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Declining Acidic Deposition Begins Reversal of Forest-Soil Acidification in the Northeastern U.S. and Eastern Canada

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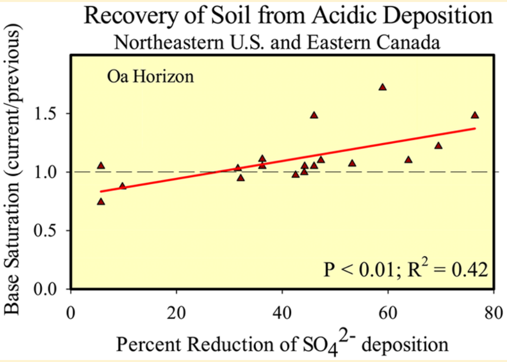
Ⓢ *Supporting Information*

ABSTRACT: Decreasing trends in acidic deposition levels over the past several decades have led to partial chemical recovery of surface waters. However, depletion of soil Ca from acidic deposition has slowed surface water recovery and led to the impairment of both aquatic and terrestrial ecosystems. Nevertheless, documentation of acidic deposition effects on soils has been limited, and little is known regarding soil responses to ongoing acidic deposition decreases. In this study, resampling of soils in eastern Canada and the northeastern U.S. was done at 27 sites exposed to reductions in wet SO_4^{2-} deposition of 5.7–76%, over intervals of 8–24 y. Decreases of exchangeable Al in the O horizon and increases in pH in the O and B horizons were seen at most sites. Among all sites, reductions in SO_4^{2-} deposition were positively correlated with ratios (final sampling/initial sampling) of base saturation ($P < 0.01$) and negatively correlated with exchangeable Al ratios ($P < 0.05$) in the O horizon. However, base saturation in the B horizon decreased at one-third of the sites, with no increases. These results are unique in showing that the effects of acidic deposition on North American soils have begun to reverse.



INTRODUCTION

The acidification of surface waters by acidic deposition and its accompanying effects on aquatic biota have been well documented in North America.[1,2] Reductions in S emissions have resulted in partial chemical recovery of surface waters, expressed by decreased SO_4^{2-}concentrations and increased pH and acid-neutralizing capacity (ANC).[3] However, decreases in base cation concentrations (largely Ca) have limited ANC increases.[2,4] The decrease of base cations in recovering surface waters is in part due to decreased atmospheric deposition of S and N compounds but is also tied to the depletion of base cations in soils from decades of elevated leaching by acidic deposition.[1] Because base cations are necessary to buffer acid inputs, depletion of base cations in soils has increased the vulnerability of both terrestrial and aquatic ecosystems to acidification and slowed the recovery of surface waters.[5,6]

Depletion of base cations in soils, particularly Ca, has also been cited as a contributor to lagging biological recovery of surface waters. Decreased Ca, an essential nutrient, has impaired the growth of key zooplankton species in pelagic food webs,[7] and extremely low base cation concentrations have been linked to reduced health of trout populations in water bodies recovering from acidification.[8] Concentrations of Ca were also found to correlate strongly with benthic algae species composition in rivers being monitored for recovery from acidification.[9]

In terrestrial systems, depletion of soil Ca has been linked to multiple components of forest ecosystems. These effects include reduced cold tolerance[10,11] and general physiological stress[12] in red spruce trees, and poor reproduction, low canopy vigor,[13] elevated branch dieback,[14] and reductions in stand health and growth[15,16] in sugar maple trees. Availability of soil Ca was also found to be a primary controlling factor in (1) the presence and abundance of vascular plant species,[17] (2) snail community richness and abundance,[18] and (3) salamander

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Table 1. Base Saturation (BS) of the Initial Sampling for O and B Horizons, Years of Initial and Final Sampling, and SO_4^{2-} Decline Expressed As the Percent Decrease in Wet Atmospheric Deposition of SO_4^{2-} ($kg\ SO_4^{2-}\ ha^{-1}\ y^{-1}$) from 4 y Prior to Initial Sampling to the Year of Final Sampling[a]

	BS		sampling years		
site	O	B	initial	final	SO_4^{2-} decrease
BB-TMT, CF; 1992−2010	14	5.4	1992−93	2010	9.8
BB-TMT, CF; 1998−2006	21	5.2	1998	2006	5.7
BB-TMT, HW; 1998−2006	50	13	1998	2006	5.7
BB-REF, HW	53	11	1998	2006	36
BB-REF, CF	37	6.3	1998	2006	36
Duchesnay, QC	72	9.4	1989	2009	53
Kossuth, ME	35	7.1	1992−93	2004	46
Howland, ME	40	8.3	1992−93	2004	46
Crawford Notch, NH	28	8.3	1992−93	2003	44
Bartlett, NH	36	6.3	1992−93	2003	44
Sleepers River, VT, MF	56	11	1992−93	2009	44
Groton, VT	50	14	1992−93	2003	32
Buck Creek, NY, HW	29	9.1	1998	2014	59
Buck Creek NY, MF	29	9	1997	2009−10	47
Big Moose Lake, NY	25	8.3	1992−93	2003	43
Little Margaret Lake, ON	80	12	1985	2009	54
Craighurst, ON	100	57	1985	2009	59
Auburn, ON	100	96	1985	2009	56
Turkey Lakes, ON	97	47	1985	2009	64
Kirkland Lake, ON	72	17	1985	2009	64
Flame Lake, ON	69	13	1985	2009	70
Wawa, ON	67	20	1985	2009	76
Dryden, ON	92	18	1985	2009	32
Hubbard Brook, NH	8.7	7.2	1996−98	2009	46
Jeffers Brook, NH	39	20	1996−98	2009	46
Sleepers River, VT, HW	95	24	1996−98	2009	44
Mt. Equinox, VT	100	100	1996−98	2009	29

[a] BB-TMT represents sites at Bear Brook, ME, that were treated with $(NH_4)_2SO_4$; BB-REF represents untreated reference sites. CF, HW, and MF stand for conifer, hardwood, and mixed forest, respectively.

species composition.[18] Furthermore, depletion of Ca has been linked to adverse effects on forest bird species through reduced availability and nutritional value of food sources.[19,20]

In comparison to surface waters, documentation of acidic deposition effects on North American soils has been both sparse and recent, with most literature having been published since 2000. This is due in large part to the relatively recent development of soil resampling as a method of monitoring environmental change.[21] In the northeastern U.S. and Canada, only four studies have included soil data that predate 1980,[22−25] although SO_2 emissions peaked in the U.S. in 1973.[26] Of these studies, Yanai et al.[24] did not detect changes, whereas the other three studies linked acidic deposition to measured increases in soil acidity expressed by one or more of the following: decreased exchangeable Ca, decreased pH, and or increased exchangeable Al. An additional six studies have evaluated soil changes in the northeastern U.S. and Canada over various periods between 1983 and 2005,[27−32] when deposition was decreasing. Of these studies, four measured increases in soil acidity linked to acidic deposition, one study did not detect changes other than decreased exchangeable Na,[30] and one study measured possible recovery expressed as higher pH and lower exchangeable Al in Oa horizons of six northeastern U.S. spruce stands.[28] To our knowledge, Lawrence et al.[28] is the only North American study in which soil-resampling measurements have suggested the onset of soil recovery from acidic deposition. Similar results have been obtained from soil resampling studies in Europe,[33−35] although the number of the studies documenting soil acidification and recovery has also been limited.[36]

