CHEMICAL WEATHERING AND CALCIUM DEPLETION IN ADIRONDACK SOILS

RICHARD APRIL
Dept. of Geology
Colgate University
Hamilton, NY 13346
rapril@mail.colgate.edu

MICHELE HLUCHY
Division of Geology and Environmental Studies
Alfred University
Alfred, NY 14802
fhluchy@alfred.edu

INTRODUCTION

Acid Rain and the Adirondack Mountains

The term 'acid rain' was first coined in 1872 in *Air and Rain: The Beginnings of Chemical Climatology*, a book published by Angus Smith, an English chemist, who was the first to systematically analyze the chemistry of precipitation in industrialized Britain. The effects of acidic deposition on aquatic and terrestrial ecosystems have been studied intensively since the late 1960's and early 1970's, first in Scandinavia, then in Europe, and eventually in the U.S when acid rain emerged as an important ecological issue (Oden, 1968; Likens et al., 1972).

The Adirondack Mountains receive elevated inputs of sulfur and nitrogen in the form of acid deposition. The acid emissions that cause acid deposition began in the late 19th century and increased well into the 20th century, peaking in the 1970's. Annual emissions of sulfur dioxide in the U. S., for example, peaked in 1973 at 28.8 million metric tons. By 2003, following implementation of the Clean Air Act Amendments (CAAA) of 1970 and passage of Title IV of the Acid Deposition Control Program by Congress in 1990, sulfur dioxide emissions had decreased 50%, to 14.3 million tons.

Prevailing winds from the west carry pollutants emitted in the Midwest, mainly from coal-burning electric utilities, over the northeastern United States and Canada. Precipitation in the Adirondacks averages 100 – 150 cm/yr, with about 30% falling as snow (Johannes et al. 1985). This large quantity of precipitation results in high acid loadings. H^+ deposition averaged about 500 eq/ha/yr over the Adirondacks in the early 1990s, but decreased to about 300 eq/ha/yr by 2002. Average deposition of H^+ and SO_4^{-2} in the Adirondacks has been declining over the past few decades due to significant decreases in SO_2 emissions. Average annual pH values of precipitation have risen over this period from about 4.2 to 4.5. Because precipitation amounts decrease from the western to eastern Adirondacks due to orographic effects, H^+ deposition decreases by about 10% across the mountain range, a distance of about 150 km (Charles 1991, Driscoll et al. 2003). There has been no significant change in nitrogen deposition during this same period because CAAA legislation did not specify limits for NO_x emissions (Driscoll et al. 2001).

Cumulative and lingering effects of over a century of acid rain has led to renewed interest in determining whether terrestrial and aquatic ecosystems in the Adirondacks are showing signs of recovery (i.e., to more natural states, although "natural" is oftentimes difficult to determine because of two centuries of anthropogenic perturbations and lack of historical data). In these studies detailed knowledge of the geology, hydrogeology and geochemistry of the Adirondacks plays a critical role. For example, recent studies of the terrestrial system have shown that base cation depletion in soils, particularly low levels of available calcium in forested watersheds, negatively impacts forest health and the ability of surface waters to recover from acid inputs (c.f. DeHayes et al. 1999, Lawrence et al. 1995, 1999). Because Spodosols (a predominant soil type in the Adirondacks) naturally have low base saturation, leaching of base cations by acidic inputs exacerbates an already fragile balance between nutrient supply for vegetation and organisms that live on or within the forest floor and replenishment of these nutrient cations by litter decay and mineral weathering. Adirondack soils consist mainly of the primary minerals quartz, K- and Na-rich feldspar, and muscovite (April and Newton 1983, April et al. 1986), all of which are highly resistant to chemical weathering. Minerals such as Ca-rich plagioclase, biotite, hornblende, diopside, garnet and calcite are much less abundant in these soils, but they are more susceptible to chemical weathering and therefore can provide base cations to exchange sites at rates comparable with depletion rates accelerated by acidic deposition (April and Newton 1992).

The effects of acid deposition on aquatic systems in the Adirondack Mountains have been studied intensively since the 1970's. Findings show that the acidification status of streams and lakes is strongly influenced by the geology and hydrology of watersheds. Deposition input quantity and quality, the mineralogy and depth of surficial materials, the hydrological properties of soils, groundwater flow paths, wetland processes, snowmelt, etc., all contribute to the final chemical composition of surface waters.

Geology of the Adirondacks

The Adirondack Park comprises about 2.4 million ha (~6 million acres) of predominantly forested land dotted with more than 3,000 lakes and ponds. Water drawn from five major drainage basins flows along 2,400 km of rivers fed by an estimated 48,000 km of brooks and streams. Geologically, the Adirondack region forms the southwestern extension of the Grenville Province of the Canadian Shield with rocks ranging in age from 1.3 to 1.0 billion years old (McLelland and Chiarenzelli 1990, McLelland 2001). The major rock units underlying the area can be broadly divided into three types: granitic gneisses, anorthosites, and metasediments. Marble and other calcite-bearing bedrock occur in a few scattered localities within the metasedimentary units. The mountains and uplands are mantled by till, with deposits thickest in the valleys and thinner at higher elevations. Glacial meltwater deposits composed primarily of stratified sand and gravel fill lowland areas, primarily in the northwestern part of the region. Soils in the region are generally acidic Spodosols, which have developed on till or outwash since deglaciation 12,000 to 14,000 years ago. Soil profiles are typically less than a meter deep.

Primer on Acid Deposition

Deposition of sulfur (S) and nitrogen (N) in the form of acid deposition has impacted soils, surface waters, and biotic components of terrestrial and aquatic ecosystems worldwide. In the northeastern United States (US) the effects of acid deposition on ecosystems has been the focus of numerous field and laboratory investigations over the past quarter century. In acid-sensitive regions, such as the Adirondack region of New York (Adirondacks), acid deposition has reduced fish populations and biological diversity in lakes and streams (Schofield 1976, Baker and Schofield 1982, Gallagher and Baker 1990), reduced growth rates of plants (Worrall 1994, DeHayes et al. 1999), lowered pH and decreased the acid-neutralizing capacity (ANC) of surface waters (Galloway et al. 1983, Driscoll and Newton 1985, Driscoll et al. 1989), caused changes in nutrient cycling and uptake in forests (Cronan 1994, Currie et al 1999, DeHayes et al. 1999), and mobilized metals, such as aluminum, that can be toxic to plants and animals (Tyler 1978, Cronan and Schofield 1990, Cronan and Grigal 1995, Baker et al. 1996, Van Sickle et al. 1996). Acid deposition causes significant changes in soil chemistry, including the depletion of base cations, the release of monomeric aluminum, and the accumulation of S and N compounds, which result in the alteration of soil biotic communities (Wolters and Schaefer 1994).

