INFLUENCE OF GEOLOGY ON THE ACIDIFICATION STATUS OF ADIRONDACK LAKES AND STREAMS

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INTRODUCTION

The effects of acid deposition on surface water quality 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. This fieldtrip will explore the processes and conditions that influence the acid-base status of surface waters as we visit lake watersheds in the eastern and central Adirondacks that display a wide range of geochemical, geologic and hydrologic characteristics.

As it turns out, for reasons to be described later, most acidic lakes and streams (pH < 5) are found in the western and southwestern Adirondacks, and also at high elevation and remote areas of the high peaks region. With the 2002 NYSGA/NEIGC meeting and field trips based out of Lake George, it was not feasible to design a one-day trip to encompass all of these areas; they were simply too far away, or too inaccessible. However, the stops selected for this field trip will illustrate how both geology and hydrology play a pivotal role in determining the acid-base status of surface waters contained within watersheds. Lakes and ponds to be visited include Clear Pond, Harris Lake, Arbutus Lake, and Echo and Little Echo Ponds.

THE ADIRONDACK REGION - BACKGROUND

Geology

The Adirondack Park, the largest park in the contiguous United States, comprises about 6 million acres of predominantly forested land dotted with more than 3,000 lakes and ponds (Figure 1). Water drawn from five major drainage basins flows along 1,500 miles of rivers fed by an estimated 30,000 miles of brooks and streams (State of the Park, Adirondack Council). 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; Figure 2). The major rock units underlying the area can be broadly divided into three types: granitic gneisses, anorthosites, and metasediments. Marble and other calcite-bearing

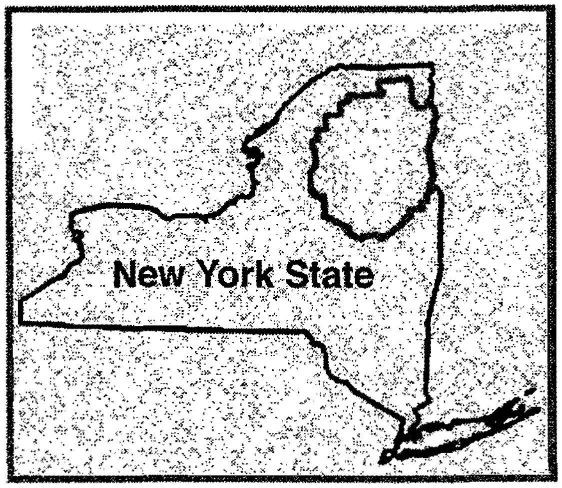

Figure 1. Area encompassed by the Adirondack Park.

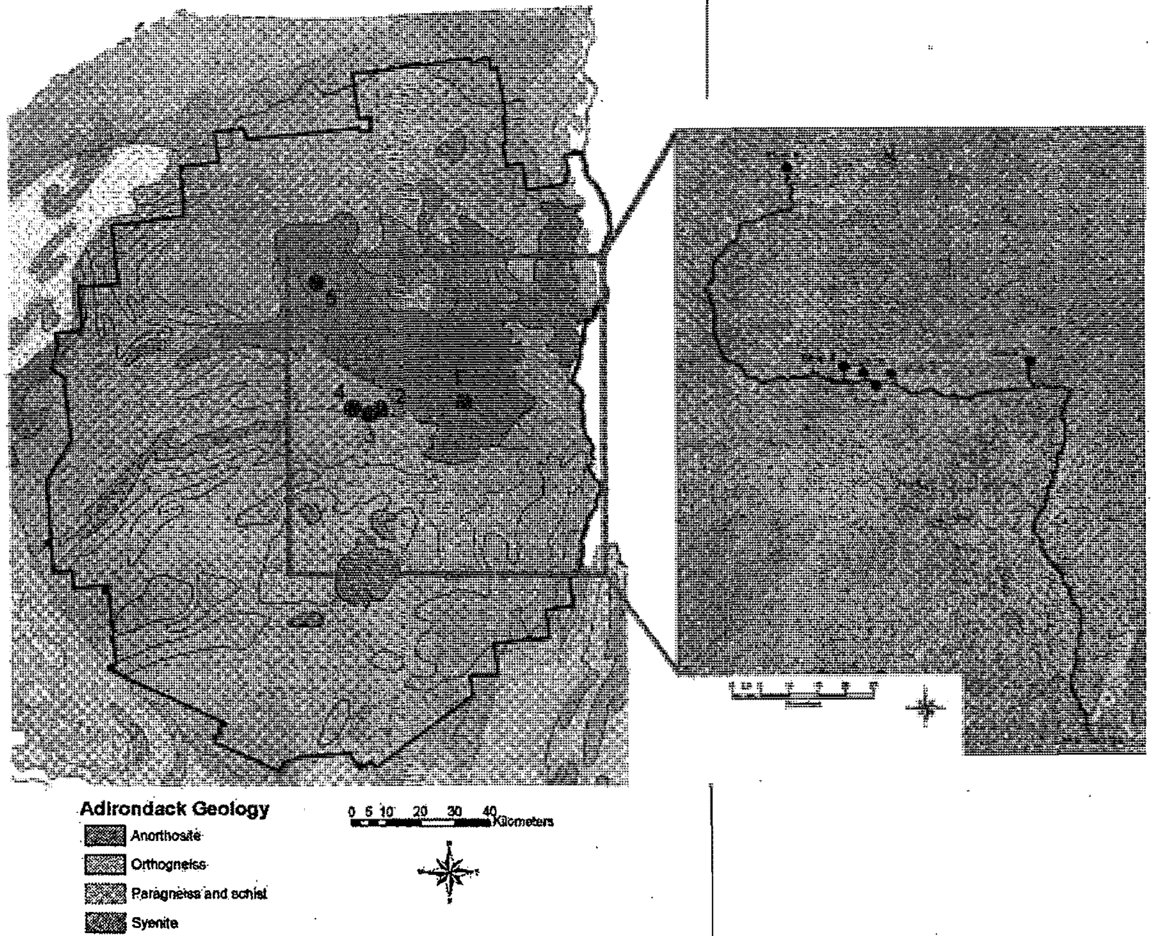

Figure 2. Generalized geologic map of the Adirondacks with field trip stops shown.

Acid Rain

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 Mountain region of New York State receives elevated inputs of sulfur and nitrogen in the form of 'acid rain.' Prevailing winds from west to east carry pollutants emitted in the Midwest, mainly from coal burning electric utilities, over the northeastern United States and Canada. Acid rain forms when SO_2 and NO_x emissions derived from the combustion of fossil fuels transform in the atmosphere to sulfuric and nitric acids. Long-range transport and deposition of these strong acids over time has resulted in the acidification of surface waters in northeastern North America, and in the Adirondacks in particular. Because components of 'acid rain' may enter terrestrial ecosystems as precipitation (both rain and snow), fog or mist (wet deposition), or as gases or particles (dry deposition), a more appropriate term used for 'acid rain' is acid deposition.

Precipitation in the Adirondacks averages about 100 -150 cm/yr, with about 70% falling as rain and 30% as snow (Johannes, 1985). This large quantity of precipitation results in high amounts of acid being delivered to the region. H^+ deposition averaged about 500 eq/ha/yr over the Adirondacks in the early 1990's. But because precipitation amounts decrease from west to east due to orographic effects, H^+ deposition decreases from west to east, as well, from about 520 eq/ha/yr to 470 eq/ha/yr (Charles, 1991). This is one reason why most acidic lakes and streams are located in the western Adirondacks. 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 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. Average annual H^+ deposition fell to about 400 eq/ha/yr over the past decade and average annual pH values have risen from about 4.2 to 4.5 (http://nadp.sws.uiuc.edu/). There has been no significant change in nitrogen deposition, during this same period because CAAA legislation did not specify caps for NO_x emissions (Driscoll et al., 2001).

SURFACE WATER ACIDIFICATION

Most surface water in the Adirondacks is naturally dilute, with low amounts of dissolved solids, low ionic strengths, and low acid neutralizing capacity (ANC). Acid neutralizing capacity is a measure of the ability of water (or soil) to neutralize inputs of strong acid. ANC may be generated by terrestrial processes such as mineral weathering, cation exchange, and adsorption of SO_4^{-2} and N (Charles, 1991), or it may be generated in lakes or marshes by sulfate reduction. The higher the ANC of a water body, the more strong acid it takes to reduce the pH to the equivalence point. Bicarbonate ion, HCO_3^-, is the major acid neutralizing species in most surface waters, but all proton acceptors can contribute to ANC. Stumm and Morgan (1981) define ANC as follows:

$$\text{ANC} = [HCO_3^-] + [CO_3^-] + [OH^-] + [\text{other } H^+ \text{ ion acceptors}] - [H^+ \text{ ion donors}]$$

A study conducted by the Adirondack Lakes Survey Corporation (ALSC) in the mid-to late-1980's on 1469 lakes found that lakes with low pH and low ANC are prevalent in the Adirondacks, and that 26% of the waters surveyed had air-equilibrated pH values <5.0 and ANC's <0 (Kretser et al., 1989). Sulfate was identified as the dominant mineral acid anion in the ALSC study, indicating that sulfuric acid is the major source of mineral acidity. Waters with low pH and low ANC were found throughout the region, but were concentrated in the western and southwestern Adirondacks (see Figure 3). This area, which contains large numbers of small, high elevation lakes, also receives the highest levels of precipitation in the region. Another survey (EMAP; Larsen et al., 1994; Stevens 1994) conducted over the period 1991-1994 indicated that 41% of the 1812 Adirondack lakes studied were chronically acid or sensitive to episodic acidification. Of these lakes, 10% had ANC values less than 0 µeq/L, and 31% had ANC values between 0 and 50 µeq/L. Acid sensitive lakes and streams in the northeast U.S. are normally defined as those with ANC values less than 50 µeq/L.