Acidification of soil by acidic deposition is conceptualized as the acid leaching of bases at a rate that exceeds soil inputs from weathering and atmospheric deposition.[1] Prior to acidic deposition, naturally low rates of leaching allowed for the gradual increase of base cations in an exchangeable form.[37] Large decreases in acidic deposition may therefore enable soils to restore pools of exchangeable bases reduced during the period of high leaching rates. This conceptualization forms the basis of critical loads modeling for forest soils,[38] which has received heightened attention in recent years as a tool for developing air quality policy.[39−41] However, both the capacity of soils to recover and the time frame needed to achieve recovery remains uncertain.[1,6,41]

To provide needed information on the response of forest soils to declining acidic deposition we applied soil resampling techniques to assess changes in soil chemistry in the northeastern U.S. and eastern Canada, over a wide range of forest soils that had been exposed to varying levels acidic deposition. Data from Lawrence et al.[28] are included with this analysis to investigate recovery of soils through comparison with more recent data and to provide additional data that enables soil changes to be related to acidic deposition decreases across the study region. At each site in our study, acidic deposition decreased over the period between initial and final soil collections, but rates of decrease and lengths of time between soil collections varied among sites. The primary objective of this study was to answer the basic question of whether soils in recent decades have (1) continued to acidify, (2) stabilized, or (3) begun to recover as acidic deposition levels have declined. In addressing this question we also sought to expand our knowledge of soil recovery processes through analysis of this diverse, long-term data set.

■ EXPERIMENTAL METHODS

Study Design. In the U.S., locations of soil sampling extended from coastal Maine through the Adirondack region of New York, and in Canada, from near Quebec City to western Ontario (locations mapped in Figure S1, Supporting Information). Differing sampling designs were included so long as (1) the original sample collection methods were fully documented and repeatable, (2) the location of the original sampling was known, and (3) soil from the original collection had been archived. Although some resampling investigations occurred in close proximity, they were considered individually if site characteristics or methods differed. The resampling investigations defined on this basis are listed in Table 1 and are hereafter referred to as resampling sites. These sites reflected the most common forest types and soil Great Groups of this region (site characteristics listed in Table S1, Supporting Information). At 13 sites, forests were comprised of a variety of sub boreal and boreal conifer species, at 12 sites northern hardwood species predominated, and at 2 sites northern conifer and hardwood species were similarly abundant. Soils were classified in one of five U.S. Great Groups; Haplorthods were the most common. Base saturation in the initial sampling ranged from 25 to 100% in the O horizon (either Oe, Oa, or combined Oe−Oa horizons), and 6.3−100% in the upper B horizon. The earliest soil sampling was done in 1985 at the Ontario sites, and the most recent sampling was done in 2014 at the Buck Creek, NY, hardwood site. The duration between initial and final sampling ranged among sites from 8 to 24 y.

Soil measurements were related to wet (rain and snow) atmospheric deposition of SO_4^{2-} measured at the monitoring station closest to the soil sampling site or, for Ontario sites, calculated by distance weighting deposition values from several proximate stations to account for the large geographical distances. Deposition data for U.S. sites were from the National Atmospheric Deposition Network (http://nadp.sws.uiuc.edu/; accessed June 1, 2015), except for Bear Brook.[42] Ontario data were available from the Canadian Air and Precipitation Monitoring Network (http://www.on.ec.gc.ca/capmon/; accessed January 15, 2015), and Quebec data, from monitoring at Lake St. Clair watershed, Quebec.[43] Because SO_4^{2-} deposition decreased at all study sites, changes in deposition between samplings were expressed as the percent reduction of wet SO_4^{2-} deposition (kg SO_4^{2-} ha^{-1} y^{-1}), calculated as $[1 - [\text{final value}/\text{initial value}] \times 100]$, for the period that extended from 4 y prior to the initial sampling to the year of final sampling (Table 1; Supporting Figure S2). This starting point was used to include prior acidic deposition history, which could possibly affect soil chemistry in the initial collection. Prior deposition was limited to 4 y by data availability.

Atmospheric wet deposition of N (NO_3^- and NH_4^+) also decreased at nearly all sites, but N deposition trends and soil changes were either weakly correlated or uncorrelated and therefore not presented in this paper. This result may be related to a lack of change in N deposition up to about 1996, which was then followed by a distinct decrease. Resampling investigations captured the different deposition phases to varying degrees depending on the sampling interval. In contrast, the trend in SO_4^{2-} deposition showed an approximately linear decrease throughout the records of all sites. The potential for an N fertilization effect may have also complicated relationships with soils. Three of the soil resampling investigations were conducted within an experimental watershed at Bear Brook, ME, referred to as BB-TMT (Table 1). In addition to ambient acidic deposition, this watershed received continuous annual inputs of 1800 eq ha^{-1} of S and N in the form of bimonthly aerial applications of $(NH_4)_2SO_4$, from 1989[42,44] to the year of final sampling (2010). Two additional resampling investigations were also conducted in an adjacent, untreated reference watershed at Bear Brook, ME, referred to as BB-REF (Table 1).

Based on wet SO_4^{2-} data, the decrease in ambient deposition among untreated sites ranged from 31% at Groton, VT, to 76% at Wawa, ON but was minimal (decreases of 5.7−9.8%) at the BB-TMT sites due to the experimental additions (Table 1). Annual deposition of SO_4^{2-} 4 y prior to initial soil sampling ranged between 13 and 30 kg SO_4^{2-} ha^{-1} at all untreated sites except Dryden, where deposition was 6.5 kg SO_4^{2-} ha^{-1} y^{-1}. Deposition data for all sites is summarized in Figure S2, Supporting Information. At the BB-TMT sites the total deposition (ambient plus experimental addition) initially exceeded 100 kg SO_4^{2-} ha^{-1} y^{-1} and was near or above 95 kg SO_4^{2-} ha^{-1} y^{-1} for the years of final soil collection (Figure S2, Supporting Information).

Methods of Collection and Analysis. Through collaborations of the Northeastern Soil Monitoring Cooperative,[21] soil collections of six previous studies that met the necessary criteria were identified for resampling. In each case, resampling and chemical analysis was supervised by an investigator involved in the original sampling to ensure that the initial and final methods were closely replicated. Details of collections and analyses for each resampling investigation are provided in Supporting Information Section S1, Methods of Sampling and Analysis.