Quantities of sulfur and nitrogen compounds released by power plants and industry in the United States have markedly decreased pursuant to the 1970 Clean Air Act Amendments (CAAA) and Title IV of the Acid Deposition Control Program of the CAAA of 1990. Amounts of sulfur dioxide (SO_2) in emissions and sulfate (SO_4^{2-}) concentrations in precipitation have shown declines over the past three decades, and sulfate concentrations in surface waters in the northeastern US have decreased over this same period (Jenkins et al. 2007). Despite decreases in acidic inputs to the Adirondacks, ANC has seemingly not improved much because decreased SO_4^{2-} in surface waters largely has been offset by decreases in concentrations of base cations (Stoddard et al. 1999). However, a more recent study of 188 long-term monitoring sites in the eastern United States, from 1990 to 2000, by Stoddard et al. (2003) shows evidence of ANC increases of about 1 μeq/l per year in Adirondack lakes. Slow recovery of chemical water quality in the Adirondacks may be due to historical leaching of base cations from soils, continued deposition of nitrogen compounds, or accumulation of sulfur in soil (Driscoll et al. 2003). The effects of acid deposition in the Adirondacks will be detectable for a very long time. Nevertheless, improvements in water and soil quality are expected. Scientists now have the opportunity to measure ecosystem structure and function at a time when the impacts of acid deposition may be at their worst. Only by establishing a baseline of appropriate geochemical and biotic parameters can we monitor ecosystem recovery in the Adirondack region.

Base cation depletion in soils and decreases in stream and lake water ANC are of particular concern in acid-impacted watersheds. Roy and Driscoll (2001) reported that the concentrations of base cations have decreased in 26 of 48 lakes designated as long-term monitoring sites by the Adirondack Lakes Survey Corporation. Adirondack soils naturally have low base saturation and, therefore, any process that accelerates the removal of base cations from exchange sites decreases the ability of the soil to sustain plant growth and contribute to the ANC of surface waters. In soils that are composed primarily of resistant minerals the potential for base cation supply is low and exchange sites may become occupied by hydrogen ions and aluminum, rather than calcium, magnesium, and potassium. The extent to which calcium has decreased and whether calcium is currently decreasing in soils of the Adirondack region are unclear. The amount of available calcium in soils affects the structure and function of terrestrial ecosystems and the ability of surface waters to recover from acid deposition.

Studies of the effects of acid deposition on terrestrial biota have been primarily aimed at commercially important forest plants. Acid deposition has been linked to the decline of sugar maple (*Acer saccharum*) in eastern North America (Duchesne et al. 2002, Sharpe 2002), although other factors are probably involved (Minorsky et al. 2003). Similarly, acid deposition is implicated in the high mortality of pines (*Pinus*) in southwestern China (Feng et al. 2002) and spruces (*Picea*) in Europe (Roberts et al. 1989) and North America (Fowler et al. 1989). Calcium apparently plays a large part in these effects because of its role in membrane stabilization and cold tolerance (DeHayes et al. 1999, Horsley et al. 2000). Effects of acid deposition on terrestrial animals have received little attention; however, available evidence suggests that calcium also is important here. Abundance and diversity of land snails are negatively associated with acid deposition (Wäreborn 1992, Graveland and van der Wal 1996). Snails have greater demands for calcium than other invertebrates because of the composition of their shell, and abundance and diversity of snails have been associated with calcium abundance in soil (Wäreborn 1969, Gärdenfors 1992, Graveland and van der Wal 1996, Johannessen and Solhoy 2001, Hotopp 2002). Caterpillars had a lower calcium concentration at an acidified forest than a reference forest in Ontario (Mahony et al. 1997). Acid-induced calcium depletion can negatively affect insectivorous birds (Graveland and van der Wal 1996, Graveland and Drent 1997, Hames et al. 2002), which use calcium-rich invertebrates as important sources of dietary calcium during egg-laying (Graveland and Van Gijzen 1994, Graveland 1996, Taliaferro et al. 2001). A similar connection might be postulated for insectivorous mammals, but we are unaware of any work that bears upon this topic. The effects of acid deposition on terrestrial insectivores and their prey remain unclear (Ormerod and Rundle 1998). However, changes in the physical structure of the environment and the availability of calcium are likely mechanisms for changes in terrestrial animal assemblages (Mahoney et al. 1997).

Effects of acid deposition on stream biota have been studied extensively in eastern North America and throughout northern and central Europe. Typically, these studies have compared chronically acidified stream systems ($pH < 5$) to streams with moderate to circum-neutral (5 – 7) pH values (Mulholland et al. 1992, Hermann et al. 1993, Fitzhugh et al. 1999). Densities of bacteria living on decomposing leaves are not severely changed by acidification, but bacterial productivity is negatively affected (Palumbo et al. 1987, Osgood and Boylen 1990, Mulholland et al. 1992, Hermann et al. 1993, Maltby 1996, Dangles and Guerold 2001). Surprisingly, periphyton abundance often increases at low pH, but there is a concomitant shift in species composition to filamentous green algae and acid tolerant diatoms (Planas et al. 1989, Mulholland et al. 1992, Rosemond et al. 1992, Hermann et al. 1993, Junger and Planas 1993, Ledger and Hildrew 2000). Thus, energy sources for stream macroinvertebrates are affected by stream acidification.

There have been several different mechanisms proposed to explain the negative impacts of acidification on stream macroinvertebrates. The most common effect is the toxicity of aluminum, which increases in concentration when calcium is depleted from soils (Hermann and Anderson 1986, Hermann 1987, Mulholland et al. 1992, Rosemond et al. 1992, Hermann et al. 1993), but experiments in simulated stream chambers where soil aluminum does not play a role in toxicity have shown different species to vary in their sensitivity to low pH (Bell 1971, Courtney and Clements 1998). Mayflies (Ephemeroptera) are the most sensitive macroinvertebrates to acidification, and their loss appears to be related to aluminum toxicity (Hermann and Anderson 1986, Hermann 1987, Rosemond et al. 1992, Hermann et al. 1993, Brakke et al. 1994, Ledger and Hildrew 2000). Some caddisflies (Trichoptera) are also lost from acidified systems, but there are caddisfly species that are acid tolerant (Mulholland et al. 1992, Rosemond et al. 1992, Hermann et al. 1993, Courtney and Clements 1998). In addition to aluminum toxicity, calcium depletion in acidified streams negatively affects macroinvertebrates with high calcium requirements such as snails and crustaceans (Mulholland et al. 1992, Hermann et al. 1993, Brakke et al. 1994, Rukke 2002).

Besides physiological effects of acidification on stream macroinvertebrates, changes in trophic dynamics have also been proposed. Most acidified systems are small, forested streams where allochthonous sources of energy predominate (Vannote et al. 1980, Wallace and Webster 1996, but see McCutchan and Lewis 2002). Because of the negative effects of acidification on microbial communities that colonize leaf detritus, the quality of coarse particulate organic matter (CPOM) is reduced and leaf decomposition rates are decreased due to fewer shredders and reduced feeding rates of shredders (Mulholland et al. 1992, Rosemond et al. 1993 Hermann et al. 1993, Dangles and Guerold 1999, 2001, Guerold et al. 2000, Ledger and Hildrew 2000, Dangles 2002). Also, if light is not limiting in these forested streams, algal abundance can increase favoring grazing macroinvertebrates. However, it is the grazing mayflies and caddisflies that are the most sensitive to acidification, and the lack of grazers has been used as a partial explanation for the increase in algae in acidified streams. Thus, a typical detritivore-based system may support few shredders because only a few species can tolerate the acid conditions, and because the quality of the CPOM does not support the same growth rates or production of macroinvertebrate shredders. Also, whereas algae are abundant in these systems, grazers are not that important because most are lost due to physiological limitations.

