observed; however, soil resampling studies indicated that soils in the region were more acidic and Ca depleted in 2001 to 2004 than in 1984 (Johnson et al., 2008a; Warby et al., 2009). We are unaware of any studies in North America that have shown recovery of soils in terms of decreased acidity, decreased exchangeable Al, or increased Ca availability. Deposition levels in North America may not have decreased enough to reverse the depletion of soil Ca or the response of soils may lag behind the response of surface waters. Also, if soil acidification occurred in the first half of the northeastern studies (1984 to about 1993), a leveling off or an increase in soil Ca in the second half of the records might not be apparent from the data collected at these two points in time. Therefore, it's not clear whether soils continued to worsen in the 1990s or if the declining deposition trend had led to the start of soil recovery.

In addition to acidic deposition, climate change was also occurring within the northeastern United States during this period (Hayhoe et al., 2007). The average annual temperature for New York and New England in the 1990s was 0.6°C warmer than the long-term mean of 1900 to 1999 for this region (Huntington et al., 2009), and precipitation increased in some areas within the region (Hayhoe et al., 2007). The effects of climate warming on soils is highly uncertain but would probably accelerate organic decomposition and could increase nutrient cycling and Ca availability (Rustad et al., 2001).

To evaluate possible changes in soils during this period of regional environmental change, soils in red spruce stands first sampled in 1992 to 1993 were resampled in 2003 to 2004. The specific objectives of this study were to: (i) determine if changes in the chemistry of the forest floor and upper mineral soil could be detected in 10 to 12 yr; (ii) investigate possible relationships between trends in atmospheric deposition and changes in soil chemistry; and (iii) determine if changes in climate could have any bearing on the results. The overall purpose was to evaluate these relationships in a variety of northeastern red spruce stands to improve our understanding of anthropogenic effects on soil processes that operate on a decadal time scale.

## MATERIALS AND METHODS

### Study Sites

The six sites where soil samples were collected in 1992 to 1993 were located in the northeastern United States (Fig. 1) in coniferous forests where red spruce was a major species in the canopy. Site selections were made to encompass varying site characteristics by including four physiographic regions in the Northeast where red spruce are common—the Adirondack region of New York, the Green Mountains of Vermont, the White Mountains of New Hampshire, and low-elevation areas of Maine (Lawrence et al., 1997). Red spruce was the most common species at all of these predominantly coniferous sites. At each site, 36 trees were cored (Shortle et al., 1997), which indicated that the stands were mature and uneven aged. At Groton, VT, Howland, ME, and Kossuth, ME, trees 100 to 150 yr old were common. At Bartlett, NH, Crawford Notch, NH, and Big Moose Lake, NY, trees >150 yr old were common. Elevated mortality had occurred at Crawford Notch in the 1970s and 1980s, but appeared to have subsided by the early 1990s. Elevated mortality began at Big Moose Lake in the early 1990s and continued for about a decade. There were no other indications of disturbance or damage to the stands before or during the study at any of the sites.

The general topography at Howland, Kossuth, and Big Moose Lake was flat, whereas the sites at Bartlett, Crawford Notch, and Groton were on middle to lower slope positions in these mountainous areas. The mineralogy of the soil parent material varied from slowly weathering silicates with low to moderate Ca content at Big Moose Lake, Crawford Notch, Kossuth, and Bartlett, to a silicate substrate that contained small amounts of highly weatherable carbonates at Howland and Groton (Lawrence et al., 1997). The soils were all classified as Spodosols, with well-defined E horizons underlying forest floors that ranged widely in thickness from 5 cm at Groton to 21 cm at Big Moose Lake in 2003 to 2004 (Table 1).

Annual values of atmospheric wet deposition of  $\text{SO}_4^{2-}$  at the five National Trends Network sites within the region (Fig. 1) decreased ( $P < 0.05$ ),

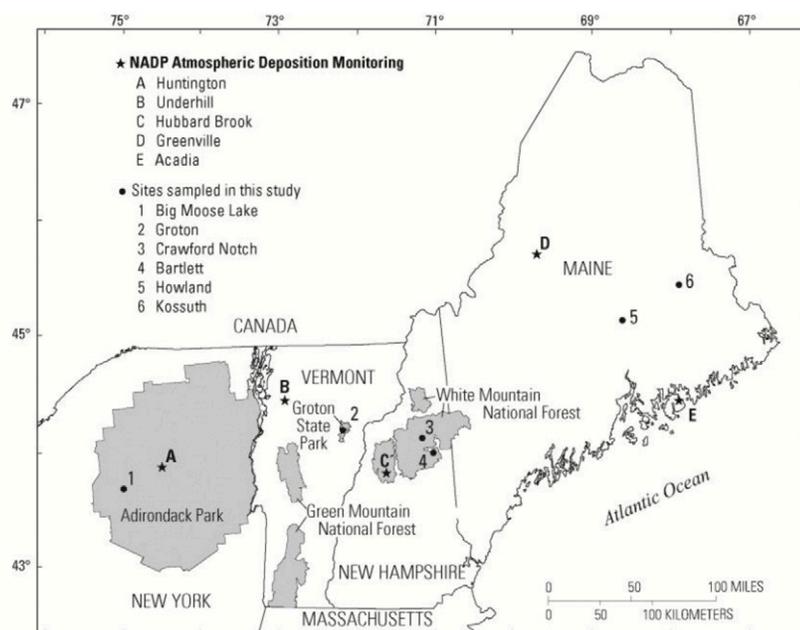


Fig. 1. Locations of study sites and National Trends Network atmospheric deposition monitoring stations, which are part of the National Atmospheric Deposition Program (NADP).

**Table 1. Study site characteristics.**

Site	Location	Elevation	Climate trend <sup>†</sup>		Soil drainage class <sup>‡</sup>	Mean thickness of forest floor <sup>§</sup>
			ΔTemp	ΔPrecip		
		m	°C	cm		cm
Big Moose Lake, NY	43°49'2" N, 74°52'49" W	550	+1.5*	+20*	moderately well	21 (6.2)
Groton, VT	44°15'59" N, 72°19'22" W	510	+1.35*	+24*	somewhat excessively	5 (1.3)
Crawford Notch, NH	44°12'54" N, 71°24'9" W	810	+0.95*	+35*	well	12 (3.0)
Bartlett, NH	44°3'31" N, 71°18'29" W	480	+0.95*	+35*	well	13 (4.0)
Howland, ME	45°12'34" N, 68°44'41" W	80	+2.2*	+6	moderately well	10 (3.5)
Kossuth, ME	45°25'7" N, 67°44'7" W	150	+0.5	+9	well	7 (2.5)

\* Significant at  $P < 0.05$ .