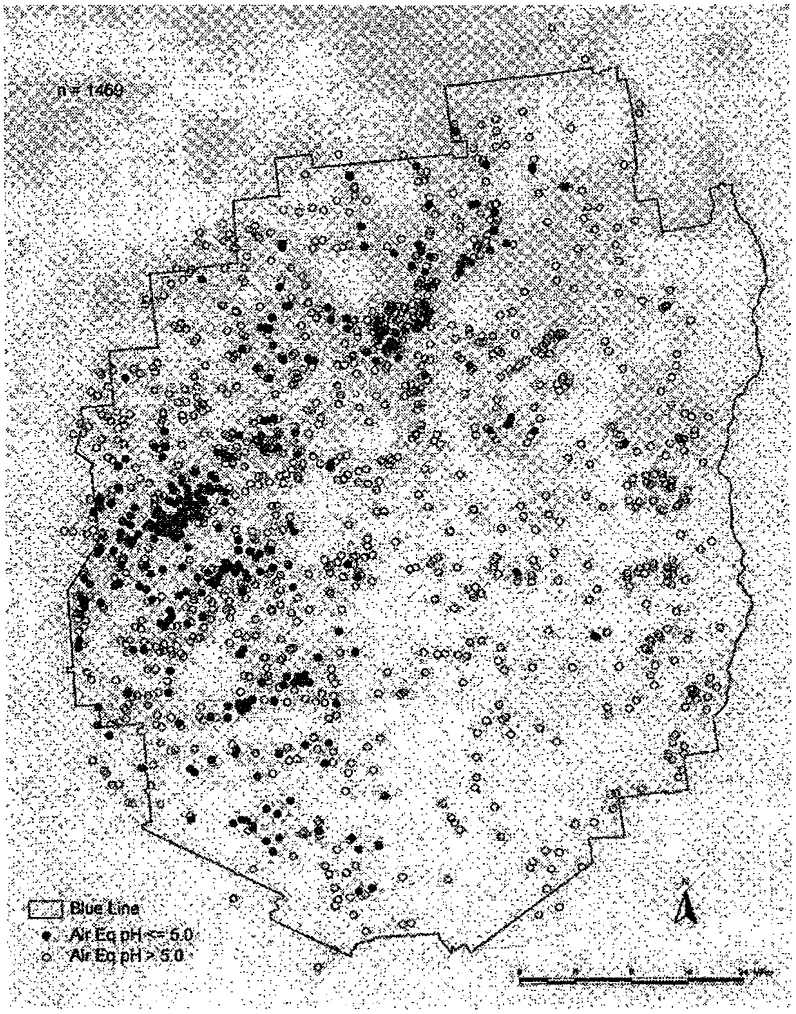

Figure 3. ALSC pH distribution (from Kretser et al., 1989, Adirondack Lakes Study 1984-1987: An Evaluation of Fish Communities and Water Chemistry).

Over the past century, inputs of acid deposition have led to the acidification of surface waters in the Adirondacks. Lakes, ponds, and streams with low ANC were the first affected and continue to be the most severely impacted today. Effects of acid deposition on surface water chemistry may vary with season and with the hydrologic processes prevalent in watersheds. For example, during winter months acidic components of precipitation are stored in the snowpack, which may reach depths of 1-2 m. During spring snowmelt, normally covering about a two-week period in April, large quantities of acid are released and cause surface waters to become more acidic than at other times during the year. This is called an episodic acidification event, and pH and ANC values may drop to less than 5.0 and 0 µeq/L, respectively, for days or weeks at a time. Usually, it is just the upper meter or two of a lake that acidifies during the event, but in streams the entire water column is affected. Episodic acidification of surface water can also occur after a particularly heavy rainfall, for example, from an air mass that might have originated in the Midwest where it encountered high levels of SO_2 and NO_x emissions.

BRIEF SUMMARY OF EFFECTS OF ACID DEPOSITION ON AQUATIC AND TERRESTRIAL ECOSYSTEMS

Introduction

The literature is rich with studies on the effects of acidic deposition on terrestrial and aquatic ecosystems, therefore, for more detail and further reading on this topic we refer you to both the scientific and popular literature that has been produced over the past three decades on this topic. Several excellent summaries worth mentioning here are those written by: Driscoll et al., 2001; Sullivan, 2000; Lawrence and Huntington, 1999; Charles, 1991; and Schindler, 1988.

We also direct your attention to several important and information-rich web sites, including:

http://www.adirondacklakessurvey.org/index.html
http://www.epa.gov/airmarkets/progress/arpreport/index.html
http://www.dec.state.ny.us/website/dar/index.html
http://www.epa.gov/oar/oaq_caa.html
http://nadp.sws.uiuc.edu/

Brief Summary of Effects

Acid deposition results in the mobilization of Al in soil solution, which subsequently enters streams and lakes. Spodosols in the Adirondacks are naturally acidic, but elevated concentrations of inorganic monomeric Al are enhanced by strong mineral acid additions to soils from atmospheric deposition (Cronan and Schofield, 1990). The source of the aluminum in soils is organically bound Al, exchangeable Al, Al-hydroxides and oxides, paracrystalline Al compounds, interlayer Al (in phyllosilicates), and ultimately, primary mineral weathering. Low pH and concomitant elevations of Al in surface waters contribute to the decline of fish, zooplankton and macroinvertebrate species in affected systems (Schindler et al., 1985; Schindler, 1988). Al concentrations in surface waters may reach toxic levels that are sustained throughout the year, or may rise only during episodic acidification events. In the latter case, elevated Al levels may coincide with critical biological events, such as the hatching of fry in the spring. High rates of fish mortality have been linked with acidic water and elevated aluminum concentrations (Baker and Schofield, 1982; Baker et al., 1996).

High levels of Al in soil solution along with the leaching of essential nutrients from soils may lead to reduced tree growth and dieback of forests (Shortle et al., 1997; DeHayes et al., 1999). 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. Replenishment of exchangeable bases for nutrient uptake depends heavily on primary mineral weathering, but in acid-sensitive soils mineral weathering may be sluggish. In soils that are composed of fairly resistant minerals, such as quartz, K-feldspar and muscovite, base cation supply is low and exchange sites may become occupied by H^+ and Al, rather than Ca^{2+}, Mg^{2+}, and K^+. Minerals such as Ca-plagioclase, biotite, hornblende, diopside, and calcite are much more susceptible to chemical weathering and can provide base cations at rates comparable with depletion rates accelerated by acidic deposition. Important here is consideration of the *quantity* of weatherable minerals present in the soil, the *residence time* of the subsurface water, and the *flowpath* of water through the soil. Calcium depletion seems to be a critical factor in Adirondack and other northeastern forest soils and studies are currently under way to assess the effect of Ca depletion on the dieback of tree species, such as red spruce and sugar maple among others (Driscoll et al., 2001; Lawrence et al., 1999).

Over time, soils receiving acidic deposition will accumulate both S and N, mainly in the form of SO_4^{-2} and NO_3^-. Driscoll et al. (2001) suggest that even though S deposition is declining because of emission controls on SO_2, the slow release of previously accumulated SO_4^{-2} from soils will delay the recovery of surface waters. NO_3^- concentrations are usually low in surface and soil waters because it is generally considered to be a growth-limiting nutrient in forest ecosystems. . However continued nitrate deposition can lead to nitrate saturation of the ecosystem. At this point nitrogen deposition exceeds nutrient uptake and excess nitrate is exported to surface waters. In the Adirondack region there does not seem to be any significant regional change in NO_3^- in surface waters, or in atmospheric deposition

PROCESSES INFLUENCING SURFACE WATER CHEMISTRY

Although much of the Adirondack region is underlain by acid-sensitive bedrock, the chemistry of surface waters varies widely across the region from about neutral to acidic. The extent of neutralization of acidic inputs to surface waters is determined by the interaction of a complex series of factors, including soil, hydrology, vegetation, geology, climate and atmospheric deposition. The relative contribution of these factors in regulating the acid-base status of surface waters is highly variable, even within very small regions. For example, hydrologic factors may dictate drainage water chemistry in one watershed, while an adjoining watershed may be largely influenced by geologic factors (e.g., the presence of carbonate minerals). Base cations are derived primarily from cation exchange and mineral weathering reactions occurring in the soil and in the surficial materials within a watershed (April et al., 1986; Newton et al., 1987). The rate at which these are supplied largely determines the acid-base status of surface water in the watershed.

For most watersheds in the Adirondacks, the routing of water through the soils and geologic materials is the major factor determining the base cation supply rate (Figure 4). The relative routing of water, or flow path, is a function of both the nature of the surficial material within the watershed, as well as the hydrologic retention time, or residence time, within the deposits. Surficial materials in the Adirondacks range from highly acidic upper soil horizons to more base-rich, relatively unweathered till and stratified drift. Rarely do drainage waters in the Adirondacks contact carbonate minerals. However, when carbonate minerals are present in the bedrock, the resulting surface water is enriched in base cations (particularly Ca^{2+} and Mg^{2+}) and ANC.

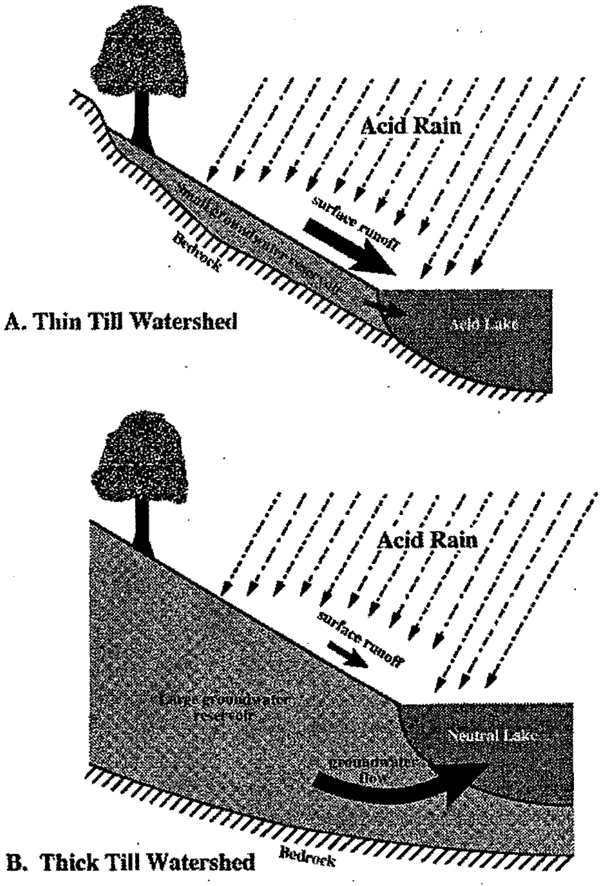

Figure 4. How flow paths of water through unconsolidated glacial sediments influence lake water chemistry.