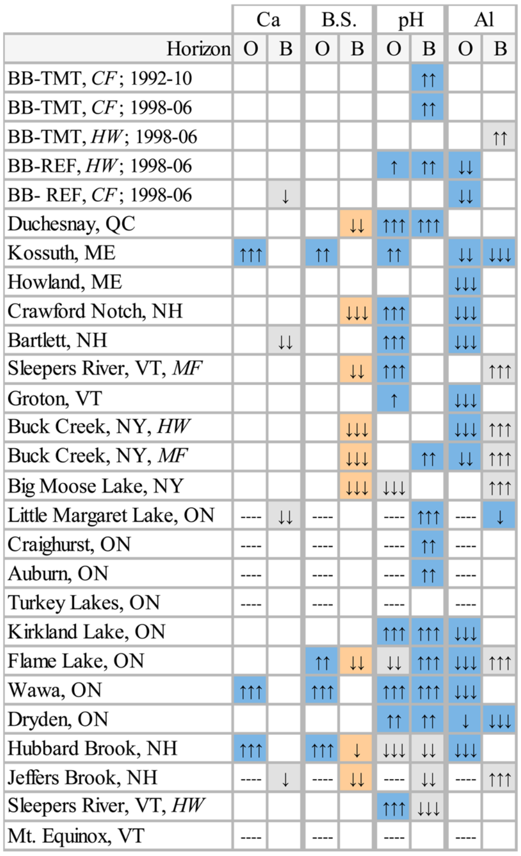
Methods of soil sampling were sufficiently similar among investigations to reflect the chemistry of the O (Oe, Oa, or combined Oe−Oa) and upper B horizons (0−5, 0−10 cm, or the uppermost B subhorizon). Some variation in methods of chemical analysis also occurred among sites, but Oa and B horizon reference samples shared among 15 laboratories, including 4 of the 5 laboratories used in this study, showed that variability in measurements of reference samples among laboratories was similar to that within laboratories for exchangeable Ca, Mg, Na, K, Al, and pH.[45] For all soil resampling studies, base saturation was determined as the sum of exchangeable base cations (Ca, Mg, Na, and K; 1 M NH_4Cl extraction, measurement by ICP) divided by the sum of base cations plus exchangeable acidity (extraction with 1 M NH_4Cl or 1 M KCl; measured by titration or pH probe) with the exception of the Ontario sites where base saturation was based on cation exchange capacity determined by NH_4 replacement[46] At all sites, pH was measured in 0.01 M $CaCl_2$ and Al was determined by extraction with 1 M NH_4Cl or 1 M KCl and measurement by ICP

As a first step, all investigations were evaluated for changes in soil measurements over time, both individually and as a group. Statistical differences between measurements of initial and final soil collections for individual soil investigations were evaluated using two-tailed *t* tests, unless normality was disproven, in which case the Mann−Whitney rank sum test was used. For the sugar maple plots (Supporting Information, Section S1) a one-sample *t* test was used because the initial sampling was not replicated ($n = 1$). For this reason, the test for differences between initial and final sampling measurements at these sites had greater uncertainty than for the other sites because the variance of the initial sampling was unknown and therefore assumed to equal the variance of the final sampling. To determine if changes had occurred if soil investigations were grouped as a whole, paired *t* tests were used on initial and final soil chemical data for all soil investigations except (1) BB-TMT sites, which were excluded because they received the experimental additions of NH_4SO_4, and (2) the sugar maple study sites in which initial values were based on a single pit. Relationships between reductions in atmospheric deposition and ratios of soil chemistry (value of final sampling/value of initial sampling) were evaluated using Pearson Product Moment correlation. The BB-TMT hardwood (HW) and conifer (CF) sites were included in the correlations because they provided additional information on whether soil changes varied as a function of deposition decreases. However, the sugar maple study plots were not included in the correlations due to the lack of replication in the initial sampling.

RESULTS

Changes in Soil Chemistry. The concentration measurements of exchangeable Ca and exchangeable Al will hereafter be referred to as Ca and Al. Comparison of soil measurements between initial and final sample collections revealed numerous statistically significant differences in both O and B horizons and at three or more sites for all soil measurements (Figure 1). Average values obtained in the initial and final sampling for each site are listed in Table S2, Supporting Information). The number of measurements that showed decreased acidification was nearly twice the number that showed increased acidification (Figure 1). Concentrations of Ca showed the least number of differences for individual sites, and the few significant differences seen in the O suggested recovery whereas the few significant differences in the B suggested acidification (Figure 1). When all sites were grouped, there were no significant differences ($p > 0.10$) in O or B horizon Ca concentrations. Mean O horizon values for initial and final samples for grouped sites were 9.7 and 10.7 $\text{cmol}_c\ \text{kg}^{-1}$, respectively, and for the upper B horizon were 1.2 and 1.0 $\text{cmol}_c\ \text{kg}^{-1}$, respectively. These results suggested that Ca concentrations were generally stable across the region for the periods of study.

Decreases in Ca have been commonly observed in previous studies, but few decreases were observed in our study. This difference may be related to more recent sampling windows in our study than in previous studies. The final sampling by Johnson et al.[29] was in 2004, but the initial sampling was in 1984. The earliest sampling in our study was done in 1985 at the Ontario sites, but the final sampling at these sites was in 2009. None of the other previous studies included data more recent than 2001, whereas the final samplings in our study ranged from 2003 to 2014. Our results suggest stabilization or possible reversal of soil Ca depletion.



	Ca		B.S.		pH		Al	
Horizon	O	B	O	B	O	B	O	B
BB-TMT, *CF*; 1992-10						↑↑		
BB-TMT, *CF*; 1998-06						↑↑		
BB-TMT, *HW*; 1998-06								↑↑
BB-REF, *HW*; 1998-06					↑	↑↑	↓↓	
BB- REF, *CF*; 1998-06		↓					↓↓	
Duchesnay, QC				↓↓	↑↑↑	↑↑↑		
Kossuth, ME	↑↑↑		↑↑		↑↑		↓↓	↓↓↓
Howland, ME							↓↓↓	
Crawford Notch, NH				↓↓↓	↑↑↑		↓↓↓	
Bartlett, NH		↓↓			↑↑↑		↓↓↓	
Sleepers River, VT, *MF*				↓↓	↑↑↑			↑↑↑
Groton, VT					↑		↓↓↓	
Buck Creek, NY, *HW*				↓↓↓			↓↓↓	↑↑↑
Buck Creek, NY, *MF*				↓↓↓		↑↑	↓↓	↑↑↑
Big Moose Lake, NY				↓↓↓	↓↓↓			↑↑↑
Little Margaret Lake, ON	----	↓↓	----		----	↑↑↑	----	↓
Craighurst, ON	----		----		----	↑↑	----	
Auburn, ON	----		----		----	↑↑	----	
Turkey Lakes, ON	----		----		----		----	
Kirkland Lake, ON					↑↑↑	↑↑↑	↓↓↓	
Flame Lake, ON			↑↑	↓↓	↓↓	↑↑↑	↓↓↓	↑↑↑
Wawa, ON	↑↑↑		↑↑↑		↑↑↑	↑↑↑	↓↓↓	
Dryden, ON					↑↑	↑↑	↓	↓↓↓
Hubbard Brook, NH	↑↑↑		↑↑↑	↓	↓↓↓	↓↓	↓↓↓	
Jeffers Brook, NH	----	↓	----	↓↓	----	↓↓	----	↑↑↑
Sleepers River, VT, *HW*					↑↑↑	↓↓↓		
Mt. Equinox, VT	----		----		----		----	