† ΔTemp and ΔPrecip are the total change from 1960 to 2010 for air temperature and precipitation.

‡ Soil drainage classes are defined in Schoeneberger et al. (2002).

§ Combined thickness of Oe and Oa horizons in 2003 and 2004; standard deviations in parentheses.

based on linear regression (normality could not be disproven for any site), by approximately 40% from 1985 to 2003 (Fig. 2). Annual values of atmospheric wet deposition of  $\text{NO}_3^-$  plus  $\text{NH}_4^+$  did not show significant trends at any of the sites between 1985 and 2003, although the Hubbard Brook and Acadia sites showed small but significant decreases ( $P < 0.10$ ) from 1992 to 2003. Most of the decrease in  $\text{SO}_4^{2-}$  deposition occurred after 1990, in large part due to compliance with the Clean Air Act Amendments of 1990, which began in 1992 to 1994 (Driscoll et al., 2001). Atmospheric deposition was not measured at the individual sampling sites but was likely to be lowest at the Maine sites as a result of regional deposition patterns (Ollinger et al., 1993) and lower elevation than at the other sites (Weathers et al., 2006).

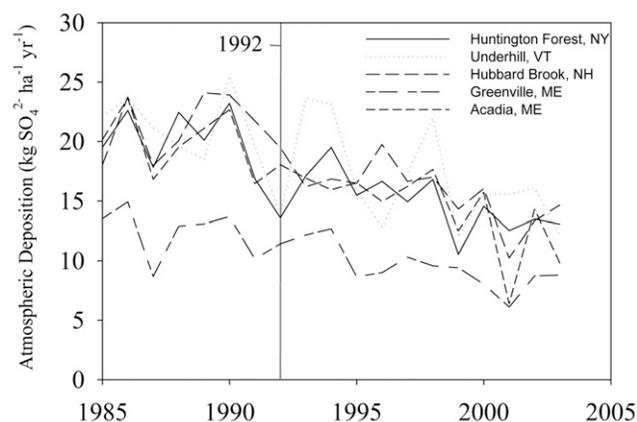
There were NOAA weather stations (Indian Lake, NY; Barre-Montpelier, VT; Pinkham Notch, NH; Orono, ME; Grand Lake Stream, ME) within approximately 50 km of each of the sites. Stations near all of the sites, except Kossuth, showed significant ( $P < 0.05$ ) increases in air temperature (1.0–2.6°C) from 1960 to 2010 (Table 1), and stations near Crawford Notch, Bartlett, Groton, and Big Moose Lake showed significant increases ( $P < 0.05$ ) in precipitation (23–26%) for the same period (Table 1). There was no trend in the Palmer Drought Severity Index for the study region from 1970 to 2000 (<http://www.esrl.noaa.gov/psd/data/gridded/data.pdsi.html>), presumably because the increase in temperature was offset by increased precipitation. The only abnormal weather during the study period (1992–2004) was a drought during 2001, in which precipitation during July and August in New York and New Hampshire and August in Maine were two standard deviations outside of the long-term average for these stations. Temperatures during the summer of 2001, however, were near the long-term averages. The sampling summers of 1992 to 1993 and 2003 to 2004 were near the long-term averages for temperature and precipitation. Monthly averages were used to assess climate trends.

### Sample Collection and Analysis

In 1992, 18 small pits were excavated in groups of three to enable collection of samples from the Oa horizon (middle 8 cm if the Oa was thicker than 10 cm) and the upper 10 cm of the

B horizon at each of the six sites. Soil from the pits within each group of three were combined, by horizon (Oa and upper B), to provide a total of six samples per horizon. Horizon depths were recorded at the time of sampling. Before chemical analysis, the soil samples were used for expelling solution to provide a soil water sample. This involved passing approximately 30 mL of dilute solution, chemically similar to throughfall, through field-moist Oa or B horizon (upper 10 cm) soil. All samples received the same solution. Analysis of the soils determined with and without prior solution expulsion showed that expulsion had no detectable effect on the soil chemistry (Lawrence and David, 1996). All details of the expulsion procedure were given in Lawrence and David (1996).

The soil sampling conducted in 1992 was repeated in 1993 at the same six sites to provide a total of 12 Oa horizon samples and 12 upper B horizon samples from each site. The locations of soil sampling were marked by aluminum tags nailed into trees adjacent to each set of three pits. Sampling was repeated by the same team of investigators in 2003 at Big Moose Lake, Groton, Bartlett, and Crawford Notch and in 2004 at Howland and Kossuth. For resampling, soil was collected from 12 individual pits, resulting in the same 12 samples per horizon as was collected in 1992 and 1993. Horizon depths were again recorded at the time of sampling.



**Fig. 2. Atmospheric deposition of  $\text{SO}_4^{2-}$  at five National Trends Network northeastern U.S. sites from 1984 to 2003.**

In both the 1992 and 1993 sampling and the 2003 to 2004 resampling, soil was collected from the midpoint of the Oa horizon and the upper 10 cm of the B horizon from the face of the excavated pits. In these soils, the upper 10 cm of the B horizon was primarily a Bs1 horizon, but about one-third of the samples included Bh or Bhs horizons, 1 to 3 cm thick, and in a few cases the Bh horizon was up to 9 cm thick. Nearly all pits had a clearly visible E horizon that ranged in thickness from 1 to 20 cm. In 2003 and 2004, a sample from the Oe horizon was also collected in association with each of the 12 pits dug at each site,

All soil samples collected in 1992 and 1993 were air dried and sieved (4 mm for the Oe and Oa horizon samples; 2 mm for the upper B horizon samples) before analysis. These samples were analyzed in 1992 to 1994 for moisture content (oven drying at 65 and 105°C for organic and mineral samples, respectively), exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> (1 mol L<sup>-1</sup> NH<sub>4</sub>Cl extraction), pH (0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> slurry), loss-on-ignition, and total N (Kjeldahl digestion, NH<sub>4</sub><sup>+</sup> analyzer) following USEPA standard methods (Blume et al., 1990), plus exchangeable Al and H<sup>+</sup> (1 mol L<sup>-1</sup> KCl extraction) following the method of Thomas (1982). About 20% of the samples collected in 1992 to 1993 were also analyzed for total C by a LECO C analyzer to develop a relationship between organic C and loss-on-ignition that was used to estimate the total C concentration for the remaining 80% of samples, as described in David (1988). Because there were no measureable amounts of inorganic C in these highly acidic soils, the total C measurement was assumed to represent organic C concentrations. All analyses were conducted under the supervision of Mark David at the University of Illinois. The remaining sample not used in the analyses was stored, air dry, in plastic bags placed in cardboard containers at room temperature.

