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The relationship between surface water chemistry and geology in the North Branch of the Moose River

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Abstract. The chemistry of lakes and streams within the North Branch of the Moose River is strongly correlated with the nature and distrubution of geologic materials in the watershed. The dominance of thin glacial till and granitic gneiss bedrock in the region north and east of Big Moose Lake results in a geologically sensitive terrain that is characterized by surface water with low alkalinity and chemical compositions only slightly modified from ambient precipitation. In contrast, extensive deposits of thick glacial till and stratified drift in the lower part of the system (e.g. Moss-Cascade valley) allow for much infiltration of precipitation to the groundwater system where weathering reactions increase alkalinity and significantly alter water chemistry.

The hypothesis that surficial geology controls the chemistry of surface waters in the Adirondacks holds true for 70 percent of the Moose River watershed. Exceptions include the Windfall Pond subcatchment which is predominantly covered by thin till, yet has a high surface water alkalinity due to the presence of carbonate-bearing bedrock. The rapid reaction rates of carbonate minerals allow for complete acid neutralization to occur despite the short residence time of water moving through the system. Another important source of alkalinity in at least one of the subcatchments is sulfate reduction. This process appears to be most important in systems containing extensive peat deposits.

An analysis of only those subcatchments controlled by the thickness of surficial sediments indicates that under current atmospheric loadings watersheds containing less than 3 percent thick surficial sediments will be acidic while those with up to 12 percent will be extremely sensitive to acidification and only those with over 50 percent will have a low sensitivity.

Introduction

The extent of the impact of acid rain on surface water chemistry is determined primarily by the chemical reactions which occur as precipitation moves along the various flow paths through the terrestrial system- (Newton and April, 1982). Reactions within the surface water bodies themselves are generally of secondary importance (Driscoll and Newton, 1985).

Precipitation falling on a watershed may travel as; surface runoff, shallow interflow, groundwater flow through unconsolidated surficial materials, or through bedrock fractures. Water which moves as surface runoff and interflow moves rapidly to rivers and lakes and has little time to react with the minerals in the soil; only reactions which occur rapidly (i.e. cation exchange) can occur. Water flowing through the groundwater reservoir moves much more slowly and has time to react with the mineral comprising the aquifer skeleton. The residence time is generally long enough for even relatively low solubility minerals such as feldspar to react enough to neutralize incoming acidity. Water moving through fractures in the bedrock generally moves quite rapidly and probably reacts only with those minerals which have high solubilities (i.e. calcite).

In Adirondack surface water bodies the most important alkalinity producing reaction is sulfate reduction (Driscoll and Newton, 1985). Sulfate reduction usually occurs in areas where there is an abundance of organic sediments such as bogs and swamps. It appears to be a dominant process in only a few of the Adironack systems.

The results from the Integrated Lake Watershed Acidification Study (ILWAS) have shown that the thickness of unconsolidated surficial sediments is most important in determining the flow path and thus the impact of acid rain on the three watersheds of that project (April and Newton, 1984). The watershed of Woods Lake, an acid system, is predominantly overlain by thin glacial till with numerous bedrock outcrops while the watershed of Panther Lake (pH 7) is covered by thick till(>3 m). Both watersheds are underlain by similar bedrock of granite-gneiss composition. The thick till cover in Panther Lake watershed provides a large groundwater reservoir. Only during spring melt is the capacity of this reservoir exceeded, causing significant surface runoff. The infiltration capacity of the soils is high enough so that during most precipitation events the water infiltrates the soils, moves down through the till and is slowly discharged to the lake through groundwater seepage. In the watershed of Woods lake the thin till can only support a small groundwater reservoir. The capacity of this reservoir is exceeded by most precipation events, therefore, most of the precipitation falling on this watershed moves directly to the lake as surface runoff (Newton and April, 1982).

The chemistry of deep groundwater in Panther Lake watershed reveals the extent to which silicate minerals may react with ground water. Samples collected from observation wells installed at a depth of 20 m within the glacial till had an average pH of 7.87 and an average alkalinity of 1740 μeq/1. This indicates considerable chemical reaction between the minerals in the till (feldspar and hornblende) and the infiltrated rainwater.

To test the applicability of these ILWAS findings to the entire Adironack region, 22 watersheds have been examined as part of the Regionalized Integrated Lake Watershed Acidification Study (RILWAS). Thirteen of these are subcatchments within the North Branch of the Moose River.