SOILS

Soils in the Adirondacks are typical Spodosols that have developed on glacial till and outwash overlying bedrock. They average less than 1 meter in depth and consist of five distinct horizons: O, A, E, B and C, which are described below. Please note that while all of the thickness and soil pH values included in the following descriptions represent data from the three sites visited on this trip, they are typical values for soils developed on this kind of parent material throughout the Adirondacks. A soil profile representative of the field area is shown in Figure 1.

The uppermost organic (O) horizon ranges from 3-10 cm in thickness and is composed of plant and animal debris in the beginning stages of decomposition. The A horizon directly underlies the O horizon. It is generally dark brown to black in color and rich in decomposed organic material, but also contains clays and other resistant minerals. A horizons vary in thickness from 3 to 16 cm at these sites. Field moist soil pH values for the O and A horizons are extremely low, ranging from 2.8 to 4.4, with A horizons being slightly more acidic (avg. = 3.1) than O horizons (avg. = 3.6).

The organic poor E horizon has a distinctive light gray color and sandy texture in Spodosols. Anywhere from 4 to 20 centimeters thick, it is the zone of maximum leaching in the soil profile and is composed of predominantly clay minerals (April et al., 1986; 2004) and very resistant primary minerals, such as quartz. Soil pH of this horizon is also very acidic, ranging from 3.4 to 3.7 (avg = 3.6). The A and E horizons are referred to as eluvial horizons in the soil profile because they are the layers where the most leaching takes place. These horizons are thicker and better developed under coniferous trees than under deciduous stands.

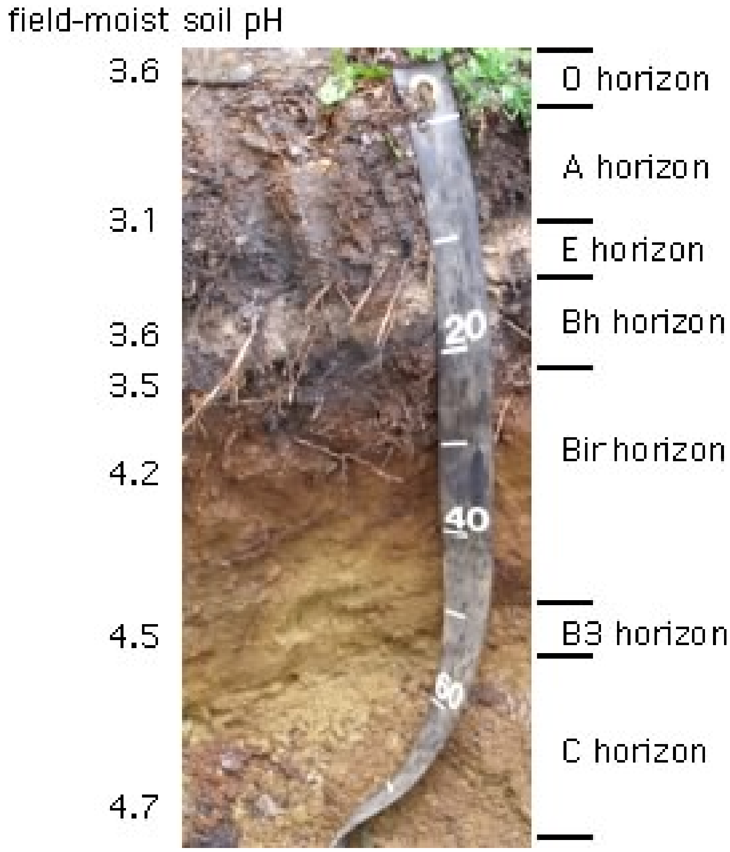

Figure 1: Typical soil profile in field area, delineating horizons and average soil pH values. Depths are in cm.

The illuviated B horizon is much thicker than the upper horizons, with an average thickness of about 40 cm. The B or "spodic" horizon is diagnostic for Spodosols and is characterized by accumulation of Al and Fe oxides and organic matter compounds which have been leached from above and re-deposited in this horizon. The B horizon is usually divided into subhorizons based on the type of material that accumulates, usually seen in the field as color differences in the soil profile. An 'h" designation (e.g. Bh subhorizon) signifies accumulation of humic organic material, giving the soil a dark brown color. "Bir" refers to accumulations of iron in the subhorizon and is indicated by soil with a reddish color. At these sites, both Bh and Bir subhorizons are present in almost all soil pits. Bh horizons are typically just below E horizons; Bir horizons are located below Bh horizons. Field moist soil pH values in the B horizon are slightly higher than in the upper horizons and increase with depth throughout the B from an average of 3.5 at the top of the horizon (Bh) to 4.5 near the bottom (B3 subhorizon).

The lowest horizon in the soil profile is the C horizon, which consists of partially weathered parent material. In this region, the parent material upon which the soil profiles have developed is till or sandy glacial outwash. The highest soil pH values are measured in the C horizon (avg. = 4.7).

SOIL MOISTURE

Soil moisture collectors, or lysimeters, are used to sample water from unsaturated soils. The chemical composition of soil moisture can give a good indication what nutrients are readily available to vegetation as well as what kinds of exchange reactions are taking place in the soil zone. In 2005, we installed soil moisture collectors at Town of Webb Site 10 (STOP 1) and Covewood (STOP 3) at different depths in the soil profiles. Two types of lysimeters were installed: suction lysimeters and passive lysimeters. Installing both types of lysimeters allows us to determine if there are any chemical differences between water that is tightly bound to soil particles (suction) and water that moves freely in the pore spaces (passive). Suction lysimeters use a vacuum to pull pore water from unsaturated soils. Suction lysimeters used here consist of a porous ceramic cup through which water is pulled from the soil, a length of PVC pipe which holds the water, and a stopper to maintain the vacuum. (Fig. 2)

Figure 2: Suction lysimeter used at Town of Webb Site 10 and Covewood – stops 1 and 3 on the field trip. (from http://www.soilmoisture.com/prod_details.asp?prod_id=1096&cat_id=16)

Passive lysimeters are devices that capture water moving downward through the soil by gravity; they do not use suction to pull water out of the soil. Two types of passive lysimeters used here are "wick" lysimeters, which employ fiberglass wicks to collect soil moisture and carry it to a collection container (Fig. 3); and simple rectangular containers of clean, pure quartz sand with a drainage tube to carry water to a collection container. Samples of soil moisture have been collected from these devices over the past three years to determine differences in soil moisture chemistry with horizon.

