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Hydrogeologic controls of surface-water chemistry in the Adirondack region of New York State

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Abstract. Relationships between surface-water discharge, water chemistry, and watershed geology were investigated to evaluate factors affecting the sensitivity of drainage waters in the Adirondack region of New York to acidification by atmospheric deposition. Instantaneous discharge per unit area was derived from relationships between flow and staff-gage readings at 10 drainage basins throughout the region. The average chemical composition of the waters was assessed from monthly samples collected from July 1982 through July 1984. The ratio of flow at the 50-percent exceedence level to the flow at the 95-percent exceedence level of flow duration was negatively correlated with mean values of alkalinity or acid-neutralizing capacity (ANC), sum of basic cations (SBC), and dissolved silica, for basins containing predominantly aluminosilicate minerals and little or no carbonate-bearing minerals. Low ratios are indicative of systems in which flow is predominately derived from surface- and ground-water storage, whereas high ratios are characteristic of watersheds with variable flow that is largely derived from surface runoff.

In an evaluation of two representative surface-water sites, concentrations of ANC, SBC, and dissolved silica, derived primarily from soil mineral weathering reactions. decreased with increasing flow. Furthermore, the ANC was highest at low flow when the percentage of streamflow derived from ground water was maximum. As flow increased, the ANC decreased because the contribution of dilute surface runoff and lateral flow through the shallow acidic soil horizons to total flow increased. Basins having relatively high ground-water contributions to total flow, in general, have large deposits of thick till or stratified drift. A major factor controlling the sensitivity of these streams and lakes to acidification is the relative contribution of ground water to total discharge.

Introduction

The Adirondack region of New York State receives acidic atmospheric deposition (Cogbill and Likens, 1974; Johannes et al., 1981. Raynal et al., 1983) and many lakes and streams in the region are acidic, with pH values less than 5.0 (Schofield, 1977; Pfeiffer and Festa, 1980; Colquhoun et al., 1981, 1982 and 1984).

It has been hypothesized that a major factor regulating the chemistry in Adirondack surface waters is flow paths (Galloway et al., 1980; Newton and April, 1982; Troutman and Peters, 1982; Chen et al., 1984; Gherini et al., 1985; Murdoch et al., 1985 Peters and Murdoch, 1985). This hypothesis was developed from an analysis of data collected from 1977 through

1981 from an acidic-lake basin and a neutral-lake basin in the west-central Adirondack mountains, New York, as part of the Integrated Lake-Watershed Acidification Study (ILWAS). The rationale was that ground water has a circumneutral pH, elevated alkalinity or acid neutralizing capacity (ANC), and sum of basic cations [Ca^{++}, Mg^{++}, Na^{+} and K^{+}] which are produced by weathering. The addition of ground water to surface water tends to increase pH and ANC.

Surface-water composition has been modeled as a mixture of two solutions, ground water and surface runoff (Johnson et al., 1969; Pinder and Jones, 1969). As discharge increases, the contribution of surface runoff, which is dilute, to total discharge increases. Furthermore, surface waters are derived from ground water become diluted by inputs of surface runoff during hydrologic events and therefore may be susceptable to acidification (Peters and Murdoch, 1985). The relative contribution of ground water to surface-water flow is primarily controlled by the distribution and thickness of till and the permeability (rate at which water is transmitted) of these deposits.

One technique of identifying differences in the relative contribution of base flow (ground water) to stream discharge is to compare flow-duration curves. A flow-duration curve is a cumulative frequency function indicating the percentage of time a given discharge (basin runoff) is equaled or exceeded during a given period (Searcy, 1959). The slope of the duration curve at high flows (low exceedence levels) is controlled largely by climate, physiography and plant cover of a basin, whereas the slope at low flows (high exceedence levels) is controlled largely by geology. Steep slopes are indicative of systems dominated by surface runoff whereas flatter slopes are indicative of systems dominated more by ground-water discharge or extensive surface storage which tend to equalize the flow. The relative extent of active storage (ground water plus surface water) or surface runoff can be elevated among basins by comparing low-flow characteristics, such as 'slope', as estimated by the ratio of flows at intermediate exceedence levels (50 percent) to high exceedence levels (95 percent) or some such index of flow variability (Lane and Lei, 1950).

Peters and Murdoch (1984) used flow duration to compare the discharge characteristics from the acidic (Woods Lake) and neutral pH (Panther Lake) ILWAS lakes (Figure 1), for which the surface-water component of storage was comparable. Runoff from the acidic lake was highly variable and the corresponding flow-duration curve had a steep slope, particularly for the low flows or high exceedence levels, which suggested that water traveled rapidly over or through the acidic upper soil horizons to the lake (Figure 1). In contrast, the runoff from the neutral-lake basin was less variable and the corresponding flow-duration curve had a flatter slope (Figure 1), because flow was attenuated as water percolated through the till. Moreover, during dry periods, ground water from the thick till maintained discharge at a relatively high level.