The North Branch of the Moose River is of particular interest because it contains surface water having a broad range of alkalinities (Driscoll et al., 1987). Also, the size of the watershed together with the variability of

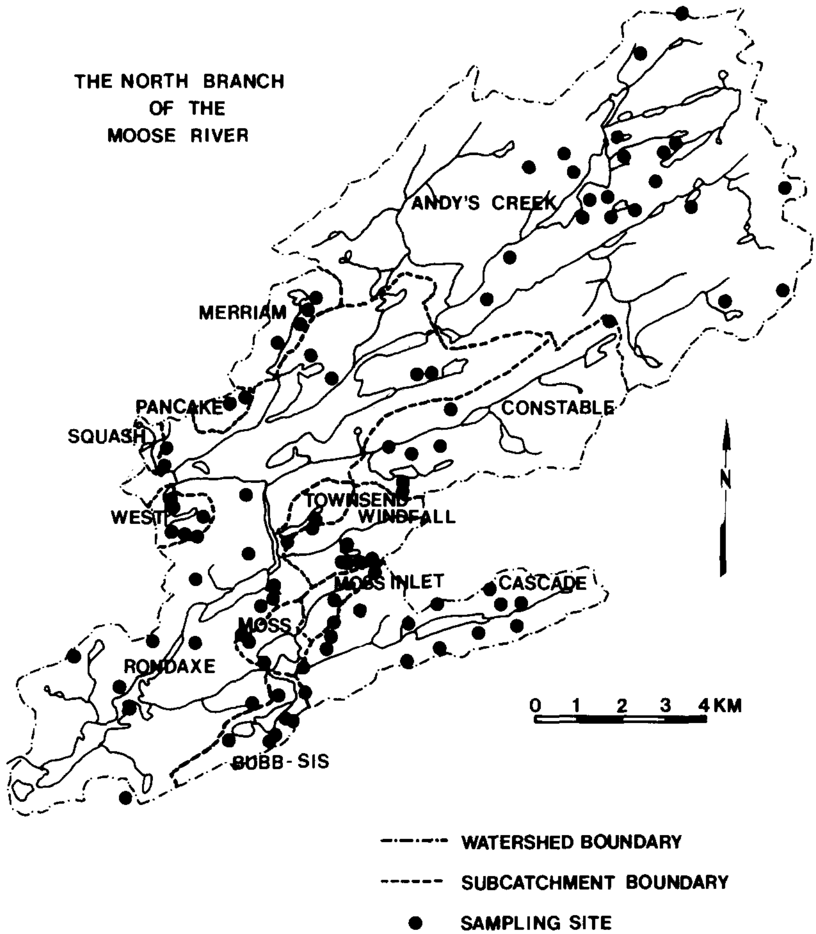

Figure 1. Sampling locations and subcatchments of the North Branch of the Moose River.

its geology allows us to evaluate the relative importance of bedrock geology and surficial geology in determining surface water alkalinity. Bedrock types range from granite gneiss to carbonate-bearing metasediments. Surficial geologic materials include both thick and thin till as well as significant areas of glaciofluvial stratified sand and gravel.

Field and analytical method

During the 1983 field season a total of 383 samples of soil, glacial drift and bedrock were collected from 77 sites in the watershed of the North Branch of the Moose River (Figure 1). Sampling and soil profile descriptions were made in excavated pits approximately 1 meter deep. A surficial geological

