# MAJOR ION HYDROGEOCHEMICAL BUDGETS AND ELEVATED CHLORIDE CONCENTRATIONS IN SENECA LAKE, NEW YORK

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**ABSTRACT:** Water samples were periodically collected from four lake sites (surface and 2 deep water samples) and seventeen streams within the Seneca Lake watershed from May 2000 through November 2004 and analyzed for the major ions ($Cl^-$, $Na^+$, $SO_4^{2-}$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$) by ion chromatography to investigate the relative importance of groundwater inputs to Seneca Lake. Lake concentrations do not reveal significant spatial trends, suggesting that the lake and these ions are well-mixed on annual time scales. On annual and longer time frames, ion concentrations vary and appear to inversely correlate with annual precipitation. Comparison between lake and stream concentrations and mass balance calculations define three ion groups: chloride, sodium and sulfate; calcium, magnesium and alkalinity; and potassium. Chloride, sodium, and to a lesser extent sulfate concentrations are up to four times greater in the lake than the streams ($Cl^-$ 140 *vs.* 33 mg/L, $Na^+$ 80 *vs.* 20 mg/L, $SO_4^{2-}$ 40 *vs.* 30 mg/L, respectively).

Chloride and sodium concentrations are 2 to 3 orders of magnitude larger in the lake sediment pore waters than the lake, substantiating a groundwater input hypothesis for chloride from the underlying Silurian beds of rock salt proposed by earlier researchers. Mass balance and diffusion rates calculations indicate diffusive as well as advective transport through the bottom sediments. Sulfur-rich springs from the Devonian Bertie Formation provide a likely groundwater source for the sulfur. Conversely, calcium and magnesium stream concentrations ($Ca^{2+}$ 60 mg/L, $Mg^{2+}$ 17 mg/L) are larger than the lake concentrations ($Ca^{2+}$ 42 mg/L, $Mg^{2+}$ 11 mg/L). Existing sediment composition and mussel abundance data suggest that the excess fluvial flux is probably removed by precipitation of low-Mg carbonates during summer whiting events and utilized by zebra and quagga mussel shell formation. Fluvial inputs of potassium are at equilibrium with the lake.

## INTRODUCTION

Seneca Lake is the largest of the eleven, north-south trending, elongated, Finger Lakes in central and western New York (Fig. 1). It has with a maximum depth, width, length, surface area, drainage area, and volume of 188 m, 5.2 km, 57 km, 175 km$^2$, 1,181 km$^2$, and 15.54 km$^3$, respectively (Bloomfield 1978). Erosion by Pleistocene glacial ice and subglacial meltwaters deepened pre-existing river valleys into the surrounding Paleozoic carbonates and clastic sedimentary rocks. The subsequent glacial retreat deposited thick sequences of glacial till and proglacial silty clays (Mullins and Hinchey 1989; Mullins et al. 1996). Approximately half of the basin is filled with glacial and postglacial sediments, and the remainder with water. A number of excavated valleys, especially to the east and west of the existing Finger Lakes are completely filled with glacial debris and are lake free.

Seneca Lake is warm monomictic, completely freezing only four times in recorded history. It is borderline oligotrophic/mesotropic, is hydrologically open and currently drains to the north eventually into Lake Ontario. Estimates of water residence time range from 12 to 18 years based on tritium, water budget and isolated stable isotopic indicators (Bloomfield 1978; Michel and Kraemer 1995). The lake is a critical natural resource as it provides Class AA drinking water to approximately 100,000 residents in and near the watershed. Yet the resource is listed on New York State Department of Environmental Conservation (NYS DEC) Priority Waterbodies List (PWL) due to elevated chloride ion concentrations and other concerns.

Berg (1963) and Schaffner and Oglesby (1978) noted that chloride concentrations were significantly larger in Seneca and Cayuga Lakes than the other Finger Lakes and streams in the region. The elevated concentrations required an extra source of chloride beyond fluvial fluxes to the lake. Wing et al. (1995) expanded and substantiated arguments initiated by Berg (1963) and Ahrnsbrak (1975) to hypothesize that the source of the extra chloride originated from the Silurian beds of commercial-grade rock salt ~450 to 600 m below the lake's surface. Wing et al. (1995) showed that: (1) a deep water mass up to 10% saltier than the rest of Seneca Lake was observed to expand and partially fill the hypolimnion from the bottom up during the summer of 1991 and 1992; and, (2) chloride concentrations in the sediment pore waters were as high as 30‰ several meters below the sediment water interface. The large chloride concentration gradients in the sediment pore waters indicate that chloride diffuses to the lake from the lake floor. Interpretation of seismic profiles collected during the mid-1990s revealed the extensive thickness of glacial fill and the great depth of the bedrock floor in Seneca Lake, and to a lesser extent, Cayuga Lake (Mullins and Hinchey 1989; Mullins et al. 1996). These two lakes are the only Finger Lakes that are deep enough, up to twice the water depth, to intersect the Silurian evaporate formations below the lake. Their depth provides an avenue for brine migration to the lake from the bedrock below (Wing et al. 1995).