Figure 3: Wick lysimeters sampling soil moisture from two different horizons in an Adirondack soil pit.

As part of an NSF-funded research project investigating calcium depletion in Adirondack watersheds resulting from acid precipitation, we applied 2.25 tonnes of powdered limestone (in three separate applications of 0.75 tonnes each) over 50-meter diameter circular areas at Town of Webb Site 10 (STOP 1) and Covewood (STOP 3) between 2005 and 2007. These soils are being monitored for exchangeable cations associated with the solid phases (minerals and organic material), and pH and calcium concentrations in the liquid phase (soil moisture) in order to determine the effects of the calcium additions on the soil system. Other scientists working on the project are investigating effects of calcium depletion and calcium additions on terrestrial and aquatic biota.

ACKNOWLEDGEMENTS

Many thanks go to Yaicha Winters for help with the preparation of figures for this field guide. Thanks also to Otto Muller and Yaicha Winters for reviewing this manuscript.

REFERENCES CITED

April, R.H. and R.M. Newton 1983. Mineralogy and chemistry of some Adirondack Spodosols. Soil Science 135: 301-307.

April, R.H., M. Hluchy and R.M. Newton. 1986. The nature of vermiculite in Adirondack soils and tills. Clays and Clay Minerals 34: 549-556.

April, R. H. and R.M. Newton. 1992. Mineralogy and Mineral Weathering: In Atmospheric Deposition and Forest Nutrient Cycling, D. W. Johnson and S. E. Lindberg, eds., Ecological Studies 91: 378-425, Springer-Verlag, New York, 707 pp.

April, R. H., Keller, D. M. and Driscoll, C., 2004, Smectite in Spodosols from the Adirondack Mountains of New York. Clay Minerals, v. 39, 99-113.

Baker, J. and C. L. Schofield. 1982. Aluminum toxicity to fish in acidic waters. Water, Air and Soil Pollution 18:289-309.

Baker, J.P., J. Van Sickle, C.J. Gagen, D.R. DeWalle Jr, W.F. Sharpe, R.F. Carline, B.P. Baldigo, P.S. Murdoch, D.W. Bath, W.A. Kretser, H.A. Simonin and P.J. Wigington. 1996. Episodic acidification of small streams in the northeastern United States: effects on fish populations. Ecological Applications 6: 422-437.

Bell, H.L. 1971. Effect of low pH on the survival and emergence of aquatic insects. Water Res. 5:313-319.

Braake, D.F., J.P. Baker, J. Bohmer, A. Hartmann, M. Havas, C. Kelly, S.J. Ormerod, T. Paces, R. Putz, B.O. Rosseland, D.W. Schindler and H. Segner. 1994. Physiological and ecological effects of acidification on aquatic biota. *In* Acidification of freshwater ecosystems: implication for the future. *Edited by* C.E.W. Steinberg and R.F. Wright. John Wiley and Sons Ltd., Chichester. pp. 275-312.

Charles, D.F., ed. 1991. Acidic Deposition and Aquatic Ecosystems, Regional Case Studies. New York, Springer-Verlag.

Courtney, L.A. and W.H. Clements. 1998. Effects of acidic pH on benthic macroinvertebrate communities in stream microcosms. Hydrobiologia 379: 135-145.

Cronan, C. S. and C. L. Schofield. 1990. Relationships between aqueous aluminum and acidic deposition in forested watersheds of North America and northern Europe. Environmental Science and Technology 24:1100-1105.

Cronan, C. S. 1994. Aluminum biogeochemistry in the ALBIOS forest ecosystems: the role of acidic deposition in aluminum cycling. Pp. 51-81 *in* Godbold, D. and A. Huttermann (eds.) Effects of Acid Rain on Forest Processes. John Wiley and Sons, New York.

Cronan, C.S. and D.F. Grigal. 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. Journal of Environmental Quality 24: 209-226.

Currie, W. S., J. D. Aber, and C. T. Driscoll. 1999. Leaching of nutrient cations from the forest floor: effects of nitrogen saturation in two long-term manipulations. Canadian Journal of Forest Research 29:609-620.

Dangles, O. 2002. Functional plasticity of benthic macroinvertebrates: implications for trophic dynamics in acid streams. Can. J. Fish. Aquat. Sci. 59: 1563-1573.

Dangles, O. and F. Guerold. 1999. Impact of headwater stream acidification on the trophic structure of macroinvertebrate communities. Internat. Rev. Hydrobiol. 84: 287-297.

Dangles, O. and F. Guerold. 2001. Influence of shredders in mediating breakdown rates of beech leaves in circumneutral and acidic streams. Arch. Hydrobiol. 151: 649-666.

DeHayes, D. H., P. G. Schaberg, G. J. Hawley, and G. R. Strimbeck. 1999. Acid rain impacts on calcium nutrition and forest health. BioScience 49:789-800.

Driscoll, C. T. and R. M. Newton. 1985. Chemical characteristics of Adirondack lakes. Environmental Science and Technology 19:1018-1024.

Driscoll, C. T., G. E. Likens, L. O. Hedin, J. S. Eaton, and F. H. Bormann. 1989. Changes in the chemistry of surface waters. Environmental Science and Technology 23:137-142.

Driscoll, C. T, G. B. Lawrence, A. J. Bulger, T. J. Butler, C. S. Cronin, C. Eager, Lambert, G. E. Likens, J. L. Stoddard, and K. C. Weathers. 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. BioScience 51:180-198.

Driscoll, C.T, K.M. Driscoll, M.J. Mitchell and D.J. Raynal. 2003. Effects of acidic deposition on forest and aquatic ecosystems in New York State. Environ. Pollution 123: 327-336.

Duchesne, L., R. Ouimet, and D. Houle. 2002. Basal area growth of sugar maple in relation to acid deposition, stand health, and soil nutrients. Journal of Environmental Quality 31:1676-1683.

Feng, Z., H. Miao, F. Zhang, and Y. Huang. 2002. Effects of acid deposition on terrestrial ecosystems and their rehabilitation strategies in China. Journal of Environmental Sciences 14:227-233.

Fitzhugh, R.D., T. Furman, J.R. Webb, B.J. Cosby and C.T. Driscoll. 1999. Longitudinal and seasonal patterns of stream acidity in a headwater catchment on the Appalachian Plateau, West Virginia, USA. Biogeochemistry 47: 39-62.

Fowler, D., J. N. Cape, and M. H. Unsworth. 1989. Deposition of atmospheric pollutants on forests. Philosophical Transactions of the Royal Society of London, B 324:247-265.

Gallagher, J. and J. Baker. 1990. Current status of fish communities in Adirondack Lakes. Pp. 3-11 to 3-48 *in* Adirondack Lakes Survey: An Interpretive Analysis of Fish Communities and Water Chemistry, 1984-1988. Adirondack Lakes Survey Corporation, Ray Brook, New York.