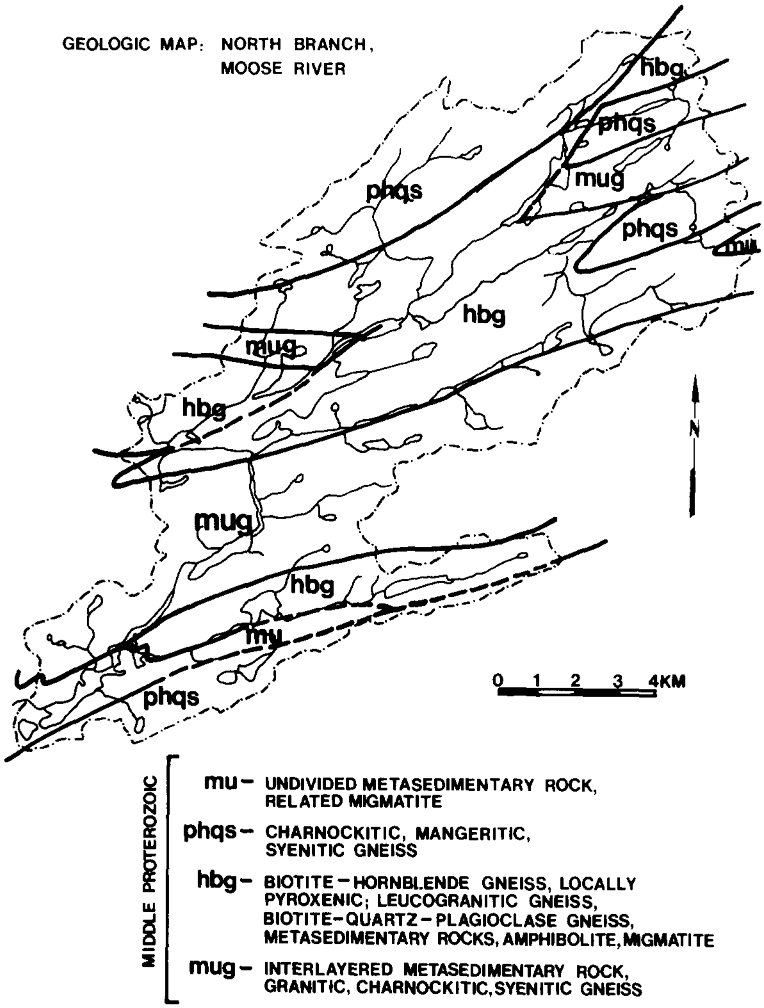

Figure 2. Bedrock geology of the North Branch of the Moose River.

map of the area was prepared using information from the pits and from geomorphological observations made directly in the field and from aerial photographs. Where necessary, seismic refraction was used to determine the thickness of the surficial sediments.

The particle size distribution of soils and glacial sediments was determined in the laboratory using standard wet sieve, dry sieve and hydrometer methods (Folk, 1968). Heavy minerals were separated from the fine to very fine sand fraction by gravity settling in tetrabromoethane (specific gravity 2.95), mounted in balsam and identified with a petrographic microscope. The mineralogy of bulk samples was determined by standard powder X-ray diffraction (XRD) techniques. The mineralogy of the $< 2\,\mu m$ clay-fraction was determined by XRD analysis of oriented samples after the following treatments; air dried, ethylene glycol, potasium saturation, heat to 350 °C, heat to 500 °C. Bedrock mineralogy and petrology was determined by examination of thin sections with the petrographic microscope. Bulk soil chemical analysis were obtained by X-ray fluorescence using a modified version of the method of Norrish and Hutton (1969). The presence of carbonate minerals was determined using the manometric method of Presley (1975).

Results

Bedrock geology

Dominant rock types underlying the North Branch of the Moose River basin include granitic and charnockitic gneisses of Precambrian age. Scarce to abundant amphibolite and metasedimentry interlayers occur scattered through the area. Of less widespread occurrence, but of importance nonetheless, are areas underlain by metasedimentary rocks of similar Precambrian age with relatively abundant calcareous layers that may contain marble, calcsilicate, quartzite, biotite schist and assorted leucogneisses and amphibolites (Figure 2).

Field examination of the bedrock geology in the North Branch of the Moose River revealed the occurrence of at least two small, isolated outcrops of carbonate-bearing calcsilicate rocks. One such outcrop, in the Windfall Pond subcatchment, displayed a surface morphology characteristic of carbonate-mineral dissolution. Six samples collected from this outcrop averaged 12 percent carbonate by weight. A second carbonate-bearing outcrop was located at the base of the waterfall just northeast of Cascade Lake. Samples collected here averaged 3.5 weight percent carbonate. The only other areas of carbonate mineralization occurred in fresh bedrock exposures (recently bared by blasting) both in the Upper Sister watershed and along the north shore of Big Moose Lake. At these locations thin carbonate veins (< 1 centimeter wide) were found intruding granitic gneiss. No carbonate mineralization was observed occuring within the bedrock fractures exposed at either of these two locations.

Lastly, it should be noted that small pockets of metamorphosed olivine gabbro and anorthositic gabbro occur just to the north and west of Big Moose Lake near Pocket and Squash Ponds.

Surficial geologic materials

Surface materials mantling the bedrock were primarily deposited by continental glaciers which covered this region during the Pleistocene epoch about 12,000–14,000 years ago. The following mapping units were used to