Callinan (2001) offered alternative hypotheses. He reported a 20% decline in sodium levels from the 1970s to the late 1990s in Seneca Lake, and suggested that changes in analytical accuracy or potentially a suspected decrease in

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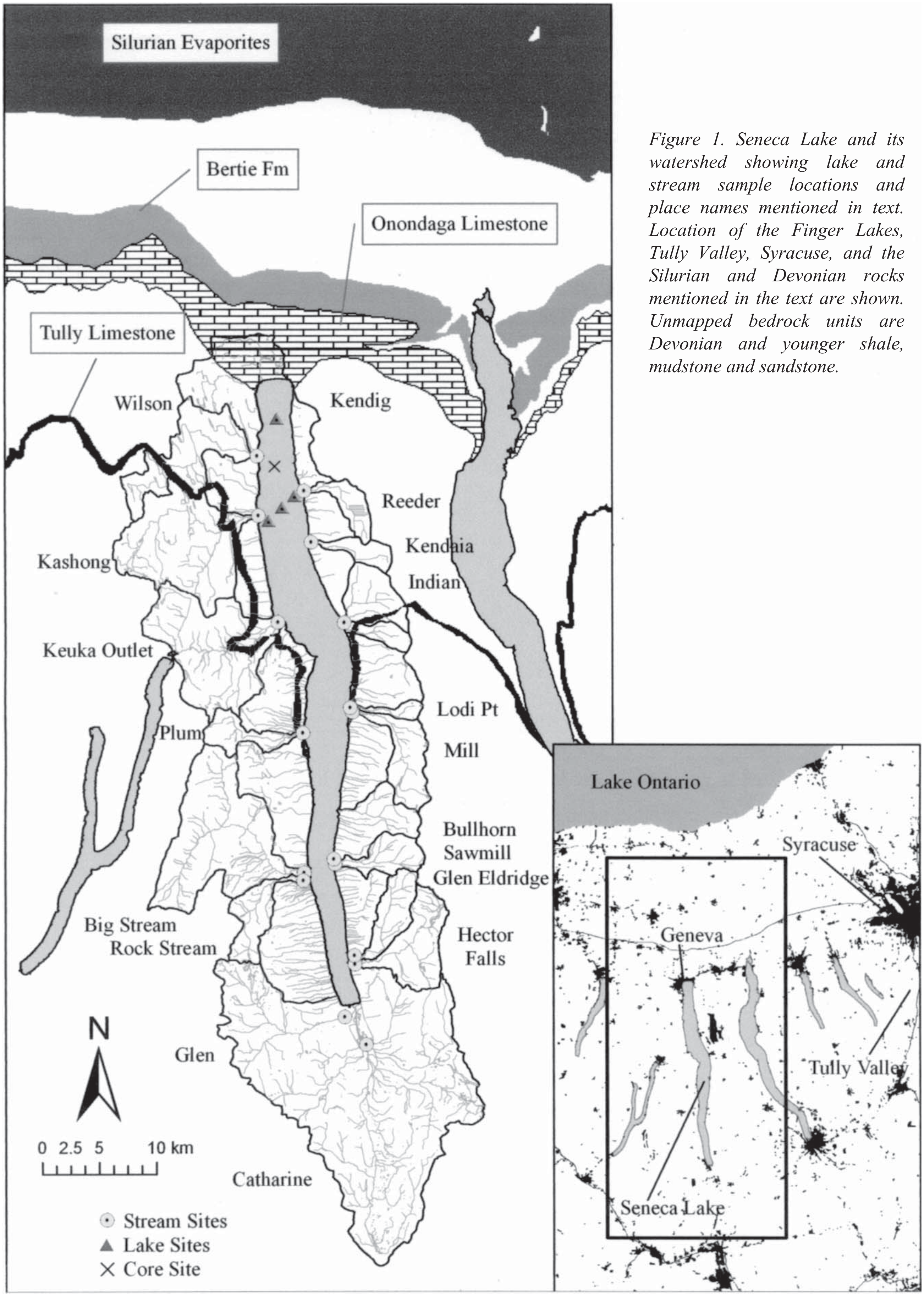


*Figure 1. Seneca Lake and its watershed showing lake and stream sample locations and place names mentioned in text. Location of the Finger Lakes, Tully Valley, Syracuse, and the Silurian and Devonian rocks mentioned in the text are shown. Unmapped bedrock units are Devonian and younger shale, mudstone and sandstone.*

the discharge of brine-water waste from the local salt mines may cause the decade-scale variability in chloride ion concentrations. Modeling efforts suggested that salt mine drainage can be significant in Cayuga Lake (Effler et al. 1989). Wing et al. (1995) also reported that high chloride concentrations in the 1970s may correspond with the direct discharge of salt-mine wastes to the lake but the reported 3,600 kg/day discharge would only increase the lake concentration by a few mg/L. This manuscript investigates the impact of groundwater on the hydrogeochemistry of the lake by extending the analysis to the other majors ions.

## METHODS

Surface water samples from four lake sites and up to 17 streams were filtered through a 0.45 µm HA Millipore or 0.45 µm glass fiber filter (Fig. 1). Different filters should not bias the results (Makarewicz, personal communication). Bottom water samples (within three meters of the lake floor) were collected from the two deepest lake sites (25 and 110 m water depth) by a 10-L Niskin bottle and filtered in an identical manner. In both cases, the filtrate was saved in Nalgene bottles and kept refrigerated at 4°C until analysis in the lab. The lake sites were sampled up to four times a month from May through November. Seven stream sites were also sampled up to four times a month from May through July, as the streams are typically dry by mid-summer. Ten additional streams were sampled once or twice a year in May or June to acquire some data from every 3rd order or higher stream in the watershed. Each stream site was located near the terminus of the stream, typically just upstream from where it emptied into the lake.

The 1999 and 2000 water samples were analyzed for chloride by silver nitrate titration using a potassium chromate indicator (LaMotte PSC-DR), and total alkalinity with sulfuric acid using a phenolphthalein and bromocresol green/methal red indicator (LaMotte WAT-MP-DR). Analytical precision for the field titration kits determined from replicate analyses was generally ±3 to 5 mg/L. The 2001 through 2004 samples were analyzed for major ions by ion chromatograph (Dionex DX-120) using an AS14 analytical column and carbonate/bicarbonate eluent for the anions ($Cl^-$ and $SO_4^{2-}$) and a CS12A analytical column and methanesulfuric acid eluent for the cations ($Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$). Alkalinity was measured by titration. Accuracy for the ion chromatograph was determined by analyzing standard solutions. The difference between the known and reported concentration averaged less than 1 mg/L. Due to the higher precision and analysis of a more complete suite of ions, the ion chromatograph data are the focus of this study using the alkalinity data to check the charge balance. The average difference between anions and cations was 0.2 meq/L, less that 5% of the total charge (meq/L).