The flow path of water moving through a watershed can be a function of a number of lake/watershed characteristics including thickness of unconsolidated sediments, hydraulic conductivity, and land slope. However, for most Adirondack watersheds, the dominant flow path is determined by the thickness of the unconsolidated glacial sediments overlying the bedrock (Newton et al., 1987). The thickness is also important, as it defines the size of the potential groundwater reservoir (Figure 4). Watersheds with thick surficial deposits have a large groundwater storage capacity. During precipitation events water infiltrates through soil and moves downward to the groundwater table where it is slowly discharged to streams and lakes. In these basins, deeper flow paths dominate and result in surface waters with higher ANC. In contrast, those watersheds with thin deposits of surficial sediments, or high proportions of bedrock outcrop, have only a small groundwater reservoir, which is rapidly filled during the early part of precipitation and snowmelt events. Subsequent rainfall or snowmelt is forced to move rapidly as shallow interflow through the upper acidic soils horizons, or as overland flow to streams and lakes, resulting in low ANC surface water.

Lakes and watersheds can be classified according to lake type and dominant flowpath. Drainage and seepage lakes represent the two major hydrologic lake types that occur in the Adirondacks. Drainage lakes are defined as lakes having a distinct surface outlet, whereas seepage lakes have none. Approximately 86% of the 1,469 Adirondack lakes surveyed by the ALSC are of the drainage type and 14% are seepage lakes (Figure 5; Kretser et al., 1989). On this trip we will look at three drainage lakes, Clear Pond (thick till), Harris Lake (carbonate and salt impacted), and Arbutus Lake (intermediate), and two seepage lakes, Echo Pond (flow-through) and Little Echo Pond (mounded).

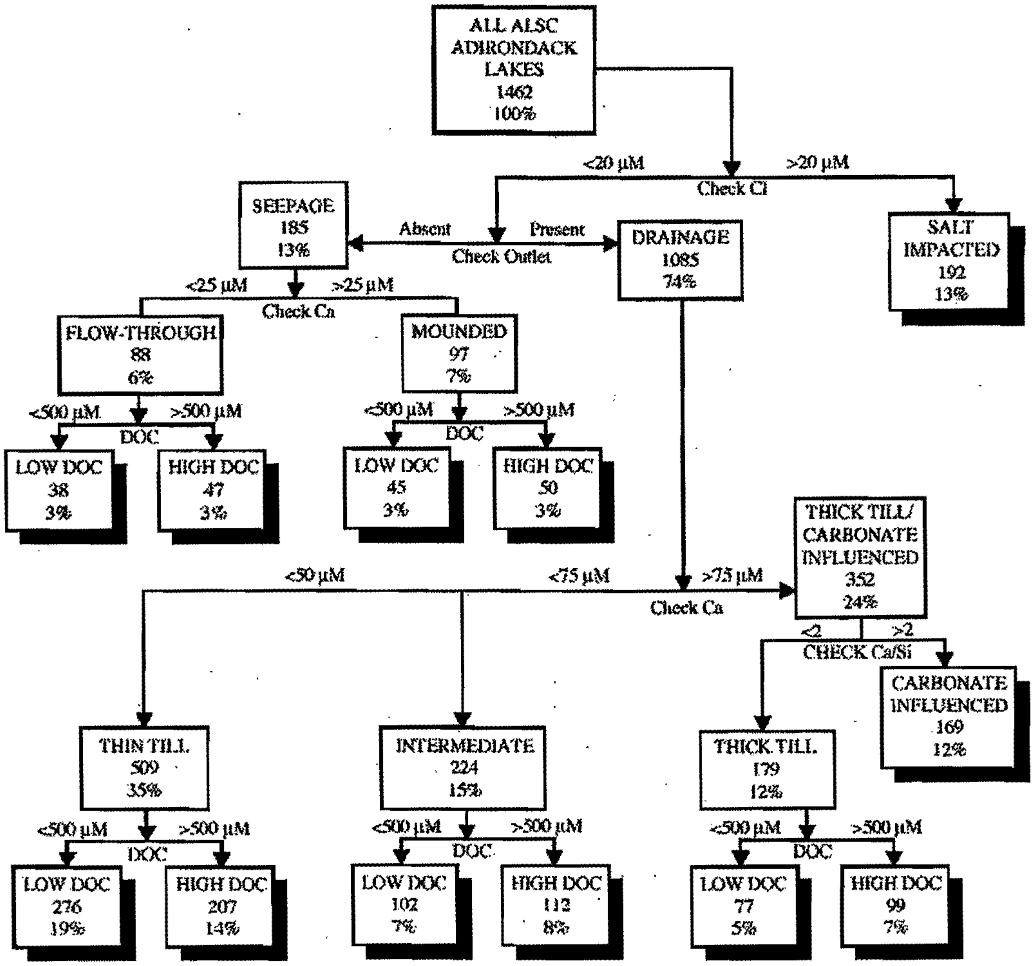

Figure 5. Lake classification diagram for 1,469 Adirondack lakes surveyed by the ALSC (Kretser et al., 1989)

CASE STUDIES OF ADIRONDACK LAKES

Clear Pond – STOP 1.

Clear Pond is a 73 hectare drainage lake occupying a watershed located just a few miles north of the Blueridge Highway (county route 2) (Figure 6). The area of the watershed is 12.06 km^2 and the lake surface elevation is 582 m. A number of fish species are present, including brook trout, cutlips minnow, common shiner, bluntnose minnow, white sucker, pumpkinseed, and banded killfish. The watershed sits at the southern edge of the high peaks region and is underlain by bedrock consisting primarily of metanorthosite with some granitic gneiss. Thin section examination of two bedrock samples (CL 102 and CL-108) revealed the first to be a garnet-biotite-quartz-oligoclase gneiss (metapelitic) with 5% garnet, 5-10% red-brown biotite, 40-50 % quartz and 40-50% oligoclase. The second, CL-108, was a gabbroic anorthosite with 90% plagioclase (~An_{45}) and 10% hypersthene.

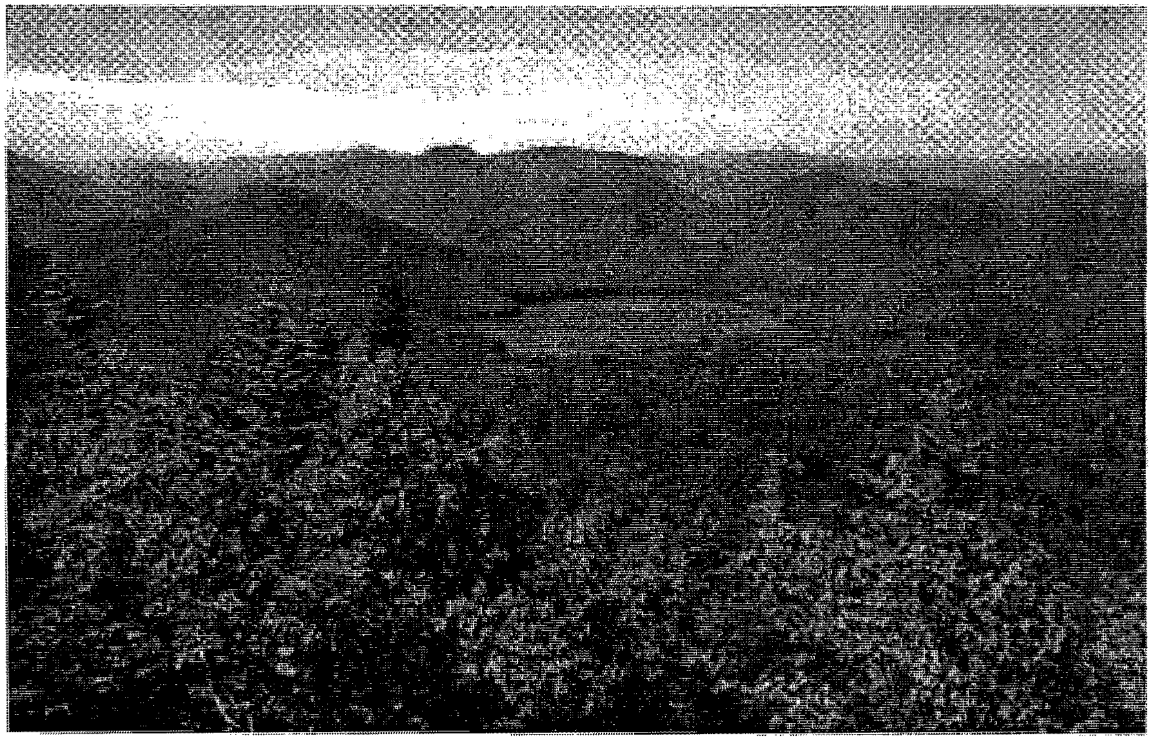

Figure 6. Clear Pond as seen from Sunrise Mountain looking south.

Areas of thick (>3 m) till and stratified drift cover approximately 33% of the watershed, with the remaining area covered by thin (<3 m) glacial deposits and bedrock outcrops (Figure 7). (Some nice till cuts can be seen on the right side of Elk Lake Road as we drive into Clear Pond.) Tills in the watershed contain on average 68% sand, 28% silt, and 4% clay. Quartz and plagioclase are the major minerals present in both the soil and glacial sediments. Vermiculite, mixed layer mica-vermiculite and kaolinite constitute the bulk of the clay mineral fraction. Heavy minerals make up 16.2% of the soil, with major constituents as follows: garnet 36.9%, pyroxene 34.4%, opaques 10.1%, epidote 8.6%, and hornblende 3.8%.