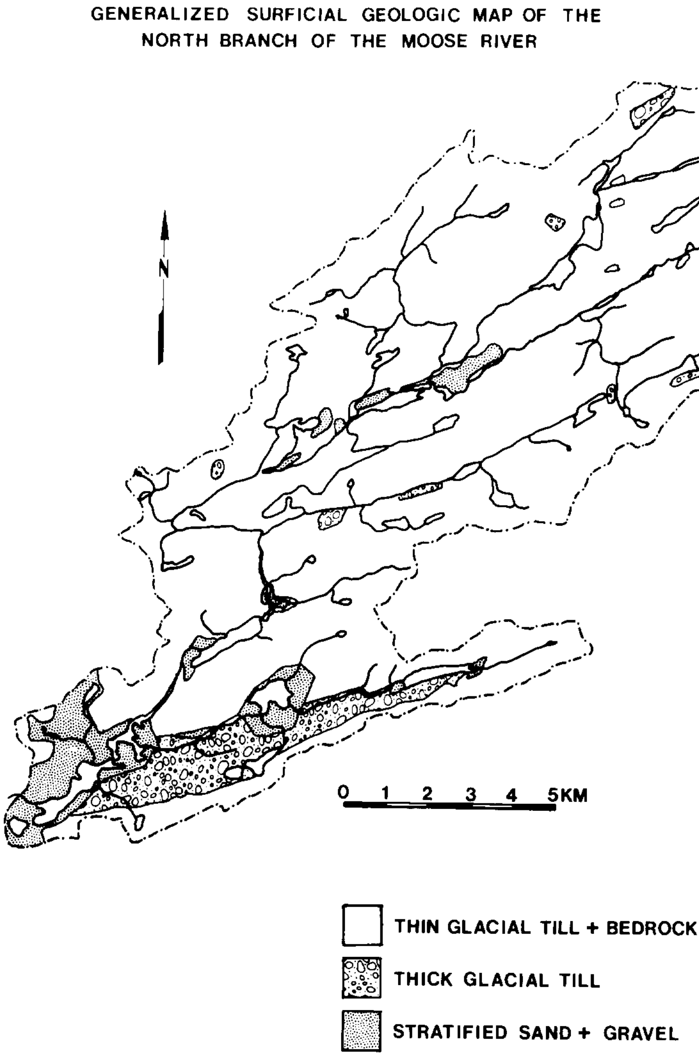

Figure 3. Generalized surficial geologic map of the North Branch of the Moose River.

describe these materials: 1) glacial till, 2) glaciofluvial sand and gravel, and 3) swamp deposits. Most abundant in the study area is locally derived, unsorted, unstratified glacial till. This material averages 68 percent sand, 29 percent silt and 3 percent clay. The till is subdivided into thick and thin units based on whether it is greater than or less than 3 meters thick, respectively. Less abundant in the watershed are glaciofluvial sand and gravel deposits left by melt water streams during glacial retreat. These deposits are composed of well-sorted, stratified sands that average 98

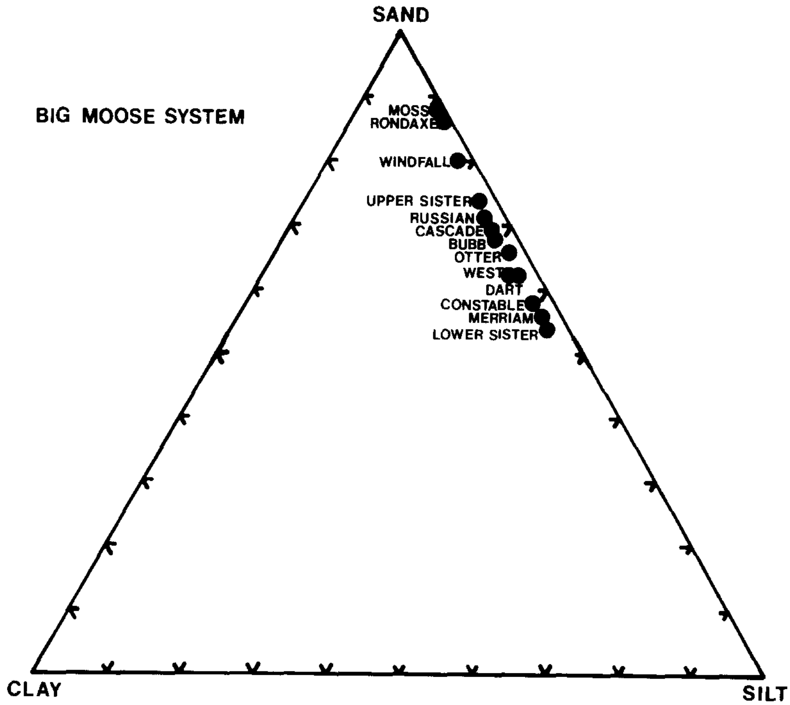

Figure 4. Average grain-size of samples from each subcatchment.

percent sand and 2 percent silt. Swamp deposits, post-glacial in origin, range from 1 to 10 meters in thickness and are composed primarily of peat.