A sediment core (located at 42°47.44'N & 76°57.39'W) ( Fig. 1) was recovered using a 3-m Alpine Geophysical piston corer to collect, isolate and analyze sediment pore waters. The sediment was recovered in a plastic liner (3.2 cm i.d.), capped and extruded in the lab. Sediment was subsampled at 40 cm intervals, and each subsample was centrifuged for 45 minutes at 5,000 rpm to extract the sediment pore waters. The resulting sediment pore water was then filtered through a 0.45 µm glass fiber filter, and 1.5 mL of the filtrate was diluted to 250 mL before analysis by ion chromatograph as outlined above.

## RESULTS AND DISCUSSION

*Water Chemistry*–The salinity in the lake is dominated by chloride (139 mg/L, Cl-) and sodium (79 mg/L, $Na^+$). Calcium (42 mg/L, $Ca^{2+}$), sulfate (38 mg/L, $SO_4^{2-}$), alkalinity (106 mg/L, $CaCO_3$), and magnesium (11 mg/L, $Mg^{2+}$) provide the bulk of the remaining salts with smaller amounts of potassium (2.7 mg/L, $K^+$) (Fig. 2, Table 1). Variability in ion concentrations for each ion at each lake site is small, especially for chloride and sodium, with standard deviations of the individual site data typically less than 10% of the average value for each site. This suggests that the lake is well-mixed on annual time scales and in equilibrium. In contrast, the average streams concentrations indicate that the streams are dominated by alkalinity (183 mg/L, $CaCO_3$), calcium (59 mg/L, $Ca^{2+}$) and sulfate (38 mg/L, $SO_4^{2-}$), with smaller amounts of chloride (33 mg/L, Cl-), sodium (18 mg/L, $Na^+$), magnesium (17 mg/L, $Mg^{2+}$) and potassium (2.4 mg/L, $K^+$). Variability in ion concentrations for each ion at each stream site and between stream sites is larger for the streams than the lake, with standard deviations of the individual site data between 15 and 50% of the average for the site. Annual scale temporal trends were not consistently observed in the stream data.

### Ion Fluxes

Stream and lake ion concentration comparisons segregate the ions into three groups: (1) chloride, sodium and sulfate; (2) calcium and magnesium; and (3) potassium (Fig. 2). Chloride, sodium and to a lesser extent sulfate concentrations are much larger in the lake than the streams; calcium magnesium and alkalinity concentrations are much smaller in the lake that the streams; and average potassium concentrations for the lake and the streams are the same, i.e., within 1 standard deviation. To quantify these differences while accounting for the removal of each dissolved ion from the lake as lake water flows through its outlet and the concentration of ions in the lake by the evaporation of water from the lake, the flux ($Flux_{ion}$) of each ion to the lake was calculated to attain the measured lake concentration assuming equilibrium, steady-state conditions (after Harte 1988).

$$Flux_{ion} = (C_{ion}\ Q_{outflow}) / 10^3 \quad (1)$$

where:

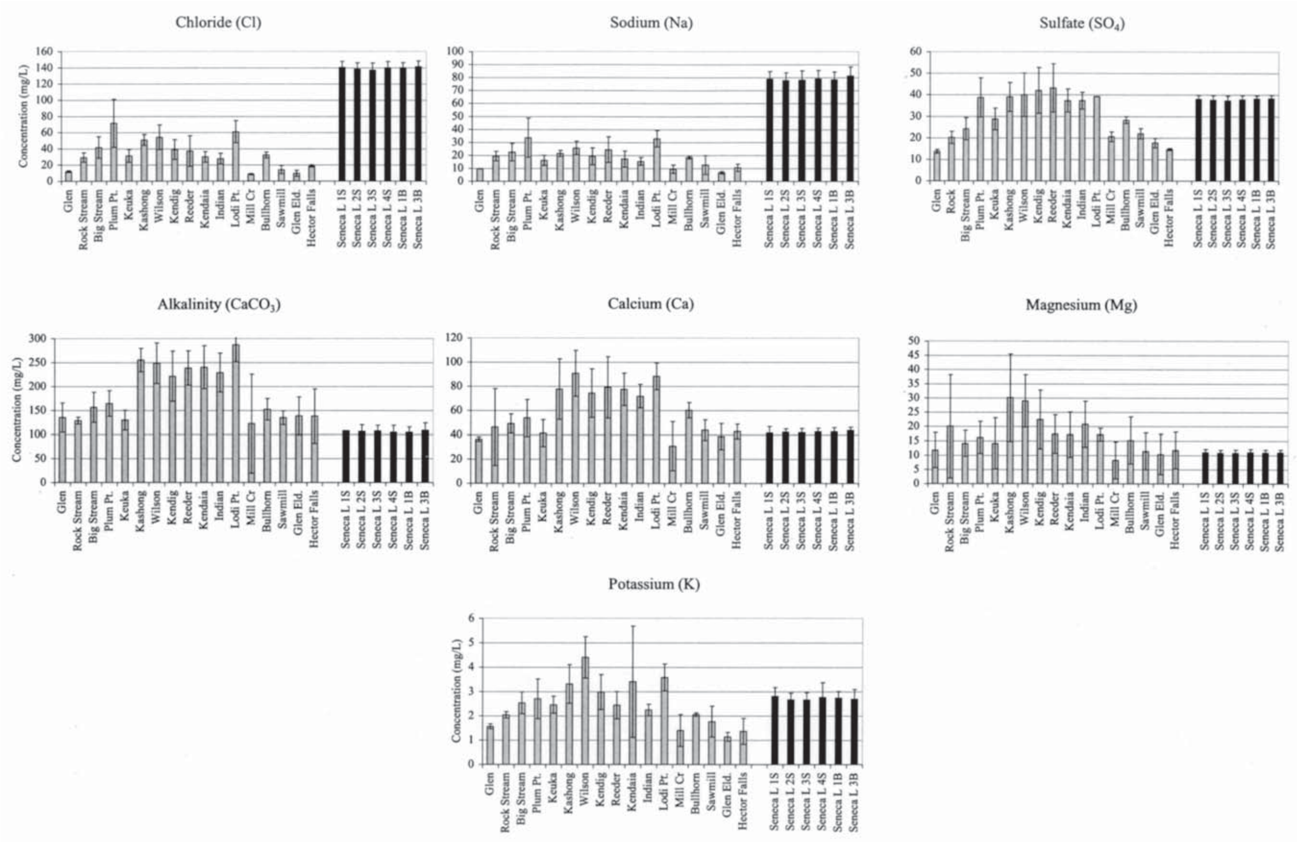


*Figure 2. Average major ion concentrations from 4 surface (S) and 2 bottom (B) water lake samples, and 17 streams sites in the Seneca Lake watershed. Samples were collected from May through November (2000-2004). The streams are arranged in order starting in the south and moving clockwise around the watershed. The error bar represents ±1 standard deviation of the analyses from each site.*

Table 1. Average lake and stream major ion concentrations from May through November of 2000 – 2004 in Seneca Lake, New York. The standard deviations reflect a ±1 standard deviation of all the analyses at the site.

| | Chloride (Cl, mg/L) | Sodium (Na, mg/L) | Sulfate (SO$_4$, mg/L) | Alkalinity (CaCO$_3$, mg/L) | Calcium (Ca, mg/L) | Magnesium (Mg, mg/L) | Potassium (K, mg/L) |
|---|---|---|---|---|---|---|---|
| **Lake Sites:** | | | | | | | |
| Site 1 Surface | 140 ± 7.5 | 78.9 ± 5.9 | 38.0 ± 1.8 | 107.4 ± 14 | 41.6 ± 5.1 | 11.0 ± 1.1 | 2.8 ± 0.4 |
| Site 2 Surface | 137 ± 9.1 | 77.8 ± 6.0 | 37.6 ± 2.1 | 106.1 ± 12 | 42.2 ± 2.6 | 10.8 ± 1.0 | 2.7 ± 0.3 |
| Site 3 Surface | 137 ± 8.7 | 78.1 ± 7.0 | 37.4 ± 2.1 | 107.0 ± 14 | 41.9 ± 3.4 | 10.8 ± 1.1 | 2.7 ± 0.3 |
| Site 4 Surface | 139 ± 8.8 | 78.1 ± 9.0 | 37.8 ± 1.8 | 104.7 ± 11 | 42.6 ± 2.8 | 11.0 ± 1.1 | 2.8 ± 0.6 |
| Site 1 Bottom | 140 ± 6.4 | 78.5 ± 6.0 | 38.2 ± 1.4 | 104.6 ± 16 | 42.7 ± 3.1 | 10.9 ± 1.0 | 2.7 ± 0.3 |
| Site 3 Bottom | 141 ± 7.2 | 79.9 ± 10.5 | 38.3 ± 1.5 | 108.6 ± 16 | 43.6 ± 2.7 | 10.9 ± 0.9 | 2.7 ± 0.4 |
| Avg. Lake | 139 ± 8.0 | 78.6 ± 7.4 | 37.9 ± 1.8 | 106.4 ± 13.8 | 42.4 ± 3.3 | 10.9 ± 1.0 | 2.7 ± 0.4 |
| **Stream Sites:** | | | | | | | |
| Glen | 11.9 ± 1.2 | 9.7 ± 0.2 | 13.6 ± 0.9 | 135.0 ± 7.1 | 36.3 ± 1.8 | 11.7 ± 6.2 | 1.6 ± 0.1 |
| Rock Stream | 29.2 ± 5.8 | 19.3 ± 3.6 | 20.1 ± 2.9 | 128.5 ± 31.3 | 46.2 ± 31.8 | 20.1 ± 18.1 | 2.0 ± 0.1 |
| Big Stream | 41.6 ± 13.2 | 22.4 ± 6.8 | 24.1 ± 5.1 | 156.3 ± 26.7 | 49.1 ± 8.0 | 14.1 ± 4.5 | 2.5 ± 0.4 |
| Plum Pt. | 71.4 ± 29.6 | 33.5 ± 15.1 | 38.7 ± 9.1 | 164.3 ± 20.6 | 53.7 ± 15.3 | 16.2 ± 5.6 | 2.7 ± 0.8 |
| Keuka Outlet | 31.2 ± 8.1 | 16.1 ± 3.9 | 28.7 ± 5.0 | 129.6 ± 24.5 | 41.3 ± 11.2 | 14.1 ± 9.0 | 2.5 ± 0.3 |
| Kashong | 50.7 ± 6.7 | 20.7 ± 4.6 | 38.9 ± 6.8 | 255.0 ± 42.3 | 77.6 ± 25.0 | 30.1 ± 15.3 | 3.3 ± 0.8 |
| Wilson | 54.2 ± 15.1 | 24.8 ± 6.5 | 40.0 ± 10.1 | 248.4 ± 52.6 | 90.6 ± 19.1 | 29.0 ± 9.2 | 4.4 ± 0.9 |
| Kendig | 39.1 ± 12.2 | 19.3 ± 6.5 | 42.0 ± 10.7 | 221.4 ± 35.8 | 74.2 ± 20.1 | 22.5 ± 10.3 | 3.0 ± 0.7 |
| Reeder | 37.1 ± 18.7 | 24.4 ± 9.9 | 43.2 ± 11.2 | 238.4 ± 45.1 | 79.1 ± 25.5 | 17.4 ± 6.8 | 2.4 ± 0.6 |
| Kendaia | 29.8 ± 6.6 | 17.2 ± 6.2 | 37.3 ± 5.4 | 240.0 ± 40.7 | 77.4 ± 13.5 | 17.2 ± 7.9 | 3.4 ± 2.3 |
| Indian | 27.5 ± 6.7 | 15.4 ± 3.0 | 37.3 ± 3.9 | 228.8 ± 35.7 | 71.8 ± 9.8 | 20.8 ± 8.1 | 2.2 ± 0.2 |
| Lodi Pt | 60.9 ± 13.8 | 32.9 ± 6.4 | 39.2 ± 0.1 | 287.0 ± 103.2 | 88.2 ± 11.1 | 17.2 ± 2.2 | 3.6 ± 0.6 |
| Mill | 8.4 ± 0.8 | 7.1 ± 5.1 | 20.5 ± 2.3 | 122.3 ± 22.6 | 30.6 ± 20.3 | 8.2 ± 6.5 | 1.4 ± 0.7 |
| Bullhorn | 32.2 ± 3.6 | 18.3 ± 1.2 | 28.2 ± 1.6 | 152.0 ± 14.4 | 60.2 ± 6.4 | 15.2 ± 8.2 | 2.1 ± 0.1 |
| Sawmill | 14.3 ± 5.0 | 12.5 ± 7.3 | 21.9 ± 2.4 | 134.5 ± 39.4 | 43.8 ± 8.4 | 11.3 ± 6.4 | 1.8 ± 0.6 |
| Glen Eldridge | 9.6 ± 3.8 | 6.6 ± 1.0 | 17.6 ± 2.2 | 138.7 ± 56.8 | 38.6 ± 10.7 | 10.3 ± 7.1 | 1.1 ± 0.2 |
| Hector Falls | 18.6 ± 1.4 | 10.4 ± 2.8 | 14.6 ± 0.5 | 138.0 ± 21.1 | 42.8 ± 6.0 | 11.7 ± 6.4 | 1.4 ± 0.5 |
| Avg. Streams | 33.4 ± 9.0 | 18.3 ± 5.3 | 29.8 ± 4.7 | 183.4 ± 36.5 | 58.9 ± 14.4 | 16.9 ± 8.1 | 2.4 ± 0.6 |

