

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

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

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## 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  $\text{SO}_4^{2-}$  deposition of 5.7% to 76%, over intervals of 8 to 24 years. 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  $\text{SO}_4^{2-}$  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.

## 1 Introduction

2  
3 The acidification of surface waters by acidic deposition and its accompanying effects on  
4 aquatic biota have been well documented in North America<sup>1,2</sup>. Reductions in S emissions have  
5 resulted in partial chemical recovery of surface waters, expressed by decreased  $\text{SO}_4^{2-}$   
6 concentrations and increased pH and acid-neutralizing capacity (ANC)<sup>3</sup>. However, decreases in  
7 base cation concentrations (largely Ca) have limited ANC increases<sup>2,4</sup>. The decrease of base  
8 cations in recovering surface waters is in part due to decreased atmospheric deposition of S and  
9 N compounds, but is also tied to the depletion of base cations in soils from decades of elevated  
10 leaching by acidic deposition<sup>1</sup>. Because base cations are necessary to buffer acid inputs,  
11 depletion of base cations in soils has increased the vulnerability of both terrestrial and aquatic  
12 ecosystems to acidification and slowed the recovery of surface waters<sup>5,6</sup>.

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

19 In terrestrial systems, depletion of soil Ca has been linked to multiple components of  
20 forest ecosystems. These effects include reduced cold tolerance<sup>10, 11</sup> and general physiological  
21 stress<sup>12</sup> in red spruce trees, and poor reproduction, low canopy vigor<sup>13</sup>, elevated branch dieback  
22<sup>14</sup>, and reductions in stand health and growth<sup>15, 16</sup> in sugar maple trees. Availability of soil Ca  
23 was also found to be a primary controlling factor in (1) the presence and abundance of vascular  
24 plant species<sup>17</sup>, (2) snail community richness and abundance<sup>18</sup>, and (3) salamander species  
25 composition<sup>18</sup>. Furthermore, depletion of Ca has been linked to adverse effects on forest bird  
26 species through reduced availability and nutritional value of food sources<sup>19, 20</sup>.

27 In comparison to surface waters, documentation of acidic deposition effects on North  
28 American soils has been both sparse and recent, with most literature having been published since  
29 2000. This is due in large part to the relatively recent development of soil resampling as a  
30 method of monitoring environmental change<sup>21</sup>. In the northeastern U.S. and Canada, only four  
31 studies have included soil data that predate 1980<sup>22-25</sup>, although SO<sub>2</sub> emissions peaked in the U.S.  
32 in 1973<sup>26</sup>. Of these studies, Yanai et al.<sup>24</sup> did not detect changes, whereas the other three  
33 studies linked acidic deposition to measured increases in soil acidity expressed by one or more of  
34 the following: decreased exchangeable Ca, decreased pH, and or increased exchangeable Al. An  
35 additional six studies have evaluated soil changes in the northeastern U.S. and Canada over  
36 various periods between 1983 and 2005<sup>27-32</sup>, when deposition was decreasing. Of these  
37 studies, four measured increases in soil acidity linked to acidic deposition, one study did not  
38 detect changes other than decreased exchangeable Na<sup>30</sup>, and one study measured possible  
39 recovery expressed as higher pH and lower exchangeable Al in Oa horizons of six northeastern  
40 U.S. spruce stands<sup>28</sup>. To our knowledge, Lawrence et al.<sup>28</sup> is the only North American study in  
41 which soil-resampling measurements have suggested the onset of soil recovery from acidic  
42 deposition. Similar results have been obtained from soil resampling studies in Europe<sup>33-35</sup>,  
43 although the number of the studies documenting soil acidification and recovery has also been  
44 limited<sup>36</sup>.

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

54 To provide needed information on the response of forest soils to declining acidic  
55 deposition we applied soil resampling techniques to assess changes in soil chemistry in the  
56 northeastern U.S. and eastern Canada, over a wide range of forest soils that had been exposed to  
57 varying levels acidic deposition. Data from Lawrence et al.<sup>28</sup> are included with this analysis to  
58 investigate recovery of soils through comparison with more recent data and to provide additional  
59 data that enables soil changes to be related to acidic deposition decreases across the study region.  
60 At each site in our study, acidic deposition decreased over the period between initial and final  
61 soil collections, but rates of decrease and lengths of time between soil collections varied among  
62 sites. The primary objective of this study was to answer the basic question of whether soils in  
63 recent decades have (1) continued to acidify, (2) stabilized, or (3) begun to recover as acidic

64 deposition levels have declined. In addressing this question we also sought to expand our  
65 knowledge of soil recovery processes through analysis of this diverse, long-term data set.

66

## 67 **Experimental Methods**

68

### 69 Study design

70 In the U.S., locations of soil sampling extended from coastal Maine through the  
71 Adirondack region of New York, and in Canada, from near Quebec City to western Ontario  
72 (locations mapped in Figure S1, Supporting Information). Differing sampling designs were  
73 included so long as (1) the original sample collection methods were fully documented and  
74 repeatable, (2) the location of the original sampling was known, and (3) soil from the original  
75 collection had been archived. Although some resampling investigations occurred in close  
76 proximity, they were considered individually if site characteristics or methods differed. The  
77 resampling investigations defined on this basis are listed in Table 1 and are hereafter referred to  
78 as resampling sites. These sites reflected the most common forest types and soil Great Groups of  
79 this region (site characteristics listed in Table S1, Supporting Information). At 13 sites, forests  
80 were comprised of a variety of sub boreal and boreal conifer species, at 12 sites northern  
81 hardwood species predominated, and at 2 sites northern conifer and hardwood species were  
82 similarly abundant. Soils were classified in one of five U.S. Great Groups; Haplorthods were the  
83 most common. Base saturation in the initial sampling ranged from 25 to 100 percent in the O  
84 horizon (either Oe, Oa, or combined Oe-Oa horizons), and 6.3 to 96 percent in the upper B  
85 horizon. The earliest soil sampling was done in 1985 at the Ontario sites and the most recent  
86 sampling was done in 2014 at the Buck Creek, NY hardwood site. The duration between initial  
87 and final sampling ranged among sites from 8 years to 24 years.