The distribution of these surficial geological materials is shown in the map presented as figure 3. In general, the region north of Dart's Lake is mantled by thin till with numerous bedrock outcrops. Thick till and glaciofluvial sand and gravel account for less than 5 percent of the surficial materials in this area. Swamp deposits occur along the river courses and around some of the lakes.

The lower part of the watershed south of Dart's is quite different with the Moss-Cascade valley system containing significant areas of thick till and stratified drift (Figure 3). These deposits merge with an extensive area of outwash sand around Rondaxe Lake. The distribution of surficial materials is reflected in the average grain size of sediments in each subcatchment as shown in figure 4. The surficial materials in Moss and Rondaxe average over 85 percent sand while in Merriam and Lower Sisters, areas mantled mainly by thin till, the average sand content is less than 60 percent.

Extensive areas in the North Branch of the Moose River were covered by a thin discontinuous veneer of aeolian silt shortly after deglaciaton. The silt is now typically found disseminated throughout the B horizon of the

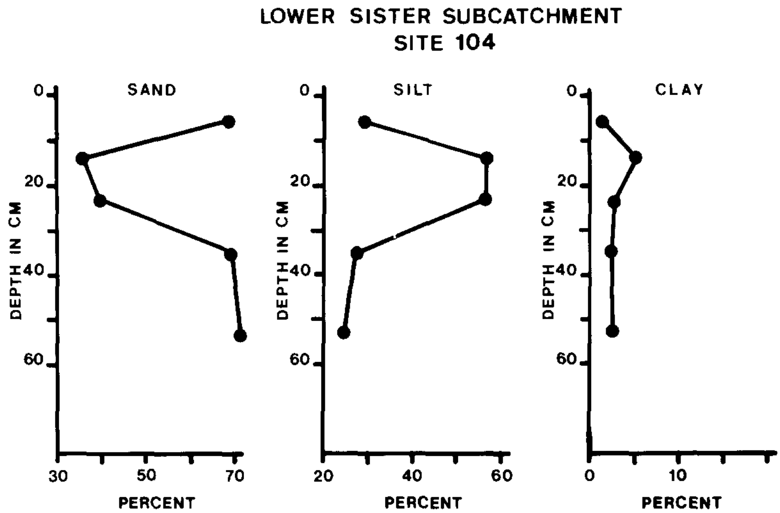

Figure 5. Typical distribution of sand, silt, and clay in a soil profile containing aeolian silt.

soil as it later mixed with underlying materials during pedogenesis, tree throw and frost processes. The soil profile in figure 5 illustrates the typical enrichment of silt in the upper part of the profile which is diagnostic of the presence of aeolian silt. The soils within the watershed can generally be classified as Spodosols.

Mineralogy and chemistry of surficial materials

Results from powder XRD analyses indicate that the surficial materials are composed mainly of quartz, potassium feldspar, sodic plagioclase and assorted heavy minerals. Heavy minerals are defined as those with a specific gravity greater than 2.95. Stratified drift has the highest heavy mineral concentration (16–18 percent) probably because selective sorting processes occurred during deposition. Most of the till contains about 8–10 percent heavies except for deposits in the Cascade and Windfall subcatchments which contain approximately 16 percent heavies. The higher concentrations here are likely a result of the occurrence of metasedimentary bedrock in these basins. The heavy mineral suite for each subcatchment is shown in Table 1. The dominant minerals are hornblende, opaques (e.g. ilmentite and magnetite), and clinopyroxene. The distribution of minerals does vary between subcatchments, but differences are especially noticeable in the Windfall subcatchment where there is an abundance of pyroxenes and little hornblende. No carbonate minerals (i.e. calcite or dolomite) were found to be present in any of the surficial materials.

The clay mineral suite in the soils and tills is dominated by vermiculite which is most abundant in the upper part of the soil horizons. Some kaolinite and illite is also present.

Table 1. Heavy mineral suite (in weight percent heavies)