$Flux_{ion}$ is the flux of each ion to the lake to attain the lake concentration (kg/year),
$C_{ion}$ is the measured concentration of the ion in the lake (mg/L), and
$Q_{outlet}$ is the annual outflow of water from the lake (760 x $10^6$ $m^3$/year).

The fluvial flux ($Fluvial\ Flux_{ion}$) was subtracted from the total flux ($Flux_{ion}$) estimated above to determine the extra flux ($Extra\ Flux_{ion}$) required to balance the hydrochemical budget (Table 2).

$$Extra\ Flux_{ion} = Flux_{ion} - Fluvial\ Flux_{ion} \quad (2)$$

where:

$Extra\ Flux_{ion}$ is the extra flux (kg/year) required to attain $C_{ion}$,
$Flux_{ion}$ is the total ion flux to the lake to achieve equilibrium (kg/year), and
$Fluvial\ Flux_{ion}$ is the fluvial flux of the ion to the lake (kg/year).

The fluvial flux ($Fluvial\ Flux_{ion}$) was calculated in two ways: (1) using an average stream concentration for the entire watershed, and (2) summing fluxes calculated individually for each watershed using the average concentration from each subwatershed. The latter interpolated an ion concentration from neighboring subwatersheds for subwatersheds without concentration data, and assumed an annual discharge for each subwatershed proportional by surface area to the annual fluvial discharge to the lake (863 x $10^6$ $m^3$/yr). The sampled subwatersheds represented 68% of the entire watershed area.

Both methods provided similar fluxes for each ions (Table 2). The largest differences are in chloride, sodium, and sulfate fluvial fluxes. These differences result from relatively large measured concentrations from small watersheds, e.g., Plum Point and Lodi Point (Fig. 1), that skew the flux based on a mean stream concentration to an inappropriately larger value. The flux calculated by the sum of individual subwatershed was used in the subsequent analysis.

The flux calculations indicate that: (1) the lake must gain 80.0 x $10^6$ kg/year of chloride, 45.5 x $10^6$ kg/year of sodium, and 6.9 x $10^6$ kg/year of sulfate from an extra non-fluvial source to augment the fluvial flux of these ions to the lake and achieve the measured concentration in the lake; (2) the lake must loose 14.9 x $10^6$ kg/year of calcium and 6.0 x $10^6$ kg/year magnesium to maintain the measured concentrations in the lake; and (3) lake is in equilibrium with the present-day fluvial flux of potassium.

### Extra Source of Chloride and Sodium

These fluxes support and expand on the chloride hypothesis of Wing et al. (1995). The extra, non-fluvial source of chloride, sodium and to a lesser degree sulfate is from a groundwater source interacting with the Silurian evaporates beneath the lake. The following findings from this study support the bedrock/groundwater source hypothesis. Chloride and sodium molar concentrations in the Seneca Lake watershed co-vary ($r^2 = 0.96$) (Fig. 3, Table 3). The covariance is consistent with a common groundwater source like the dissolution of the Silurian evaporate deposits (NaCl). A slope of the best fit line is slightly less than 1 and suggests that chloride ions are slightly more conservative than sodium. Interestingly, a slightly different trend was observed for the stream samples and suggests that sodium is not as conservative as chloride in the streams. More importantly, the different trends imply two unique sources of chloride and sodium to the lake, e.g., surface and subsurface inputs.