Galloway, J. J., C. L. Schofield, N. E. Peters, G. R. Hendrey, and E. R. Altwicker. 1983. Effect of atmospheric sulfur on the composition of three Adirondack lakes. Canadian Journal of Fish and Aquatic Science 40:799-908.

Gärdenfors, U. 1992. Effects of artificial liming on land snail populations. Journal of Applied Ecology 29:50-54.

Graveland, J. R. 1996. Avian eggshell formation in calcium-rich and calcium-poor habitats: importance of snail shells and anthropogenic calcium sources. Canadian Journal of Zoology 74:1035-1044.

Graveland, J. R. and R. H. Drent. 1997. Calcium availability limits breeding success of passerines on poor soils. Journal of Animal Ecology 66:279-288.

Graveland, J. R. and R. van der Wal. 1996. Decline in snail abundance due to soil acidification causes eggshell defects in forest passerines. Oecologia 105:351-360.

Graveland, J. R. and T. Van Gijzen. 1994. Arthropods and seeds are not sufficient as calcium sources for shell formation and skeletal growth in passerines. Ardea 82:299-314.

Guerold, F., J.P. Boudot, G. Jacquemin, D. Vein, D. Merlot and J. Rouiller. 2000. Macroinvertebrate community loss as a result of headwater acidification in the Vosges Mountains (N-E France). Biodiversity and Conservation 9: 767-783.

Hames, R. S., K. V. Rosenberg, J. D. Lowe, S. E. Barker and A. A. Dhondt. 2002. Adverse effects of acid rain on the distribution of the wood thrush Hylocichla mustelina in North America. Proceedings of the National Academy of Sciences 99:11235-11240.

Hermann, J. and K.G. Anderson. 1986. Aluminum impact on respiration of lotic mayflies at low pH. Water, Air and Soil Pollution 30: 703-709.

Hermann, J. 1987. Aluminum impact on freshwater invertebrates at low pH – a review. In: Speciation of Metals in Water, Sediment, and Soil Systems. Landner L. (ed.). Lecture notes in Earth Sciences 11, 157-175. Springer and Verlag, Berlin.

Hermann, J., E. Degerman, A. Gerhardt, C. Johansson, P.E. Lingdell and I.P. Muniz. 1993. Acid-stress effects on stream biology. Ambio 22: 298-307.

Horsley, S. B., R. P. Long, S. W. Bailey, R. A. Hallett, and T. J. Hall. 2000. Factors associated with the decline disease of sugar maple on the Allegheny Plateau. Canadian Journal of Forest Research 30:1365-1378.

Hotopp, K. P. 2002. Land snails and soil calcium in central Appalachian Mountain forest. Southeastern Naturalist 1:27-44.

Jenkins, J., K. Roy, C. Driscoll, and C. Buerkett.2007. Acid Rain in the Adirondacks. Cornell University Press, Ithaca, NY, 246 p.

Johannes, A.H., E.R. Altwicker and N.L. Clesceri. 1985. The Integrated Lake-Watershed Acidification Study: Atmospheric inputs. Water Air Soil Pollution 26: 339-353.

Johannessen, L. E., and T. Solhoy. 2001. Effects of experimentally increased calcium levels in the litter on terrestrial snail populations. Pedobiologia 45:234-242.

Junger, M. and D. Planas. 1993. Alteration of trophic interactions between periphyton and invertebrates in an acidified stream: a stable carbon isotope study. Hydrobiologia 262: 97-107.

Lawrence, G.B. David, and W. C. Shortle. 1995. A new mechanism for calcium loss in forest-floor soils. Nature 378:162-164.

Lawrence, G. B., M. B. David, G. M. Lovett, P. S. Murdoch, D. A. Burns, J. L. Stoddard, B. P. Baldigo, J. H. Porter, and A. W. Thompson. 1999. Soil calcium status and the response of stream chemistry to changing acidic deposition rates. Ecological Applications 9:1059-1072.

Ledger, M.E. and A.G. Hildrew. 2000. Herbivory in acid stream. Freshwat. Biol. 43: 545-556.

Likens, G.E., Bormann, F.H., and Johnson, N.M., 1972, Acid Rain: Environment, v. 14, no.3, p.33-40.

Mahony, N., E. Nol, and T. Hutchinson. 1997. Food-chain chemistry, reproductive success, and foraging behaviour of songbirds in acidified maple forests of central Ontario. Canadian Journal of Zoology 75:509-517.

Maltby, L. 1996. Detritus processing. *In*: River biota: Diversity and dynamics. G. Petts and P Calow (*Eds.*). Blackwell Sci. London. pp. 98-110.

McCutchan, J.H. and W.M. Lewis. 2002. Relative importance of carbon sources for macroinvertebrates in a Rocky Mountain stream. Limnol. Oceanogr. 47: 742-752.

McLelland, J. and J. Chiarenzelli. 1990. Isotopic constraints on emplacement age of anorthositic rocks of the Marcy massif, Adirondack Mtns., New York. Journal of Geology 98: 19-41.

McLelland, J. 2001. Rock of Ages: From volcanic islands to Himalayan ranges: the geologic evolution of the Adirondack Mountains. Adirondack Life, July/August, 2001.

Minorsky, P. J., C.T. Driscoll, J.W. Elwood, M.P. Osgood, A.V. 2003. The decline of sugar maples (*Acer saccharum*). Plant Physiology 133:441-442.

Mulholland, P.J., C.T. Driscoll, J.W. Elwood, M.P. Osgood, A.V. Palumbo, A.D. Rosemond, M.E. Smith and C. Schofield. 1992. Relationships between stream acidity and bacteria, macroinvertebrates and fish: a comparison of north temperate and south temperate mountain streams, USA. Hydrobiologia 239: 7-24.

Oden, S., 1968, The acidification of air precipitation and its consequences in the natural environment: Bull. Ecological Research Communications NFR. Ecology Comm. Bull. no. 1, Stockholm.

Ormerod, S. J., and S. D. Rundle. 1998. Effects of experimental acidification and liming on terrestrial invertebrates: implications for calcium availability to vertebrates. Environmental Pollution 103:183-191.

Osgood, M.P. and C.W. Boylen. 1990. Seasonal variations in bacterial communities in Adirondack streams exhibiting pH gradients. Microb. Ecol. 20: 211-230.

Palumbo, A.V., M.A. Bogle, R.R. Turner, J.W. Elwood and P.J. Mulholland. 1987. Bacterial communities in acid and circumneutral streams. Appl. Environ. Microbiol. 53: 3370344.

Planas et al., D.L., L. Lapierre, G. Moreau and M. Allard. 1989. Structural organization and species comopsitiopn of a lotic periphyton community in response to experimental acidification. Can. J. Fish. Aquat. Sci. 46: 827-835.

Roberts, T. M., R. A. Skeffington, and L. W. Blank. 1989. Causes of type I spruce decline in Europe. Forestry 62:179-222.

Rosemond et al., A.D., S.R. Reice, J.W. Elwood and P.J. Mulholland. 1992. The effects of stream acidity on benthic invertebrate communities in the south-eastern United States. Freshwat. Biol. 27: 193-209.