All samples collected in 2003 and 2004 were analyzed following the same methods used for the 1992 to 1993 samples, with the exception that all samples collected in 2003 and 2004 were analyzed for total N and total C with a Thermo NC analyzer. Analyses of the 2003 and 2004 samples were done under the supervision of Gregory Lawrence in the USGS New York Water Science Center laboratory.

The cation exchange capacity (CEC) was determined as the sum of cations extracted by unbuffered NH<sub>4</sub>Cl and KCl and therefore can be considered the effective CEC. Base saturation was calculated as the sum of exchangeable base cations (Ca<sup>2+</sup>,

Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) divided by the sum of exchangeable base cations plus exchangeable Al and H<sup>+</sup>. Estimates of Oa horizon mass were based on bulk density estimates determined by measurements of loss-on-ignition and the model of Federer et al. (1993), which was based on organic soils that were passed through 2-, 6-, or 12-mm sieves.

All data analyses presented were based on concentrations expressed per unit of soil mass. Data analysis was also done for Oa horizon samples with concentrations expressed per unit of organic matter mass. Only minor differences in results were observed and none that changed the interpretations of the study. Concentrations are presented on a soil mass basis because changes in organic matter concentrations were observed between sampling periods, which would complicate the analysis if concentrations were expressed per organic matter mass. Statistical differences between measurements of the two sampling periods were determined by *t*-test unless the data distribution was non-normal, in which case the Mann-Whitney rank sum test was used.

### Assessment of Analytical Biases and Long-Term Storage Effects

Analysis of the 1992 to 1993 samples by the University of Illinois in 1992 to 1994 were repeated in the USGS laboratory in 2007 to 2008 following procedures identical to those used for the analysis of the samples collected in 2003 to 2004. This was done to compare the results obtained by the two laboratories and to evaluate whether storage altered the sample chemistry.

Most measurements of the 1992 to 1993 samples made in the 1992 to 1994 analyses closely approximated the measurements made in 2007 to 2008 with the exceptions shown in Table 2. In the 2007 to 2008 analysis, exchangeable Ca<sup>2+</sup> concentrations in the upper B horizon were lower for all six sites and significantly lower (*P* < 0.05) for three sites than in the 1992 to 1994 analysis (Table 2). Exchangeable Ca<sup>2+</sup> results for the Oa horizon, however, were not different for any sites (*P* > 0.1). Measurements of exchangeable Al in the upper B horizon were also lower in the 2007 to 2008 analyses than in 1992 to 1994 analyses for all sites and significantly lower (*P* < 0.05) for four sites (Table 2) but were not significantly different for Oa horizon samples for any site. Similarly, measurements of pH for the upper B horizon were significantly lower (*P* <

**Table 2. Means of individual sites for 1992 and 1993 samples analyzed in 1992 and 1994 and reanalyzed in 2007 and 2008 that showed differences in measurements for at least one site.**

Site	Upper B horizon						Oa horizon			
	Ca <sup>2+</sup>		Al		pH		Exchangeable H <sup>+</sup>		Exchangeable H <sup>+</sup>	
	1992–1994	2007–2008	1992–1994	2007–2008	1992–1994	2007–2008	1992–1994	2007–2008	1992–1994	2007–2008
	cmol <sub>c</sub> kg <sup>-1</sup>						cmol <sub>c</sub> kg <sup>-1</sup>			
Big Moose Lake, NY	0.18	0.10	9.9	3.6*	3.93	3.71*	1.60	1.94	15.8	19.8*
Groton, VT	0.32	0.11	1.6	1.3	3.91	3.73*	0.25	0.14*	11.5	16.9*
Crawford Notch, NH	0.30	0.17*	8.0	3.6*	4.46	4.28*	1.10	1.47	14.8	19.0*
Bartlett, NH	0.19	0.10	4.4	2.9*	4.13	3.91*	0.59	0.64	14.9	19.7*
Howland, ME	0.19	0.10*	4.1	2.9	4.15	3.92*	0.50	0.66	13.1	15.6*
Kossuth, ME	0.37	0.21*	6.4	4.4*	3.58	3.39*	0.50	1.21*	11.9	15.3

\* Significantly different values in 2007 and 2008 than in 1992 and 1993 (*P* < 0.05).

0.05) at all sites in the 2007 to 2008 analyses than in the 1992 to 1994 analyses by approximately 0.2 pH units (Table 2), but there were no differences between analyses for the Oa horizon samples. Concentrations of exchangeable H<sup>+</sup> in the B horizon were generally higher in 2007 to 2008 than 1992 to 1994 but were only significantly different ( $P < 0.05$ ) at one site, and one site showed a significant decrease (Table 2). Concentrations of exchangeable H<sup>+</sup> in the Oa horizon were significantly higher ( $P < 0.05$ ) in 2007 to 2008 than in 1992 to 1994 (Table 2) at five of six sites.

In the case of Ca<sup>2+</sup>, the lower concentrations in the upper B horizon soils in the 2007 to 2008 analysis than in the 1992 to 1994 analysis were considered to more probably be the result of analytical factors than changes due to storage. Hazlett et al. (2011) found that storage for 19 yr did not affect exchangeable Ca<sup>2+</sup> concentrations that ranged from approximately 0.05 to 0.9 cmol<sub>c</sub> kg<sup>-1</sup>, and in the study of Bailey et al. (2005), small differences observed in low-Ca<sup>2+</sup> soils after 30 yr of storage were attributable to using buffered extractant for the original analysis and unbuffered extractant for the recent analysis. The study of Blake et al. (2000) also did not show a significant change ( $P > 0.1$ ) in Ca concentrations after long-term storage, although only four samples were analyzed. Some of the differences between laboratory results may have been related to the low concentrations (overall average of 0.13 cmol<sub>c</sub> kg<sup>-1</sup>), which increases the difficulty of making accurate measurements.

The lower concentrations of exchangeable Al in the upper B horizon soils in the 2007 to 2008 analyses than in the 1992 to 1994 analyses were also considered to be more probably the result of analytical factors than storage. The studies of Bailey et al. (2005) and Hazlett et al. (2011) did not observe any storage effects on exchangeable Al concentrations.

Besides the limited number of studies that did not show storage effects on these measurements, we are not aware of any studies that have shown differences in exchangeable concentrations of Ca or Al before and after long-term storage of air-dried soil, other than our results. Participation by the USGS laboratory in interlaboratory comparisons of reference samples (Oa and upper B horizon samples from northeastern forest soils) showed, however, that the differences observed between results from the University of Illinois laboratory and the USGS laboratory are not uncommon among different laboratories.