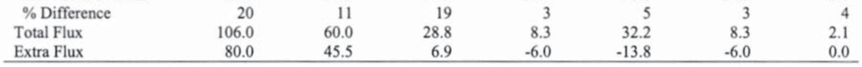
Chloride and sodium molar concentrations of sediment pore waters extracted from a 3-m core also co-vary and increase down core with concentrations 2 to 3 orders of magnitude larger three meters below the sediment-water interface than their concentrations in the lake, whereas the other ions do not increase by the same order of magnitude (Fig. 4). The gradient indicates diffusion of chloride and sodium into the lake from below. The diffusive flux was estimated by (after Fetter 2001):

$$Flux_{diffusion} = -D\,(\partial C / \partial dx)\,A \quad (3)$$

where:

$Flux_{diffusion}$ is the ion flux (kg/year),

Table 2. Ion fluxes in the Seneca Lake watershed. The fluvial fluxes ($Fluvial\ Flux_{ion}$) were calculated using two methods: (1) mean concentrations of all the stream data and (2) individual subwatershed concentrations. The percent difference is the difference between the two fluvial fluxes relative to the individual stream flux. The total flux ($Flux_{ion}$) is the required ion flux to attain the measured lake concentration assuming equilibrium conditions. The extra flux ($Extra\ Flux_{ion}$) is the flux that is required to balance the hydrochemical budget based on the individual stream and total flux results.



| | Chloride ($10^6$ kg/yr) | Sodium ($10^6$ kg/yr) | Sulfate ($10^6$ kg/yr) | Alkalinity ($10^6$ kg/yr) | Calcium ($10^6$ kg/yr) | Magnesium ($10^6$ kg/yr) | Potassium ($10^6$ kg/yr) |
|---|---|---|---|---|---|---|---|
| Fluvial Flux: | | | | | | | |
| Avg. Stream | 31.1 | 16.1 | 26.0 | 14.7 | 48.4 | 14.7 | 2.1 |
| Individual Streams | 26.0 | 14.5 | 21.9 | 14.7 | 46.0 | 14.3 | 2.0 |
| % Difference | 20 | 11 | 19 | 3 | 5 | 3 | 4 |
| Total Flux | 106.0 | 60.0 | 28.8 | 8.3 | 32.2 | 8.3 | 2.1 |
| Extra Flux | 80.0 | 45.5 | 6.9 | -6.0 | -13.8 | -6.0 | 0.0 |

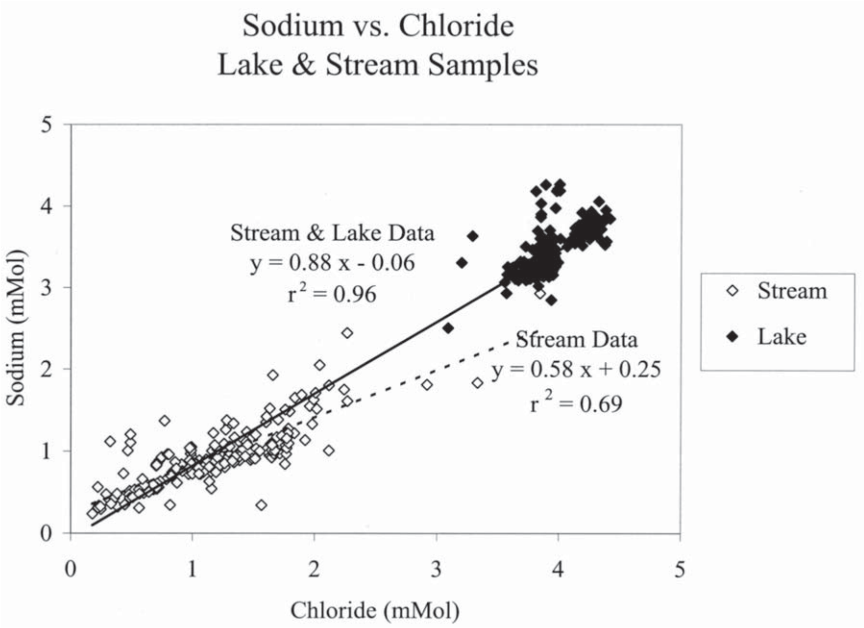


*Figure 3. Chloride and sodium concentrations from individual analyses in the Seneca Lake watershed. Best-fit linear interpolations are also shown (solid – all samples, dashed – stream samples). Note the unit change from mg/L to mMol for the concentrations to reveal Na and Cl molar consistencies.*

Table 3. Correlation (r) matrix of the 410 lake and stream ion concentrations collected from 2001 through 2004 determined by ion chromatograph, and correlation of the 2001 through 2004 annual precipitation totals to annual average ion concentration data (Fig. 5).

| | Chloride | Sodium | Sulfate | Calcium | Magnesium | Potassium |
|---|---|---|---|---|---|---|
| Chloride, Cl | 1.00 | 0.98 | 0.38 | -0.39 | -0.37 | 0.10 |
| Sodium, Na | | 1.00 | 0.33 | -0.42 | -0.42 | 0.09 |
| Sulfate, $SO_4$ | | | 1.00 | 0.33 | 0.17 | 0.38 |
| Calcium, Ca | | | | 1.00 | 0.46 | 0.43 |
| Magnesium, Mg | | | | | 1.00 | 0.37 |
| Potassium, K | | | | | | 1.00 |
| Precipitation | -0.59 | -0.50 | 0.02 | -0.36 | -0.50 | -0.67 |

