Do the competitions among calcium, aluminum and hydrogen ion for organic binding sites determine soil pH and aluminum solubility in Adirondack Forest soils?

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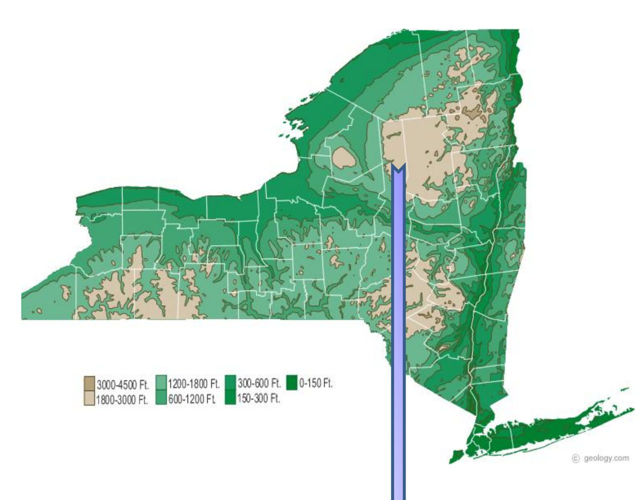
Abstract: Long-term acid deposition has resulted in a decrease in soil pH, the depletion of labile calcium (Ca) and the mobilization of aluminum (Al) in Adirondack forest ecosystems. In acidic soils, the labile Al^{3+} is highly toxic to most organisms, affects the growth of plants, and can displace base cations (such as Ca^{2+}, Mg^{2+}, K^+, Na^+) on the exchange sites of soil organic matter (SOM). Liming is generally applied to mitigate soil acidity and to improve soil base status. After liming, the acid cations (Al^{3+}, H^+) may be neutralized by base cations (Ca^{2+}), and the soil pH may be improved, suggesting that the competition between Ca^{2+} and Al^{3+} binding on SOM is the key process controlling soil pH and Al solubility. However, some researchers have noted that the fraction of exchangeable base cations and Al to cation exchange capacity (CEC) is correlated with soil pH, and it has been suggested that Al^{3+} might act as a base cation. Furthermore, researchers have hypothesized that the composition of hydrogen ions (H^+) and Al^{3+} adsorbed to the SOM determines the soil pH and Al solubility. The goal of this project is to explore the relationships between Al^{3+}, Ca^{2+} and H^+ bound to the organic exchange sites of SOM, and to improve understanding of the key acid-base processes determining the soil pH and Al solubility in the acidic forest ecosystem. We have conducted experiments to determine the acid-base chemistry of thirty-six samples from three horizons (Oe, Oa and mineral) of two limed subcatchments (II and IV) and two control subcatchments (III and V) at the Woods Lake watershed in the Adirondack Region.

Objectives

- ❑ Comparisons of soil chemistry of Woods lake subcatchments between pre-liming in 1989 and post-liming in 1991 and 2008
- ❑ Exploration of the relationships between Al^{3+}, Ca^{2+} and H^+ bound to organic exchange sites from three soil horizons from Woods lake subcatchments

Sampling Sites

Woods Lake Watershed (43°52'00 " N 75°57'30" W)
Sampled in 2008
6 sites from limed subcatchments: II and IV
6 sites from control subcatchments: III and V
Each pit has 3 horizons: Oe, Oa, and mineral



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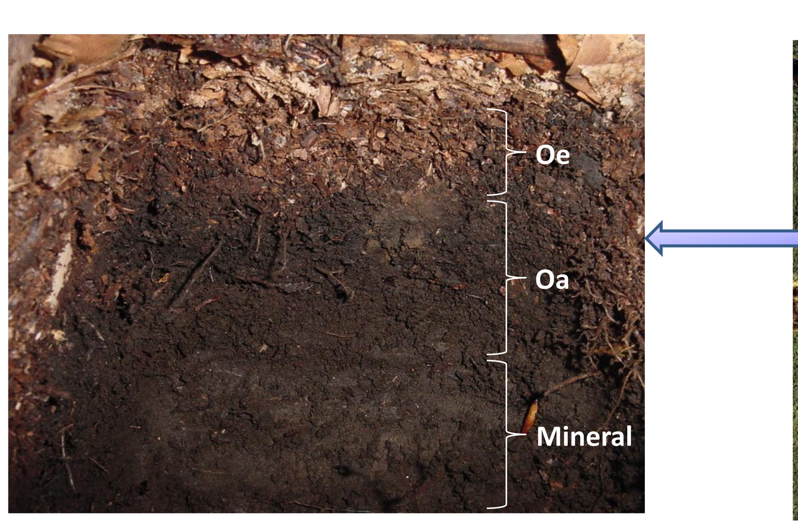

