Soil Chemistry and the Recovery of Sensitive Watersheds from Chronic Acidification

Chris E. Johnson¹, Charles T. Driscoll¹, Richard A.F. Warby², Jeremy Tamargo¹, Wei Li¹, April Melvin³

¹Syracuse University
²Arkansas State University
³Cornell University

W. M. Keck Foundation
Decline in Acid Deposition

Huntington Forest, NY

Annual Deposition (eq/ha)

- Sulfate
- H Ion

Data: National Atmospheric Deposition Program (http://nadp.sws.uiuc.edu/)
Surface Waters Are Showing Chemical Recovery

- Decreased $\text{SO}_4^{2-}$ in drainage waters.
- Increased pH, ANC.
- Decreased Al concentrations.

**BUT:**

- ANC recovery is sluggish.
- Base cation concentrations continue to decline.

Warby et al. (2005)
Hypothesis

• The recovery of surface waters in the northeastern U.S. from acid rain is hindered by continuing acidification of soils.
Approach

• Sample soils from watersheds studied in the Direct/Delayed Response Program (DDRP) – 1984.

• Samples collected in 2001-02.

• Same chemical methods as DDRP, to the extent possible.
## Region-Wide Results: Oa Horizons

<table>
<thead>
<tr>
<th></th>
<th>1984 Median</th>
<th>2001 Median</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium, cmol(_c) (kg C(^{-1}))</td>
<td>23.5</td>
<td>10.6</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>Aluminum, cmol(_c) (kg C(^{-1}))</td>
<td>8.8</td>
<td>21.3</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>Acidity, cmol(_c) (kg C(^{-1}))</td>
<td>23.6</td>
<td>38.0</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>CEC(_e), cmol(_c) (kg C(^{-1}))</td>
<td>62.7</td>
<td>60.6</td>
<td>None</td>
</tr>
<tr>
<td>pH</td>
<td>3.14</td>
<td>2.98</td>
<td>P &lt; 0.05</td>
</tr>
<tr>
<td>Base Saturation, %</td>
<td>56.2</td>
<td>33.0</td>
<td>P &lt; 0.01</td>
</tr>
</tbody>
</table>

(Warby et al. 2009)
Sub-Regional Results: Oa Horizon

(Warby et al. 2009)

Sample Size (N):

<table>
<thead>
<tr>
<th>Region</th>
<th>1984</th>
<th>2001</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>75</td>
<td>55</td>
</tr>
<tr>
<td>ADR</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>CATPOC</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>CNE/Maine</td>
<td>37</td>
<td>19</td>
</tr>
</tbody>
</table>

* Indicates P < 0.05
Bhs Horizon?
or Bs Horizon?
here?

Bhs Horizon
or here?

Bhs Horizon
Two Horizons?
or Three?
**Equal-Area Quadratic Splines**

- A series of local quadratic polynomials that join at “knots” located at the horizon boundaries (Bishop et. al, 1999).

- Area to the left of the fitted spline (“X”) is equal to the area to the right of the spline (“Y”) (Ponce-Hernandez, 1986).

- Mean value of each horizon is maintained by the spline.

- Minimizes the true mean squared error (Bishop et. al, 1999).

(Ponce-Hernandez et al., 1986)
Equal-Area Quadratic Splines

- Continuous depth-concentration function computed by the spline-fitting program.
- Mean concentration of analyte calculated for user-specified depth segment (e.g., 0-10 cm).
## Adirondack Results: Mineral Soils

<table>
<thead>
<tr>
<th>Depth</th>
<th>1984 Mean</th>
<th>2001 Mean</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0-10 cm</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium, cmol_c kg^{-1}</td>
<td>0.77</td>
<td>0.43</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>Aluminum, cmol_c kg^{-1}</td>
<td>4.34</td>
<td>4.82</td>
<td>NS</td>
</tr>
<tr>
<td>Acidity, cmol_c kg^{-1}</td>
<td>5.57</td>
<td>5.79</td>
<td>NS</td>
</tr>
<tr>
<td><strong>10-20 cm</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium, cmol_c kg^{-1}</td>
<td>0.60</td>
<td>0.37</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>Aluminum, cmol_c kg^{-1}</td>
<td>3.58</td>
<td>6.25</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>Acidity, cmol_c kg^{-1}</td>
<td>4.40</td>
<td>7.25</td>
<td>P &lt; 0.01</td>
</tr>
</tbody>
</table>
Woods Lake Watershed Liming Experiment

- Sub-watersheds II and IV limed in 1989.
- Sub-watersheds III and V not limed - controls.
- Transects sampled in 2008.
- Pre-treatment data – Blette et al. (1996)
Liming Effects on Soil Chemistry
Ca-Al Dynamics After Liming

[Graphs showing the relationship between CEC (cmol c kg⁻¹) and Bound Hydrogen (cmol c kg⁻¹) for Control and Ca Treated samples, and another graph showing the relationship between CEC (cmol c kg⁻¹) and Bound Aluminum (cmol c kg⁻¹) for Control and Ca Treated samples.]
Conclusions

1. Oa horizons in the northeastern USA experienced substantial decreases in exchangeable Ca, and increases in exchangeable Al between 1984 and 2001-02.

2. These changes appear to be occurring in the upper layers of mineral soils in the region as well.

3. The continuing acidification of soils may help explain the sluggish recovery of ANC in regional surface waters.

4. Soils at Woods Lake were significantly less acidic 19 years after liming.

5. Increased Ca levels in Woods Lake soils appear to be equivalent to decreases in bound Al.