Figure 1. Statistical results by site where initial and final measurements increased or decreased at $P \leq 0.1$ (↑ or ↓), $P < 0.05$ (↑↑ or ↓↓), or, $P < 0.01$ (↑↑↑ or ↓↓↓). Empty boxes indicate $P > 0.10$. Dashes indicate that data were not available. Gray shading indicates increased acidification; blue shading indicates decreased acidification. Tan shading indicates increased acidification in the B horizon that may be part of a recovery response. BB-TMT represents sites at Bear Brook, ME, that received experimental additions of $(NH_4)_2SO_4$. BB-REF represents untreated reference sites. CF, HW, and MF stand for conifer, hardwood, and mixed forest, respectively.

In the O horizon base saturation increased at four sites and no decreases were observed, whereas in the B horizon decreases were observed at nine sites and no increases were observed (Figure 1). No changes were observed for the BB-TMT sites. When values for individual sites were grouped, base saturation in the O horizon increased from 49% to 56% ($p < 0.01$). In contrast, values decreased from 19% to 17% ($p < 0.10$) in the B horizon. These results suggest a cessation of Ca depletion in the O but also that declining base saturation in the B horizon remains common within the region. Prior soil resampling studies reporting base saturation are limited, but Warby et al.[31] showed consistent decreases in O horizon base saturation throughout New York and northern New England between 1985 and 2001, and Sullivan et al.,[47] showed decreases in the Adirondack region in the B horizon between the mid-1980s and 2003.

Values of pH in O horizons increased at 11 sites and decreased at three sites (Figure 1), and in B horizons, increased at 12 sites and decreased at three sites (Figure 1). No changes in pH were observed in the O horizon of BB-TMT sites, but an unexpected increase in pH was observed in the B horizon of the BB-TMT CF sites (Figure 1). When sites were grouped, pH in the O increased from 3.06 to 3.26 ($p < 0.05$) and increased in the B from 4.26 to 4.43 ($p < 0.05$). These results were counter to the common decreases in base saturation in the B horizon. No studies other than that of Lawrence et al.[28] have reported pH increases in the O horizon, and none to our knowledge have reported pH increases in the B horizon in the region.

Concentrations of Al in the O horizon decreased at 14 locations and showed no increases, whereas in the B horizon, increases were observed at seven locations and decreases were observed at three locations (Figure 1). At the BB-TMT sites there were no changes other than a decrease in the B horizon of the HW site. When sites were grouped, Al decreased in the O horizon ($p < 0.01$) from 5.9 to 3.5 cmol$_c$ kg^{-1} but was not different ($P > 0.1$) in the B horizon, with initial and final means of 3.2 and 3.3 cmol$_c$ kg^{-1}, respectively. The O horizon Al showed the most consistent recovery response in this study, but in contrast, the B horizon showed mixed responses, with Al increases more common than decreases.

Links between Acidic Deposition and Soil Changes. Among the numerous soil changes identified, some suggested further acidification, some suggested recovery, and some showed no response. This mixed set of results occurred under decreasing deposition levels at all locations, although the magnitude of decreases and the length of time over which they occurred was variable. To investigate a link between atmospheric deposition and soil changes, the ratio of mean soil concentrations (final sampling: initial sampling) was related to the percent reduction in SO_4^{2-} deposition at each site. Results of the BB-TMT sites were included to show effects of minimal decreases in SO_4^{2-} deposition.

Ratios of Ca in the O horizon were positively correlated ($P < 0.05$) with SO_4^{2-} deposition reductions (Figure 2a), although no correlation ($P > 1.0$) was observed if the exceptionally high value for the Wawa site was excluded. Ratios for all soil investigations other than Wawa were clustered around the 1.0 line throughout the range of SO_4^{2-} reduction, with an average ratio of 1.02. Ratios of Ca in the B horizon were not related to the SO_4^{2-} reduction, and most fell below the 1.0 line (Figure 2a). A positive correlation was also observed for base saturation in the O horizon, and this relationship was considerably stronger than that observed for Ca (Figure 2b). In the B horizon, there was no relation between base saturation and SO_4^{2-} reduction, and most ratio values were less than 1.0 (Figure 2b).

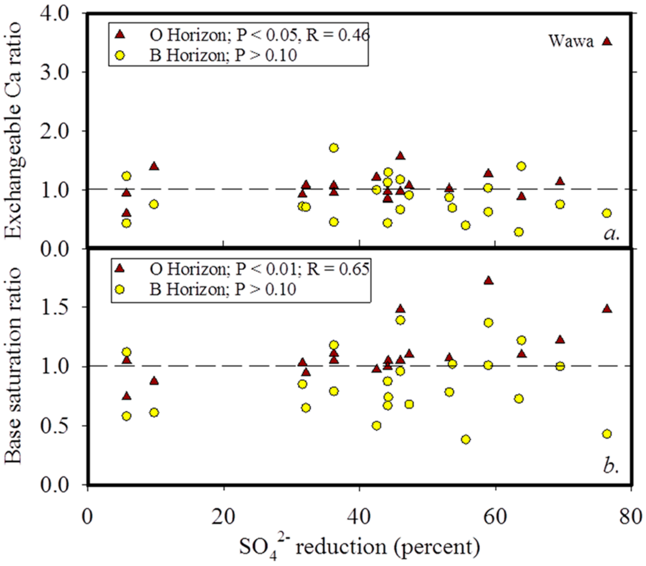


Figure 2. Ratio of site means (final sampling/initial sampling) for (a) Ca (cmol$_c$ kg^{-1}) and (b) base saturation (percent), versus the reduction of wet SO_4^{2-} deposition. The ratio for O horizon Ca at the Wawa site differed greatly from all other sites. SO_4^{2-} reduction is expressed as the percent decrease in wet deposition of SO_4^{2-} (kg SO_4^{2-} ha^{-1} y^{-1}) from 4 y prior to the first sampling to the year of final sampling. A ratio of 1.0 (dashed line) indicates no difference between initial and final soil values. Correlation coefficients (R) are listed for P values <0.10.

Measurements of pH were not correlated with SO_4^{2-} deposition reduction for O or B horizons ($P > 0.1$), although for SO_4^{2-} reductions greater than 40% there was a strong positive correlation (0.74; $P < 0.01$) for the B horizon (Figure 3a). Concentrations of Al showed a strong negative correlation with SO_4^{2-} deposition reduction in the O horizon, and nearly all ratio values were near or below the 1.0 line. In the B horizon there was no correlation for all sites (Figure 3b). For SO_4^{2-} reductions greater than 40%, correlations of −0.84 and −0.61 ($P < 0.01$) were observed for O and B, respectively. The pH and Al results suggest a link between reduction of SO_4^{2-} deposition and a reversal of acidification of O and B horizons within the study region.