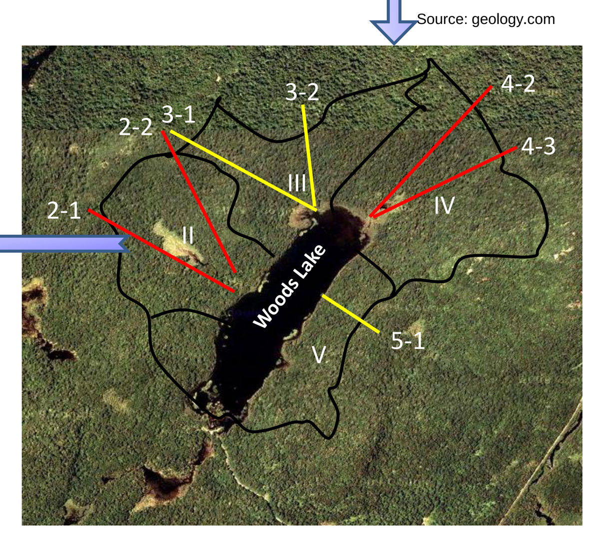

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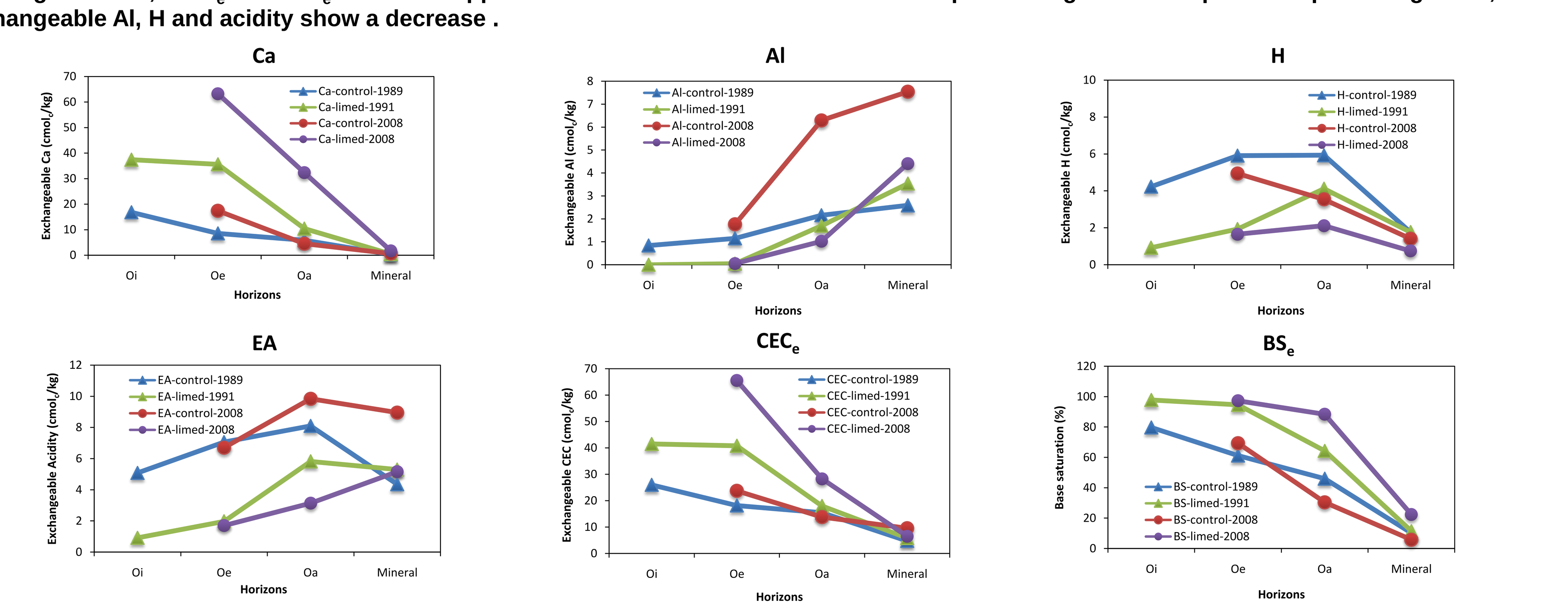
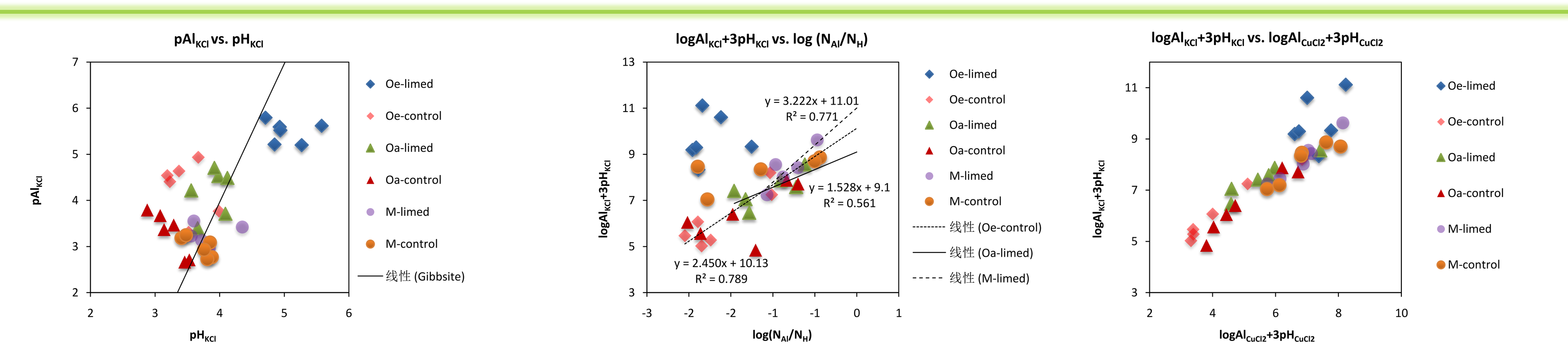
Methods