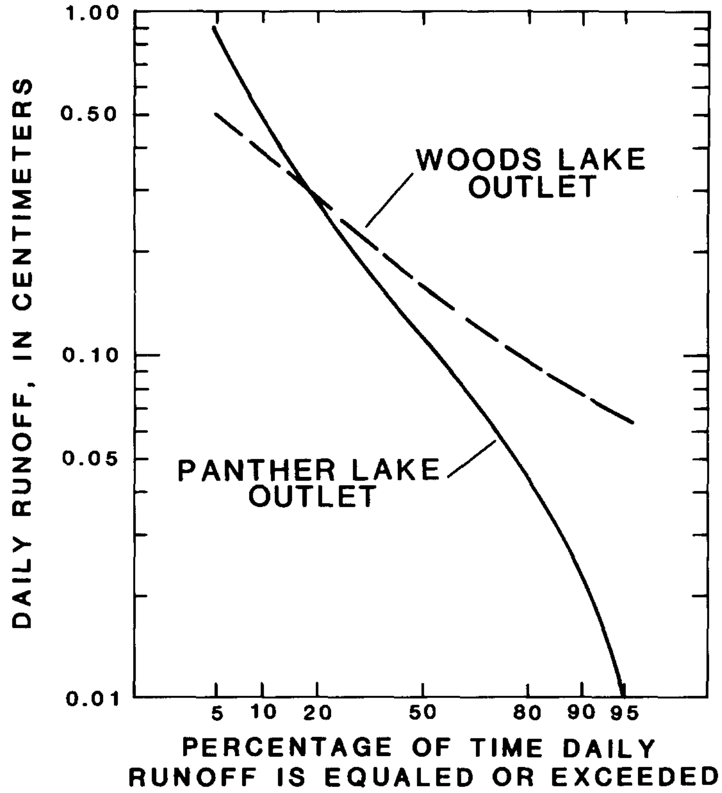

Figure 1. Flow-duration curves for daily runoff from acidic Woods and neutral pH Panther Lakes, January 1980 through December 1981.

Reflecting the difference in slopes, the ratio of runoff at the 50-percent exceedence level to that at the 95-percent exceedence level was much larger for the acidic-lake basin than that for the neutral-lake basin. For 1980–81, the 50 to 95 percent flow ratio was 13.0 for the acidic-lake basin and 2.3 for the neutral-lake basin. These differences in flow characteristics reflect differences in ground-water discharge which is controlled by the amount of thick till (> 3 m) in the basins. The acidic-lake basin contained approximately 20 percent thick till, whereas the neutral-lake basin contained approximately 65 percent thick till.

The intent of our investigation was to test the hypothesis that residence time and the relative contribution of ground water to stream discharge is the primary factor controlling surface-water acidifcation on several lake and stream watersheds distributed throughout the Adirondack Mountains. This project was part of the Regionalization of the Lake-Watershed Acidification Study (RILWAS). The 'slope' of the flow duration curves during low-flow (ratio of flow at the 50-percent exceedence level to flow at the 95-percent exceedence level) and average water chemistry of RILWAS

Table 1. Location and drainage areas of sites studied

USGS Station identification number	Stream	Tributary to	Latitude	Longitude	Location	Drainage Area (km^2)
01311992	Arbutus Pond Outlet	Fishing Brook	43°58′56″	74°14′09″	Essex County, Hydrologic Unit 02020001, at bridge on private road at outlet of dam, and 5.9 km northwest of Newcomb	3.16
01311998	Woodruff Pond Outlet	Harris Lake	43°58′10″	74°09′51″	Essex County, Hydrologic Unit 02020001, at culvert on State Highway 28N, 0.8 km downstream from Woodruff Pond, at Newcomb	8.73
01316154	Clear Pond Outlet	The Branch	43°59′44″	73°49′53″	Essex County, Hydrologic Unit 02020001, at culvert on Elk Lake Road 5.1 km northwest of Blue Ridge, and 9.6 km northwest of North Hudson.	5.67
01347260	Otter Lake Outlet	Green Lake	43°10′52″	74°30′13″	Fulton County, Hydrologic Unit 02020004, at a site along side a private road, just downstream from pond, and 1 km northeast of Canada Lake.	4.09
04253628	Constable Creek	Big Moose Lake	43°49′28″	74°50′05″	Herkimer County, Hydrologic Unit 04150101, at site 0.3 km upstream from town road, and 6.2 km east of Big Moose.	13.70
04253633	Pancake Creek	Big Moose Lake	43°49′47″	74°51′56″	Herkimer County, Hydrologic Unit 04150101, at site 0.1 km downstream from town road, 2.6 km east of Big Moose.	1.37
04253640	West Pond Outlet	Big Moose Lake	43°49′02″	74°52′50″	Herkimer County, Hydrologic Unit 04150101, at culvert on Big Moose Road, 2.7 km east of Big Moose.	1.84
04253650	North Branch Moose River (Big Moose Lake outlet)	Middle Branch Moose River	43°48′59″	75°51′21″	Herkimer County, Hydrologic Unit 04150101, at culvert on town road, just downstream from dam of Big Moose Lake, and 4.8 km east of Big Moose.	95.6
04253655	Townsend Pond Outlet	North Branch Moose River	43°48′30″	74°51′05″	Herkimer County, Hydrologic Unit 04150101, at culvert on Big Moose Road, just upstream from mouth, and 5.3 km southeast of Big Moose.	1.50