88 Soil measurements were related to wet (rain and snow) atmospheric deposition of  $\text{SO}_4^{2-}$   
89 measured at the monitoring station closest to the soil sampling site or, for Ontario sites,  
90 calculated by distance weighting deposition values from several proximate stations to account for  
91 the large geographical distances. Deposition data for U.S. sites were from the National  
92 Atmospheric Deposition Network (<http://nadp.sws.uiuc.edu/>; accessed June 1, 2015), except for  
93 Bear Brook<sup>42</sup>. Ontario data were available from the Canadian Air and Precipitation Monitoring  
94 Network (<http://www.on.ec.gc.ca/capmon/>; accessed January 15, 2015) and Quebec data from  
95 monitoring at Lake St. Clair watershed, Quebec<sup>43</sup>. Because  $\text{SO}_4^{2-}$  deposition decreased at all  
96 study sites, changes in deposition between samplings were expressed as the percent reduction of  
97 wet  $\text{SO}_4^{2-}$  deposition ( $\text{kg SO}_4^{2-} \text{ ha}^{-1} \text{ y}^{-1}$ ), calculated as  $[1 - [\text{final value} / \text{initial value}] * 100]$ , for the  
98 period that extended from 4 years prior to the initial sampling to the year of final sampling  
99 (Table 1; Supporting Figure S2). This starting point was used to include prior acidic deposition  
100 history, which could possibly affect soil chemistry in the initial collection. Prior deposition was  
101 limited to four years by data availability.

102 Atmospheric wet deposition of N ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) also decreased at nearly all sites, but  
103 N deposition trends and soil changes were either weakly correlated or uncorrelated and therefore  
104 not presented in this paper. This result may be related to a lack of change in N deposition up to  
105 about 1996, which was then followed by a distinct decrease. Resampling investigations captured  
106 the different deposition phases to varying degrees depending on the sampling interval. In  
107 contrast, the trend in  $\text{SO}_4^{2-}$  deposition showed an approximately linear decrease throughout the  
108 records of all sites. The potential for an N fertilization effect may have also complicated  
109 relationships with soils. Three of the soil resampling investigations were conducted within an

110 experimental watershed at Bear Brook, ME, referred to as BB-TMT (Table 1). In addition to  
111 ambient acidic deposition, this watershed received continuous annual inputs of 1800 eq ha<sup>-1</sup> of S  
112 and N in the form of bi-monthly aerial applications of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, from 1989<sup>42,44</sup> to the year of  
113 final sampling (2010). Two additional resampling investigations were also conducted in an  
114 adjacent, untreated reference watershed at Bear Brook, ME, referred to as BB-REF (Table 1).

115 Based on wet SO<sub>4</sub><sup>2-</sup> data, the decrease in ambient deposition among untreated sites ranged  
116 from 31 percent at Groton, VT, to 76 percent at Wawa, ON, but was minimal (decreases of 5.7 to  
117 9.8 percent) at the BB-TMT sites due to the experimental additions (Table 1). Annual deposition  
118 of SO<sub>4</sub><sup>2-</sup> four years prior to initial soil sampling ranged between 13 and 30 kg SO<sub>4</sub><sup>2-</sup> ha<sup>-1</sup> at all  
119 untreated sites except Dryden, where deposition was 6.5 kg SO<sub>4</sub><sup>2-</sup> ha<sup>-1</sup> y<sup>-1</sup>. Deposition data for  
120 all sites is summarized in Figure S2, Supporting Information. At the BB-TMT sites the total  
121 deposition (ambient plus experimental addition) initially exceeded 100 kg SO<sub>4</sub><sup>2-</sup> ha<sup>-1</sup> y<sup>-1</sup> and was  
122 near or above 95 kg SO<sub>4</sub><sup>2-</sup> ha<sup>-1</sup> y<sup>-1</sup> for the years of final soil collection (Figure S2, Supporting  
123 Information).

124

### 125 Methods of collection and analysis

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

132 Methods of soil sampling were sufficiently similar among investigations to reflect the  
133 chemistry of the O (Oe, Oa, or combined Oe-Oa) and upper B horizons (0-5 cm, 0-10 cm or the  
134 uppermost B subhorizon). Some variation in methods of chemical analysis also occurred among  
135 sites, but Oa and B horizon reference samples shared among 15 laboratories, including four of  
136 the five laboratories used in this study, showed that variability in measurements of reference  
137 samples among laboratories was similar to that within laboratories for exchangeable Ca, Mg, Na,  
138 K, Al, and pH.<sup>45</sup> For all soil resampling studies, base saturation was determined as the sum of  
139 exchangeable base cations (Ca, Mg, Na, and K; 1 M NH<sub>4</sub>Cl extraction, measurement by ICP)  
140 divided by the sum of base cations plus exchangeable acidity (extraction with 1 M NH<sub>4</sub>Cl or 1 M  
141 KCl; measured by titration or pH probe) with the exception of the Ontario sites where base  
142 saturation was based on cation exchange capacity determined by NH<sub>4</sub> replacement<sup>46</sup>. At all sites  
143 pH was measured in 0.01 M CaCl<sub>2</sub> and Al was determined by extraction with 1 M NH<sub>4</sub>Cl or 1 M  
144 KCl and measurement by ICP.