Soil pH	Measured in deionized water and 0.01 M $CaCl_2$
Exchangeable Ca	Measured in 1 M NH_4Cl extracts
Exchangeable Al and acidity (EA)	Measured in 1 M KCl extracts
Exchangeable H	Difference between EA and exchangeable Al
Base cations (BC)	Summation of Ca, Mg, K, and Na measured in 0.5 M $CuCl_2$ extracts
Effective CEC (CEC_e)	Summation of BC and EA
Total C and N	Measured by elemental analysis
Organically bound Al	Measured in 0.5 M $CuCl_2$
Total acidity (TA)	Measured in 0.5 M $BaCl_2$-TEA, buffered at pH 8.2
Total CEC (CEC_t)	Summation of BC and TA
Effective base saturation (BS_e)	Percentage of BC divided by CEC_e

Results

Comparisons of soil chemistry of Woods Lake subcatchments between Year 1989, 1991 (Blette et al., 1996) and Year 2008. Exchangeable Ca, CEC_e and BS_e show an apparent increase for forest floor soils in post-liming sites compared to pre-liming sites, while Exchangeable Al, H and acidity show a decrease.

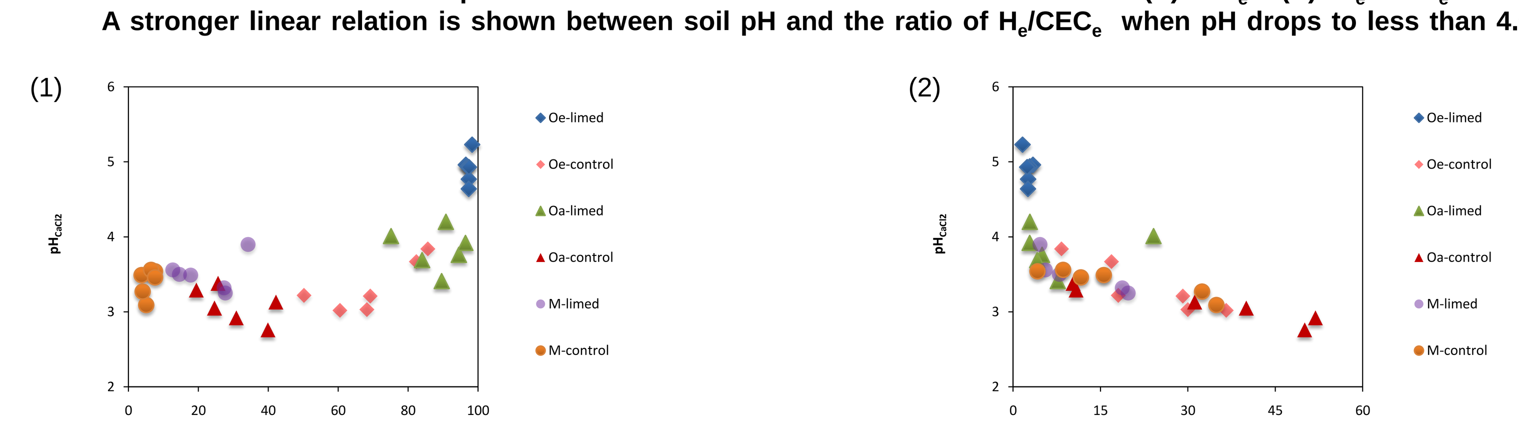




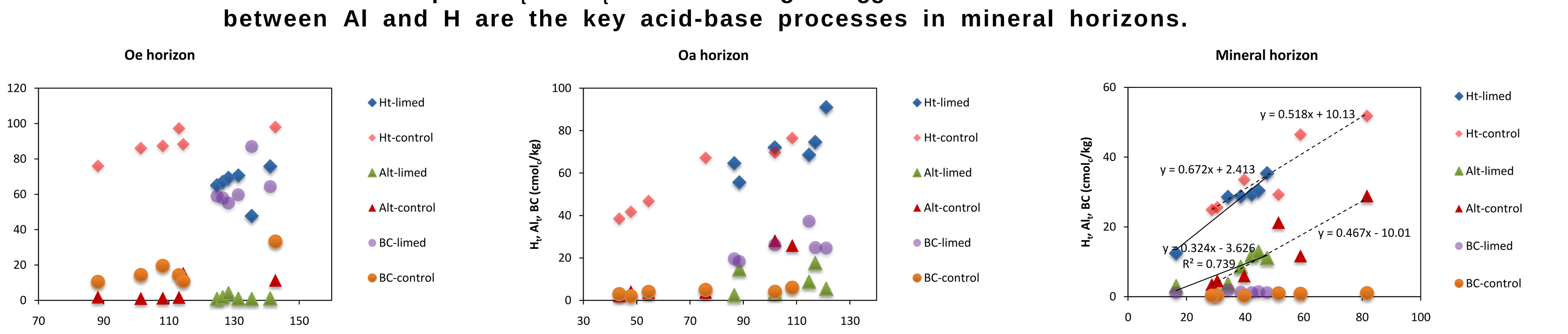
Model of Gibbsite solubility does not explain the soil pH and Al solubility completely.

Model of organic Al complexes failed to describe cation-exchange reactions between H^+ and Al^{3+} in SOM for all horizons using an unifying equation.

Relations between soil pH and two soil acid-base status indicators (1) BS_e (2) H_e/CEC_e ratio. A stronger linear relation is shown between soil pH and the ratio of H_e/CEC_e when pH drops to less than 4.0.



Horizon-specific relations between CEC_t and its three components: H_t, Al_t, and BC. The similar intercepts of H_t and Al_t with reverse signs suggest that chemical reactions between Al and H are the key acid-base processes in mineral horizons.



Conclusions

- ❑ Exchangeable Ca, CEC_e and BS_e have experienced a large increase in organic horizons of limed sites , compared to reference sites. Exchangeable Al, H and EA decreased after liming.
- ❑ The model of cation exchange reactions among H^+, Al^{3+} and Ca^{2+} and the pH-dependent solubility of Al hydroxide should be both considered while determining soil pH and Al solubility.