04253660	Windfall Pond Outlet	North Branch Moose River	43°48′13″	74°51′05″	Herkimer County, Hydrologic Unit 04150101, at culvert on Big Moose Road, 1.4 km west of Windfall Pond, and 5.4 km southeast of Big Moose.	3.99
04253680	North branch Moose River (Dart Lake Outlet)	Middle Branch Moose River	43°47′32″	74°52′31″	Herkimer County, Hydrologic Unit 04150101, at trail crossing, 0.6 km downstream from Dart Lake, and 4.2 km southeast of Big Moose.	107.5
04253713	Cascade Lake Outlet	Moss Lake	43°46′50″	74°50′31″	Herkimer County, Hydrologic Unit 04150101, at site 0.5 km downstream from Big Moose Road at foot bridge, and 2.6 km northwest of Eagle Bay.	7.61
04253715	Moss Lake Tributary	Moss Lake	43°47′20″	74°50′41″	Herkimer County, Hydrologic Unit 04150101, at culvert on Big Moose Road, 3.2 km northwest of Eagle Bay.	1.30
04253720	Moss Lake Outlet	North Branch Moose River	43°46′53″	74°51′11″	Herkimer County, Hydrologic Unit 04150101, at trail just downstream from Moss Lake, and 3.4 km northwest of Eagle Bay.	12.48
04253740	Bubb Lake Outlet	Moss Lake Outlet	43°46′52″	74°51′11″	Herkimer County, Hydrologic Unit 04150101, at mouth just above Moss Lake Outlet, and 3.2 km northeast of Eagle Bay.	2.61
04253780	North Branch Moose River (Lake Rondaxe Outlet)	Middle Branch Moose River	43°45′38″	74°54′49″	Herkimer County, Hydrologic Unit 04150101, at site just downstream from dam of Lake Rondaxe, and 7.7 km southeast of Eagle Bay.	141.9
04268385	Black Pond Outlet	Lower St. Regis Lake	44°25′56″	74°17′53″	Franklin County, Hydrologic Unit 04150306, staff gage on right bank, 19 m upstream from dam on Black Pond, 21 m upstream from Keese Mills Road, and 3.5 km west of Paul Smiths.	3.73
04273819	Heart Lake Outlet	MacIntyre Brook	44°10′48″	73°58′00″	Essex County Hydrologic Unit 02010004, at trail crossing about 61 m downstream from Heart Lake, and 6.9 km southwest of North Elba.	0.67

sites were compared among sites to evaluate the hypothesis. In addition, the relationships between concentration and flow at two nearby stream sites were investigated more intensively to illustrate the control of hydrogeologic characteristics on surface water chemistry.

Methods

Water level and discharge data

Staff gages were installed at 18 sites, including lake outlets and streams, in the Adirondack region, New York, during the summer and fall of 1982 (Table 1). During ice-free periods, water levels were recorded as part of the monthly collection of water-chemistry samples and, for several sites values were recorded uniformly at more frequent intervals. At each site discharge was measured using Price[1] current meters and water levels were recorded (Rantz et al., 1982). From these data, stage-discharge relationships were developed.

For those sites for which the standard error of the log-log stage-discharge relationship was less than or equal to 30 percent, instantaneous discharge normalized with respect to drainage area was calculated for each recorded stage. These discharges were ranked and the percentages of the time a given discharge was equaled or exceeded (flow duration) was determined for the calculated discharge at each site.

The ratio of flow at the 50-percent exceedence level to flow at 95-percent exceedence level ('slope' of the flow duration curve during low flow) was used as the flow indicator of a given site for comparison with those for the other sites. But because this approach has not been reported elsewhere, there was some question regarding the reliability of using discontinuous versus continuous data. The agreement between the ratio derived from discontinuous data and that of a continuous record, therefore, was assessed by computing ratios for several subsets of the continuous discharge record for 1980–81 (731 observations) from acidic and neutral-pH ILWAS lakes.

Twenty subsets for each group of 25, 50, 100, and 150 observations of daily mean discharge were randomly selected. For each subset, the 'slope' of the duration curve for the low-flow part was determined by dividing the flow at the 50-percent level by the flow at the 95-percent exceedence level. The coefficient of variation was used to assess precision of each group. Results indicate that the mean ratio did not change significantly with the number of observations, whereas the coefficient of variation decreased with both the number of observations and the value of the ratio. The coefficient of variation for the acidic-lake basin (2-year flow ratio, 13.0) decreased from 60 percent for 25 observations (mean ratio, 14.7) to 17

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[1] Use of brand names in this report is for identification purposes only and does not indicate endorsement by the U.S. Geological Survey.

percent for 150 observations (mean ratio, 13.2). The coefficient of variation for the neutral-lake basin (2-year flow ratio, 2.3) decreased from 27 percent (mean ratio, 2.6) to 10 percent (mean ratio, 2.3). For RILWAS, more than 100 observations were recorded at all but two sites. The precision of this variable, therefore, was generally better than or equal to that associated with the computed discharges.

The ratios for each subset, however, were nonnormally distributed and positively skewed which is typical for hydrologic data, i.e., values smaller than the mean were more common than values larger than the mean. The reliability of correlation analysis (or linear regression) to accurately represent the relationship among variables is diminished by nonnormal distributions of the variables through unequal weighting by extreme values. The ratios, therefore, were transformed logarithmically to adjust for the nonnormal distributions and these values were correlated with the average chemical composition of stream water at the sites. The t-test was applied to the Pearson product-moment coefficient of linear correlation to assess the statistical significance of the linear relationship between the log-transformed flow 'slope' and average composition (Till, 1974).