145 As a first step, all investigations were evaluated for changes in soil measurements over  
146 time, both individually and as a group. Statistical differences between measurements of initial  
147 and final soil collections for individual soil investigations were evaluated using two-tailed T-  
148 tests, unless normality was disproven, in which case the Mann-Whitney rank sum test was used.  
149 For the sugar maple study plots a one-sample T-test was used because the initial sampling was  
150 not replicated (n=1). For this reason, the test for differences between initial and final sampling  
151 measurements at these sites had greater uncertainty than for the other sites because the variance  
152 of the initial sampling was unknown and therefore assumed to equal the variance of the final  
153 sampling. To determine if changes had occurred if soil investigations were grouped as a whole,  
154 paired T-tests were used on initial and final soil chemical data for all soil investigations except  
155 (1) BB-TMT sites, which were excluded because they received the experimental additions of

156  $\text{NH}_4\text{SO}_4$ , and (2) the sugar maple study sites in which initial values were based on a single pit.  
157 Relationships between reductions in atmospheric deposition and ratios of soil chemistry (value of  
158 final sampling/value of initial sampling) were evaluated using Pearson Product Moment  
159 correlation. The BB-TMT hardwood (HW) and conifer (CF) sites were included in the  
160 correlations because they provided additional information on whether soil changes varied as a  
161 function of deposition decreases. However, the sugar maple study plots were not included in the  
162 correlations due to the lack of replication in the initial sampling.

163

## 164 **Results**

165

### 166 Changes in Soil Chemistry

167 The concentration measurements of exchangeable Ca and exchangeable Al will hereafter  
168 be referred to as Ca and Al. Comparison of soil measurements between initial and final sample  
169 collections revealed numerous statistically significant differences in both O and B horizons and  
170 at three or more sites for all soil measurements (Figure 1). Average values obtained in the initial  
171 and final sampling for each site are listed in Table S2, Supporting Information). The number of  
172 measurements that showed decreased acidification was nearly twice the number that showed  
173 increased acidification (Figure 1). Concentrations of Ca showed the least number of differences  
174 for individual sites, and the few significant differences seen in the O suggested recovery whereas  
175 the few significant differences in the B suggested acidification (Figure 1). When all sites were  
176 grouped, there were no significant differences ( $p > 0.10$ ) in O or B horizon Ca concentrations.  
177 Mean O horizon values for initial and final samples for grouped sites were 9.7 and 10.7  $\text{cmol}_c \text{ kg}^{-1}$   
178  $^{-1}$ , respectively, and for the upper B horizon were 1.2 and 1.0  $\text{cmol}_c \text{ kg}^{-1}$ , respectively. These  
179 results suggested that Ca concentrations were generally stable across the region for the period of  
180 study.

181 Decreases in Ca have been commonly observed in previous studies, but few decreases  
182 were observed in our study. This difference may be related to more recent sampling windows in  
183 our study than in previous studies. The final sampling by Johnson et al.<sup>29</sup> was in 2004, but the  
184 initial sampling was in 1984. The earliest sampling in our study was done in 1985 at the Ontario  
185 sites, but the final sampling at these sites was in 2009. None of the other previous studies  
186 included data more recent than 2001, whereas the final samplings in our study ranged from 2003-  
187 2014. Our results suggest stabilization or possible reversal of soil Ca depletion.

188 In the O horizon base saturation increased at four sites and no decreases were observed,  
189 whereas in the B horizon decreases were observed at nine sites, and no increases were observed  
190 (Figure 1). No changes were observed for the BB-TMT sites. When values for individual sites  
191 were grouped, base saturation in the O horizon increased from 49 percent to 56 percent ( $p <$   
192  $0.01$ ). In contrast, values decreased from 19 percent to 17 percent ( $p < 0.10$ ) in the B horizon.  
193 These results suggest a cessation of Ca depletion in the O, but also that declining base saturation  
194 in the B horizon remains common within the region. Prior soil resampling studies reporting base  
195 saturation are limited, but Warby et al.<sup>31</sup> showed consistent decreases in O horizon base  
196 saturation throughout New York and northern New England between 1985 and 2001, and  
197 Sullivan et al.,<sup>47</sup> showed decreases in the Adirondack region in the B horizon between the mid-  
198 1980's and 2003.

199 Values of pH in O horizons increased at eleven sites and decreased at three sites (Figure  
200 1), and in B horizons increased at 12 sites and decreased at three sites (Figure 1). No changes in  
201 pH were observed in the O horizon of BB-TMT sites, but an unexpected increase in pH was

202 observed in the B horizon of the BB-TMT CF sites (Figure 1). When sites were grouped, pH in  
203 the O increased from 3.06 to 3.26 ( $p < 0.05$ ) and increased in the B from 4.26 to 4.43 ( $p < 0.05$ ).  
204 These results were counter to the common decreases in base saturation in the B horizon. No  
205 studies other than Lawrence et al.<sup>28</sup> have reported pH increases in the O horizon, and none to our  
206 knowledge have reported pH increases in the B horizon in the region.