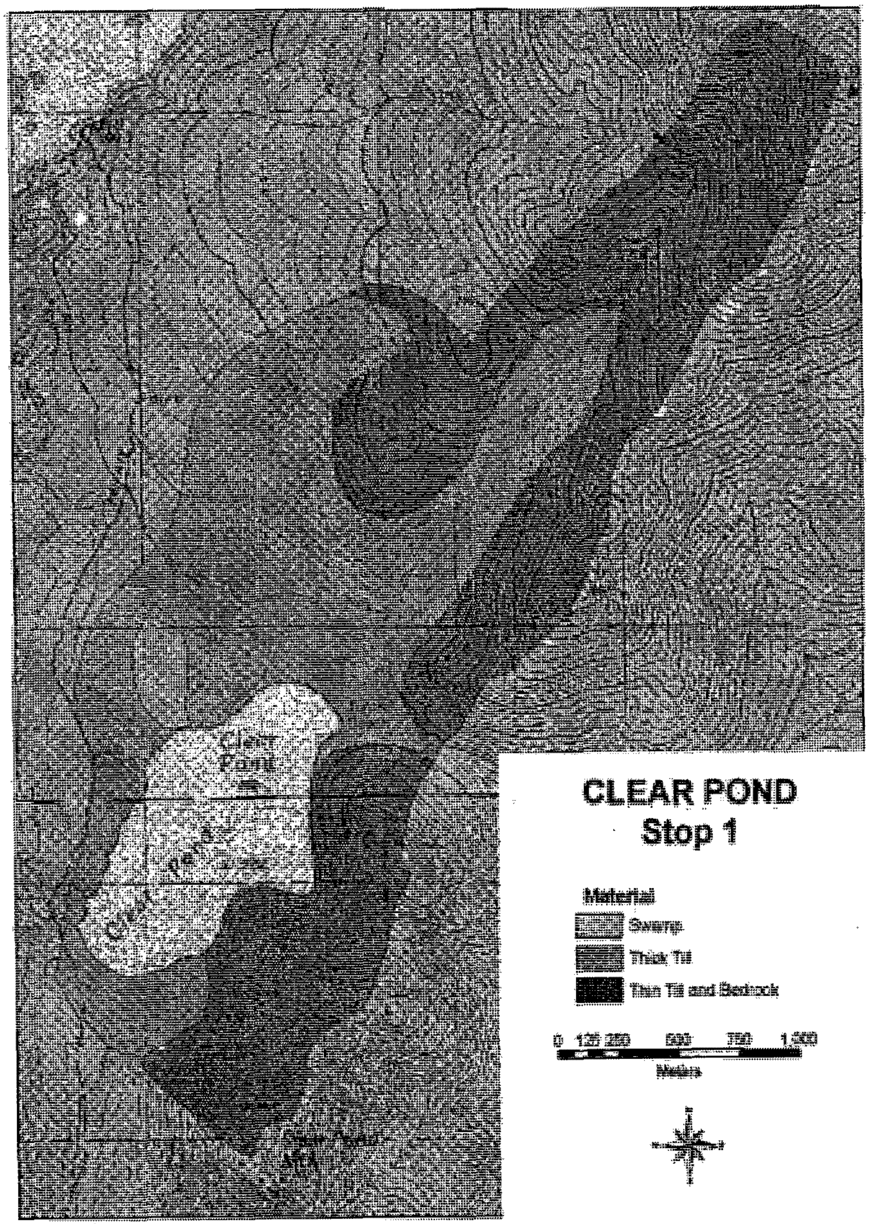

Figure 7. Surficial geology of the Clear Pond watershed.

Comparative values of the chemistry of Clear Pond in 1982-84 and 2002 are shown in Table 1. This is a circum-neutral lake with an ANC of about 100 µeq/L. Compared to other lakes we have studied (Driscoll and Newton, 1985; Table 2), Ca concentrations are relatively high but do not approach values found in some carbonate-influenced lakes. More importantly, the high Ca concentrations are coupled with high SiO_2, suggesting that the Ca is ultimately derived from silicate minerals rather than carbonates. Although there has been a significant decline in SO_4^{-2} (20 µmol/L) over the past 20 years, ANC has remained relatively constant. The nearly one-third drop in SO_4^{-2} suggests that we are seeing the effect of reduced SO_2 emissions over this period of time. The lack of response in

ANC is due to a corresponding decrease in base cations. Ca concentrations have declined by about 10% in twenty years and may reflect decreases in the flux of particulate matter to the watershed

Parameter	Clear Pond (82-84)	Clear Pond 2002
pH	7 (0.2)	7.09
ANC (µeq/L)	100 (19)	101
Ca (µmol/L	79 (11)	63.6
Mg	16 (2)	14.8
Na	37 (4)	38.7
K	4 (.7)	2.6
SO_4	63 (2)	43.7
NO_3	1 (2)	6.5
Cl	7.7 (1.5)	11.6
F	.7 (.3)	1.9
DOC	318 (64)	325
DIC	101 (52)	75.8
H_4SiO_4	70 (5)	209

Table 1. Chemistry of Clear Pond, today and 20 years ago.

Chemical characteristics of Adirondack study lakes[a]

Lake	pH	ANC (µeq/L)	NO_3^- (µeq/L)	SO_4^{2-} (µeq/L)	Ca^{2+} (µeq/L)	Monomeric Al (µmol/L)	DOC (µmol/L)
Arbutus Pond	6.2 ± 0.3	58 ± 21	10 ± 6	141 ± 10	152 ± 11	1.0 ± 0.6	420 ± 65
Barnes Lake[b]	4.7 ± 0.1	-14 ± 10	2 ± 3	65 ± 12	30 ± 4	1.1 ± 0.6	450 ± 136
Big Moose Lake	5.1 ± 0.1	1 ± 10	24 ± 5	140 ± 11	93 ± 10	8.9 ± 2.7	340 ± 78
Black Pond	6.8 ± 0.2	200 ± 21	4 ± 5	130 ± 3	191 ± 11	0.3 ± 0.6	350 ± 65
Bubb Lake	6.1 ± 0.2	41 ± 28	16 ± 7	131 ± 14	108 ± 13	1.8 ± 1.3	280 ± 82
Cascade Lake	6.5 ± 0.3	95 ± 52	29 ± 9	139 ± 10	159 ± 24	2.8 ± 1.9	310 ± 92
Clear Pond	7.0 ± 0.2	100 ± 19	1 ± 2	139 ± 11	157 ± 21	0.8 ± 0.7	320 ± 64
Constable Pond	5.2 ± 0.6	8 ± 22	17 ± 12	149 ± 19	98 ± 10	10.5 ± 4.3	420 ± 80
Darts Lake	5.2 ± 0.2	6 ± 12	24 ± 5	139 ± 7	97 ± 9	7.6 ± 2.7	320 ± 86
Heart Lake	6.4 ± 0.3	43 ± 12	5 ± 6	106 ± 11	119 ± 12	0.6 ± 0.6	310 ± 51
Little Echo Pond[b]	4.3 ± 0.1	-51 ± 17	0 ± 0	78 ± 17	36 ± 6	1.2 ± 0.5	1100 ± 153
Merriam Lake	4.5 ± 0.2	-25 ± 15	21 ± 13	137 ± 11	58 ± 7	19.0 ± 0.6	480 ± 110
Moss Lake	6.4 ± 0.2	66 ± 25	26 ± 6	141 ± 8	146 ± 15	2.2 ± 1.6	310 ± 61
Otter Lake	5.5 ± 0.5	13 ± 16	9 ± 9	138 ± 21	88 ± 11	5.0 ± 3.6	200 ± 54
Lake Rondaxe	5.9 ± 0.5	33 ± 25	23 ± 6	134 ± 7	112 ± 10	4.4 ± 3.0	300 ± 60
Squash Pond	4.6 ± 0.6	-22 ± 39	24 ± 17	131 ± 18	65 ± 28	19.2 ± 7.6	580 ± 127
Townsend Pond	5.2 ± 0.6	18 ± 21	27 ± 15	154 ± 30	95 ± 16	9.9 ± 7.9	260 ± 81
West Pond	5.2 ± 0.5	29 ± 50	10 ± 6	111 ± 13	94 ± 24	6.6 ± 2.1	670 ± 204
Windfall Pond	5.9 ± 0.4	44 ± 30	26 ± 14	141 ± 17	143 ± 19	5.6 ± 2.4	390 ± 92
Woodruff Pond	6.9 ± 0.2	410 ± 140	2 ± 3	147 ± 17	430 ± 120	1.0 ± 1.1	710 ± 161

[a] Arithmetic mean and standard deviations shown for the samples collected

[b] Barnes and Little Echo are seepage lakes; the others are drainage lakes

Table 2. Chemical characteristics of RILWAS Adirondack study lakes (from Driscoll and Newton, 1985).

Questions to consider at this stop are:

1) Is Clear Pond a typical Adirondack drainage lake? Does the preponderance of metanorthosite over granitic gneiss influence the chemistry of the lake water?

2) Is it possible to tie the decline in SO_4^{-2} in Clear Pond over the past 20 years to reductions in SO_2 emissions? Has sulfate (and nitrate) accumulated in soils over time, and if so, how long will sulfate (and nitrate) continue to leach out of soils into stream and lake water?

3) Does the increase in NO_3^- reflect the fact that Knox emissions have remained relatively steady over the past 20 years, whereas SO_4^{-2} has declined? Has the proportion of sulfuric and nitric acid in deposition changed over time?

4) Do lower Ca values reflect a decrease in the influx of Ca from particulate matter, or does it suggest lower weathering rates in the watershed? Ca depletion on exchange sites has been measured in the Adirondacks (and the Catskills, Lawrence et.al., 1999) and it has been suggested that high acid loadings in the Adirondacks have resulted in significant depletion of base cations in the soils. Because ANC values for most Adirondack lakes have not risen over time, is it possible that base cation depletion in soils will delay recovery of Adirondack lakes?

Harris Lake (and Woodruff Pond) – STOP 2

Harris Lake is a 116 hectare drainage lake occupying a watershed located just north of route 28N (Figure 8). The area of the watershed is 183 km^2 and the lake surface elevation is 473 m. Over a dozen fish species inhabit the lake, including northern pike, common shiner, white sucker, brown bullhead, rock bass, smallmouth and largemouth bass, and yellow perch. The watershed straddles a thin belt of metasedimentary rocks comprising calcitic and dolomitic marble, calcsilicate rock, quartzite and interlayered gneisses (Geologic Map of New York, NYS Museum). Harris Lake has not been included in any of our recent studies, so we cannot provide more detailed information concerning the geologic and mineralogic characteristics of the bedrock and glacial deposits within the watershed. However, in walking the southern shoreline one observes outcrops of calcsilicate rocks, containing calcium carbonate (Figure 9). In a class mapping exercise in 1990, Colgate students identified outcrops of calcsilicates on the northeastern shoreline, and also found outcrops of granitic gneiss in the northern areas of the watershed and on the easternmost shore of the lake.