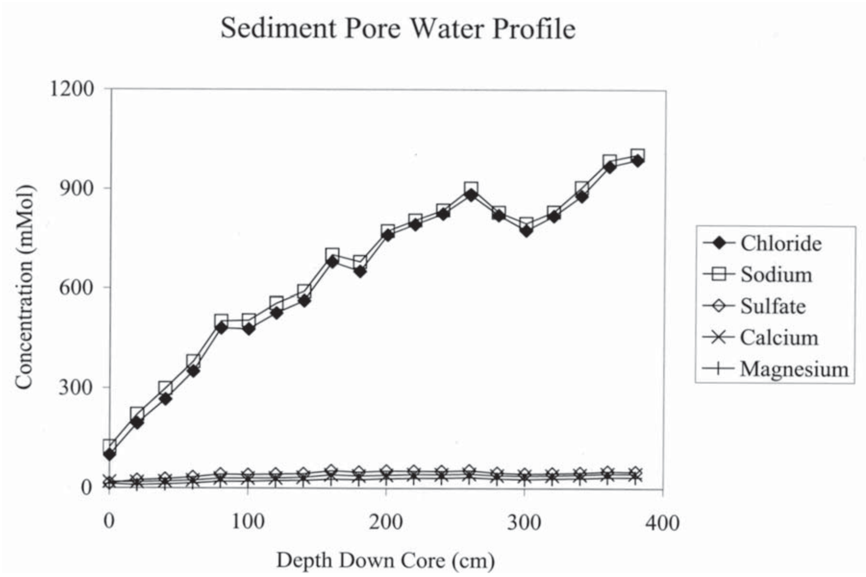


*Figure 4. Major ion concentrations in sediment pore waters of a piston core recovered from the northern portion of Seneca Lake. See Fig. 1 for core location. Note the unit change from mg/L to mMol for the concentrations to reveal Na and Cl molar consistencies.*

$D$ is the diffusion coefficient (cm$^2$/s),
$\partial C / \partial dx$ is the concentration gradient (kg/cm$^3$/cm), and
$A$ is the area of the lake floor (cm$^2$).

The diffusive flux for chloride through the lake floor sediment is 6 x 10$^6$ kg/yr. This estimate assumed the measured concentration gradient in this core, 0.08 mg/cm$^3$/cm, was uniform over the entire lake, a diffusion coefficient of 1.3 x 10$^{-6}$ cm$^2$/s for chloride through Seneca Lake mud (Grotzinger 1979), and a lake floor area of 175 km$^2$. This flux is a maximum estimate, as some of the chloride concentration gradients were smaller in the cores analyzed by Wing et al. (1995), especially in the southern half of the lake where the lake floor does not intersect the Silurian rock-salt formations and the glacial sediments are thickest (~250 m). Even at this estimated maximum rate, diffusion from the lake floor only contributes 10% of the required 80 million kg of chloride to the lake each year.

Advective groundwater transport may be another likely source of chloride and sodium. Subsurface seeps and brackish-discharging mudboils are observed at Tully Valley, about 100 km east of Seneca Lake and 20 km south of Syracuse, NY. The Tully Valley is a "dry" Finger Lake, where glacial sediments completely filled the glacially carved basin and are underlain by Silurian rock salt (Mullins et al. 1991). Kappel et al. (1996) reported that the mudboils emit brines up to 50,000 mg/L of total dissolved solids at a discharge of 0.003 m$^3$/s, and brines in wells drilled in the valley reveal total dissolved solids of over 100,000 mg/L. A discharge of 0.003 m$^3$/s and salt concentration of 50,000 mg/L yields a flux of ~0.5 x 10$^6$ kg/year, and suggests that advective transport could supply the missing chloride and sodium to Seneca Lake. Routine bottom water sampling, high resolution seismic imaging of the lake floor and hydrologic budgets could easily miss these small features in the well-mixed lake, where the suspected groundwater discharge is less than 1% of the annual input of water to the lake. Groundwater seeps are observed elsewhere in central New York State. Salt springs are found near Onondaga Lake near Syracuse, and sulfurous springs near downtown Geneva, Clifton Springs and Canandaigua, where the saline springs probably originate from the Silurian rock salt, and the sulfurous springs from the overlying Bertie Formation (Donald Woodrow personal communication 2004).

## Extra Source of Sulfate

Sulfate concentrations and fluxes mimic the chloride and sodium trends. Sulfate concentrations are higher in the lake than the fluvial flux of sulfate would predict, and requires an additional non-fluvial input of 6.9 x 10$^6$ kg of sulfate ($SO_4$) each year to attain the sulfate concentrations in the lake. We propose that the extra sulfate originates from a unique groundwater source because sulfate concentrations do not co-vary with chloride or sodium in the stream samples ($r^2$ of 0.37 for Cl & $SO_4$, and 0.24 for Na and $SO_4$). The sulfate pore water profile does not reveal a down-core concentration gradient. Rather the sulfate concentrations are uniform down-core and indicate that diffusion from the Silurian evaporate deposits is not a primary mechanism for the extra flux of sulfate to the lake (Fig. 4). The Black River Group found below the Salina formation contains black shales with pyrite but is over 1,500 to 3,000 m below the surface of the lake, limiting it as a potential source. Runoff from the sulfur-based herbicides used on the vineyards in the watershed is another possible source, although this source probably lacks sufficient mass to be a major contributor although the exact application rates are unknown. Finally, the Bertie Formation has abundance sulfate evaporate minerals and is the suspected source for the sulfurous springs observed in the Geneva area. We hypothesize that it is the extra source of sulfur to the lake. It supports our hypothesis that advective transport of chloride, sodium and sulfate from underneath the lake is important in Seneca Lake.