Roy, K. M. and C. T. Driscoll. 2001. Adirondack Lake Survey Corporation long-term monitoring project lake chemistry recovery in the Adirondack region. Proceedings of the Conference on Environmental Monitoring, Evaluation, and Protection in New York: Linking Science and Policy, September 24-25, 2001. Albany, NY. Sponsored by NYSERDA.

Rukke, N.A. 2002. Effects of low calcium concentrations on two common freshwater crustaceans, *Gammarus lacustris* and *Astacus astacus*. Funct. Ecol. 16: 357-366.

Schofield, C.L. 1976. Acid precipitation: Effects on fish. Ambio 5:228-230.

Sharpe, W. E. 2002. Acid deposition explains sugar maple decline in the east. BioScience 52:4-5.

Stoddard, J.L., D.S. Jeffries, A. Lukewille, T.A. Clair, P.J. Dillon, et al. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 401: 575-578.

Stoddard, J.L., Kahl, J.S., Deviney, F.A., DeWalle, D.R., Driscoll, C.T., Herlihy, A.T., Kellogg, J.H., Murdoch, P.S., Webb, J.R., and Webster, K.E. 2003, Response of Surface water chemistry to the Clean Air Act amendments of 1990. U.S. Environmental Protection Agency. EPA 620/R-03/001.

Taliaferro, E. H., R. T. Holmes and J. D. Blum. 2001. Eggshell characteristics and calcium demands of a migratory songbird in two New England forests. Wilson Bulletin 113:94-100.

Tyler, G. 1978. Leaching rates of heavy metal ions in forest soil. Water, Air and Soil Pollution 9:137-148.

Vannote, R.L., G.W. Minshall, K.W. Cummins, J.R. Sedell, and C.E. Cushing, 1980. The river continuum concept. Canadian Journal of Fisheries and Aquatic Sciences 37: 130-137.

Van Sickle et al., J., J.P. Baker, H.A. Simonin, B.P. Baldigo, W.A. Krester and W.E. Sharpe. 1996. Episodic acidification of small streams in the northeastern United States: Fish mortality in field bioassays. Ecological Applications 6: 408-421.

Wallace, J.B and J.R. Webster. 1996. The role of macroinvertebrates in stream ecosystem function. Ann. Rev. Entomol. 41: 115-139.

Wäreborn, I. 1969. Land mollusks and their environments in an oligotrophic area in southern Sweden. Oikos 20:461-479.

Wäreborn, I. 1992. Changes in the land mollusk fauna and soil chemistry in an inland district in southern Sweden. Ecography 15:62-69.

Wolters, V. and M. Schaefer. 1994. Effects of acid deposition on soil organisms and decomposition processes. Pp. 83-127 *in* Godbold, D. L. and A. Hütterman (eds.) Effects of acid rain on forest processes. John Wiley and Sons, New York.

Worrall, J. J. 1994. Relationships of acid deposition and sulfur dioxide with forest diseases. Pp. 163-182 *in* Godbold, D. L. and A. Hütterman (eds.) Effects of acid rain on forest processes. John Wiley and Sons, New York.

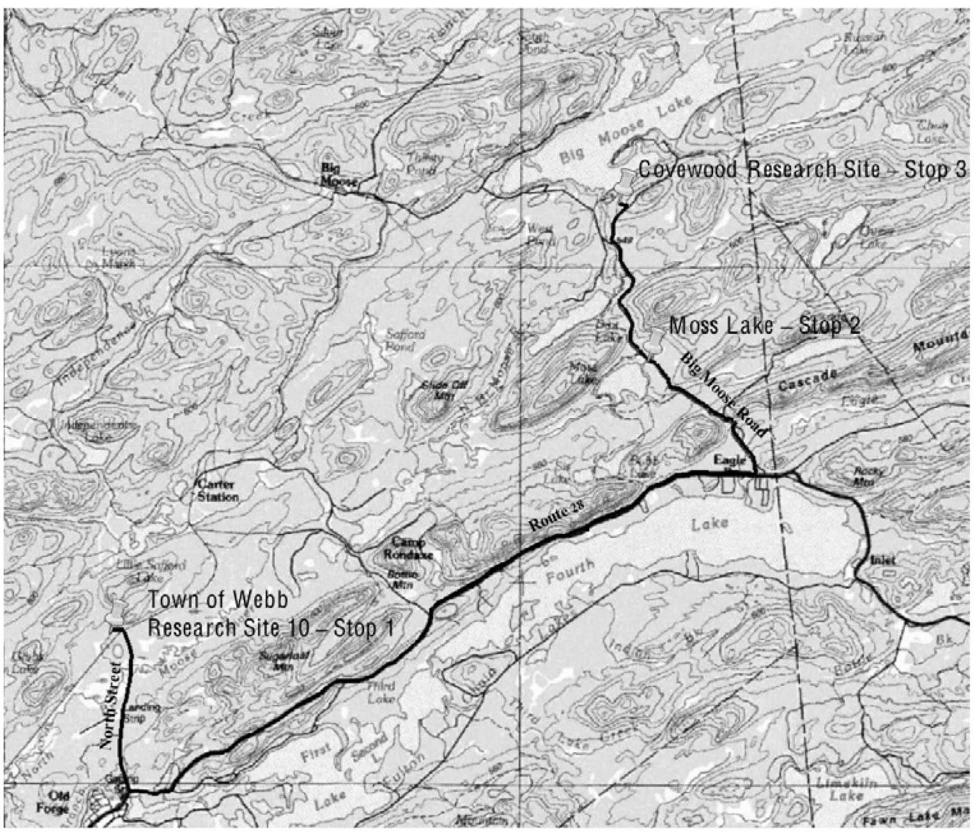

Figure 4: Location map of stops for field trip in Adirondacks.

ROAD LOG AND STOP DESCRIPTIONS

We will depart from the public parking lot located in Old Forge, NY across from the Old Forge Hardware store and the Old Forge Fire Dept, located on NYS Route 28. Head north on NYS Route 28.

Total Miles	Miles from Last Point	Route Description
0.0	0.0	Leave parking lot. Turn onto Route 28 N.
0.3	0.3	Turn left onto North St.
0.9	0.6	Note "outcrops" of glacial outwash sand on the left.
1.3	0.4	Paved road ends
1.8	0.5	Cross bridge over Moose River
2.3	0.5	Cross railroad tracks
2.4	0.1	Bear left, staying on road you are on
2.5	0.1	Pull off road to the right and park

STOP 1: TOWN OF WEBB "SITE 10"

18T: 0502060
UTM: 4843218
N43°44.519'
W074°58.464'

Note: If you wish to return to this area, permission must be obtained from the Town of Webb supervisor. During the fall months, this land is leased to a hunting club and is generally inaccessible to the public until the winter season, when the trails are re-opened for snowmobiling.