207 Concentrations of Al in the O horizon decreased at 14 locations and showed no increases,  
208 whereas in the B horizon, increases were observed at 7 locations and decreases were observed at  
209 three locations (Figure 1). At the BB-TMT sites there were no changes other than a decrease in  
210 the B horizon of the HW site. When sites were grouped, Al decreased in the O horizon ( $p <$   
211  $0.01$ ) from  $5.9 \text{ cmol}_c \text{ kg}^{-1}$  to  $3.5 \text{ cmol}_c \text{ kg}^{-1}$ , but was not different ( $P > 0.1$ ) in the B horizon, with  
212 initial and final means of  $3.2$  and  $3.3 \text{ cmol}_c \text{ kg}^{-1}$ , respectively. The O horizon Al showed the  
213 most consistent recovery response in this study, but in contrast, the B horizon showed mixed  
214 responses, with Al increases more common than decreases.

215

### 216 Links between Acidic Deposition and Soil Changes

217 Among the numerous soil changes identified, some suggested further acidification, some  
218 suggested recovery, and some showed no response. This mixed set of results occurred under  
219 decreasing deposition levels at all locations, although the magnitude of decreases and the length  
220 of time over which they occurred was variable. To investigate a link between atmospheric  
221 deposition and soil changes, the ratio of mean soil concentrations (final sampling: initial  
222 sampling) was related to the percent reduction in  $\text{SO}_4^{2-}$  deposition at each site. Results of the  
223 BB-TMT sites were included to show effects of minimal decreases in  $\text{SO}_4^{2-}$  deposition.

224 Ratios of Ca in the O horizon were positively correlated ( $P < 0.05$ ) with  $\text{SO}_4^{2-}$  deposition  
225 reductions (Figure 2a), although no correlation ( $P > 1.0$ ) was observed if the exceptionally high  
226 value for the Wawa site was excluded. Ratios for all soil investigations other than Wawa were  
227 clustered around the 1.0 line throughout the range of  $\text{SO}_4^{2-}$  reduction, with an average ratio of  
228 1.02. Ratios of Ca in the B horizon were not related to the  $\text{SO}_4^{2-}$  reduction, and most fell below  
229 the 1.0 line (Figure 2a). A positive correlation was also observed for base saturation in the Oa  
230 horizon, and this relationship was considerably stronger than that observed for Ca (Figure 2b).  
231 In the B horizon, there was no relation between base saturation and  $\text{SO}_4^{2-}$  reduction, and most  
232 ratio values were less than 1.0 (Figure 2b).

233 Measurements of pH were not correlated with  $\text{SO}_4^{2-}$  deposition reduction for O or B  
234 horizons ( $P > 0.1$ ), although for  $\text{SO}_4^{2-}$  reductions greater than 40% there was a strong positive  
235 correlation (0.74;  $P < 0.01$ ) for the B horizon, (Figure 3a). Concentrations of Al showed a strong  
236 negative correlation with  $\text{SO}_4^{2-}$  deposition reduction in the O horizon, and nearly all ratio values  
237 were near or below the 1.0 line. In the B horizon there was no correlation for all sites (Figure  
238 3b). For  $\text{SO}_4^{2-}$  reductions greater than 40 percent, correlations of -0.84 and -0.61 ( $P < 0.01$ ),  
239 were observed for O and B, respectively. The pH and Al results suggest a link between  
240 reduction of  $\text{SO}_4^{2-}$  deposition and a reversal of acidification of O and B horizons within the study  
241 region.

242 A link between  $\text{SO}_4^{2-}$  deposition reductions and decreased Al is further supported by the  
243 O horizon results at Bear Brook. At the BB-REF sites, where ambient  $\text{SO}_4^{2-}$  decreased 36  
244 percent, Al showed marked decreases that were similar to the average decrease of the other sites  
245 (Figure 4). However, at BB-TMT, with  $\text{SO}_4^{2-}$  decreases of only 5.7 percent, there were no  
246 significant differences in Al in the O horizon. The BB-REF  $\text{SO}_4^{2-}$  deposition was  $15.5 \text{ kg SO}_4^{2-}$   
247  $\text{ha}^{-1} \text{ y}^{-1}$  four years before the initial sampling and  $9.9 \text{ kg SO}_4^{2-} \text{ ha}^{-1} \text{ y}^{-1}$  in the final sampling year,

248 whereas the BB-TMT  $\text{SO}_4^{2-}$  deposition was 102 and 96.2 kg  $\text{SO}_4^{2-} \text{ha}^{-1} \text{y}^{-1}$  in these same years  
249 (1994 and 2006). The BB-TMT resampling for the period 1992/3-2010 also did not show a  
250 difference between initial and final sampling (Figure 4). Differences in sampling methods likely  
251 account for the higher concentrations measured for the BB TMT 1992/3-2010 resampling than  
252 either BB-TMT 1998-2006 resamplings. For the shorter time period, both the Oe and Oa were  
253 collected together, whereas for the longer time period only the Oa was collected, which tends to  
254 have higher concentrations of Al than the Oe<sup>28</sup>. The Bear Brook results provided further  
255 evidence of a link between decreasing  $\text{SO}_4^{2-}$  deposition and declining Al in the O horizon.  
256