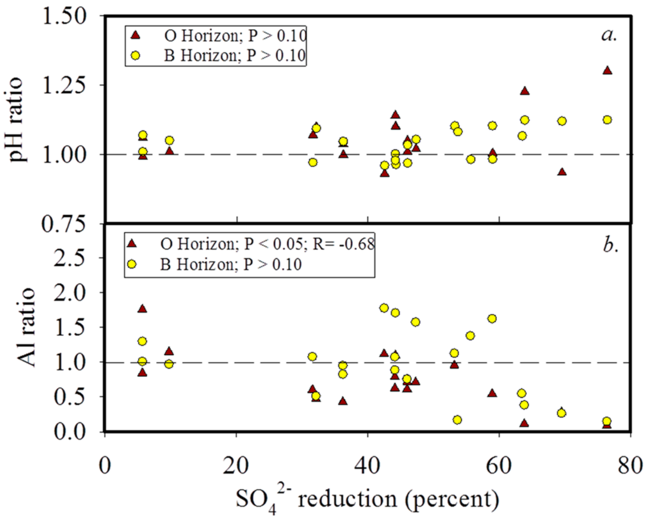


Figure 3. Ratio of site means (final sampling/initial sampling) for (a) pH and (b) Al (cmol$_c$ kg^{-1}), versus the reduction of wet SO_4^{2-} deposition. SO_4^{2-} reduction is expressed as the percent decrease in wet deposition of SO_4^{2-} (kg SO_4^{2-} ha^{-1} y^{-1}) from 4 y prior to the first sampling to the year of final sampling. A ratio of 1.0 (dashed line) indicates no difference between initial and final soil values. Correlation coefficients (R) are listed for P values <0.10.

A link between SO_4^{2-} deposition reductions and decreased Al is further supported by the O horizon results at Bear Brook. At the BB-REF sites, where ambient SO_4^{2-} decreased 36%, Al showed marked decreases that were similar to the average decrease of the other sites (Figure 4). However, at BB-TMT, with SO_4^{2-} decreases of only 5.7%, there were no significant differences in Al in the O horizon. The BB-REF SO_4^{2-} deposition was 15.5 kg SO_4^{2-} ha^{-1} y^{-1} 4 y before the initial sampling and 9.9 kg SO_4^{2-} ha^{-1} y^{-1} in the final sampling year, whereas the BB-TMT SO_4^{2-} deposition was 102 and 96.2 kg SO_4^{2-} ha^{-1} y^{-1} in these same years (1994 and 2006). The BB-TMT resampling for the period 1992/3−2010 also did not show a difference between initial and final sampling (Figure 4). Differences in sampling methods likely account for the higher concentrations measured for the BB TMT 1992/3−2010 resampling than either BB-TMT 1998−2006 resamplings. For

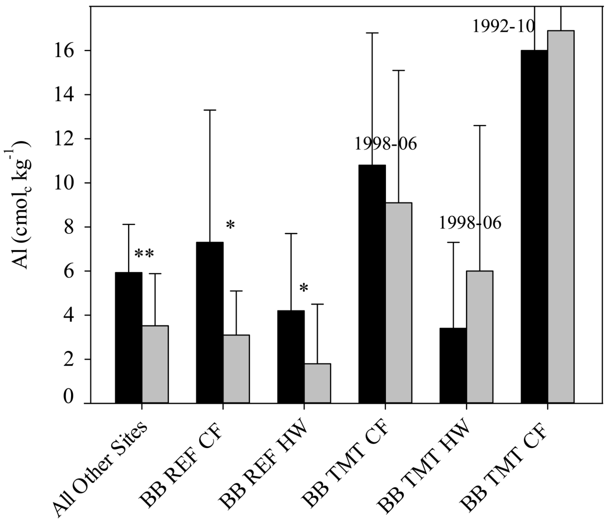


Figure 4. Mean Al concentrations and standard deviations (vertical lines) in O horizons for initial (black) and final (gray) collections for all resampling investigations other than BB-REF sites (untreated reference sites) and BB-TMT (sites treated with $\{NH_4\}_2SO_4^{2-}$). Differing sampling intervals are shown for TMT sites. CF indicates northern conifer stands; HW indicates northern hardwood stands. Significant differences are indicated by ** ($P < 0.01$) and * ($P < 0.05$). Standard deviation lines for BB TMT CF 1992/93 and 2010 extend to 21.7.

the shorter time period, both the Oe and Oa were collected together, whereas for the longer time period only the Oa was collected, which tends to have higher concentrations of Al then the Oe.[28] The Bear Brook results provided further evidence of a link between decreasing SO_4^{2-} deposition and declining Al in the O horizon.

■ DISCUSSION

The overall results of O horizon soil measurements provided strong evidence that acidic deposition is no longer acidifying this horizon and that some of the acidic deposition effects have begun to reverse. This was most evident in the decreases in O horizon Al, as widespread increases had been documented in previous studies.[22,23,29,31] The decrease in O horizon Al was correlated with the increase in pH in the O horizon ($R = -0.43$; $P = 0.07$), and the increase in pH in the B horizon ($R = -0.50$; $P = 0.03$). Although these correlations were similar, they can be attributed to different processes in the respective horizons. The increase in Oa pH increased the solubility of organic matter and associated complexed Al, thereby increasing the opportunity for leaching of organic Al out of the O horizon. In the B horizon, where organic matter concentrations were much lower, abundant mineral surfaces readily adsorb dissolved organic matter, thereby retaining organic-Al complexes received from upper horizons. Increased pH and decreased SO_4^{2-} within the B horizon also likely contributed to decreased mobility of Al in this horizon. The upper B horizon has been previously established as the primary location within the profile where Al was mobilized by acidic deposition through studies of soil processes[23] and measurements of soil waters.[48] Therefore, increases in B-horizon pH would be expected to reduce Al transport from the B into the O horizon through hydrologic and vegetative mechanisms. In sum, the increases in pH of both horizons combined to reduce Al in the O horizon by increasing outputs and decreasing inputs. Decreases in Al without changes in Ca also led to the strong increase in base saturation for grouped data. These soil responses are consistent with trends of increasing organic Al and decreasing inorganic Al in Adirondack lakes.[49]

Like increases in O horizon Al, past increases of exchangeable Al in the B horizon have also been linked to acidic deposition,[22,50] but recovery effects on Al in this horizon are uncertain. The decreases in O horizon Al observed in this study were likely to have increased movement of Al into the B horizon. Accumulation of this Al would contibute to increases in this horizon. Increased movement of Al from the O to the upper B horizon may have contributed to the decrease in B horizon base saturation that was commonly observed. For the B horizon, the increases in pH had the effect of increasing inputs in the B horizon and decreasing outputs, which is the reverse effect of pH increases in the O horizon. Alternatively, the exchangeable phase of Al may have decreased in the B horizon (as seen at three sites) due to reduced solubility from increased pH and an increase in the relative availability of Ca and other base cations in soil solution. Although pH increases in the B horizon were common in our study, Ca availability did not increase in the B horizon. Further monitoring of B horizon soil will be needed to understand the differing responses in the B horizon.