Basin characteristics

Field surveys for geology, soils and vegetation were performed in all the watersheds. Bedrock and soil samples were collected for petrographic and chemical analyses. Depths and distributions of surficial materials were determined from seismic refraction transects, field inspections and interpretation of aerial photographs and topographic maps (Harstad, 1983; Newton et al., 1987). Vegetation maps were compiled for most of the watersheds using line transects and infared aerial photographs (Cronan et al., 1987).

Water-quality data

Water samples were collected monthly from July 1982 through July 1984 at each site and analyzed for all major solutes. A description of the sampling procedures, sample custody and analytical methods used in this study are described in detail elsewhere (Driscoll and Newton, 1985; Driscoll et al., 1987). As for constitutents discussed in this report, acid-neutralizing capacity was determined by Gran titration (Gran, 1952). Silica was determined by autoanalyzer (American Public Health Assoc., 1975) and each of the major cations (calcium, magnesium, sodium and potassium by atomic adsorbtion spectrophotometry (Salvine, 1968).

Concentration-discharge relationships

The relationship between concentration and discharge in surface waters is generally consistent with a 2-component mixing model, in which base flow (ground water) is diluted by surface runoff (Johnson et al., 1969; Pinder and Jones, 1969). This concept was assumed to be valid for the two stream

Table 2. Stage-discharge relationships and ratios of flow at the 50-percent to 95-percent duration level for RILWAS sites

[Back-transformed equations are in the form $Q = a\ (\text{stage} - X)^b$, where Q is the instantaneous discharge, in liters per second per square kilometer; a and b are the regression constants; stage is the staff gage reading of water level in feet, and X is the stage offset, corresponding approximately to the water stage at zero flow, in feet.]

Site	Type[1]	a	X	b	Number of measurements	Standard error of estimate in percent	Ratio of flow at 50-percent to 95-percent duration level	Number of observations
Arbutus	L	66	3.29	2.89	9	23	—	—
Woodruff Pond Outlet	S	171	13.91	1.99	10	25	64.3	125
Clear Pond Outlet	L	12	13.84	3.38	11	15	5.6	456
Otter Lake Outlet	L	61	0.62	0.82	5	10	—	—
Constable Creek	S	27	6.41	2.32	9	20	10.2	148
West Pond Outlet	S	8.6	14.13	0.80	8	30	13.4	234
Big Moose Lake Outlet	L	44	17.49	1.55	6	4	5.5	217
Townsend Pond Outlet	S	70	13.83	1.71	9	9	7.6	246
Windfall Pond Outlet	S	60	17.56	2.04	10	5	11.5	252
Dart Lake Outlet	L	1.7	30.61	3.60	7	9	10.0	232
Cascade Lake Outlet	S	42	0.08	2.84	8	9	2.9	159
Moss Lake Tributary	S	238	17.68	1.79	12	30	3.9	253
Moss Lake Outlet	L	—	—	—	—	—	—	—
Bubb Lake Outlet	S	—	—	—	—	—	—	—
Lake Rondaxe Outlet	L	19	13.87	2.04	7	15	4.9	26
Black Pond Outlet	L	—	—	—	—	—	—	—
Heart Lake Outlet[2]	L	126	17.26	2.57	5	9	12.1	27

[1] L = lake, S = stream.

[2] Relationship applied to data through August 1983.

sites investigated. The relationship between concentration(C) and flow (Q), Therefore, was calculated using the hyperbolic relationship formulated by Johnson et al., (1969).

$$C = [1/(1 + B.Q)]a + b \tag{1}$$

where:

B = a constant related to the volume of water stored in the basin at zero discharge and residence time,

a = the slope, and

b = the concentration, as discharged approaches infinity.

Results and discussion

Discharge

The stage-discharge relationships for each of the sites are summarized in Table 2. The absence of a stage-discharge relationship for a site indicates that a meaningful relationship could not be determined for that site. The water levels at Black Pond Outlet, Bubb Lake Outlet, Moss Lake Outlet, and Arbubus Lake Outlet were affected by beaver activity and the staff gage at Squash Pond Outlet was vandalized.

Of the remaining sites, 50 percent of the stage-discharge relationships had standard errors of an estimated discharge less than 10 percent. The stage-discharge relationship for Otter Lake Outlet was acceptable for medium to high flow but leakage through the dam at the outlet caused the water level to drop below the top of the dam during low-flow periods; discharge data for Otter Lake Outlet, therefore, were excluded from the flow-duration analysis. The larger standard errors for the relationships at the remaining sites were probably the result of scour or deposition of sediment, or vegetative growth in the stream reach which controlled the water level at the staff gages.

Flow ratios

In this study, basins that had a higher portion of surface runoff were expected to have flow characteristics similar to the acidic ILWAS lake and to have a steeper 'slope' or a large ratio of flow at the 50-percent exceedence level to flow at the 95-percent exceedence level. According to the hypothesis, these sites should have lower average concentrations of constituents, such as SBC, dissolved silica and ANC, than sites which have a flatter 'slope' or small ratio indicating that a larger percentage of the runoff at these sites is derived from ground water. This concept of processes regulating the acid/base chemistry is simplified to some extent because it assumes that other major identifiable processes controlling the concentration of SBC, dissolved silica and ANC within the watersheds, streams or lakes (e.g., biological assimilation or dissimilatory reduction) were insignificant.