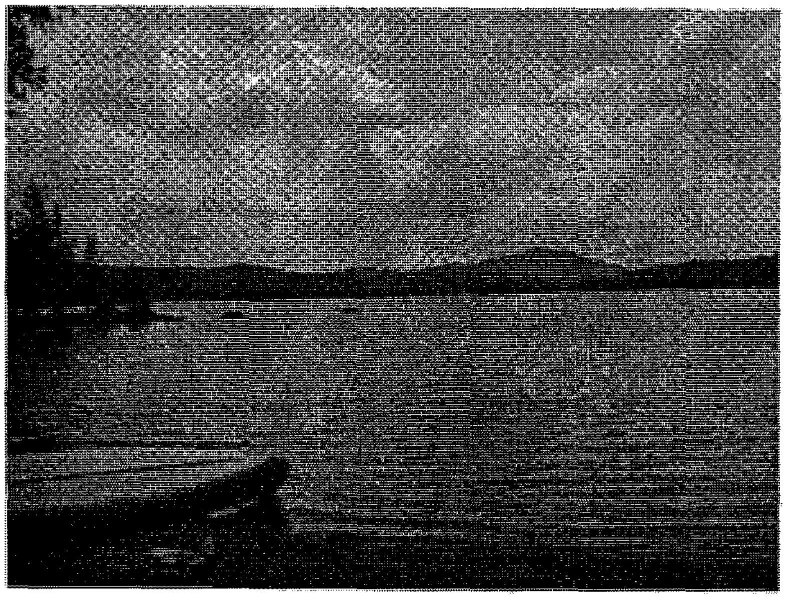

Figure 8. Harris Lake as seen from the NYS campground area.

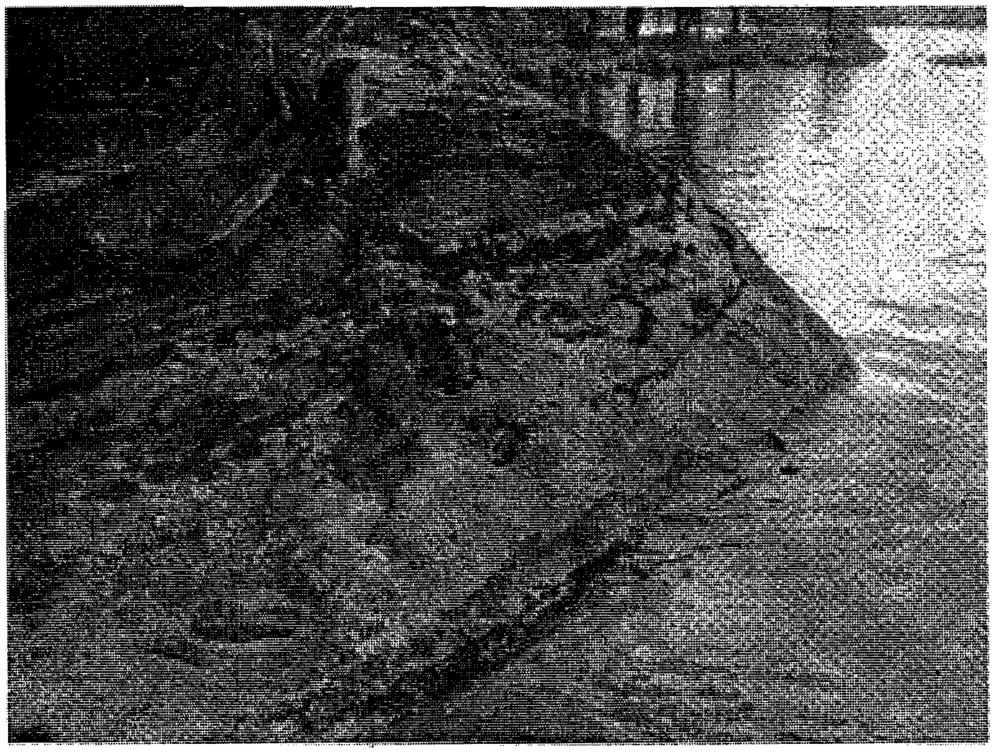

Figure 9. Outcrop of calcsilicate containing calcium carbonate on the southern shore of Harris Lake.

Harris Lake is classified as a salt-impacted lake using the ALSC classification (Figure 5). This reflects the proximity of the highway and other anthropogenic influences within this watershed. Throughout the Adirondacks, developed lakes with cottages and their associated septic systems, roads, etc have relatively high concentrations of Cl^-. We stop at Harris Lake to consider the effect of the presence of carbonate-bearing rock on the chemistry of the lake water. As Table 3 shows, Ca values are high, but compared with other Adirondack lakes (Table 2) the values do not seem so unusually high to suggest that the chemistry of Harris Lake is controlled solely by the dissolution of carbonate minerals. In fact the lake does not have a high enough Ca/Si ratio (2) to qualify as a carbonate controlled lake. Perhaps a better indicator of the impact of carbonate minerals in this watershed is the high ANC of about 200 μeq/L, which is one of the higher values observed in the Adirondack lakes we have studied.

Parameter	Harris Lake 1987 (ALSC data)	Harris Lake 2002
pH	7.17	7.20
ANC (μeq/L)	193.7	232
Ca (μmol/L	119.5	136.5
Mg	35.8	46.9
Na	77.9	134.8
K	8.7	8.2
SO_4	50.0	48.3
NO_3	1.13	16.3
Cl	64.6	117.6
F	3.42	0.95
DOC	558	492

Table 3. Chemistry of Harris Lake, today and 15 years ago.

Only Woodruff Pond, a drainage lake that sits a stone's throw to the south of Harris Lake and whose watershed also sits within the calcsilicate – marble belt, has a higher ANC (and Ca concentration; Table 2). Three bedrock samples from Woodruff Pond were thin sectioned and analyzed with the petrographic microscope. The first was an amphibolite with 40% hornblende, 10% hypersthene, 50% plagioclase and 1-2% biotite. The second was a quartz-diopside calcsilicate with 30-40% quartz, 20-30% diopside, 20% phlogopite, 5-10% calcite and a trace of tremolite. The third was a quartzite with 60% quartz, 20% hornblende, 5% garnet, 5% hypersthene, and 2% calcite. Areas of thin (<3 m) till and stratified drift cover most of Woodruff watershed; calcsilicate boulders are common. Quartz, plagioclase, K-spar, hornblende and pyroxene are the major minerals present in both the soil and glacial sediments. Vermiculite, mixed layer mica-vermiculite, kaolinite and talc constitute the bulk of the clay mineral fraction. Heavy minerals make up 21.1% of the soil, with the major constituents as follows: pyroxene 23.5%, opaques 23.5%, hornblende 20.3%, garnet 11.9%, and epidote 5.8%.

On the basis of the thickness of the surficial deposits one might expect Woodruff Pond to have low ANC. In fact, Woodruff Pond has the highest ANC (410-480 µeq/L) observed of all lakes in the Regional Integrated Lake Watershed Acidification Study (RILWAS; Driscoll and Newton, 1985). The relationship between base flow discharge and sum of the base cations (SBC) for several of the RILWAS lakes is shown in Figure 10. All lakes except Woodruff Pond fall between end members Woods Lake, with a watershed dominated by thin till (average depth 2.3 m), and Panther Lake, with a watershed dominated by thick till (average depth 24.5 m) (April and Newton, 1985). Woodruff Pond has a base flow discharge that is almost as low as Woods Lake, yet it has an ANC of 410 µeq/L and SBC of 600 µeq/L. Woodruff Pond watershed provides a dramatic example of the influence that carbonate minerals have on surface water chemistry. Although the water moves rapidly along shallow flow paths, there is sufficient time for carbonate minerals to react. The dissolution of calcium carbonate is rapid and base cations, in this case Ca, are readily supplied to the drainage water. Hence, flow path is not the major determinant in regulating the acid-base status of Woodruff Pond. Rather, the presence of carbonate in the till, and also in the underlying bedrock, is the chief controlling factor.

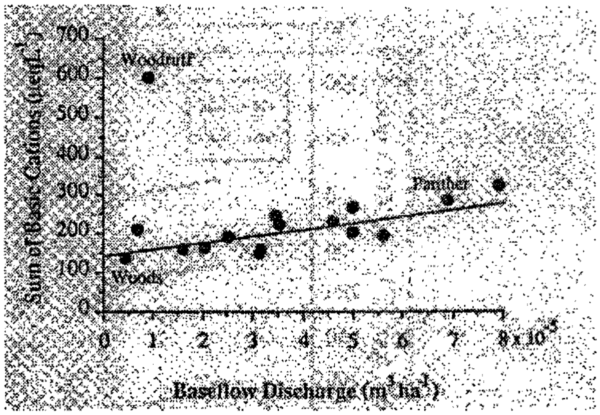

Figure 10. Average ANC as a function of low-flow discharge for the RILWAS and ILWAS watersheds (from Charles, 1991)

Harris Lake watershed probably falls somewhere in between and can be considered a carbonate-influenced (but not controlled) lake. Although carbonate is present in the watershed materials, the entire watershed is not within the calcsilicate-marble belt. Indications are that at least half of the watershed area is underlain by granitic gneiss, and although some of the till in the watershed may contain carbonate minerals, much of the glacial cover is likely 'granitic' in composition and devoid of carbonate minerals. Water in contact with carbonate-bearing outcrops along the shore may contribute to increasing lake water Ca concentrations and ANC. However, the relative contribution of this water to the overall chemistry of Harris Lake, although significant, is probably small. We still have much more to do in Harris Lake watershed, but it serves as a good example of an area where surface water chemistry is influenced, somewhat, by the presence of carbonate minerals.

Questions to consider at this stop are:

1) How do we measure the influence of carbonate minerals on lake water chemistry? Is it the carbonate in the bedrock, or the carbonate in the till, or both, that is most important in raising ANC and pH?
2) Does the Ca to Si ratio in surface water give us an indication of the amount of carbonate mineral weathering taking place? That is, can carbonate influenced water be differentiated from non-carbonate influenced water by calculating the molar ratio of Ca^{2+} to H_4SiO_4?
3) With ANC values of 200 µeq/L or more, are lakes like Harris and Woodruff essentially insensitive to changes caused by acid deposition?
4) Can we artificially create carbonate-influenced lakes by liming techniques? And is it best to lime the lake, or the watershed?