Increases in the mean of ratios of Ca to Al in the O horizon (1.6−3.1 for all sites except BB-TMT) contrasted with decreases found in the B horizon, (0.38−0.30 for the same sites) largely because of the different Al responses between horizons without clear changes in Ca. The decrease of the ratio in the B horizon occurred despite the pH increase. A lack of increase in either O or B horizon Ca may have in part been related to a decreasing trend of atmospheric wet deposition of Ca that was common throughout the study region in the 1980s and was followed by stable levels through the 1990s[51] (http://nadp.sws.uiuc.edu/; accessed June 1, 2015). Further reductions in SO_4^{2-} deposition and/or a greater length of time may be needed to increase B horizon Ca to Al ratios.

The seemingly dynamic nature of Al at these study sites was linked to the low base saturation values of the B horizon measured in the initial samplings. All but five of the sites had base saturation values less than 20% (Table 1), the threshold below which the dominance of cation exchange shifts from Ca to Al.[52] Therefore, most sites were highly susceptible to mobilization of Al by the addition of protons associated with a mobile anionic charge in the form of sulfate. However, the reversal of Al accumulation in the O horizon was not the result of increasing base saturation in the B horizon above this threshold—increases in base saturation were not measured at any site and decreases were common. Furthermore, the increases in soil pH that were seen in the B horizon were not likely to have been sufficient to render Al insoluble in soil solution. Reduced mobilization of Al can be largely attributed to the decrease of SO_4^{-2} concentrations in soil solutions. As a result, the recovery response of Al in the O horizon occurred in advance of any increases in the availability of B horizon Ca. The decrease in base saturation seen in the B horizon can be attributed to increased Al that moved out of the O horizon ($P < 0.01$ at 6 of 9 sites where base saturation decreased), and therefore may be a recovery response. It should be noted that four of the five sites with initial base saturation higher than 20% had O horizons that were too thin for consistent sampling.

Results from the Wawa site provided unique information on recovery processes because this site had the largest reduction in

SO_4^{2-} deposition (76%) as well as the greatest increase in O horizon Ca (Figure 2a, Table S2). Deposition of SO_4^{2-} in the Wawa area was elevated by a local iron sintering plant that lacked emission abatement equipment. Although data are not available, deposition in the 1970s was likely to have been much greater than in the 1980s due to high factory production.[53] The pronounced decline in deposition at the Wawa site[54] resulted in large increases in base saturation and pH, and a large decrease in Al in the Oe horizon ($P < 0.05$), but no change in base saturation or Al ($P > 0.01$) in A or B horizons. Soil data for three samplings are presented for the Wawa site in Figure S3, Supporting Information.

Ongoing release of Ca through mineral weathering under greatly reduced SO_4^{2-} leaching could potentially increase Ca concentrations in the B horizon, but increases in Ca were not observed in this horizon at Wawa. One explanation for this result is suggested by the large increase in Ca concentrations in the Oe horizon. Transfer of Ca from the B to the Oe through biocycling, coupled with recycling within the Oe, may play an important role in limiting increases of Ca in the B under the conditions of decreased SO_4^{2-} leaching. Transfer of Ca from the mineral soil into the forest floor may also be facilitated by decay fungi that bridge these horizons.[55] Shortle et al.[56] found that decay fungi enrich wood residues with Ca to concentrations that approximate those of the surrounding forest floor, while maintaining extremely low concentrations of Al. The high Ca to Al ratio creates a source of Ca that can be readily utilized by trees, thereby enhancing the fertility of the forest floor.

The changes in soils identified in this study were generally consistent across the large study region, over differing time periods, using varying methods of resampling. Responses in the O horizon provided strong evidence that (1) further acidification was not occurring and (2) reversal of Al accumulation was underway at nearly all sites and pH increases were occurring at half of the sites. The response of the B horizon was less clear, however, and not consistent with the conceptual model of recovery that assumes replenishment of bases from weathering as cation leaching fluxes are reduced by decreases in deposition. A more complete understanding of how soil processes are responding to decreasing deposition throughout the profile is needed to determine the capacity of soils to improve Ca availability and the length of time over which this could occur. This study demonstrates the value of long-term soils investigations to understand complex processes in systems with high spatial and temporal variability. Future remeasurements will be essential to determine the trajectory of recovery and what type of new stability might be achieved under lowered acidic deposition levels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02904.

> Section S1: text and references providing details on methods of sampling and analysis. Table S1: characteristics of individual sites. Table S2: mean values and results of tests for differences between initial and final measurements of Ca, base saturation, pH, and Al. Figure S1: map of site locations. Figure S2: atmospheric deposition of all sites, initial and final. Figure S3: trends of atmospheric deposition and soil measurements at Wawa, Ontario, site (PDF)

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Notes

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■ REFERENCES

(1) Driscoll, C. T.; Lawrence, G. B.; Bulger, A. J.; Butler, T. J.; Cronan, C. S.; Eagar, C.; Lambert, K. F.; Likens, G. E.; Stoddard, J. L.; Weathers, K. C. Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies. *BioScience* **2001**, *51* (3), 180−198.

(2) Jeffries, D. S.; Clair, T. A.; Couture, S.; Dillon, P. J.; Dupont, J.; Keller, W.; McNicol, D. K.; Turner, M. A.; Vet, R.; Weeber, R. C. Assessing the recovery of lakes in southeastern Canada from the effects of acidic deposition. *Ambio* **2003**, *32*, 176−182.

(3) Kahl, J. S.; Stoddard, J. L.; Haeuber, R.; Paulsen, S. G.; Birnbaum, R.; Deviney, F. A.; Webb, J. R.; Dewalle, D. R.; Sharpe, W.; Driscoll, C. T.; Herlihy, A. T.; Kellogg, J. H.; Murdoch, P. S.; Roy, K. M.; Webster, K. E.; Urquhart, N. S. Have U.S. surface waters responded to the 1990 Clean Air Act Amendments? *Environ. Sci. Technol.* **2004**, *38*, 484A−490A.

(4) Waller, K.; Driscoll, C. T.; Lynch, J.; Newcomb, D.; Roy, K. M. Long-term recovery of lakes in the Adirondack region of New York to decreases in acidic deposition. *Atmos. Environ.* **2012**, *46*, 56−64.

(5) Rice, K. C.; Herman, J. S. Acidification of Earth: an assessment across mechanisms and scales. *Appl. Geochem.* **2012**, *27*, 1−14.

(6) Likens, G. E.; Driscoll, C. T.; Buso, D. C. Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* **1996**, *272* (5259), 244−246.