At this site, we will walk a few hundred meters into the woods to dig a soil pit and view monitoring and collection equipment used to study soil and soil moisture. This site is part of an NSF-funded research project studying calcium depletion in Adirondack watersheds exposed to acid precipitation – the "site 10" designation is our own internal label. Soils here, as in most of the Adirondacks, are typical spodosols. In this area, soils are developed on a sandy outwash material, which could be seen in roadside "outcrops" as we traveled from Old Forge into the site. Few cobbles or boulders are encountered when digging soil pits in this area.

As part of the research project, a 50-meter diameter circular area on one side of the small stream flowing through the site was treated 3 times with 0.75 tonnes (each time) of powdered limestone and an identically-sized untreated area on the opposite side of the stream was used as a control. Soil and soil moisture chemistry has been monitored at this site since 2005. Figures 5 and 6 show soil pH and exchangeable calcium with depth over time before and after application of powdered limestone. As expected, additions of calcium carbonate raised the soil pH in the upper horizons and, over time, that effect is being translated lower into the soil profile. Similarly, exchangeable calcium is increased in the upper horizons of the soils treated with powdered limestone, although that increase is only seen down to about 15 cm, even 3 years after the first application of calcium carbonate.

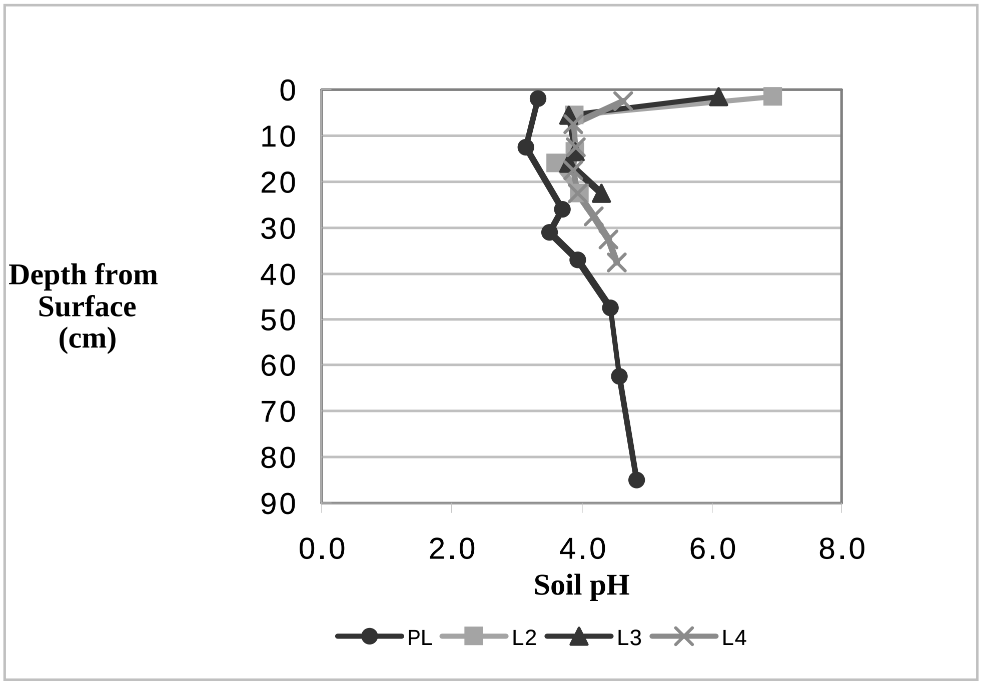

Figure 5: Soil pH in Town of Webb Site 10 soil pit. PL = pre-liming; L2 = after second application; L3 = 9 months after third application; L4 = 20 months after third application. Note that successive application of limestone raises soil pH in the upper horizons (approximately the top 40 cm).

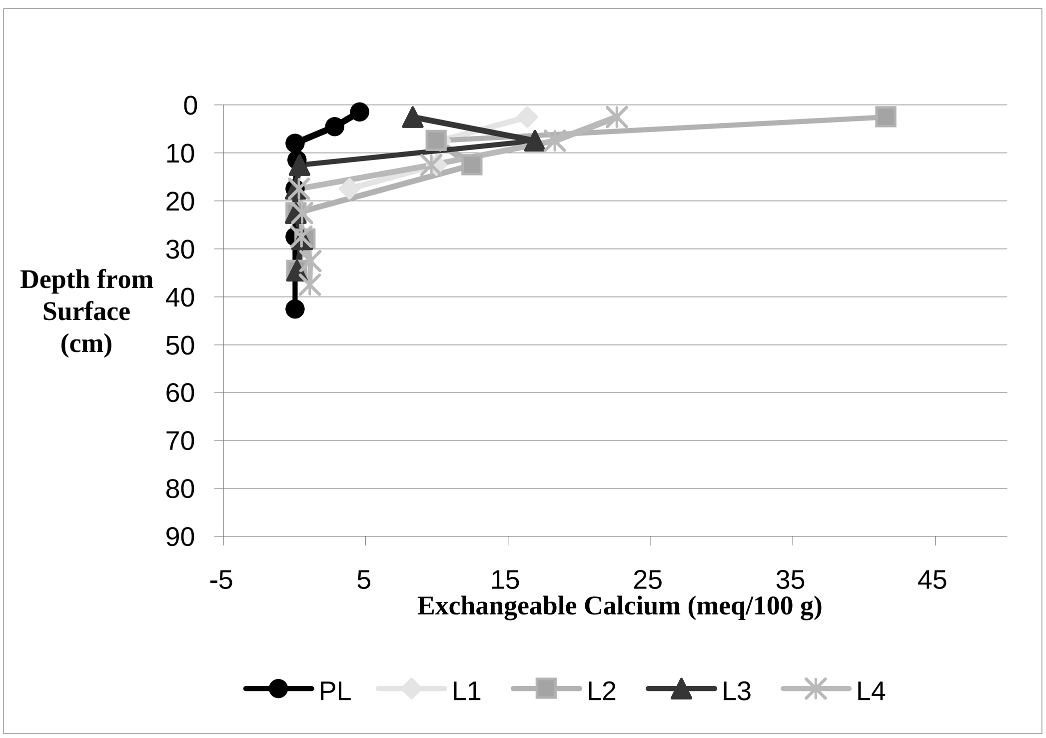

Figure 6: Exchangeable calcium in Town of Webb Site 10 soil pit. PL = pre-liming; L1 = after first limestone application; L2 = after second application; L3 = after third application. Note that successive application of limestone increases exchangeable calcium in the upper horizons (approximately the top 20 cm).

Return to vehicle. Retrace route back to intersection of North St. and NYS Route 28N.

Total Miles	**Miles from Last Point**	**Route Description**
4.7	2.2	Turn left onto NYS Route 28N
13.7	9.0	Turn left onto Big Moose Rd
15.9	2.2	Turn left into parking lot for Moss Lake trailhead and park

STOP 2: MOSS LAKE TRAILHEAD

18T: 0512455
UTM: 4848383
N43°47.304'
W074°50.712'

We will take a short walk here to the shore of Moss Lake and take a reading of water pH. The south side of the Moss Lake watershed consists of thick sand-covered bedrock and much of the north side has a thinner cover of till and bedrock close to the surface. Flow paths of water moving through the soils and underlying materials determine how well buffered the incoming acid precipitation becomes and therefore affects the lake pH. At this location, we will also view the Moss Lake National Atmospheric Deposition Program data collection site (site NY29 – Fig. 7). Precipitation pH for the past few years is shown in Figure 8.