Marble Outcrop – STOP 3

Lunch at Adirondack Visitors Center

Arbutus Lake – Huntington Wildlife Forest – STOP 4.

Arbutus Lake is a 49 hectare drainage lake occupying a watershed located in the Huntington Wildlife Forest (Figure 11). The area of the watershed is 3.75 km^2 and the lake surface elevation is 513 m. The watershed is underlain by granitic gneiss, but small outcrops of amphibolite and biotite-rich gneiss have been identified. The watershed has been gauged at the lake outlet since October 1991 with a V-notch weir. Huntington Forest has also participated in the National Atmospheric Deposition Program (NADP) and the National Trends Network (NTN) since Oct. 31, 1978 (see Figures 12 and 13 for trends in sulfate and pH). In May, installation of an EPA CASTNET dry deposition monitoring system was completed. Time permitting, we will take a short hike to view these instrumentation set-ups.

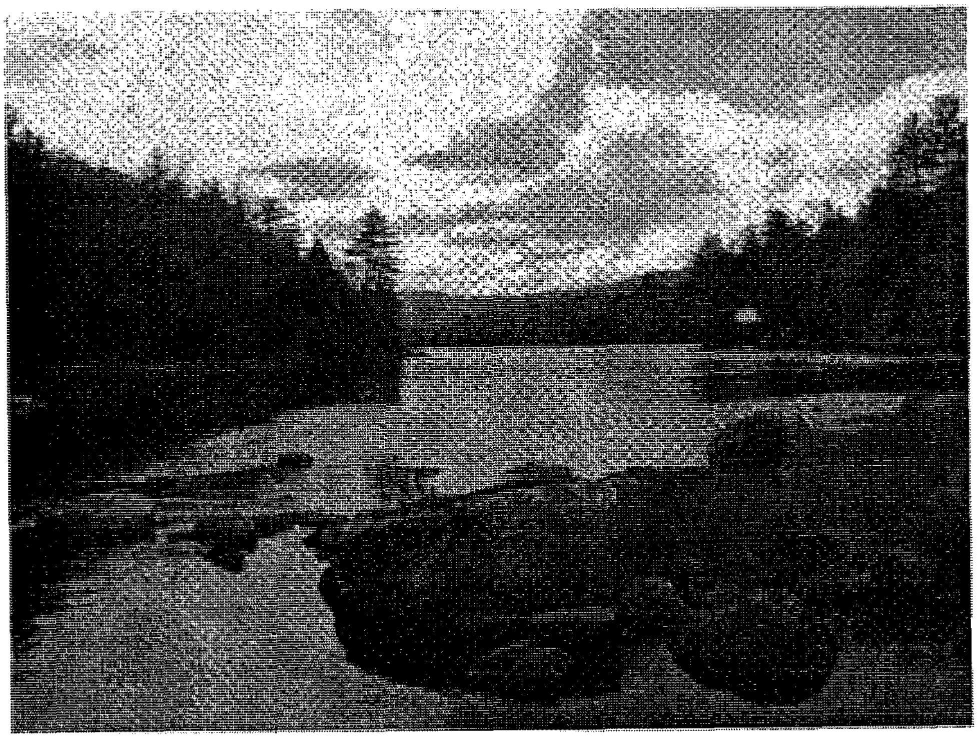

Figure 11. View of Arbutus Lake from the outlet.

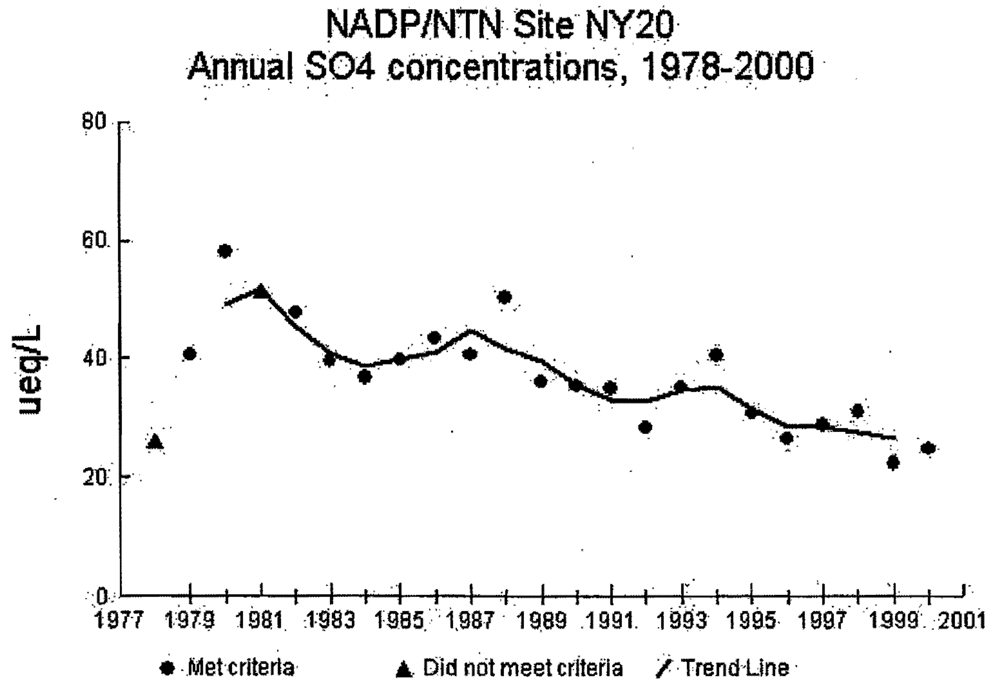

Figure 12. Trends in SO_4^{2-} from the NADP/NTN site at Huntington Forest (from http://nadp.sws.uiuc.edu/nadpdata/siteinfo.asp?id=NY20&net=NADP)

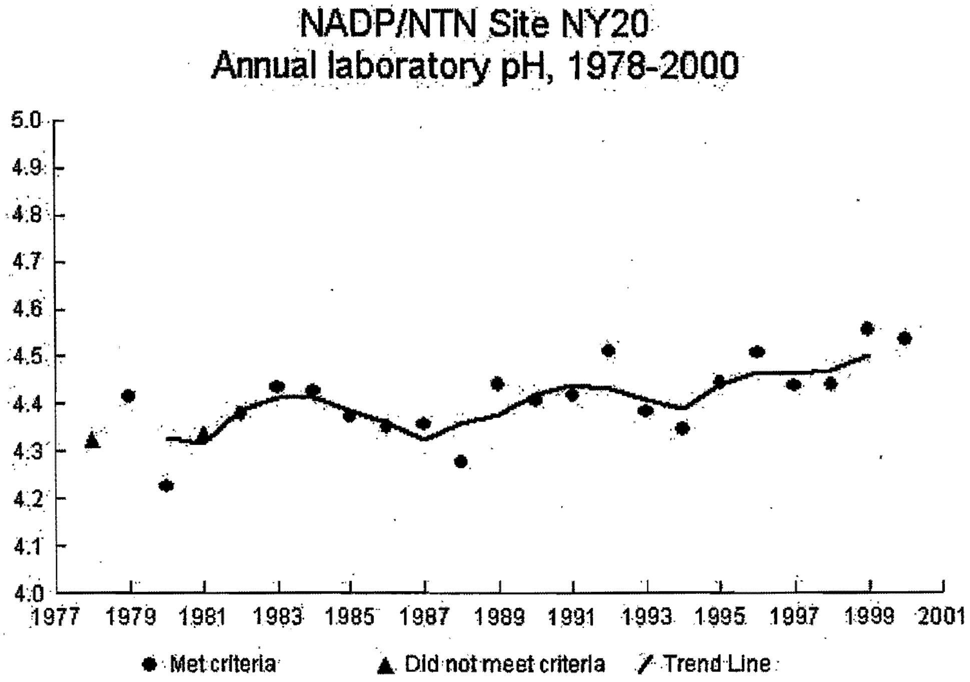

Figure 13. Trends in precipitation pH from the NADP/NTN site at Huntington Forest (from http://nadp.sws.uiuc.edu/nadpdata/siteinfo.asp?id=NY20&net=NADP)

Areas of thin (<3 m) till cover approximately 80-90% of Arbutus Lake watershed; bedrock outcrops are numerous (Figure 14). Tills contain on average 73% sand, 24% silt, and 2% clay. Quartz, K-spar and plagioclase are the major minerals present in both the soil and glacial sediments. Vermiculite, mixed layer mica-vermiculite and kaolinite constitute the bulk of the clay mineral fraction. Heavy minerals make up about 16% of the soil, with major constituents as follows: hornblende 33.6%, opaques (ilmenite and magnetite) 29.5%, pyroxene 20.1%, garnet 7.2%, and apatite 5.4%.