	Cascade	Lower sister	Bubb	Constable	Dart	Merriam	Otter
Total Heavies	16.1	8.2	10.6	12.5	9.1	7.3	9.4
Hypersthene	5.5	6.0	5.0	6.0	4.5	4.3	4.0
Hornblende	26.3	38.0	35.7	33.0	41.2	43.7	44.7
Garnet	6.2	4.0	3.0	5.7	5.3	2.7	7.3
Opaques	36.2	34.3	32.3	21.3	26.6	29.0	25.7
Zircon	2.2	0.0	1.0	2.0	1.3	2.7	1.3
Rock Frags.	2.2	2.0	1.3	2.0	1.4	2.0	2.0
Enstatite	1.5	1.0	4.7	3.7	2.0	2.3	1.3
Epidote	0.5	1.3	0.3	0.3	0.3	0.7	0.7
Clinopyroxene	15.2	9.0	8.0	23.0	6.2	9.7	11.3
	Rondaxe	**Russian**	**Squash**	**Upper sister**	**West**	**Windfall**	
Total Heavies	18.4	9.5	8.2	10.3	10.5	15.7	
Hypersthene	5.0	6.5	3.7	5.0	4.0	15.3	
Hornblende	27.2	29.1	53.7	35.0	30.0	0.7	
Garnet	6.5	6.5	3.0	5.0	5.7	0.3	
Opaques	45.2	37.0	23.7	36.3	40.2	10.3	
Zircon	1.7	2.7	1.3	1.3	1.8	2.0	
Rock Frags.	0.8	1.5	0.7	1.7	1.0	1.3	
Enstatite	2.8	2.2	5.0	3.0	2.7	10.0	
Epidote	1.1	0.2	0.0	0.3	0.5	1.0	
Clinopyroxene	8.7	13.0	8.7	10.7	5.0	41.3	

The average bulk chemistry of surficial materials from each subcatchment is shown in Table 2. In general the chemical composition of the surficial materials does not vary significantly among watersheds and the average composition is close to that for a granite. One notable exception is Windfall Pond where calcium and magnesium concentrations in the soil and till are approximately twice as great as in any other subcatchment. The abundance of these elements and variations in others (see Table 2) reflects the anomolous geology of this subcatchment with respect to the rest of the Moose River System.

Discussion

Surface waters in the Moose River watershed north of Dart's Lake are quite acidic with pH values generally 5 or less (Driscoll et al., 1987). The acid neutralizing capacity (ANC) of water draining into Big Moose Lake ranges from 5 μeq/l at Andy's Creek to -25 μeq/l at Squash Pond. This, in large part, reflects the surficial geology in this part of the system. The thin till areas promote surface runoff and shallow interflow; hydrologic conditions which inhibit reactions between the water and soil minerals.

Surface waters draining subcatchments in the lower part of the system are generally more alkaline with ANC's that range from 95 μeq/l at

Table 2. Average bulk chemistry of surficial materials in each watershed

	Bubb	Cascade	Dart	Constable	Moss	Rond
SiO_2	74.97	77.26	74.09	71.75	80.12	72.83
Al_2O_3	11.62	10.37	11.34	12.54	10.65	10.64
Fe_2O_3	5.39	4.39	6.23	6.21	3.00	7.25
MgO	0.36	0.44	0.40	0.50	0.28	0.49
CaO	1.23	1.16	1.13	1.46	1.00	1.30
Na_2O	1.55	1.50	1.53	1.95	1.47	1.59
K_2O	3.87	3.66	3.88	4.46	3.60	4.23
TiO_2	0.99	0.99	1.21	1.03	0.64	1.39
P_2O_5	0.11	0.10	0.13	0.14	0.07	0.09
MnO	0.05	0.05	0.06	0.07	0.04	0.08
n	18	12	12	11	4	6
	Otter	Squash	Lower Sister	Upper Sister	West	Wind
SiO_2	73.90	74.47	73.26	74.44	75.56	81.48
Al_2O_3	11.95	11.70	12.65	11.39	11.47	7.54
Fe_2O_3	5.55	5.19	6.09	4.97	4.82	2.89
MgO	0.41	0.41	0.43	0.60	0.29	1.43
CaO	1.02	0.99	1.07	1.47	1.25	2.62
Na_2O	1.75	1.34	1.40	1.69	1.48	0.56
K_2O	3.96	4.59	3.70	4.07	4.08	3.16
TiO_2	0.15	0.09	0.09	0.14	0.13	0.11
P_2O_5	0.15	0.09	0.09	0.14	0.13	0.11
MnO	0.05	0.06	0.05	0.07	0.04	0.07
n	4	5	4	13	7	5

Cascade to 40–60 μeq/l in the Moss-Bubb area (Driscoll et al., 1987). The surficial geology in this part of the system is dominated by thick till and stratified drift. Although the permeability of the stratified drift is significantly greater than that of the glacial till, both materials have sufficiently high infiltration capacities to accomodate most of the water which falls during precipition events. These materials are relatively thick and have enough available pore space to store most of the incident precipitation. Thus a large fraction of the precipitation percolates down to recharge the groundwater. This water moves slowly through the system and is eventually discharged to lakes and streams.