Figure 7: NADP site NY29 at Moss Lake showing wet/dry collector, rain gage and other meteorological equipment (from http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=NY29).

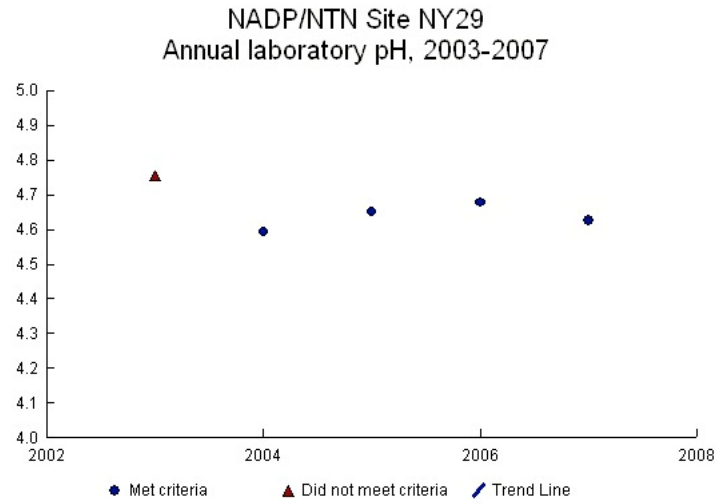

Figure 8: Mean annual pH values of precipitation samples from Moss Lake NADP site (from http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=NY29)

Return to vehicles. Turn left back onto Big Moose Rd.

Total Miles	**Miles from Last Point**	**Route Description**
17.1	1.2	Pass Windfall Pond trailhead on the right. We will not take the trail to Windfall Pond, but it is a nice walk. The trail passes over the outlet of Windfall Pond. The Windfall Pond watershed contains some calcium carbonate rock, which acts to buffer acidic precipitation. Outlet pH values are generally higher here than in other streams in the Big Moose area because of this buffering effect.
18.1	1.0	Turn right onto Covey Rd
18.2	0.1	Turn right at sign for Covewood Lodge
18.3	0.1	Turn right at sign for South Bay Rd.
18.4	0.1	Pull off to the left and park.

STOP 3: COVEWOOD

18T: 0511908
UTM: 4851626
N43°49.055'
W074°51.121'

Note: This land is private property and permission must be obtained from the owners of Covewood Lodge. On the north shore of Big Moose Lake, Covewood Lodge and surrounding property presents a somewhat different surface material than previous stops. The surficial material upon which soil are developed in this area is a thinner, bouldery till, as is evident just by looking at the surrounding landscape. Numerous cobbles and boulders are encountered when excavating soil pits around here. Depth to the saturated zone is shallower here and soils are often wetter than at Town of Webb Site 10 or Moss Lake.

The owner of Covewood Lodge uses spring water (groundwater) to supply his lodge and cabins. Several years ago, he determined that the water was very acidic (below pH of 4) and he has attempted several different methods for neutralizing the acidity. We will look at one or two these devices as well as view monitoring equipment we have set up in this area as part of the aforementioned research project.

Covewood is one of the sites where powdered limestone was applied in 2005, 2006 and 2007. Exchangeable calcium in the soils is shown in Figure 9 below. As at Town of Webb Site 10, the data show that exchangeable calcium in the soil has increased down to a depth of about 10 cm due to the addition of calcium carbonate. We have not seen any effect of the limestone additions on the groundwater yet.

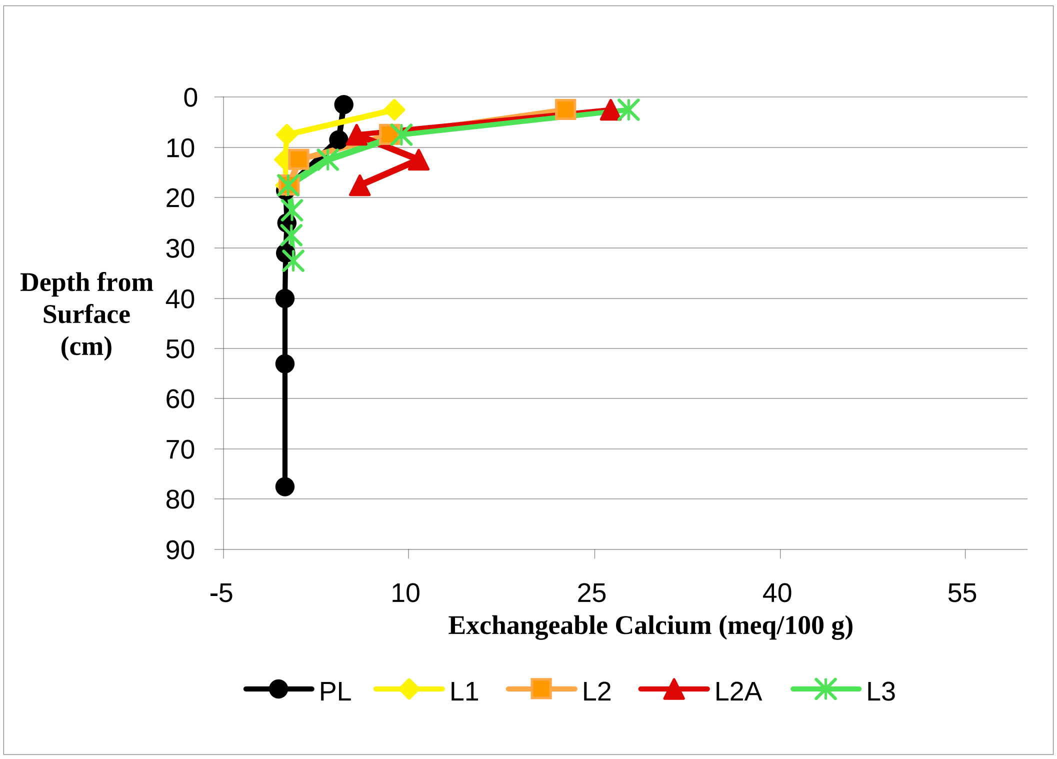

Figure 9: Exchangeable calcium in Covewood pit BIG-12. PL = pre-liming; L1 = after first limestone application; L2 and L2A = after second application; L3 = after third application. Note that successive application of limestone increases exchangeable calcium in the upper horizons (approximately the top 10 cm).

To return to Old Forge: leave Covewood property and turn left onto Covey Rd

Total Miles	Miles from Last Point	Route Description
18.6	0.2	Turn left onto Big Moose Rd
22.7	4.1	Turn right onto NYS Route 28 S
32.0	9.3	Turn left into public parking lot.

END OF FIELD TRIP