Surface-water storage in lakes, ponds, and wetlands and drainage area can affect the ratios (Lane and Lei, 1950). The longer travel time in large basins attenuates flow resulting in lower flow ratio than that for a smaller basin which has similar geologic and surface storage characteristics. Likewise, a basin with an extensive amount of surface storage would have a smaller ratio than one with a small amount of surface storage. For the analysis, herein, differences in surface storage and drainage area among basins were not quantitatively addressed and were assumed to have a minor affect on the flow ratios.

Also, we anticipated that significant correlations would only exist for basins having little or no carbonate-bearing minerals because of the relatively rapid dissolution kinetics of these mimerals. Therefore, Woodruff Pond Outlet and Windfall Pond Outlet were excluded from the flow-duration analysis because substantial amounts of carbonate-bearing minerals were found in these basins (Harstad, 1983; Newton et al., 1987).

For the 10 basins, the logarithm of the 'slopes' of flow duration curve was negatively correlated with the average dissolved silica concentration ($p < 0.01, r^2 = 0.45$), SBC ($p < 0.05, r^2 = 0.43$), and ANC ($p < 0.15$, $r^2 = 0.28$), as shown in Figure 2. The individual and average concentrations of dissolved silica, ANC, SBC, and field or air-equilibrated hydrogen ion concentrations (from pH measurements) were also found to be highly correlated, for either the subset of sites for which flow ratios were computed, or for all the sites without carbonate minerals. As anticipated, SBC was positively correlated with ANC (in μeq.l^{-1}; $p < 0.001$, $r^2 = 0.92$); the slope of a linear regression of SBC on ANC was 1.0. SBC was also negatively correlated ($p < .01$, $r^2 > = 0.55$) with the average field and air-equilibrated hydrogen ion concentration.

The consistency in results among constituents and the 'slope' of the flow duration curve support the hypothesis that residence time of water in contact with the neutralizing minerals in the till and the ground-water contribution to surface flow are primary factors controlling acidification and, in general, water chemistry in the Adirondack Region.

Further analysis of these data revealed an additional cause and effect relationship. Average ANC was more poorly correlated with dissolved silica (Figure 3, $p < 0.05$, $r^2 = 0.30$) than average SBC was with dissolved silica (Figure 4, $p < 0.01$, $r^2 = 0.45$). The data for Woodruff Pond Outlet have been included in the figures to show the effect that carbonate mineral weathering has on the outlet composition. Not only was the average dissolved silica concentration low for the respective SBC and ANC concentrations, but SBC and ANC were several times larger in the stream water draining this carbonate basin than those for any of the remaining aluminosilicate basins. Of the remaining basins, however, the

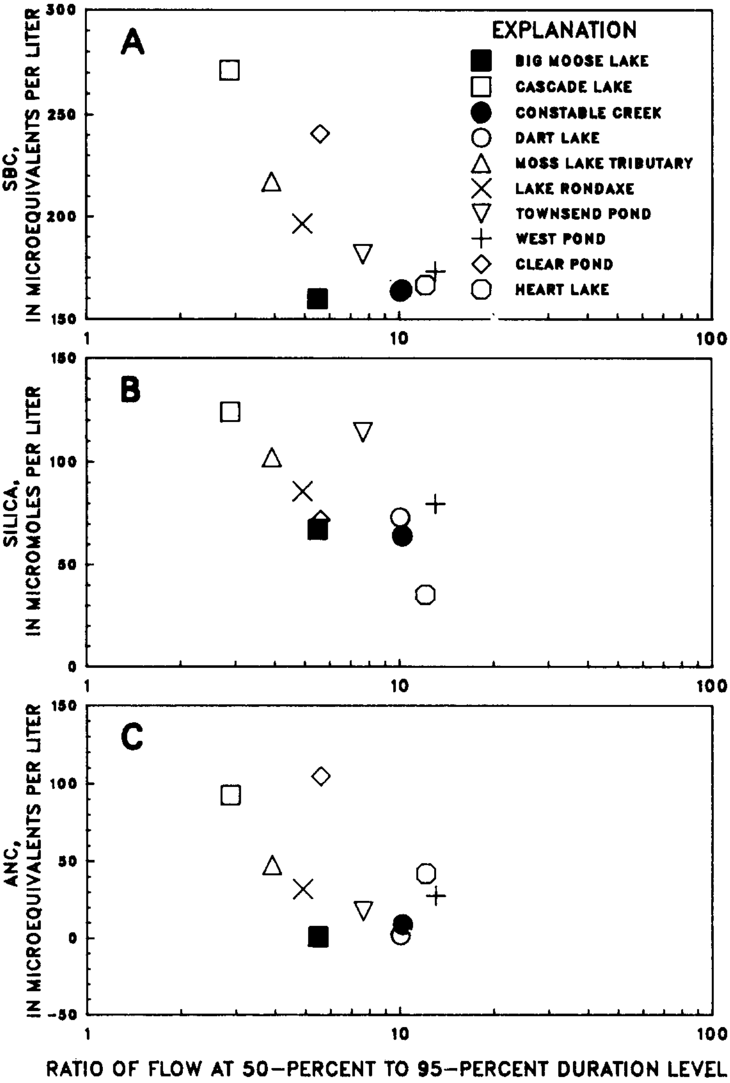

Figure 2. Average concentration as a function of ratio of flow at the 50- to 95-percent exceedence level for RILWAS sites. A, sum of basic cations (SBC); B, dissolved silica; C, acid-neutralizing capacity (ANC).