Water which does infiltrate the groundwater system comes in contact with relatively fresh mineral surfaces and resides long enough for weathering reactions to significantly alter the chemistry. Both primary and secondary mineral weathering and cation exchange reactions likely occur. Truettner (1984) found the following weathering reactions to be important in explaining the outlet chemistry of the ILWAS lakes

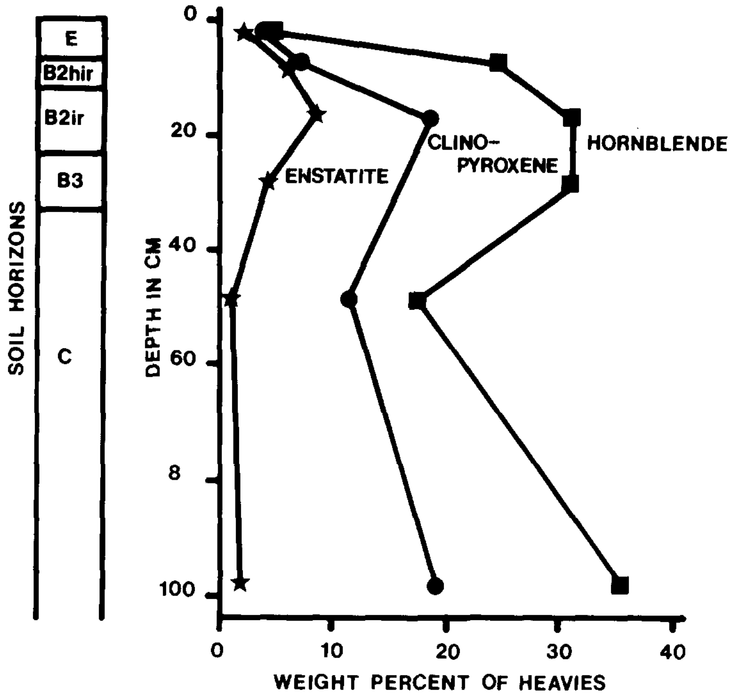

Figure 6. Variation in the percent enstatite, clinopyroxene, and hornblende as a function of depth through the soil profile. The depletion of these minerals near the surface is due to weathering.

Hornblende + acid ⟶ vermiculite

+ base cations and silica in solution

Feldspar + acid ⟶ kaolinite

+ base cations and silica in solution

Hydrogen ion + exchanger ⟶ base cation + exchanger

The distribution of heavy minerals within the soils of the North Branch of the Moose River is similar to that observed by Truettner (1984). Unstable heavies such as hornblende and pyroxene (Goldich, 1938; Grimm, 1978) have been depleted from the upper soil horizons by chemical weathering (Figure 6). Acidic water infiltrating these soils rapidly reacts with the more unstable minerals as it migrates downward to the saturated zone. By the time this is discharged to surface water it is completely neutralized.

The distribution of thick till is not the only factor controlling surface water chemistry in the North Branch of the Moose River. The water chemistry of some subcatchments is determined by the bedrock mineralogy. For example, the alkalinity of surface waters draining the Windfall system is 44 μeq/l, yet no thick till or stratified drift occurs within this basin. Here the bedrock underlying the watershed contains a number of large "pods" of carbonate bearing calc-silicate rocks. Enough water comes in contact with these rocks to allow complete neutralization of surface water in this basin. Whether or not the flow path of this water is through fractures in the bedrock or as sheet flow across the bedrock-till interface is unknown. However, it is known that there are no carbonate minerals left within the surficial materials themselves. Carbonate mineralization may also be an important process contributing to the alkalinity of Cascade lake as some carbonate-bearing bedrock was found there as well.

Alkalinity may also be generated by inlake processes. Probably both sulfate reduction and denitrification reactions are important (Rudd, et al., in press). The relatively low concentration of sulfate in the waters draining West Pond (Driscoll and Newton, 1985) is most likely due to this process. The watershed of West Pond has no thick till, stratfield drift or carbonate bearing bedrock yet the average alkalinity is 29 μeq/l. However, the pond is surrounded and is being encroached by thick peat deposits. Organic decomposition associated with peat leads to conditions favoring sulfate reduction within the Pond. These processes appear to be important in only a few watersheds within the North Branch of the Moose River, since most of the lakes have extremely short flushing times.

Occasionally a watershed will have a lower alkalinity than predicted from the distribution of thick till. Driscoll and Newton (1985) have shown that some lakes become isolated from their surrounding groundwater system due to the accumulation of low permeability organic-rich bottom sediments. This appears, for example, to be the case with most Adirondack seepage lakes.