(7) Jeziorski, A.; Yan, N. D.; Paterson, A. M.; DeSellas, A. M.; Turner, M. A.; Jeffries, D. S.; Keller, B.; Weeber, R. C.; McNicol, D. K.; Palmer, M. E.; McIver, K.; Arseneau, K.; Ginn, B. K.; Cumming, B. F.; Smol, J. P. The widespread threat of calcium decline in fresh waters. *Science* **2008**, *322*, 1374−1377.

(8) Enge, E.; Kroglund, F. Population density of Brown trout (*Salmo trutta*) in extremely dilute water qualities in mountain lakes in southwestern Norway. *Water, Air, Soil Pollut.* **2011**, *219*, 489−499.

(9) Schneider, S. C. Impact of calcium and TOC on biological acidification assessment in Norwegian rivers. *Sci. Total Environ.* **2011**, *409*, 1164−1171.

(10) Halman, J. M.; Schaberg, P. G.; Hawley, G. J.; Eagar, C. Calcium addition at the Hubbard Brook Experimental Forest increases sugar storage, antioxidant activity and cold tolerance in red spruce. *Tree Physiol.* **2008**, *28*, 855−862.

(11) Hawley, G. J.; Schaberg, P. G.; Eagar, C.; Borer, C. H. Calcium addition at the Hubbard Brook Experimental Forest reduced winter injury to red spruce in a high-injury year. *Can. J. For. Res.* **2006**, *36*, 2544−2549.

(12) Minocha, R.; Long, S. Effects of aluminum on organic acid metabolism and secretion by red spruce cell suspension cultures and the reversal of Al effects on growth and polyamine metabolism by exogenous organic acids. *Tree Physiol.* **2004**, *24*, 55−64.

(13) Sullivan, T. J.; Lawrence, G. B.; Bailey, S. W.; McDonnell, T. C.; Beier, C. M.; Weathers, K. C.; McPherson, G. T.; Bishop, K. Effects of Acidic Deposition and Soil Acidification on Sugar Maple Trees in the Adirondack Mountains, New York. *Environ. Sci. Technol.* **2013**, *47*, 12687−12694.

(14) Schaberg, P. G.; Tilley, J. W.; Hawley, G. J.; DeHayes, D. H.; Bailey, S. W. Associations of calcium and aluminum with the growth and health of sugar maple trees in Vermont. *For. Ecol. Manage.* **2006**, *223*, 159−169.

(15) Long, R. P.; Horsley, S. B.; Hallett, R. A.; Bailey, S. W. Sugar maple growth in relation to nutrition and stress in the Northeastern United States. *Ecol. Appl.* **2009**, *19*, 1454−1466.

(16) Duchesne, L.; Ouimet, R.; Houle, D. Basal area growth of sugar maple in relation to acid deposition, stand health, and soil nutrients. *J. Environ. Qual.* **2002**, *31*, 1676−1683.

(17) Horsley, S. B.; Bailey, S. W.; Ristau, T. E.; Long, R. P.; Hallett, R. A. Linking environmental gradients, species composition, and vegetation indicators of sugar maple health in the northeastern United States. *Can. J. For. Res.* **2008**, *38*, 1761−1774.

(18) Beier, C. M.; Woods, A. M.; Hotopp, K. P.; Gibbs, J. P.; Mitchell, M. J.; Dovciak, M.; Leopold, D. J.; Lawrence, G. B.; Page, B. P. Changes in faunal and vegetation communities along a soil calcium gradient in northern hardwood forests. *Can. J. For. Res.* **2012**, *42*, 1141−1152.

(19) Hames, R. S.; Rosenberg, K. V.; Lowe, J. D.; Barker, S. E.; Dhondt, A. A. Adverse Effects of Acid Rain on the Distribution of the Wood Thrush *Hylocichla mustelina* in North America. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 11235−11240.

(20) Pabian, S. E.; Brittingham, M. C. Terrestrial liming benefits birds in an acidified forest in the Northeast. *Ecol. Appl.* **2007**, *17*, 2184−2194.

(21) Lawrence, G. B.; Fernandez, I.; Richter, D. D.; Ross, D. S.; Hazlett, P. W.; Bailey, S. W.; Ouimet, R.; Warby, R. A. F.; Johnson, A. H.; Lin, H. S.; Kaste, J. M.; Lapenis, A. G.; Sullivan, T. J. Measuring environmental change in forest ecosystems by repeated soil sampling: a North American perspective. *J.Environ. Qual.* **2013**, *42* (3), 623−639.

(22) Bailey, S. W.; Horsley, S. B.; Long, R. P. Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania. *Soil Sci. Soc. Am. J.* **2005**, *69* (3), 681−690.

(23) Lawrence, G. B.; David, M. B.; Shortle, W. C. A new mechanism for calcium loss in forest-floor soils. *Nature* **1995**, *378* (6553), 162−165.

(24) Yanai, R. D.; Siccama, T. G.; Arthur, M. A.; Federer, C. A.; Friedland, A. J. Accumulation and depletion of base cations in forest floors in the northeastern United States. *Ecology* **1999**, *80* (8), 2774−2787.

(25) Johnson, A. H.; Andersen, S. B.; Siccama, T. G. Acid rain and soils of the Adirondacks. 1. Changes in pH and available calcium, 1930−1984. *Can. J. For. Res.* **1994**, *24* (1), 39−45.

(26) *National air pollution trends, 1900−1998*, Report EPA 454/R-00-002; U.S. Environmental Protection Agency: Washington D.C., 2000.

(27) Watmough, S. A.; Dillon, P. J. Major element fluxes from a coniferous catchment in central Ontario, 1983−1999. *Biogeochemistry* **2004**, *67* (3), 369−398.

(28) Lawrence, G. B.; Shortle, W. C.; David, M. B.; Smith, K. T.; Warby, R. A. F.; Lapenis, A. G. Early indications of soil recovery from acidic deposition in U.S. red spruce forests. *Soil Sci. Soc.Am. J.* **2012**, *76*, 1407−1417.

(29) Johnson, A. H.; Moyer, A. J.; Bedison, J. E.; Richter, S. L.; Willig, S. A. Seven decades of calcium depletion in organic horizons of Adirondack forest soils. *Soil Sci. Soc. Am. J.* **2008**, *72*, 1824−1830.

(30) Hazlett, P. W.; Curry, J. M.; Weldon, T. P. Assessing decadal change in mineral soil cation chemistry at the Turkey Lakes Watershed. *Soil Sci. Soc. Am. J.* **2011**, *75*, 287−305.

(31) Warby, R. A. F.; Johnson, C. E.; Driscoll, C. T. Continuing acidification of organic Soils across the Northeastern USA: 1984−2001. *Soil Sci. Soc. Am. J.* **2009**, *73*, 274−284.