- ❑ The indicator H_e/CEC_e produces a better relationship with pH than BS_e when the soil pH is less than 4.0.
- ❑ Competition between H^+ and Al^{3+} are more important for Mineral horizons than for Oe and Oa horizons.

Ongoing Study

We will optimize the WinHumicV model by using the batch titration data of reference samples and calculate equilibrium concentrations of cations in solution with changing soil Al and Ca concentrations. The model simulation results will be used to compare the liming effects of the treated subcatchments with the measured results, and further test the relationships between Al^{3+}, Ca^{2+} and H^+ on organic binding sites.

References

Blette, V.L, and Newton, R.M., 1996. Effects of watershed liming on the soil chemistry of Woods Lake, New York. *Biogeochemistry.* 32: 175-194

Driscoll, C.T., Cirmo, C.P., Fahey, T.J., Blette, V.L., Bukaveckas, P.A., Burns, D.A., Gubala, C.P., Leopold, D.J., Newton, R.M., Raynal, D.J., Schofield, C.L., Yavitt, J.B., and Porcella, D.B., 1996. The Experimental Watershed Liming Study: Comparison of lake and watershed neutralization strategies . *Biogeochemistry.* 32: 143-174

Johnson, C.E., 2002. Cation exchange properties of acid forest soils of the northeastern USA. *Eur. J. Soil Sci.* 53: 271-282.

Nissinen, A., Ilvesniemi, H., and Tanskanen, N., 1999. Equilibria of weak acid and organic Al complexes explain activity of H^+ and Al^{3+} in a salt extract of exchangeable cations. *Eur. J. Soil Sci.* 50: 675-686

Ross, D.S., David, M.B., Lawrence, G.B., and Bartlett, R.J., 1996. Exchangeable hydrogen explains the pH of Spodosol Oa horizons. *Soil Sci. Soc. Am. J.* 60: 926-1932.

Skyllberg, U., 1999. pH and solubility of aluminium in acidic forest soils: a consequence of reactions between organic acidity and aluminium alkalinity. *Eur. J. Soil Sci.* 50: 95-106.

Walker, W.J., Cronan, C.S. and Bloom, P.R. 1990. Aluminum solubility in organic soil horizons from northern and southern forested watersheds. *Soil Sci. Soc. Am. J.* 54: 369-374.

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