average ANC for the eastern basins, Heart Lake Outlet, Clear Pond Outlet and Black Pond Outlet, were relatively enriched in ANC when compared to sites with comparable concentrations of dissolved silica (Figure 4). Also, the correlation between ANC and the 'slope' of the flow duration curve was significantly improved when the data for Clear Pond Outlet and Heart Lake Outlet were excluded ($p < 0.05$, $r^2 = 0.52$). Although not as

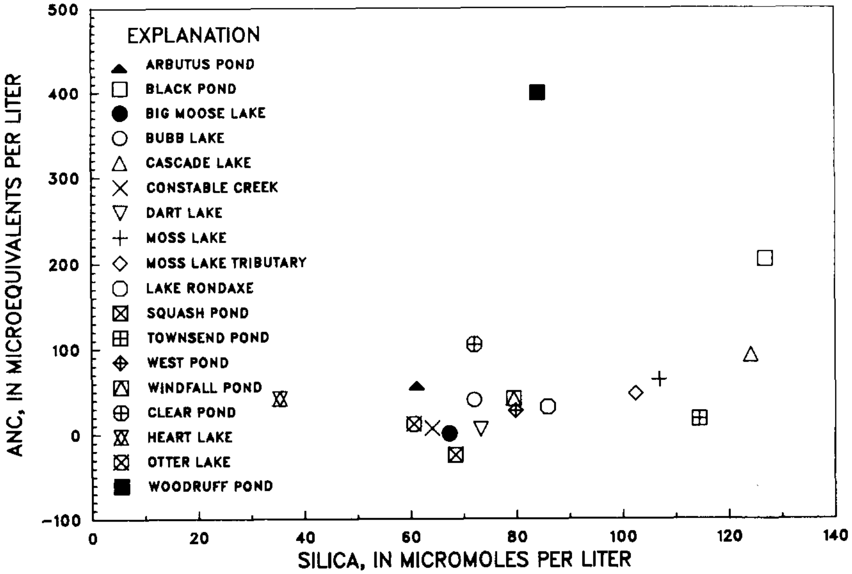

Figure 3. Average acid-neutralizing capacity (ANC) as a function of average dissolved silica concentration at RILWAS sites.

pronounced as ANC, SBC for these sites also tends to be slightly enriched when compared with sites with comparable concentrations of dissolved silica (Figure 3). Carbonate-mineral weathering could produce these results as SBC and ANC would be produced without silica. However, carbonate minerals were not found in the bedrock and soils of these basins (R. M. Newton, pers comm).

A comparison of the average SBC with average ANC for all sites indicates that these eastern sites also had lower SBC for comparable ANC relative to the remaining sites. These results are difficult to explain on the basis of mineral weathering. Streamwater at these sites, however, had a considerably lower average NO_3^- concentration, which ranged from 1 μeq. l^{-1} to 5 μeq. l^{-1}, than that at the remaining sites, which ranged from 10 μeq. l^{-1} to 31 μeq. l^{-1} (Driscoll and Newton, 1985). Yet, the atmospheric deposition of NO_3^- was comparable to that in the western Adirondacks (A. H. Johannes, pers. comm.). Biological assimilation of NO_3^- at these three sites could produce the additional ANC (Van Breeman et al., 1983; Hemond and Eshleman, 1984) which could account for the observed differences and lack of a more statistically significant relationship, i.e. at $p < 0.05$, between ANC and logarithm of the ratio of flow at the 50- to 95-percent exceedence level. Note that all three of these sites contain lakes or ponds immediately upstream of the monitoring site and are located in the eastern part of the study area where the underlying bedrock is more

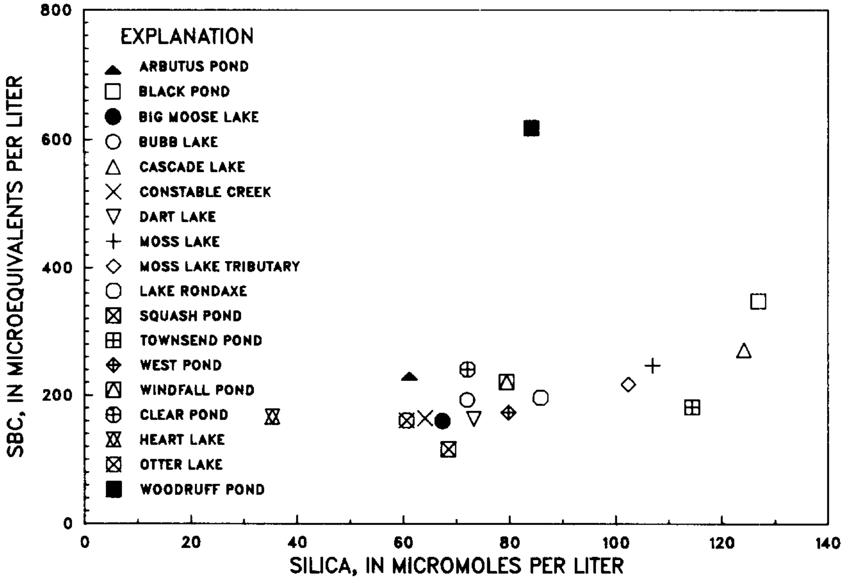

Figure 4. Average sum of basic cations (SBC) as a function of average dissolved silica concentration at RILWAS sites.

calcium rich. However, there is no other apparent causative factor to explain this variation.