The small but significant decrease in pH in the B horizon soils after 12 to 14 yr of storage is consistent with the results of Blake et al. (2000) and Bailey et al. (2005). Similarity of results from these independent studies suggests that air-dried storage does have a modest effect on pH values of acidic mineral soils. Although increases in exchangeable H<sup>+</sup> in the B horizon were not significant for most sites (and decreased at one site), they were generally consistent with the clear decreases observed in pH. In the Oa horizon samples, the clear increase in exchangeable H<sup>+</sup> concentrations and the seemingly inconsistent lack of decrease in pH values can be explained by the extremely low range of pH values. Changes in acidity from storage were likely to be large

enough to be seen in exchangeable H<sup>+</sup> measurements but would have needed to be much greater to affect pH measurements <3.0 due to the logarithmic scale.

On the basis of this assessment, the original measurements for pH and exchangeable H<sup>+</sup> of the 1992 to 1993 samples were used to compare with the analysis results of samples collected in 2003 to 2004. For all other measurements, results from the reanalysis of the 1992 to 1993 samples (done in 2007–2008) were used to compare with the results of samples collected in 2003 to 2004, which enabled soil from the original sampling and the resampling to be analyzed in the same laboratory, by the same analysts, thereby providing maximum analytical consistency.

## RESULTS

### Changes from 1992 and 1993 to 2003 and 2004

Statistical differences in soil properties from 1992 and 1993 to 2003 and 2004 were detected at all six sites. Measurements of pH in the Oa horizon in 2003 and 2004 were higher at three sites at  $P < 0.01$ , higher at one site at  $P < 0.1$ , and lower at the Big Moose Lake site ( $P < 0.05$ ) than in 1992 to 1993 (Table 3). At the four sites where pH increased, organic C concentrations significantly decreased ( $P < 0.05$ ), whereas at Big Moose Lake, the one site where the pH decreased, organic C concentrations increased ( $P < 0.01$ ) (Table 3). No change in pH or organic C concentration in the Oa horizon was observed at the Howland site ( $P > 0.05$ ). In the B horizon, no change was detected at any of the sites for pH or organic C concentration ( $P > 0.05$ ), although nonsignificant decreases in organic C concentrations were observed at all sites except Big Moose Lake (Table 3).

Concentrations of Ca<sup>2+</sup> showed no differences ( $P > 0.05$ ) between 1992 to 1993 and 2003 to 2004, with the exception of an increase in the Oa horizon at Kossuth and a decrease in the B horizon at Bartlett (Table 3). Exchangeable Mg<sup>2+</sup> concentrations were higher ( $P < 0.05$ ) in 2003 and 2004 than in 1992 to 1993 in the Oa horizon at Howland (Table 3), but no differences in exchangeable K<sup>+</sup> concentrations were measured in either horizon at any site (not shown). Exchangeable Na<sup>+</sup> concentrations were lower in 2003 and 2004 than in 1992 to 1993 in both horizons at all sites (Table 3). The highly significant decreases in Na<sup>+</sup> concentrations ( $P < 0.01$  for 11 of 12 comparisons) occurred despite the weak adsorption capacity of this ion and the already low concentrations in 1992 to 1993.

Concentrations of organic C in the Oa horizon decreased between the two sampling periods ( $P < 0.05$ ) at four of the sites (Groton, Crawford Notch, Bartlett, and Kossuth) and increased ( $P < 0.05$ ) at Big Moose Lake (Table 3). There were no significant changes in organic C concentrations in the B horizon ( $P > 0.05$ ), but five of the six sites showed nonsignificant decreases and Big Moose Lake showed a nonsignificant increase. As expected, changes in organic matter concentrations between the two sampling periods were similar to those of organic C concentrations. Although not all differences were significant ( $P < 0.1$ ), each site that showed a decrease in organic matter concentration also showed a decrease in organic C concentration

**Table 3. Mean values of soil chemistry measurements of samples collected from 1992 to 1993 and 2003 or 2004 from Oa and upper B horizons.**

Site	Year	pH	C	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Al	H <sup>+</sup>
<u>Oa horizon</u>								
Big Moose Lake, NY	1992–1993	2.56	455	5.8	1.5	0.27	7.6	15.8
	2003	2.38**	51**	7.1	1.9	0.11**	8.5	19.4**
Groton, VT	1992–1993	2.87	476	12.7	2.4	0.28	5.8	11.5
	2003	3.06†	382**	11.6	2.5	0.10**	3.5**	10.8
Crawford Notch, NH	1992–1993	2.62	481	6.2	1.8	0.38	8.0	14.8
	2003	2.98**	429*	6.0	1.6	0.13**	6.3**	14.3
Bartlett, NH	1992–1993	2.63	487	9.5	1.9	0.27	7.5	14.9
	2003	2.89**	441*	8.1	1.8	0.11**	4.7**	14.3
Howland, ME	1992–1993	2.77	456	9.5	2.4	0.37	7.2	13.1
	2004	2.80	475	9.2	3.4*	0.28*	4.4**	14.3
Kossuth, ME	1992–1993	2.87	452	6.3	1.5	0.35	6.4	11.6
	2004	3.01*	396*	9.9**	1.9	0.13**	4.6*	8.5**
<u>Upper B horizon</u>								
Big Moose Lake, NY	1992–1993	3.58	81.2	0.21	0.08	0.08	3.6	1.6
	2003	3.44	94.3	0.21	0.08	0.02**	6.4**	3.4*
Groton, VT	1992–1993	4.46	30.1	0.11	0.03	0.04	1.3	0.25
	2003	4.33	26.6	0.08	0.03	0.02**	1.4	0.33
Crawford Notch, NH	1992–1993	3.91	80.6	0.17	0.07	0.08	3.6	1.1
	2003	3.83	66.4	0.19	0.06	0.02**	3.8	2.0
Bartlett, NH	1992–1993	3.93	32.5	0.10	0.04	0.04	2.9	0.59
	2003	3.94	30.2	0.04*	0.02	0.02**	2.6	0.58
Howland, ME	1992–1993	4.13	45.3	0.10	0.07	0.05	2.9	0.50
	2004	4.27	36.3	0.12	0.05	0.02**	2.2	0.54
Kossuth, ME	1992–1993	4.15	53.5	0.15	0.08	0.06	4.4	0.50
	2004	4.02	50.7	0.10	0.07	0.03**	3.4**	0.50

\* Significant differences between sampling years at  $P < 0.05$ .

\*\* Significant differences between sampling years at  $P < 0.01$ .