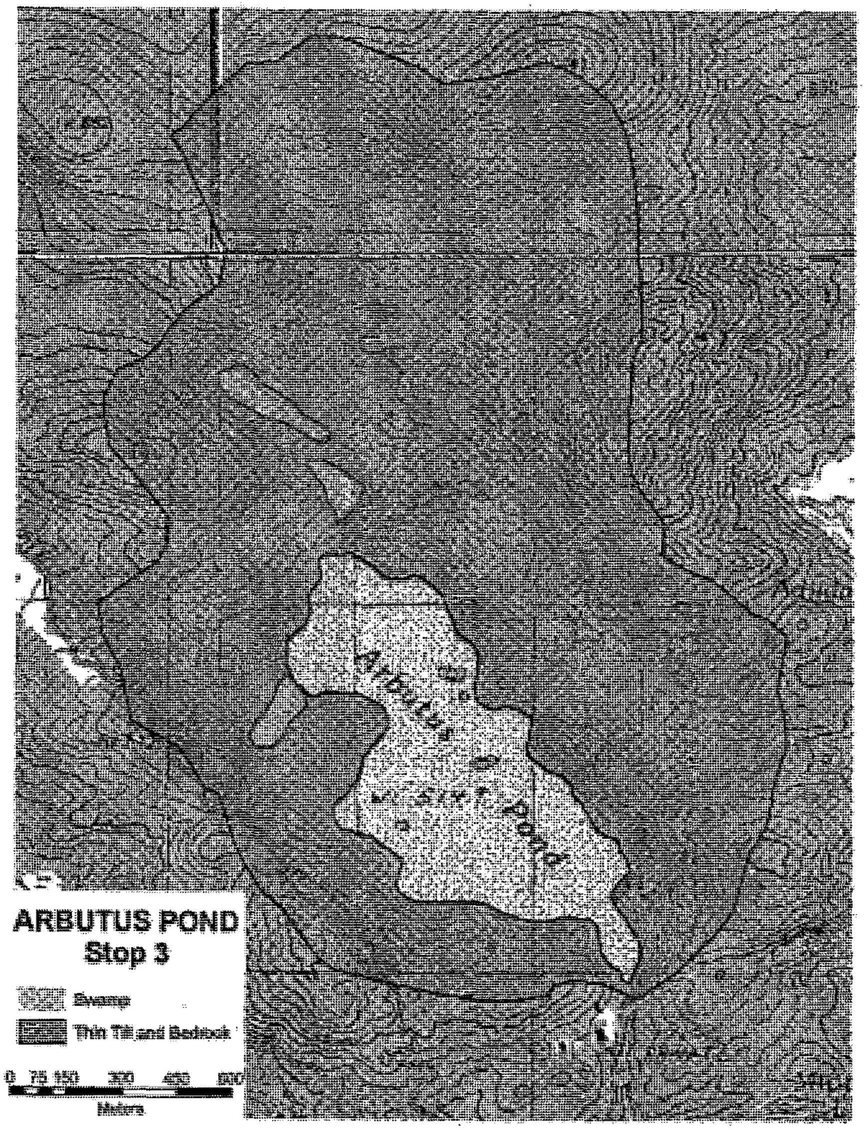

Figure 14. Surficial geology of the Arbutus Lake watershed

Comparative values of the chemistry of Arbutus Lake in 1982-84 and 2002 are shown in Table 4. This is a moderately sensitive water body with an ANC that ranges between 60 - 80 µeq/L. Ca concentrations are relatively high, and may reflect the presence of amphibolitic bedrock, and the presence of carbonate-bearing boulders in the till, especially up in the area around Archer Creek. Unlike Clear Pond, the 20 µmol/L reduction in SO_4^{-2} here has resulted in a concomitant rise of 20 µeq/L in ANC.

Parameter	Arbutus 82-84	Arbutus 2002
pH	6.2 (0.3)	6.6
ANC (μeq/L)	58 (21)	78
Ca (μmol/L	76 (6)	60.1
Mg	22 (3)	17.3
Na	31 (3)	28.7
K	11 (1)	6.1
SO_4	71 (5)	49.4
NO_3	10 (6)	5.8
Cl	10.7 (2.0)	11.9
F	4.5 (.5)	0.8
DOC	422 (65)	441
DIC	112 (20)	48.3
H_4SiO_4	68 (16)	-

Table 4. Chemistry of Arbutus Lake, today and 20 years ago.

Arbutus Lake watershed is a good example of a system in which the combination of thin till, short flow paths, and short residence times, which usually gives rise to surface waters with low ANC and high sensitivity (see Figure 4), is modified by the presence of minerals in the watershed that weather at moderately fast rates (e.g., hornblende, pyroxenes, and garnet) to provide alkalinity to drainage waters. In June of 1989-1991, Colgate students mapping and collecting water samples in Arbutus watershed measured the ANC of all running inlet streams in the watershed. Most streams had ANC values that were in the range of 20-80 μeq/L, but several streams had ANC's that were as high as 160-180 μeq/L. The highest values were measured following a particularly dry spring, and lowest values were measured following a rainy period of several days. During periods of low precipitation, or drought, base flow becomes a proportionately greater fraction of the drainage water reaching the lake and ANC values in Arbutus Lake can rise to their highest levels. Highest ANC values also seemed to be concentrated in the northern part of the watershed, near or within the Archer Creek subcatchment. We are planning to conduct future field studies in this part of the watershed to better characterize the composition of the bedrock, till, and soils.

Questions to consider at this stop are:

1) How does one measure the contribution of mineral weathering to the ANC of surface waters? Can the relative rates of mineral weathering in soils and till be measured, and if so, how do we measure or calculate the relative contribution of *each* mineral to ANC?

2) Why did a reduction in SO_4^{-2} result in an increase in ANC here and not at Clear Pond?

3) Several calcsilicate belts run east-west in the vicinity of the Arbutus watershed. Just a few miles to the east we noted the influence these rocks have on the chemistry of Harris Lake and Woodruff Pond. How much calcsilicate float is incorporated in the till of Arbutus watershed, and to what degree does this float influence the composition of soil and till in Arbutus? One clue, of course, is to look at the heavy mineral content of the till and soil, which includes significant quantities of hornblende and pyroxene.

4) A second possibility is to look at the bulk chemistry of till samples from the watershed. For example, XRF analyses of the < 2 mm (sand) fraction of 13 till samples from the Big Moose watershed, a watershed underlain by granitic gneiss and containing many acid sensitive lakes, has a mean CaO value of 1.64 wt. %. The mean CaO value for till collected from watersheds underlain by metanorthosite or calcsilicates (including samples from Clear Pond and Woodruff Pond) is 4.13 wt. %. Till from Arbutus Lake watershed has a CaO content of 2.54 wt. %, an intermediate value. Does this

indicate that source rocks for the till were both granitic gneiss and calcsilicates, and that the bulk chemistry reflects a mixture of the two? MgO values also suggest the same, as shown below.

Till from watersheds in:	**Wt. % CaO**	**Wt. % MgO**
Granitic gneiss	1.64	0.72
Metanorthosite/calcsilicates	4.13	2.02
Arbutus Lake	2.54	1.49

Echo and Little Echo Ponds – STOP 5.

Little Echo Pond is a 0.8 hectare brown water seepage lake surrounded by thick (~8 m)) peat (sphagnum bog) deposits (Figures 15 and 16). Its watershed is estimated to be about 0.11 km^2. Echo Pond, a stone's throw to the NNE, is a slightly larger seepage lake but without peat deposits edging the shoreline (Figure 17). The lake surface elevation of both ponds is 481 m. No fish species are present in Little Echo Pond; no fish population data is available for Echo Pond. The two Ponds sit in an outwash area at the eastern edge of the anorthositic massif, in the Fish Creek Ponds recreational area. Thin section examination of one bedrock sample taken in the vicinity (LE-105) revealed a typical Adirondack gabbroic anorthosite with 85% plagioclase (~An_{45}), 7% magnetite, 3% green clinopyroxene, and 5% garnet.

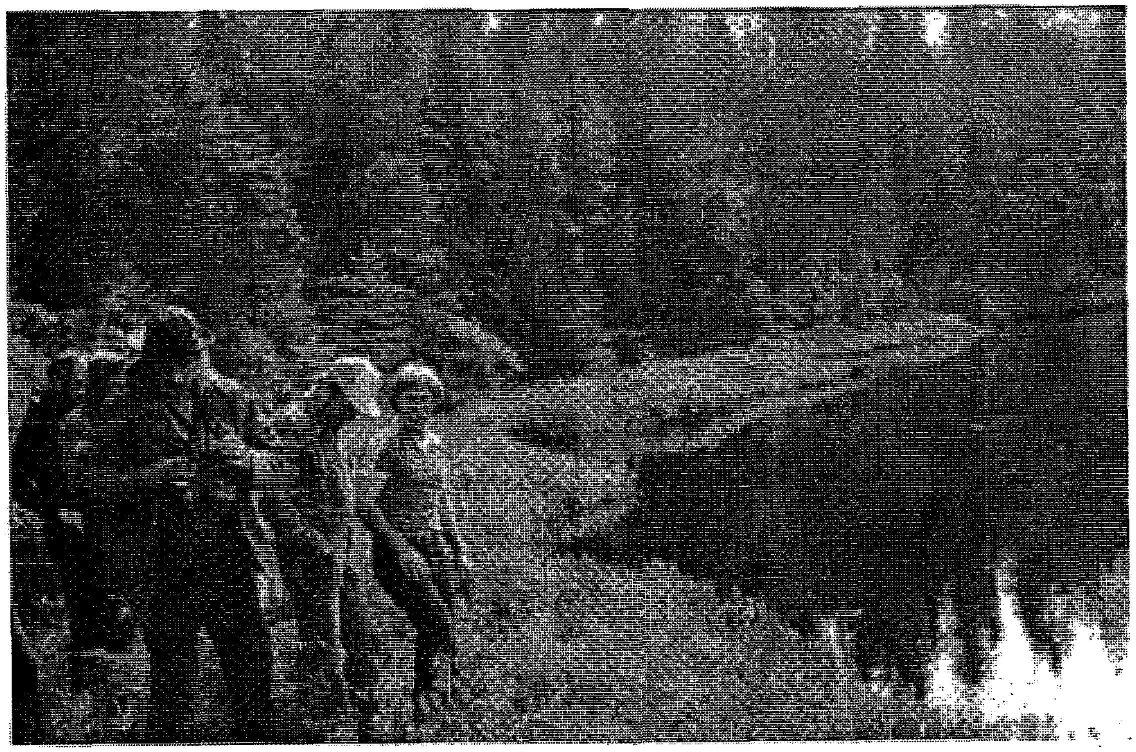

Figure 15. View of Little Echo Pond and the surrounding peat deposits.