## 257 **Discussion**

258 The overall results of O horizon soil measurements provided strong evidence that acidic  
259 deposition is no longer acidifying this horizon and that some of the acidic deposition effects have  
260 begun to reverse. This was most evident in the decreases in O horizon Al, as widespread  
261 increases had been documented in previous studies<sup>22, 23, 29, 31</sup>. The decrease in O horizon Al was  
262 correlated with the increase in pH in the O horizon ( $R = -0.43$ ;  $P = 0.07$ ), and the increase in pH  
263 in the B horizon ( $R = -0.50$ ;  $P = 0.03$ ). Although these correlations were similar, they can be  
264 attributed to different processes in the respective horizons. The increase in Oa pH increased the  
265 solubility of organic matter and associated complexed Al, thereby increasing the opportunity for  
266 leaching of organic Al out of the O horizon. In the B horizon, where organic matter  
267 concentrations were much lower, abundant mineral surfaces readily adsorb dissolved organic  
268 matter, thereby retaining organic-Al complexes received from upper horizons. Increased pH and  
269 decreased  $\text{SO}_4^{2-}$  within the B horizon also likely contributed to decreased mobility of Al in this  
270 horizon. The upper B horizon has been previously established as the primary location within the  
271 profile where Al was mobilized by acidic deposition through studies of soil processes<sup>23</sup> and  
272 measurements of soil waters<sup>48</sup>. Therefore, increases in B-horizon pH would be expected to  
273 reduce Al transport from the B into the O horizon through hydrologic and vegetative  
274 mechanisms. In sum, the increases in pH of both horizons combined to reduce Al in the O  
275 horizon by increasing outputs and decreasing inputs. Decreases in Al without changes in Ca also  
276 led to the strong increase in base saturation for grouped data. These soil responses are consistent  
277 with trends of increasing organic Al and decreasing inorganic Al in Adirondack lakes<sup>49</sup>.

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

291 Increases in the mean of ratios of Ca to Al in the O horizon (1.6 to 3.1 for all sites except  
292 BB-TMT) contrasted with decreases found in the B horizon, (0.38 to 0.30 for the same sites)  
293 largely because of the different Al responses between horizons without clear changes in Ca. The

294 decrease of the ratio in the B horizon occurred despite the pH increase. A lack of increase in  
295 either O or B horizon Ca may have in part been related to a decreasing trend of atmospheric wet  
296 deposition of Ca that was common throughout the study region in the 1980s, and was followed  
297 by stable levels through the 1990s<sup>51</sup> (<http://nadp.sws.uiuc.edu/>; accessed June 1, 2015). Further  
298 reductions in  $\text{SO}_4^{2-}$  deposition and or a greater length of time may be needed to increase B  
299 horizon Ca to Al ratios.

300 The seemingly dynamic nature of Al at these study sites was linked to the low base  
301 saturation values of the B horizon measured in the initial samplings. All but five of the sites had  
302 base saturation values less than 20% (Table 1), the threshold below which the dominance of  
303 cation exchange shifts from Ca to Al<sup>52</sup>. Therefore, most sites were highly susceptible to  
304 mobilization of Al by the addition of protons associated with a mobile anionic charge in the form  
305 of sulfate. However, the reversal of Al accumulation in the O horizon was not the result of  
306 increasing base saturation in the B horizon above this threshold—increases in base saturation  
307 were not measured at any site and decreases were common. Furthermore, the increases in soil  
308 pH that were seen in the B horizon were not likely to have been sufficient to render Al insoluble  
309 in soil solution. Reduced mobilization of Al can be largely attributed to the decrease of  $\text{SO}_4^{2-}$   
310 concentrations in soil solutions. As a result, the recovery response of Al in the O horizon  
311 occurred in advance of any increases in the availability of B horizon Ca. The decrease in base  
312 saturation seen in the B horizon can be attributed to increased Al that moved out of the O horizon  
313 ( $P < 0.01$  at 6 of 9 sites where base saturation decreased), and therefore may be a recovery  
314 response. It should be noted that four of the five sites with initial base saturation higher than 20%  
315 had O horizons that were too thin for consistent sampling.

316 Results from the Wawa site provided unique information on recovery processes because  
317 this site had the largest reduction in  $\text{SO}_4^{2-}$  deposition (76%) as well as the greatest increase in O  
318 horizon Ca (Figure 2a, Table S2). Deposition of  $\text{SO}_4^{2-}$  in the Wawa area was elevated by a local  
319 iron sintering plant that lacked emission abatement equipment. Although data are not available,  
320 deposition in the 1970s was likely to have been much greater than in the 1980s due to high  
321 factory production<sup>53</sup>. The pronounced decline in deposition at the Wawa site<sup>54</sup> resulted in large  
322 increases in base saturation and pH, and a large decrease in Al in the Oe horizon ( $P < 0.05$ ), but  
323 no change in base saturation or Al ( $P > 0.01$ ) in A or B horizons. Soil data for three samplings  
324 are presented for the Wawa site in Figure S3, Supporting Information.

325 Ongoing release of Ca through mineral weathering under greatly reduced  $\text{SO}_4^{2-}$  leaching  
326 could potentially increase Ca concentrations in the B horizon, but increases in Ca were not  
327 observed in this horizon at Wawa. One explanation for this result is suggested by the large  
328 increase in Ca concentrations in the Oe horizon. Transfer of Ca from the B to the Oe through  
329 biocycling, coupled with recycling within the Oe, may play an important role in limiting  
330 increases of Ca in the B under the conditions of decreased  $\text{SO}_4^{2-}$  leaching. Transfer of Ca from  
331 the mineral soil into the forest floor may also be facilitated by decay fungi that bridge these  
332 horizons<sup>55</sup>. Shortle et al<sup>56</sup> found that decay fungi enrich wood residues with Ca to  
333 concentrations that approximate those of the surrounding forest floor, while maintaining  
334 extremely low concentrations of Al. The high Ca to Al ratio creates a source of Ca that can be  
335 readily utilized by trees, thereby enhancing the fertility of the forest floor.