† Significant differences between sampling years at  $P \leq 0.1$ .

and vice versa (Tables 3 and 4). Exchangeable Al concentrations showed significant decreases ( $P < 0.05$ ) of 20 to 40% in the Oa horizon between 1992 to 1993 and 2003 to 2004 at all of the sites except Big Moose Lake, which showed no change (Table 3). In the B horizon, exchangeable Al also significantly decreased ( $P < 0.01$ ) at the Kossuth site, but significantly increased ( $P < 0.01$ ) at the Big Moose Lake site, and showed no significant

changes ( $P > 0.05$ ) at the other sites (Table 3). Concentrations of exchangeable H<sup>+</sup> in the Oa horizon were significantly lower at the Kossuth site, significantly higher at the Big Moose Lake site, and showed no other changes in either horizon at any other site.

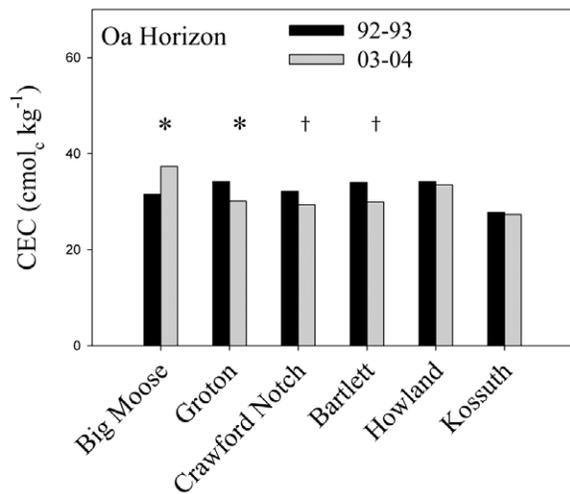
The relatively small increases in pH coupled with the pronounced decreases in exchangeable Al concentrations indicated that the Oa horizon had become less acidic during the

**Table 4. The Oa horizon organic matter (OM) concentrations, horizon thickness, total organic matter content, and differences between sampling years in mass units and percentage for 1992 to 1993 and 2003 to 2004. To emphasize the importance of horizon thickness measurements, values are also shown if no changes in horizon thickness between sampling years is assumed.**

Site	OM concentration		Horizon thickness		Total OM content		Difference	
	1992–1993	2003–2004	1992–1993	2003–2004	1992–1993	2003–2004		
	kg kg <sup>-1</sup> soil		cm		Mg ha <sup>-1</sup>		%	
Big Moose Lake, NY	0.83	0.92*	19.5	16.2*	175.0	161.7	-13	-8
Groton, VT	0.84	0.81	4.7	2.0*	42.8	17.6	-25	-59
Crawford Notch, NH	0.85	0.80†	8.5	5.3	79.0	45.7	-33	-42
Bartlett, NH	0.89	0.79*	8.9	7.8	86.2	66.3	-20	-23
Howland, ME	0.88	0.89	7.1	5.8	67.3	56.6	-11	-16
Kossuth, ME	0.80	0.78	2.5	3.7	21.6	30.6	9	41
<u>No change in thickness</u>								
Big Moose Lake, NY	0.83	0.92*	19.5		175	195	19.9	11.4
Groton, VT	0.84	0.81	4.7		43	41	-1.4	-3.4
Crawford Notch, NH	0.85	0.80†	8.5		79	74	-5.1	-6.5
Bartlett, NH	0.89	0.79*	8.9		86	75	-10.8	-12.5
Howland, ME	0.88	0.89	7.1		67	68	1.1	1.7
Kossuth, ME	0.80	0.78	2.5		22	21	-0.8	-3.5

\* Significant differences between sampling years at  $P < 0.05$ .

† Significant differences between sampling years at  $P \leq 0.1$ .



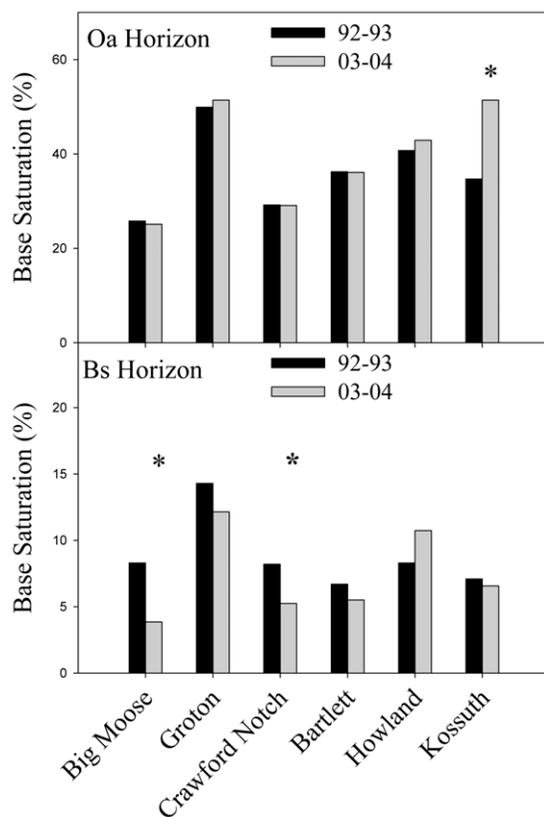
**Fig. 3.** Cation exchange capacity (CEC) of the Oa horizon for the six study sites for the 1992 to 1993 and 2003 to 2004 collection periods. \*Significant differences between sampling years at  $P < 0.05$ . †Significant differences between sampling years at  $P \leq 0.1$ .

10 to 11 yr between sampling at all of the sites except Big Moose Lake, which showed tendencies of becoming more acidic. At Kossuth and Howland, higher concentrations of exchangeable  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  and lower concentrations of exchangeable Al (and  $\text{H}^+$  at Kossuth) indicated some decrease in acidity through increased availability of base cations. At both sites, the sizeable decrease in exchangeable Al concentrations occurred without a change in CEC (Fig. 3). As a result, base saturation increased ( $P < 0.05$ ) at Kossuth and showed a nonsignificant increase ( $P > 0.05$ ) at Howland (Fig. 4).

At Groton, Crawford Notch, and Bartlett, the decrease in Al in the Oa horizons was not coupled with an increase in  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ . The decrease in acidity at these sites was probably from the decrease in organic C concentrations (Table 3), possibly resulting from higher mineralization rates or lower inputs from litterfall and root turnover. Lower organic C concentrations are indicative of lower organic acid concentrations and higher pH (Sullivan et al., 2006). The decrease in exchangeable Al concentrations at these three sites reflected lower CECs (Fig. 3) rather than exchange with base cations. No change in base saturation was observed at the three sites (Fig. 4), although these results do indicate that divalent cations were being conserved while Al was being lost, thereby increasing the relative availability of  $\text{Ca}^{2+}$  (or  $\text{Mg}^{2+}$ ).