(32) Courchesne, F.; Cote, B.; Fyles, J. W.; Hendershot, W. H.; Biron, P. M.; Roy, A. G.; Turmel, M.-C. Recent changes in soil chemistry in a forested ecosystem of southern Quebec, Canada. *Soil Sci. Soc. Am. J.* **2005**, *69*, 1298−1313.

(33) Blake, L.; Goulding, K. W. T.; Mott, C. J. B.; Johnston, A. E. Changes in soil chemistry accompanying acidification over more than 100 years under woodland and grass at Rothamsted Experimental Station, UK. *Eur. J.Soil Sci.* **1999**, *50*, 401−412.

(34) Billett, M. F.; Parker-Jervis, F.; Fitzpatrick, E. A.; Cresser, M. S. Forest soil chemical changes between 1949/50. *J. Soil Sci.* **1990**, *41* (1), 133−145.

(35) Falkengren-Grerup, U.; Linnermark, N.; Tyler, G. Changes in acidity and cation pools of south Swedish Soils between 1949 and 1985. *Chemosphere* **1987**, *16*, 2239−2248.

(36) Arrouays, D.; Bellamy, P. H.; Paustian, K. Soil inventory and monitoring. Current issues and gaps. *Eur. J. Soil Sci.* **2009**, *60*, 721−843.

(37) Fernandez, I. J.; Rustad, L. E.; Norton, S. A.; Kahl, J. S.; Cosby, B. J. Experimental acidification causes soil base cation depletion in a New England forested watershed. *Soil Sci. Soc. Am. J.* **2003**, *67*, 1909−1919.

(38) McNulty, S. G.; Cohen, E. C.; Moore Myers, J. A.; Sullivan, T. J.; Li, H. Estimates of critical acid loads and exceedances for forest soils across the conterminous United States. *Environ. Pollut.* **2007**, *149*, 281−292.

(39) Burns, D. A.; Blett, T.; Haeuber, R.; Pardo, L. H. Critical loads as a policy tool for protecting ecosystems from the effects of air pollutants. *Front. Ecol.Environ.* **2008**, *6*, 156−159.

(40) Ouimet, R.; Arp, P. A.; Watmough, S. A.; Aherne, J.; DeMerchant, I. Determination and mapping critical loads of acidity and exceedances for upland forest soils in Eastern Canada. *Water, Air, Soil Pollut.* **2006**, *172*, 57−66.

(41) Sullivan, T. J.; Cosby, B. J.; Driscoll, C. T.; McDonnell, T. C.; Herlihy, A. T.; Burns, D. A. Target loads of atmospheric sulfur and nitrogen deposition for protection of acid sensitive aquatic resources in the Adirondack Mountains, New York. *Water Resour. Res.* **2012**, *48*, W01547.

(42) Norton, S. A.; Fernandez, I. J.; Haines, T.; Rustad, L.; Nodvin, S. C.; Scofield, J.; Strickland, T.; Erickson, H.; Wigington, P. J.; Lee, J.; Kahl, J. The Bear Brook Watershed, Maine (BBWM), USA. *Environ. Monit. Assess.* **1999**, *55*, 7−51.

(43) Monson, R. K.; Lipson, D. L.; Burns, S. P.; Turnipseed, A. A.; Delany, A. C.; Williams, M. W.; Schmidt, S. K. Winter forest soil respiration controlled by climate and microbial community composition. *Nature* **2006**, *439*, 711−714.

(44) Fernandez, I. J.; Norton, S. A. The Bear Brook Watershed in Maine-The Second Decade. *Environ. Monit. Assess.* **2010**, *171*, 1−2.

(45) Ross, D. S.; Bailey, S. W.; Briggs, R. D.; Curry, J.; Fernandez, I. J.; Fredriksen, G.; Goodale, C.; Hazlett, P. W.; Heine, P. R.; Johnson, C. E.; Larson, J. T.; Lawrence, G. B.; Kolka, R. K.; Ouimet, R.; Pare, D.; Richter, D. D.; Schirmer, C. D.; Warby, R. A. Inter-Laboratory Variation in the Chemical Analysis of Acidic Forest Soil Reference Samples from Eastern North America. *Ecosphere* **2015**, *6* (5), 73 http://dx.doi.org/10.1890/ES14-00209.1,.

(46) Kalra, Y. P.; Maynard, D. G. *Methods manual for forest soil and plant analysis*, Northwest Region Information Report NOR-X-319; Forestry Canada, Northern Forestry Center: Edmonton, AB, 1991.

(47) Sullivan, T. J.; McDonnell, T. C.; Nowicki, N. A.; Snyder, K. U.; Sutherland, J. W.; Fernandez, I. J.; Herlihy, A. T.; Driscoll, C. T. Acid-base characteristics of soils in the Adirondack Mountains, New York. *Soil Sci. Soc. Am. J.* **2006**, *70* (1), 141−152.

(48) Cronan, C. S.; Schofield, C. L. Relationships between aqueous aluminum and acidic deposition in forested watersheds of North

America and Northern Europe. *Environ. Sci. Technol.* **1990**, *24*, 1100−1105.

(49) Lawrence, G. B.; Dukett, J. E.; Houck, N.; Snyder, P.; Capone, S. B. Increases in Dissolved Organic Carbon Accelerate Loss of Toxic Al in Adirondack Lakes Recovering from Acidification. *Environ. Sci. Technol.* **2013**, *47*, 7095−7100.

(50) Lawrence, G. B.; Lapenis, A. G.; Berggren, D.; Aparin, B. F.; Smith, K. T.; Shortle, W. C.; Bailey, S. W.; Varlyguin, D. L.; Babikov, B. Climate dependency of tree growth suppressed by acid deposition effects on soils in Northwest Russia. *Environ. Sci. Technol.* **2005**, *39*, 2004−2010.

(51) Ouimet, R.; Duchesne, L. Dépôts atmosphériques dans les forêts du Québec. Retombées actuelles et tendances au cours des 30 dernières années. *Nat. Can.* **2009**, *133*, 56−64.

(52) Reuss, J. O. Implications of the calcium-aluminum exchange system for the effect of acid precipitation on soils. *J.Environ. Qual.* **1983**, *12*, 591−595.

(53) *Countdown Acid Rain: Ontario's Acid Gas Control Program for 1986−1994*; Environment Ontario, 1985.

(54) Jeziorski, A.; Keller, B.; Paterson, A. M.; Greenaway, C. M.; Smol, J. P. Aquatic ecosystem responses to rapid recovery from extreme acidification and metal contamination in lakes near Wawa, Ontario. *Ecosystems* **2013**, *16*, 209−223.

(55) Thompson, T. A.; Thorn, R. G.; Smith, K. T. *Hypholoma lateritium* isolated from coarse woody debris, the forest floor, and mineral soil in a deciduous forest in New Hampshire. *Botany* **2012**, *90*, 457−464.

(56) Shortle, W. C.; Smith, K. T.; Jellison, J.; Schilling, J. S. Potential of decaying wood to restore root-available base cations in depleted forest soils. *Can. J. For. Res.* **2012**, *42*, 1015−1024.

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