Goldstein et al. (1984) hypothesized that short-term changes in the concentrations of SBC in Adirondack surface waters were regulated by cation exchange reactions, rather than mineral weathering reactions. Although weathering is clearly responsible for the long-term production of ANC, the much stronger correlation between SBC and ANC than between SBC and dissolved silica may be evidence to support this hypothesis.

Chemical-composition and flow

For lake systems, in which the lake volume is large relative to the drainage area, the chemical composition at the outlet generally does not correlate well with runoff because in-lake mixing obscures the distinct chemical composition of waters derived from various edaphic sources (e.g., surface runoff from organic and upper mineral soil; ground water from the lower mineral soil and till). This problem was evident in an evaluation of the variations of SBC, dissolved silica and ANC with discharge at the outlet of Big Moose Lake (Figure 5). In streams or streams draining lakes which are small relative to the total drainage area, concentrations of solutes were more transient due to the absence of mixing and the relatively short retention time within the hydrologic reach. Of the RILWAS sites for which discharges were computed, 5 were at lake outlets and 7 were on streams although these streams (Table 2) had lakes or ponds in their headwaters.

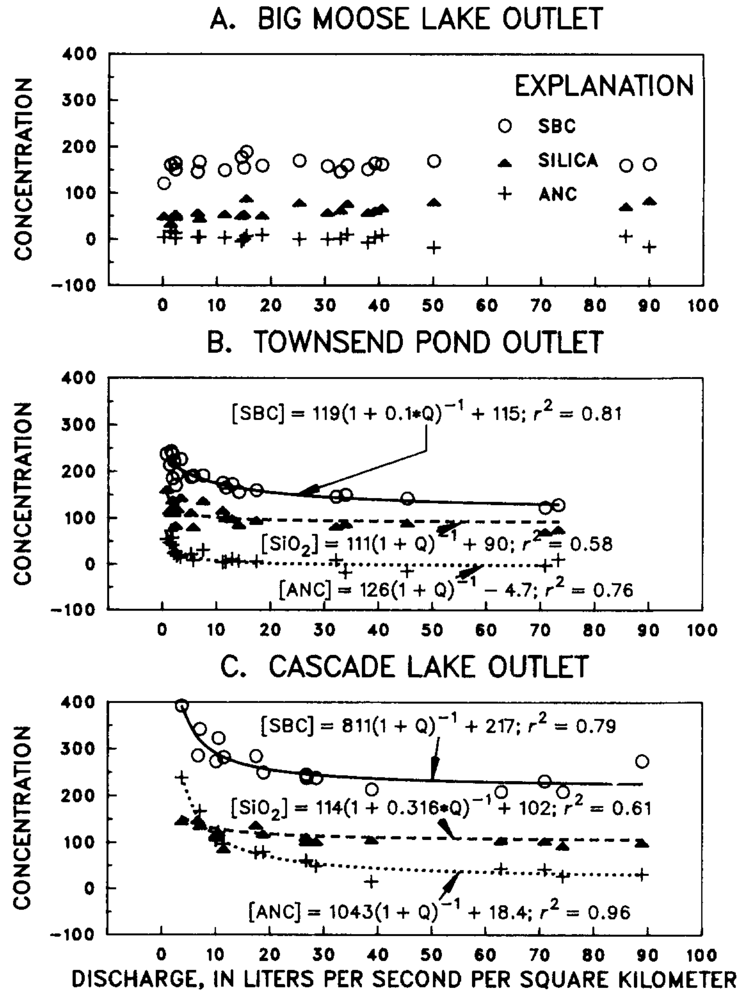

Figure 5. Concentration of basic cations (SBC) in μeq. l^{-1}, acid-neutralizing capacity (ANC) in μeq. l^{-1}, and dissolved silica in μeqll^{-1}, as a function of discharge per unit area. A, Big Moose Lake Outlet; B, Townsend Pond Outlet; and C, Cascade Lake Outlet.

An examination of the relationships between concentration and flow at two stream sites, both within the North Branch of the Moose River, illustrates the control that the hydrogeologic characteristics of a basin have on the chemical composition of drainage waters, particularly during low flow. The first stream site, Townsend Pond Outlet, drains a relatively small area (1.50 km^2) and contains a small pond (< 0.02 km^2) in its headwaters. The basin contains predominantly till (< than 3 m) and bedrock and minor (2 percent) thick till (> 3 m) and stratified drift (Newton et al., 1987). The stream water had a low ANC, which averaged 21.1 μeq. l^{-1} and ranged from $-18.2\,\mu eq.l^{-1}$ to $72.2\,\mu eq.l^{-1}$, and a low SBC, which averaged $189\,\mu eq.l^{-1}$ and ranged from $128\,\mu eq.l^{-1}$ to $249\,\mu eq.l^{-1}$ (Figure 5). In comparison, the second stream, Cascade Lake Outlet, has a larger drainage area ($7.61\,km^2$) of which 13 percent contains thick till and stratified drift and the remaining area consists mainly of thin till and bedrock (Newton et al., 1987). The basin, also, contains more open water ($0.44\,km^2$) and the stream is bordered by beaver meadows and wetlands over much of the 4–km reach between the lake outlet and the gage and sampling site. The stream water had a higher ANC, which averaged $102\,\mu eq.l^{-1}$ and ranged from $27\,\mu eq.l^{-1}$ to $239\,\mu eq.l^{-1}$, and a higher SBC, which averaged $275\,\mu eq.l^{-1}$ and ranged from $209\,\mu eq.l^{-1}$ (Figure 5).