336 The changes in soils identified in this study were generally consistent across the large  
337 study region, over differing time periods, using varying methods of resampling. Responses in  
338 the O horizon provided strong evidence that (1) further acidification was not occurring and (2)  
339 reversal of Al accumulation was underway at nearly all sites and pH increases were occurring at

340 half of the sites. The response of the B horizon was less clear, however, and not consistent with  
341 the conceptual model of recovery that assumes replenishment of bases from weathering as cation  
342 leaching fluxes are reduced by decreases in deposition. A more complete understanding of how  
343 soil processes are responding to decreasing deposition throughout the profile is needed to  
344 determine the capacity of soils to improve Ca availability and the length of time over which this  
345 could occur. This study demonstrates the value of long-term soils investigations to understand  
346 complex processes in systems with high spatial and temporal variability. Future remeasurements  
347 will be essential to determine the trajectory of recovery, and what type of new stability might be  
348 achieved under lowered acidic deposition levels.

349

### 350 Supporting Information

351 This information is available free of charge on the ACS Publications website at

352 <http://pubs.acs.org/>.

353 Section S1: Text and references providing details on methods of sampling and analysis Table S1:  
354 characteristics of individual sites Table S2: Mean values and results of tests for differences  
355 between initial and final measurements of Ca, base saturation, pH and Al Figure S1: Map of site  
356 locations Figure S2: atmospheric deposition of all sites, initial and final Figure S3: trends of  
357 atmospheric deposition and soil measurements at Wawa, Ontario site

358

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Table 1. Base saturation (B.S.) of the initial sampling for O and B horizons, years of initial and final sampling, and  $\text{SO}_4^{2-}$  decline expressed as the percent decrease in wet atmospheric deposition of  $\text{SO}_4^{2-}$  ( $\text{kg SO}_4^{2-} \text{ ha}^{-1} \text{ y}^{-1}$ ) from four years prior to initial sampling to the year of final sampling. BB-TMT represents sites at Bear Brook, ME that were treated with  $(\text{NH}_4)_2\text{SO}_4$ ; BB-REF represents untreated reference sites. CF, HW and MF stand for conifer, hardwood and mixed forest, respectively.

Site	Base Sat.		Sampling Years		$\text{SO}_4^{2-}$ Decrease
	O	B	Initial	Final	
BB-TMT, <i>CF</i> ; 1992-10	14	5.4	1992-93	2010	9.8
BB-TMT, <i>CF</i> ; 1998-06	21	5.2	1998	2006	5.7
BB-TMT, <i>HW</i> ; 1998-06	50	13	1998	2006	5.7
BB-REF, <i>HW</i>	53	11	1998	2006	36
BB-REF, <i>CF</i>	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, <i>MF</i>	56	11	1992-93	2009	44
Groton, VT	50	14	1992-93	2003	32
Buck Creek, NY, <i>HW</i>	29	9.1	1998	2014	59
Buck Creek NY, <i>MF</i>	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, <i>HW</i>	95	24	1996-98	2009	44
Mt. Equinox, VT	100	100	1996-98	2009	29

### Figure Legends

Figure 1. Statistical results by site where initial and final measurements increased or decreased at  $P \leq 0.1$  ( $\uparrow$  or  $\downarrow$ ),  $P < 0.05$  ( $\uparrow\uparrow$  or  $\downarrow\downarrow$ ), or,  $P < 0.01$  ( $\uparrow\uparrow\uparrow$  or  $\downarrow\downarrow\downarrow$ ). 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  $(\text{NH}_4)_2\text{SO}_4$ ; BB-REF represents untreated reference sites. CF, HW and MF stand for conifer, hardwood and mixed forest, respectively.

Figure 2. The ratio of site means (final sampling/ initial sampling) for (a.) Ca ( $\text{cmol}_c \text{ kg}^{-1}$ ), and (b.) base saturation (percent), versus the reduction of wet  $\text{SO}_4^{2-}$  deposition. The ratio for O horizon Ca at the Wawa site differed greatly from all other sites.  $\text{SO}_4^{2-}$  reduction is expressed as the percent decrease in wet deposition of  $\text{SO}_4^{2-}$  ( $\text{kg SO}_4^{2-} \text{ ha}^{-1} \text{ y}^{-1}$ ) from four years 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  $< 0.10$ .

Figure 3. The ratio of site means (final sampling/ initial sampling) for (a.) pH, and (b.) Al ( $\text{cmol}_c \text{ kg}^{-1}$ ), versus the reduction of wet  $\text{SO}_4^{2-}$  deposition.  $\text{SO}_4^{2-}$  reduction is expressed as the percent decrease in wet deposition of  $\text{SO}_4^{2-}$  ( $\text{kg SO}_4^{2-} \text{ ha}^{-1} \text{ y}^{-1}$ ) from four years 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  $< 0.10$ .

Figure 4. Mean exchangeable 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  $\{\text{NH}_4\}_2 \text{SO}_4^{2-}$ ). 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.

Figure 1.