In contrast with the other sites, the Oa horizon chemistry at Big Moose Lake indicated greater acidification in some measurements in 2003 to 2004 than in 1992 to 1993. Concentrations of organic C and CEC increased, pH decreased, exchangeable  $\text{H}^+$  increased, and contrary to the other five sites, exchangeable Al did not decrease. Base saturation did not differ between 1992 to 1993 and 2003 to 2004, however, despite increased exchangeable  $\text{H}^+$  concentrations.

In the B horizon, Kossuth was the only site that showed evidence that the soil conditions had become less acidic from 1992 and 1993 to 2003 and 2004, and this was limited to the decrease in exchangeable Al. The lack of significant changes in



**Fig. 4.** Base saturation of the Oa and Bs horizons for the six study sites for the 1992 to 1993 and 2003 to 2004 collection periods. \*Significant differences between sampling years at  $P < 0.05$ .

the B horizon indicated that this horizon was relatively stable between sampling periods, with, again, the exception of Big Moose Lake. The increases in exchangeable Al and exchangeable  $\text{H}^+$  and decrease in base saturation indicated that this soil was considerably more acidic in 2003 than in 1992 to 1993 (Table 3; Fig. 4). A decrease in base saturation was also observed at Crawford Notch ( $P < 0.05$ ), and Bartlett, Groton, and Howland showed nonsignificant decreases (Fig. 4).

## DISCUSSION

### Assessment of Potential Bias from Sampling Inconsistencies

The observed changes in organic C concentrations in the Oa horizon of five of the six sites suggested shifts in the C dynamics of these forests; however, similar changes might have resulted from sampling bias. If sampling in 2003 and 2004 extended deeper than in 1992 to 1993, the mineral fraction of the recent sample could be higher (and the organic C concentration lower) because the Oa horizon overlies the mineral E horizon. The likelihood of this bias was reduced in these soils because the bleached E horizon, readily visible in all profiles, provided a distinctive color contrast to the dark brown to black Oa horizon. More significantly, consistency of sampling was verifiable through comparisons of measurements among horizons. If sampling in 2003 and 2004 extended deeper toward the E horizon than in 1992 to 1993, other characteristics of the E horizon should also be reflected in the more recent samples. For

example, the E horizon has exchangeable  $\text{Ca}^{2+}$  concentrations that are typically an order of magnitude less than the Oa horizon (Likens et al., 1998). Therefore, if some E horizon material was included in the 2003 and 2004 samples but not in the 1992 to 1993 samples, then exchangeable  $\text{Ca}^{2+}$  concentrations, as well as organic C concentrations, would probably be lower in the 2003 and 2004 samples, or at the least an increase in Oa horizon Ca would be less apparent. Lower concentrations of exchangeable  $\text{Ca}^{2+}$  in the Oa horizon were not measured at any of the sites ( $P > 0.1$ ) in 2003 and 2004, however, although both higher  $\text{Ca}^{2+}$  concentrations and lower organic C concentrations were measured at Kossuth (Table 3).

### Relationships to Other Studies of Soil Change

In the northeastern United States, soil acidification for the period between 1984 and 2001 to 2004 was documented by decreases in exchangeable  $\text{Ca}^{2+}$  (Johnson et al., 2008a; Sullivan et al., 2006; Warby et al., 2009), base saturation (Sullivan et al., 2006; Warby et al., 2009), and pH (Warby et al., 2009) and increases in exchangeable Al (Warby et al., 2009). Depletion of  $\text{Ca}^{2+}$  was also documented for the periods between 1930 to 1932 and 1984 (Johnson et al., 2008a) and between 1969 to 1970 and 1987 to 1992 (Lawrence et al., 1995), and increases in acid-extractable Al were documented for the period between 1969 to 1970 and 1987 to 1992 (Lawrence et al., 1995). Other studies in the northeastern United States and eastern Ontario have shown no change in exchangeable  $\text{Ca}^{2+}$  concentrations (Hazlett et al., 2011; Yanai et al., 1999), pH (Hazlett et al., 2011), or exchangeable Al concentrations (Hazlett et al., 2011; Yanai et al., 2005). We believe that our data are the first in North America to show increases in pH and decreases in exchangeable Al concentrations in the Oa horizon. Our results are consistent, however, with the recent Czech study of Oulehle et al. (2011), in which total acidity (exchangeable Al plus  $\text{H}^+$ ) decreased in the Oa horizon from 1994 to 2009 at a site where atmospheric  $\text{SO}_4^{2-}$  deposition decreased approximately 75%. Exchangeable Al concentrations at that site also decreased in the Oa horizon during the same period, although the change was only significant for 1994 to 2003.

The decrease in exchangeable Na concentrations that we observed in both horizons at all sites was also observed by Warby et al. (2009) in the Oa horizon and by Hazlett et al. (2011) in the B horizon. The cause for these changes is not known, but they are not likely to result from acidification or neutralization processes because the soils of Hazlett et al. (2011) showed minimal changes in acid-base status, whereas the soils of Warby et al. (2009) acidified and our Oa horizon soils became less acidic. The trend of increased precipitation (Table 1) at our sites may have played a role in the lowering of Na concentrations. Because these changes have now been documented in three different studies across a large geographical region, further investigation is warranted.

We did not find other reports in North American forests of decreases in total organic matter mass in the Oa horizon similar to our results, but similar results were recently observed in the Czech Republic. In that study, the mass of the Oa horizon

decreased by  $74.2 \text{ Mg ha}^{-1}$  during 16 yr in Norway spruce [*Picea abies* (L.) H. Karst.] stands (Oulehle et al., 2011). Expressed as an annual rate, this decrease of  $4.6 \text{ Mg ha}^{-1} \text{ yr}^{-1}$  is comparable to the rate of  $3.0 \text{ Mg ha}^{-1} \text{ yr}^{-1}$  measured at Crawford Notch, our site with the highest rate of organic matter loss.