At both sites, the concentrations of SBC, silica and ANC decreased with increasing flow (Figure 5). The relationship between concentration and flow are consistent with a two component mixing model in which base flow (ground-water discharge) was diluted by surface runoff (eqn. 1). Concentrations of SBC, dissolved silica and ANC were not constant but rather fluctuated at high flow (Figure 5). These fluctuations are attributed to antecedent conditions. For example, concentrations were high during the initial stages of snowmelt as a result of flushing of solutes from the snowpack and soils (Rascher et al., 1987) whereas in the later part of the snowmelt period concentrations were low because their source had been depleted though flow remained high.

During base-flow conditions, the stream composition was controlled mainly by the composition of ground water, the predominant source of the streamflow. All constituents had higher concentrations at Cascade Lake Outlet than at Townsend Pond Outlet for a given discharge. At a discharge of zero, concentrations of SBC and ANC are predicted from the two component mixing model (eqn. 1, Figure 5) to be $230\,\mu eq.l^{-1}$ and $120\,\mu eq.l^{-1}$, respectively, for Townsend Pond Outlet, whereas values of $1{,}028\,\mu eq.l^{-1}$ and $1{,}025\,\mu eq.l^{-1}$, respectively, are anticipated for Cascade Outlet. These values theoretically represent the concentrations of ground-water inputs to the surface waters. At infinite flow, the dilution model predicts SBC values of $115\,\mu eq.l^{-1}$ and $217\,\mu eq.l^{-1}$ for Townsend and Cascade Outlets, respectively, and ANC values of $-4.7\,\mu eq.l^{-1}$ and $+18.4\,\mu eq.l^{-1}$ for Townsend and Cascade Outlets, respectively. A larger percentage of the streamflow in the Cascade Lake basin was derived from ground-water reservoirs which also provided a longer residence time and consequently, higher concentrations at low flow than in the Townsend Pond basin. The existence of thicker and more extensive glacial deposits in the Cascade Lake basin than in the Townsend Pond basin supports this observation (Newton et al., 1987).

ANC values predicted by the dilution model for extremes in discharge had a very large range, particularly for Cascade Outlet ($+18$ to $1{,}020\,\mu eq.l^{-1}$). These model calculations are significant because they indicate that although Adirondack surface waters may appear to be insensitive to acidic deposition on the basis of synoptic surveys generally conducted during the summer when flow is typically low, dilution during high low flow periods in the winter and spring may reduce the ANC to a value that is extremely sensitive to mineral acid inputs.

Summary

An understanding of the flow paths of water is a critical factor in assessing the susceptibility of surface waters to acidification. Hydrogeochemical data were collected at 10 sites in the Adirondack region of New York. For these sites, the 'slope' of the low flow part of the flow (expressed as a ratio of the flow at the 50-percent exceedence level to flow at the 95-percent exceedence level) was negatively correlated with the average SBC ($p < 0.01$) and dissolved silica ($p < 0.05$), both by-products of mineral-weathering reactions which neutralize acid inputs. Small slopes are indictive of surface-water systems that receive a large part of their flow from ground water. Large slopes are indicative of surface-water systems that receive less ground water and more surface runoff. The relatively higher contribution of surface runoff which moves over or through the shallow acidic soil horizons may acidify the base flow component in the stream. Consequently, sites with large slopes have lower concentrations. The bedrock and glacial materials in these drainages contain predominantly aluminosilicate minerals.

The 'slope' was negatively correlated with ANC at $p < 0.05$ only when sites from the eastern Adirondacks (clear and Heart Lakes) were removed from the analysis. Eastern Adirondack sites characteristically have much lower concentrations of NO_3^- than western Adirondacks although both receive comparable amounts in atmospheric deposition. These observations suggest that NO_3^- loss in the eastern Adirondacks may significantly contribute to the acidification of surface waters and a reduction in ANC. Therefore, soil weathering/exchange reactions and hydrologic flow paths are not the only factors controlling the ANC in Adirondack surface waters, but the extent of NO_3^- retention also seems to significantly contribute.

The concentrations of SBC, dissolved silica and ANC were also evaluated with respect to the discharge per unit area at two stream sites in the drainage of the North Branch of the Moose River. The data at both sites fit the general hyperbolic model for the mixing of two components in which ground water was diluted by surface runoff. Concentrations of SBC, dissolved silica and ANC were higher, in particular, at Cascade Lake Outlet than those for Townsend Pond Outlet. This observation was consistent with distribution of aquifer materials in the two basins. Thirteen percent of the Cascade Lake basin consisted of thick till ($> 3\,\text{m}$) and stratified drift whereas no thick till or stratified drift was found in the Townsend Pond basin. The thick till or stratified drift provides groundwater storage. Water that infiltrates these deposits has a longer residence time than that of surface runoff. Water that contacts the lower mineral soil on till generally has higher ANC due to weathering reactions than water that flows through shallow acidic upper soil horizons. Consequently, the relative contribution of ground-water discharge containing elevated ANC to streams or lakes is a major factor controlling the sensititivity to acidification.

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