Horizon	Ca		B.S.		pH		Al	
	O	B	O	B	O	B	O	B
BB-TMT, <i>CF</i> ; 1992-10						↑↑		
BB-TMT, <i>CF</i> ; 1998-06						↑↑		
BB-TMT, <i>HW</i> ; 1998-06								↑↑
BB-REF, <i>HW</i> ; 1998-06					↑	↑↑	↓↓	
BB- REF, <i>CF</i> ; 1998-06		↓					↓↓	
Duchesnay, QC				↓↓	↑↑↑	↑↑↑		
Kossuth, ME	↑↑↑		↑↑		↑↑		↓↓	↓↓↓
Howland, ME							↓↓↓	
Crawford Notch, NH				↓↓↓	↑↑↑		↓↓↓	
Bartlett, NH		↓↓			↑↑↑		↓↓↓	
Sleepers River, VT, <i>MF</i>				↓↓	↑↑↑			↑↑↑
Groton, VT					↑		↓↓↓	
Buck Creek, NY, <i>HW</i>				↓↓↓			↓↓↓	↑↑↑
Buck Creek, NY, <i>MF</i>				↓↓↓		↑↑	↓↓	↑↑↑
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, <i>HW</i>					↑↑↑	↓↓↓		
Mt. Equinox, VT	----		----		----		----	

Figure 2.

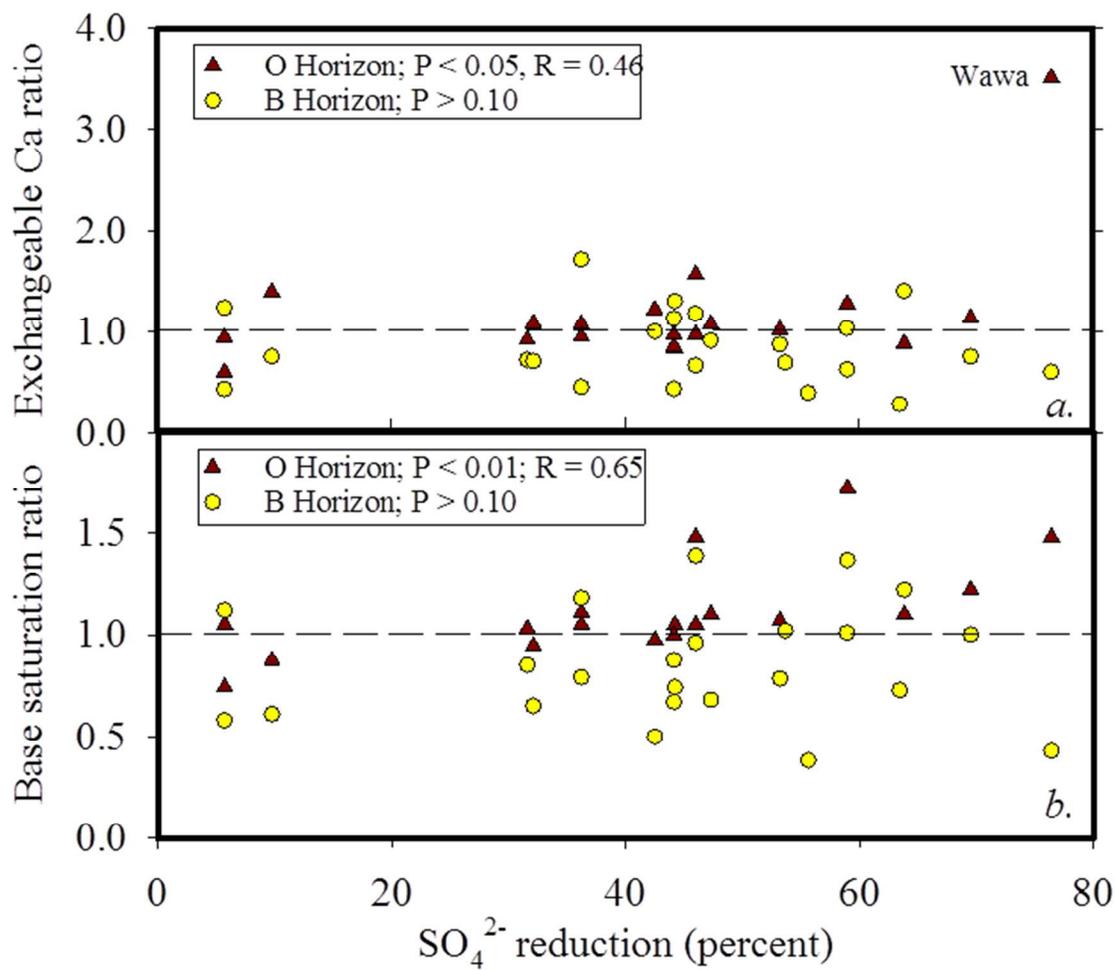


Figure 3.