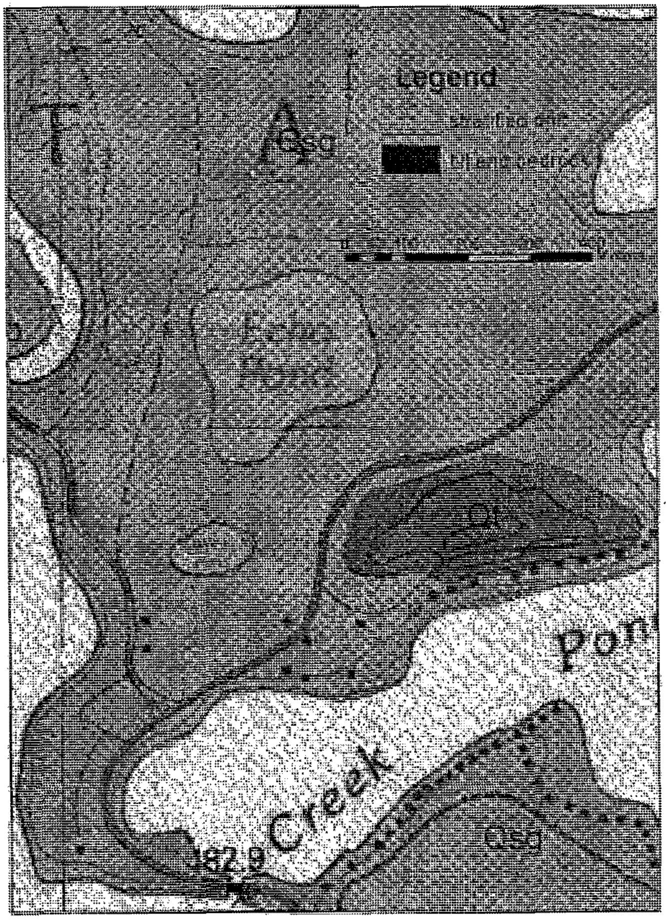

Figure 16. Surficial geology of Little Echo and Echo Ponds.

Figure 17. View of Echo Pond.

Outwash deposits of quartz, K-spar, and plagioclase are composed of 97% sand and 3% silt. Heavy minerals constitute 12.8% of the sand fraction and include 46.3% opaques, 20.1% hornblende, 10.6% pyroxene, 5.6 % garnet, and 2.3% zircon. What little clay is in the soil consists of vermiculite, mixed layer mica-vermiculite, kaolinite, and possibly a trace of talc.

Values of the chemistry of Little Echo Pond in 1982-84 and 2002, and Echo Pond in 2002 are shown in Table 5. What is immediately striking is the difference in water chemistry between these two seepage lakes located not more than 100 m apart. Little Echo is an acidic pond with an ANC that averages about of –50 µeq/L (range from ALSC data is –79.6 to –7.4 µeq/L). The pH is 4.3, the SBC and dissolved Si concentrations are low, and the DOC is high. Concentrations of organic anions are high and are comparable to SO_4^{2-} (on an equivalence basis) (Driscoll and Newton, 1985). The kettle hole that formed Little Echo Pond and the surrounding peatland has almost completely filled in. There is at least one ephemeral channel that drains the lake-peatland system during periods of high water. This lake is virtually isolated from the groundwater in the surrounding outwash aquifer system due to the extremely low hydraulic conductivity of the peat and bottom sediments, both of which form a nearly impermeable barrier around the lake-edge and bottom. Recharge of lake water must depend primarily on direct precipitation, and from runoff through the upper "active" zone of the peat. Although much of the acidity of the pond can be attributed to atmospheric deposition of H_2SO_4, it appears that the peat deposits and the sphagnum mat surrounding the pond release substantial quantities of organic acids that contribute to the overall acidity.

Sulfate concentrations in both the seepage lakes are much lower than in the drainage lakes both in the 1982 and 2002 data (Table 5 and Table 2). This is due to sulfate reduction occurring in the bottom waters of these lakes. The high DOC and long residence time of waters in seepage lakes provide conditions conducive to sulfate reduction. Measured profiles of dissolved oxygen show anoxic conditions in the deeper water of Little Echo Pond. Sulfate reduction is an ANC producing reaction making these lakes less acidic than they would have been had the water column been fully oxygenated.

Silica concentrations are very low in seepage lakes. This is likely due to a combination of a reduced input of groundwater and the removal of silica by the action of diatoms. The long residence time of water in seepage lakes makes it likely that diatoms will remove a substantial amount of silica from the water column.

Parameter	**Little Echo 82-84**	**Little Echo 2002**	**Echo 2002**
pH	4.3 (0.1)	4.3	6.4
ANC (µeq/L)	-51 (17)	-25	40
Ca (µmol/L	18 (3)	8.2	23.7
Mg	7 (1)	14.0	27.2
Na	8 (4)	15.2	9.1
K	4 (1)	13.0	4.9
SO_4	39 (9)	21.7	25.1
NO_3	0 (0)	1.8	3.4
Cl	5.8 (3.1)	19.2	18.9
F	1.3 (0.3)	2.3	1.7
DOC	1038 (153)	1236	450
DIC	113 (31)	0	12
H_4SiO_4	9 (5)	5	8

Table 5. Chemistry of Little Echo Pond and Echo Pond.

Echo Pond is marginally classified as a "flow-through" seepage lake (Figure 18). There is sufficient groundwater contribution in this class of lake to provide enough ANC to neutralize acidic deposition. However, with a pH of 6.4, an ANC of 40 μeq/L, and relatively low SBC compared with drainage lakes we have studied (Table 2), the chemistry of Echo Pond is still greatly influenced by direct precipitation. Despite the good hydraulic connection between the groundwater and the lake, groundwater inflow is limited. This is likely due to the low hydraulic gradient within the groundwater system. Therefore, the influence of direct precipitation is still relatively high especially during rainy periods and snowmelt. We don't have much time series chemical or hydrologic data from Echo Pond, so, at best, our comments should be taken as suggestions based on work completed at similar seepage lakes.

Questions to consider at this stop are:

1) Why doesn't Echo Pond have a surrounding peat layer?
2) Would Little Echo Pond be acidic if there was no acid rain?
3) How important is sulfate reduction in generating alkalinity?
4) Can we determine the relative proportions of groundwater and precipitation entering Little Echo and Echo Ponds?

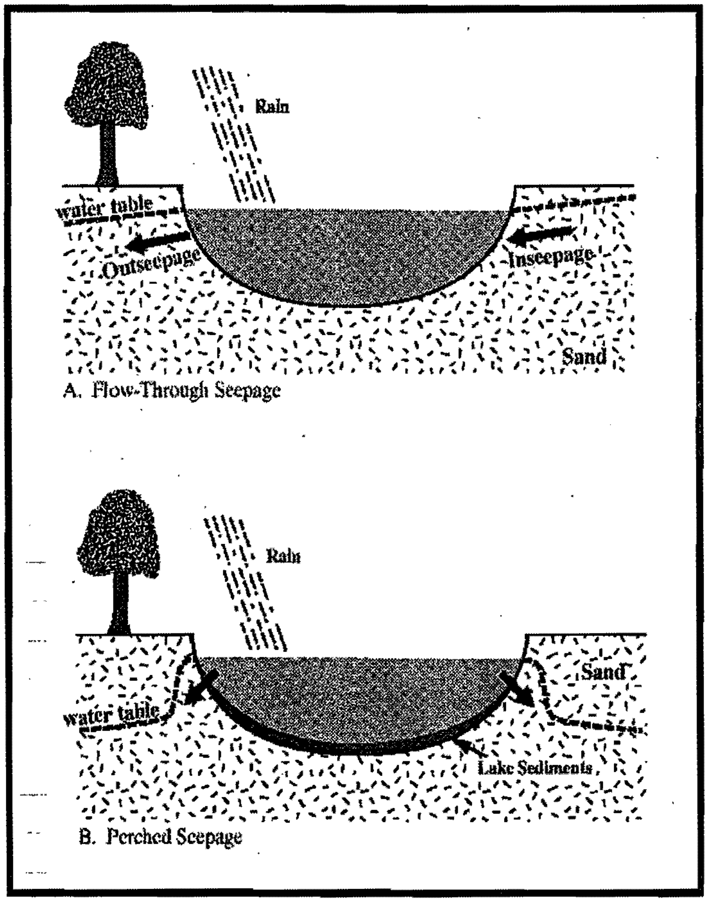

Figure 18. Schematic of the hydrology of flow-through and perched seepage lakes.

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http://nadp.sws.uiuc.edu/

ACKNOWLEDGEMENTS

Many thanks go to Di Keller in the Department of Geology at Colgate University who assisted in putting together this field guide while getting ready to leave for two weeks in Alaska.

Road Log

Cumulative Mileage	
0.0	Fort William Henry, Lake George, NY
1.0	Turn south onto 9N
1.1	Turn Right onto entrance ramp to I87 northbound
43.2	Exit highway at Exit 29 (Newcomb)
43.4	Turn left at end of ramp onto County Rd #2
47.6	Turn Right onto Elk Lake Road
51.6	**STOP 1 -** Park in area on right side of road at the outlet of Clear Pond
51.6	Return to County Rd#2 on Elk Lake Road
55.6	Turn Right on County Rd#2
68.7	Tahawus Rd enters from right
69.6	Bear left
69.8	Turn Right at stop sign onto Rt 28N
73.0	Turn Right onto access road to Harris Lake Campground
73.6	Cross Hudson River on Campground Access Rd
74.4	Entrance to Campground
75.1	**STOP 2 -** Camp sites 50 - 52 and Lake boat access
75.1	Return to Rt 28N
77.2	Turn Right onto Rt 28N
77.6	Cross Hudson River on Rt 28N
78.6	**STOP 3 -** Marble outcrop on Left side of Rd at Newcomb School
80.3	Marble outcrops along side of Rt 28N
80.5	Turn Right entrance to Adirondack Visitors Center
80.8	**LUNCH STOP** - Parking area
81.1	Return to Rt 28N
83.6	Turn right onto Arbutus Rd - Huntington Wildlife Forest
84.4	Bear right at buildings and cross Arbutus Outlet
84.5	**STOP 4 -** Arbutus Pond outlet
85.4	Return to 28N and Turn right (west) on 28N
95.6	Turn right onto Rt 30 in Long Lake
117.9	Turn right at first traffic light in Tupper Lake (east on Rt 3)
118.1	Straight through second traffic light
123.7	Turn Left to continue on Rt 30 north
129.2	Pass entrance to Fish Creek Ponds Camping area on left
	STOP 5 -
	Park in small parking area on right side of road
	Trail to Echo Pond and Little Echo Pond is on the opposite side of the road
129.3	
	Return to Lake George

Contact Info:

Percy Flemming – Elk Lake Lodge 518-332-7616
Harris Lake Campground – 518-582-2503
Adirondack Visitors Center – 518-582-2000