In our study, decreases in total organic matter mass during the 11-yr study ranged from 11 to  $33 \text{ Mg ha}^{-1}$ . These values represent large percentages of the total Oa mass (Table 4) but are not unrealistic when compared with rates of organic matter (OM) inputs to the forest floor in spruce forests. In a Maine spruce–fir forest, Rustad and Cronan (1989) measured litterfall inputs of  $2.5 \text{ Mg OM ha}^{-1} \text{ yr}^{-1}$  and coarse woody debris inputs of  $2.7 \text{ Mg OM ha}^{-1} \text{ yr}^{-1}$ . These rates sum to a total input for 11 yr of  $57 \text{ Mg OM ha}^{-1} \text{ yr}^{-1}$ . Furthermore, Gower et al. (2001) showed that belowground net primary production (NPP) of Norway spruce could be approximately twice that of foliage NPP. Therefore, total above- and belowground inputs during 11 yr are of similar magnitude to the total mass of organic matter in the Oa horizon of these soils, which suggests dynamic C cycling with the potential to cause changes in total mass such as those reported in our study and that of Oulehle et al. (2011) in the Czech Republic.

The Oa horizon mass loss was further examined by calculating values under the assumption of no change in horizon thickness (Table 4). When 1992 to 1993 thickness measurements were applied to organic matter concentrations for both 1992 to 1993 and 2003 to 2004, it became apparent that most of the differences between sampling times were due to decreases in the measurements of horizon thickness rather than organic matter concentration. This analysis emphasizes the importance of accurate measurements of horizon thickness for the purpose of estimating mass on an areal basis. Because we made only one measurement of horizon thickness per soil pit, the changes in concentration measurements of organic matter and C provide less uncertainty than the changes in total Oa horizon organic mass.

We present data from only six sites, but when viewed regionally, the pattern of most acidified (Big Moose Lake) to least acidified (Kossuth) from west to east fits the general pattern of acidic deposition that decreases from west to east (Driscoll et al., 2001). Mineralogic analyses were not done at these sites, but the potential was previously estimated to range from low in calcium silicate parent material to moderate in formations that contained small amounts of  $\text{CaCO}_3$  (Lawrence et al., 1997). Despite variation in deposition levels and weathering potential, the direction of changes in the measured soil properties for all the sites, with the notable exception of Big Moose Lake, showed a high degree of similarity. Generally, Oa horizons increased in pH, decreased in Al, and showed no change in  $\text{Ca}^{2+}$ , whereas B horizons exhibited minimal changes in acidification status.

Our B horizon data showed decreases in base saturation that were somewhat similar to the Adirondack data of Sullivan et al. (2006), although decreases were only significant ( $P < 0.05$ ) at Big Moose Lake and Crawford Notch. Differences in our results for the Oa horizon and those of Johnson et al. (2008a) and Warby

et al. (2009) may be related to differences in sampling years. Johnson et al. (2008a) and Warby et al. (2009) collected samples in 1984 and 2001 or 2004, whereas our collections were in 1992 to 1993 and 2003 to 2004. Atmospheric  $\text{SO}_4^{2-}$  deposition in the region showed only a small decrease from 1984 to 1992 but a steeper decline from 1992 to 2003 (Fig. 2). Further soil acidification may have occurred from 1984 up through the mid-1990s that was only partially offset by decreases in acidity in the late 1990s. With our sampling interval, we would have missed most of this period of acidification if it had occurred in this way.

Differing results between this study and the Warby et al. (2009) study may also have been related to vegetation effects on soil properties. Whereas our study was done in spruce-dominated stands with Oa horizons that were, in almost all cases, >4 cm thick, many of the sites in the Warby et al. (2009) study were in deciduous forests with thinner Oa horizons. Therefore, a comparison was made with a subset of nine watersheds from the Warby et al. (2009) study that included only Oa horizons thicker than 4 cm and were sampled in both 1984 and 2001. These data showed higher pH, lower CEC, lower exchangeable Al, and lower total acidity in 2001 than in 1984, although these differences were not significant ( $P > 0.05$ ). These data also showed significant decreases ( $P < 0.05$ ) in exchangeable Ca concentrations, however, and nonsignificant ( $P > 0.05$ ) decreases in base saturation. For samples with C concentrations >40% (which was exceeded by nearly all our samples), Warby et al. (2009) also did not detect decreases in pH or increases in exchangeable Al or total acidity. This comparison raises the possibility that the C content of the forest floor may play a role in the soil acidification and recovery process.

### Processes of Acidification and Recovery

Most assessments of soil change in North America have studied either the Oa horizon or the upper B horizon but not both. With data from both the Oa and upper B horizon, possible interactions between these horizons can be evaluated to interpret acidification and recovery processes. Changes in soil chemistry between the two sampling periods indicate that these soils are becoming less acidic, but these changes represent a nascent recovery. Depletion of  $\text{Ca}^{2+}$  has been identified as the key change resulting from acidic deposition in soils, but the only indication of increased Ca availability was the modest increase in the Oa horizon at Kossuth. The lack of decreases in exchangeable  $\text{Ca}^{2+}$  concentrations, however, can be considered a positive change because it is probable that Ca depletion did occur previously in these soils (Lawrence et al., 1995).

Recovery has generally been viewed as a decrease in  $\text{SO}_4^{2-}$  deposition that is sufficient to lower the  $\text{Ca}^{2+}$  leaching rate below the rate at which  $\text{Ca}^{2+}$  is released through weathering in the B horizon (Driscoll et al., 2001). With increased  $\text{Ca}^{2+}$  availability in the B horizon, acid neutralization increases, Al is no longer mobilized, and exchangeable Al is replaced by  $\text{Ca}^{2+}$  (and other base cations). Base saturation is thereby increased and the CEC may also increase as the pH-dependent charge increases. At our

study sites, however, decreases in Oa horizon exchangeable Al occurred without increases in  $\text{Ca}^{2+}$  availability in the B horizon. Nevertheless, this change may be attributable to decreased acidic deposition (Fig. 2), which lowered  $\text{SO}_4^{2-}$  concentrations in soil solutions and reduced mobilization of Al in the B horizon. Under previous conditions of high Al mobilization, the exchangeable Al concentration in the B horizon increased, and vegetative cycling and hydrologic transport elevated the exchangeable Al concentrations in the Oa horizon as well (Lawrence et al., 1995). The decreasing trend of  $\text{SO}_4^{2-}$  deposition during the interval between sampling periods reduced Al mobilization in the B horizon, thereby decreasing transport from the B to the Oa horizon. Decreased Al mobilization was indicated by a decreasing trend of Al concentrations in soil solutions of the B horizon in the White Mountains of New Hampshire from 1984 to 1998 (Palmer et al., 2004). This trend occurred without concomitant decreases in pH in the soil solution of the B horizon.