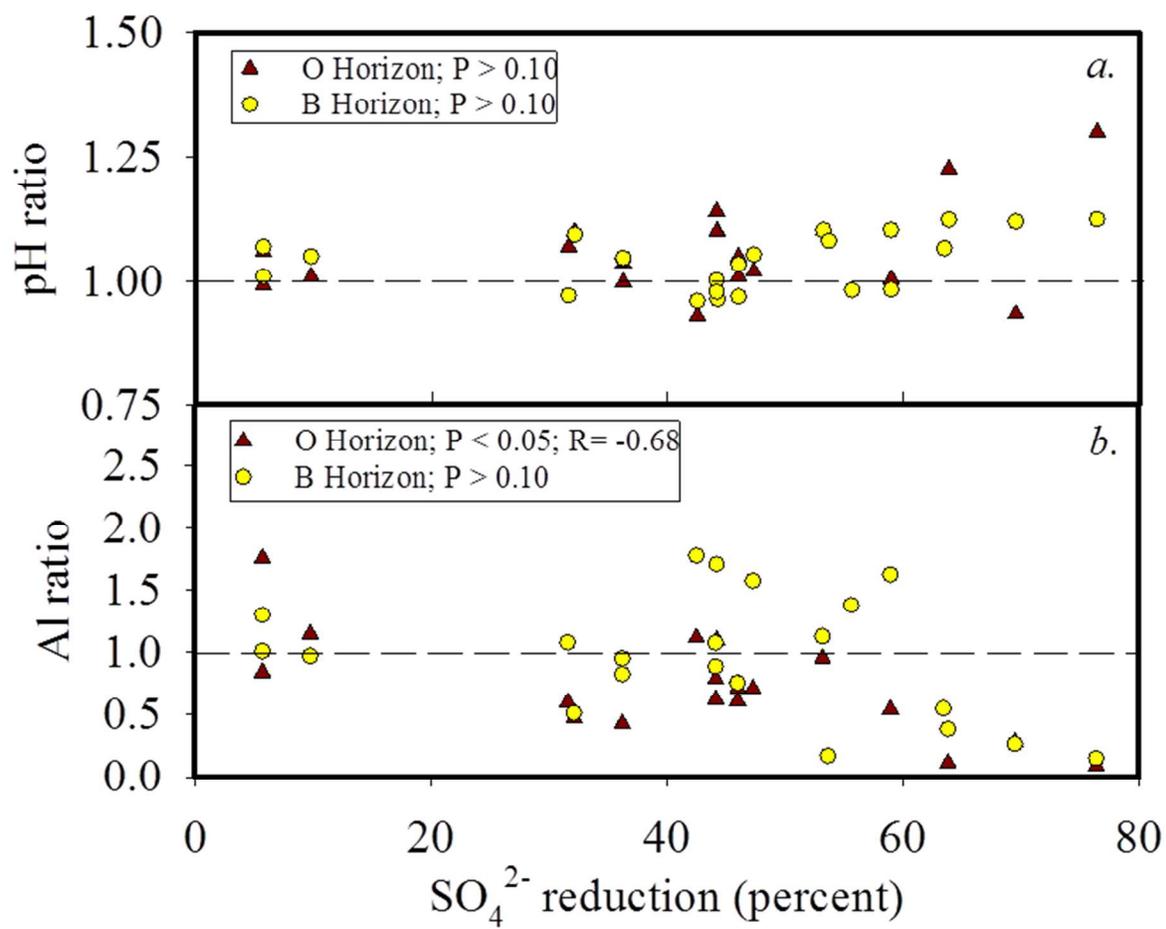
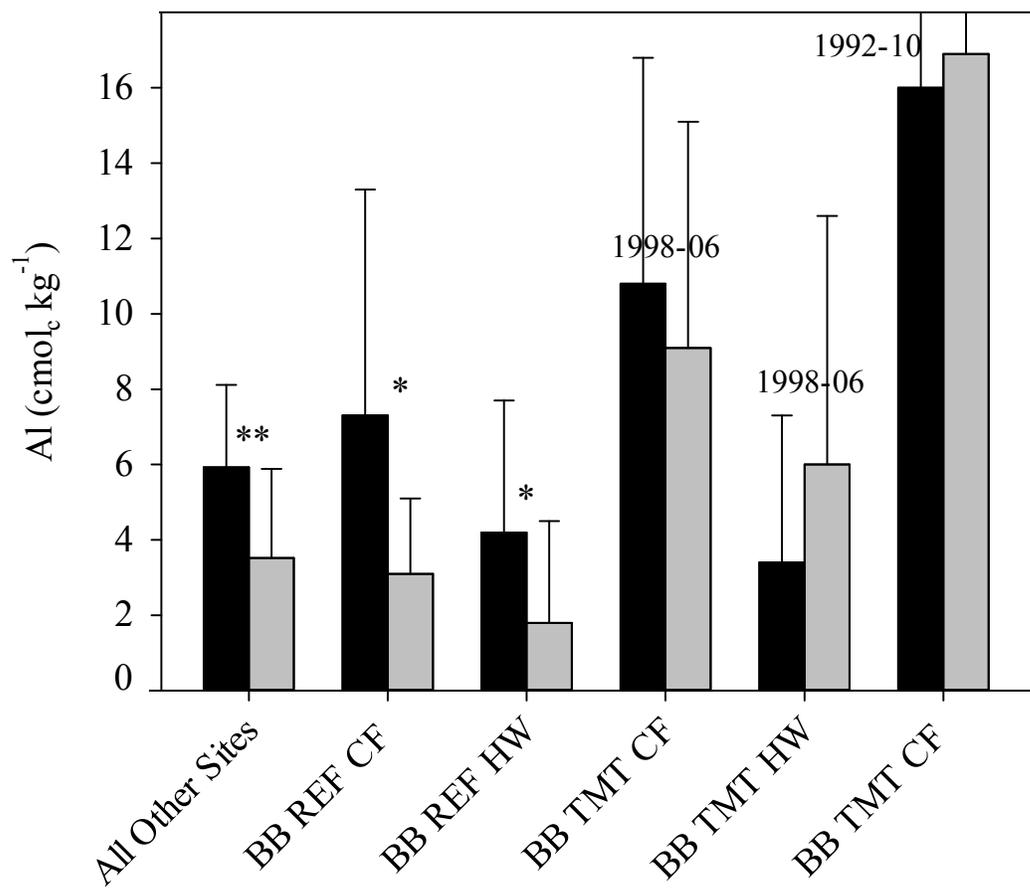


Figure 4.



**TOC Art to be used in publication**