The Bubb-Sis lake system which is underlain by 43 percent thick till and stratified drift (the highest percentage in the Moose River Watershed), yet has a surface water alkalinity of only 41 μeq/l appears to be another example. Thick organic-rich bottom sediments partially isolate this lake from the underground reservoir. Hence, much of the surface water comes from direct precipitation and runoff originating on the steep thin till covered slopes to the south. Groundwater in the thick till area directly north of the Bubb and Sis lakes probably drains northward under the topographic divide to Moss lake outlet. The effective area of thick till and stratified drift is, therefore, less than that calculated by considering only the topographic drainage basin.

The ILWAS findings show a direct correlation between surface water alkalinity and the percentage of a watershed covered by thick till. Although this relationship holds true for most of the subcatchments of the

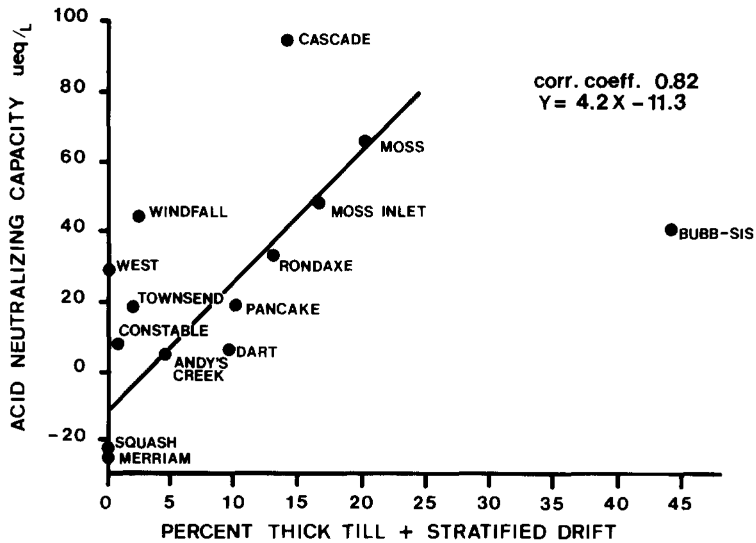

Figure 7. Plot of average alkalinity as a function of the percent of the watershed covered by thick till and stratified drift.

North Branch of the Moose River a significant number are controlled by other processes. A plot of the average alkalinity of surface water versus the percentage of the watershed covered by thick till and stratified drift is shown in figure 7. Datum points for most of the subcatchments plot on a linear trend with the following exceptions: 1) Windfall — which is controlled by carbonate, 2) West — which has a component of sulfate reduction and 3) Bubb-Sis which may be partially isolated from the groundwater system. In addition, the alkalinity of Cascade may, in part, be controlled by carbonate-bearing bedrock as previously suggested. The correlation coefficient for the remaining subcatchments is 0.89, or 0.82 if Cascade is included in the data set. The importance of carbonate in Cascade watershed is difficult to evaluate, especially in light of the fact that water draining the catchment had the highest concentration of dissolved silica, an element mainly associated with silicate mineral weathering.

Colquhoun, Kretser, and Pfeiffer (1984) classified Adirondack waters in terms of sensitivity to acidification according to the following scheme; acidified less than 0 μeq/l alkalinity, extremely sensitive 0–40 μeq/l, moderately sensitive 41–200 μeq/l. If the thickness of glacial till and stratified drift is the only variable considered then the regression of the relationship shown in figure 7 would predict that watersheds with less than 3 percent thick till would be acidic under the current rates of acidic deposition. Those with 3–12 percent would be extremely sensitive and those 12–50 percent would be moderately sensitive.

Conclusion

The application of the ILWAS results to the watershed of the North Branch of the Moose River allows us to explain the alkalinity of approximately 70 percent of the subcatchments. The remaining 30 percent are controlled by other processes, such as carbonate dissolution and sulfate reduction. These increase the alkalinity of the surface waters above the level estimated by just considering the area of thick till and stratified drift. It is possible that in some watersheds the surface waters are not fully coupled hydraulically to the surrounding groundwater systems. In these cases, the alkalinity of surface waters is below that predicted from the area of thick till and stratified drift.

Thick till and stratified drift is not uniformly distributed throughout the watershed of the North Branch of the Moose River. Many of the headwater subcatchments have little or no thick till and stratified drift, hence their high susceptibility to acidification. In contrast, many of the subcatchments in the lower portion of the watershed contain significant accumulations of these deposits and therefore resist the acidification process.

Thick glacial sediments are unevenly distributed throughout the Adirondacks. The thicker materials are in general going to be concentrated in the lower elevations due to both glacial depositional and postglacial erosional processes. This may in part explain the correlation between elevation and surface water acidity observed by Colquhoun, Kretser and Pfeiffer (1984).

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