The increases in pH observed in the Oa horizon are consistent with decreases in organic C concentrations, but the cause for the decrease in organic C concentrations and mass is less clear. Lower concentrations of  $\text{SO}_4^{2-}$  and associated  $\text{H}^+$  may have increased the solubility of organic matter, which could reduce concentrations of soil organic matter. Increasing trends in concentrations of dissolved organic C in surface waters have been attributed to this mechanism (Monteith et al., 2007). Loss of organic matter at the Czech site was interpreted largely as a remobilization of organic C that had previously accumulated when high levels of atmospheric deposition suppressed decomposition rates (Oulehle et al., 2011). The pH of the Oa horizons at our sites were likely to be too low to show much effect from changes in the acidity of atmospheric deposition (Lawrence et al., 1995). Experiments showing the effects of  $\text{SO}_4^{2-}$  concentrations on the solubility of dissolved organic C suggest, however, that the decreases in atmospheric deposition of  $\text{SO}_4^{2-}$  may have played a role in mobilizing organic C in the Oa horizon (Clark et al., 2006).

Loss of organic C from the Oa horizon could also be related to changes in the C cycle driven by climate warming that was measured in proximity to all the sites, with the possible exception of Kossuth (Table 1). In a climate gradient study in Maine, Simmons et al. (1996) found that the turnover time of forest floor C was 6.1 yr in the coastal region but 11 yr in the northern region, which had significantly lower air temperatures. In this study, soil respiration was also found to increase exponentially with temperature, suggesting that increased temperatures could decrease C storage in the forest floor. Organic C increased at Big Moose Lake, however, despite an increase in temperature. Increases in precipitation occurred at three sites where organic C concentrations decreased but also at Big Moose Lake. Soil moisture measurements at each site would be needed to evaluate the possible effects of increased annual precipitation. Discerning the effects of warming air temperatures and changes in soil moisture from the effects of decreasing concentrations of  $\text{SO}_4^{2-}$

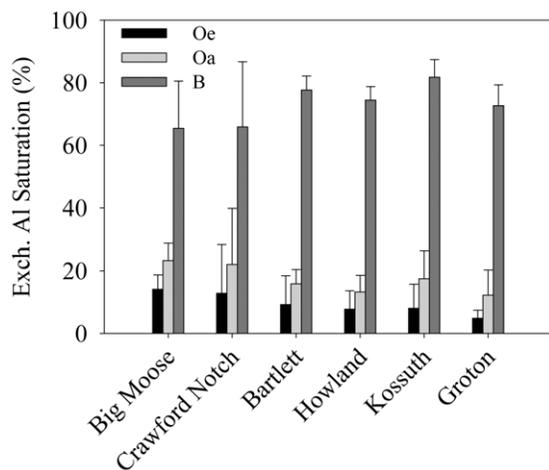


Fig. 5. Exchangeable Al saturation of Oe, Oa, and upper B horizons for the six study sites in 2003 and 2004.

on Oa horizon C concentrations will require more detailed measurements of local conditions.

The results of this study provide insight into the processes involved in the recovery of soils from acidification. The lack of increase in base saturation in the upper B horizon (Fig. 4) between sampling periods indicates that mineral weathering fluxes were not sufficient to increase base availability under the leaching regime of the study period. Vegetation will continue to extract some  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the B horizon, however, even if at very low rates, and other processes such as wood decay by fungi have the capacity to maintain Ca availability in the forest floor at the exclusion of Al by extracting Ca from the mineral soil (Smith et al., 2007).

The role of vegetation in recovery can be seen by comparing values of exchangeable Al in Oe horizons, which are derived almost entirely from litter, woody debris, and fine roots, with those in the Oa and B horizons (Fig. 5). At all sites, Al concentrations were lower in the Oe horizon than in the Oa or B horizons, but differences among sites in the Oe horizon (Fig. 5) tend to reflect the differences among sites in the base saturation of the B horizon in the 2003 and 2004 sampling (Fig. 4). Less mobility of Al within the B horizon resulting from decreased atmospheric deposition of  $\text{SO}_4^{2-}$  lowered the hydrologic inputs of Al into the Oa horizon (Lawrence et al., 1995), and as the Oa horizon decomposed and was replaced by organic matter from the Oe horizon, exchangeable Al concentrations in the Oa horizon were further lowered.

Further analysis of the exchange chemistry of these soils suggests that minimal increases in base saturation in the B horizon will be achieved solely through increases in base availability resulting from declining atmospheric deposition. Concentrations of exchangeable Al as a percentage of the CEC in the upper B horizon were approximately 25 times higher than concentrations of exchangeable Ca for the six sites (Fig. 6), and Al is more strongly attracted to charged surfaces than Ca (Buol et al., 2003). Displacement of adsorbed Al under these conditions would be minimal without high concentrations of Ca in the soil solution (Reuss, 1983). Even with a 40% decrease in atmospheric depo-

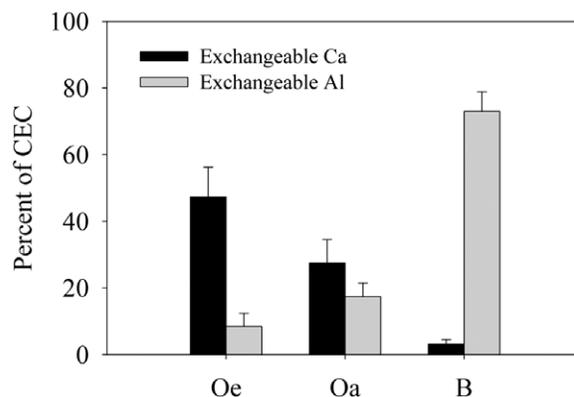


Fig. 6. Exchangeable Ca and Al concentrations ( $\text{cmol}_c \text{kg}^{-1}$ ) expressed as a percentage of the cation exchange capacity (CEC) averaged by horizon for all six study sites in 2003 and 2004.

sition of  $\text{SO}_4^{2-}$  from the mid-1980s to 2003, Ca concentrations remained essentially unchanged at a low level (Table 2). Additional decreases in atmospheric deposition are not likely to cause substantial increases in Ca availability; however, future increases in B-horizon base saturation may be achieved through the creation of new exchange sites as dissolved organic matter from the Oa horizon is immobilized in the B horizon. If atmospheric deposition decreases to levels at which little or no Al is mobilized from bound or solid phases (which appears to have already begun), concentrations of Al in soil solutions will be controlled by exchangeable Al. Without the dissolution of solid-phase Al, the pool of Al available for adsorption will not increase. With the creation of new adsorption sites, however, soil solution enriched in Ca relative to Al that drains from the Oa horizon into the B horizon (as suggested by Fig. 6) will adjust the ratio of Ca to Al in the solution of this horizon, and in doing so, will increase exchangeable Ca concentrations. Decreased Al mobilization through reduction of  $\text{SO}_4^{2-}$  concentrations will be a key component of this process.

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