Sulfate concentrations are larger in the streams draining the northern than the southern portion of the watershed. It suggests that pyrite in the fine-grained mudstones to the south is not abundant enough to release significant quantities of sulfate to the lake. Plum Point Creek (Fig. 1) is an exception as it drains clastic sedimentary rocks yet has relatively high sulfate, sodium and chloride concentrations. The elevated salt concentrations in this creek probably originate from an abandoned rock-salt mining operation in the watershed. The basin-wide fluvial concentration gradients may reflect a greater abundance of gypsum/anhydrite in the soils and glacial tills underlying the northern watershed just like carbonates are more abundant in the northern soils and tills, as both were eroded from the outcropping evaporite and carbonate rocks to the north of the lake, but it is unlikely as the sulfate evaporate minerals most likely weathered in the early Holocene. Sulfurous springs discharging from the Bertie Formation, like the one in Geneva, are a more likely surface source of sulfur to the lake. The watershed data presented here however, clearly indicate that none of these surface sources are sufficient to balance the sulfate hydrochemical budget, and the source of sulfur is unique from chloride and sodium.

## Calcium and Magnesium

Calcium and magnesium concentrations are larger in the streams than the lake, and their fluxes indicate that 14 x 10$^6$ kg of calcium and 6 x 10$^6$ kg of magnesium are removed from the water column of the lake each year. The excess fluvial source indicates that diffusion and/or advection from the lake floor does not dominate the hydrogeochemistry of calcium and magnesium as it does for chloride and sodium. Two likely scenarios exist for the removal of calcium and to a lesser extent magnesium from the lake: autochthonous precipitation of fine-grained, low-Mg carbonates and precipitation of biogenic shell matter.

Whiting events are observed and fine-grained, autochthonous, low-Mg carbonates have accumulated in the profundal sediments of most of the Finger Lakes (e.g., Mullins and Hinchey 1989; Anderson et al. 1997; Mullins 1998; Halfman et al. 2001; Lajewski et al. 2003). In Seneca Lake, the carbonates accumulate on the lake floor and are buried in the profundal postglacial sediments. The flux of calcium to the lake floor was estimated by:

$$Flux_{carbonate} = C_{Ca}\, S\, (1 - \phi)\, A_{mud} \quad (4)$$

$Flux_{carbonate}$ is calcium flux by inorganic carbonates to the lake floor (kg/year),
$C_{Ca}$ is the calcium concentration in the sediment (g Ca/g dry mud),
$S$ is the linear sedimentation rate of the historic sediments (cm/yr),
$\phi$ is the sediment porosity (unitless), and
$A_{mud}$ is the surface area of Seneca Lake accumulating postglacial mud (cm$^2$).

We assumed the following: The recent profundal muds accumulating in Seneca Lake contain 5 to 10% fine-grained carbonate by weight ($CaCO_3$) of dry sediment which equates to an average calcium concentration in the sediment of 0.03 ± 0.01 g Ca / g dry mud (Halfman et al. 2001). A Pb-210 and Cs-137 dated box core revealed a historic sediment accumulation rate of 0.21 cm/year (Callinan 2001; Lajewski et al. 2003). The rate is slightly faster than published postglacial sediment rates, as expected (Mullins et al. 1996; Anderson et al. 1997; Halfman and Herrick 1998). Finally, profundal muds accumulate in water depths over 50 m which corresponds to ~170 km$^2$ of the lake floor (Halfman and Herrick 1998).

The estimated calcium flux to the lake floor by fine-grained autochthonous carbonate precipitation is $5.1 \times 10^6$ kg/year. Thus, this flux removes ~40% of the calcium from the water column that is required to balance the hydrochemical budget. The removal percentage is smaller than previously estimated (Halfman et al. 2001); however, the earlier estimate was based on stream concentration data from only six streams that were not as representative of the watershed as the 17 streams presented here and resulted in a smaller fluvial flux of calcium to the lake.

Zebra and quagga mussels (*Dreissena polymorpha* and *D. bugensis*) which invaded Seneca Lake in 1992 and ~1999, respectively, now dominate the epifaunal community in water depths less than 50 meters and are also detected in deeper depths. Halfman et al. (1999) estimated that the mussels removed $0.3 \times 10^6$ kg of calcium each year based on an average mass of calcium in shell material recovered by ponar dredges extrapolated over the surface area of the lake floor shallower than 50 m in the lake. Similar estimates were calculated in 2002 (Shelley et al. 2003). Declines in the autochthonous carbonate abundance by 2 or 3 weight percent in the uppermost cm of the profudal mud suggests that this flux only redirects the total calcium flux to the lake floor and is not an extra flux of calcium from the water column (Halfman et al. 2001; Lajewski et al. 2003).

The autochthonous and biogenic flux of calcium from the water column to the lake floor removes at least ~40% of the excess calcium from the water column of the lake. Additional analyses for carbonate abundance and accumulation rates, density of zebra and quagga mussels on the lake floor, hydrologic budgets, and perhaps the acquisition of sediment trap data may close the gap even further. These estimates, however, do support our hypothesis that calcium and magnesium are hydrochemically unique from chloride, sodium and sulfate.

Calcium, and to a lesser extent magnesium, stream concentrations are larger in the northern than the southern portion of the watershed (Fig. 2). Halfman et al. (2001) suggested that the larger concentrations reflect a higher percentage of agricultural land use in the north. A re-evaluation of the current data that expanded the analysis from 6 to 17 streams in the Seneca Lake watershed, suggests that calcium concentrations do not correlate strongly with agricultural land use ($r^2 = 0.01$, Opalka and Halfman 2003, Morgan and Halfman 2004). Instead, calcium concentrations are larger where the subwatershed is underlain by soils, till and bedrock with more carbonate ($r^2 = 0.77$), and these substrates are found in the northern portion of the watershed. The correlation suggests that successful agricultural land is found where the soils are calcium rich and reduce or eliminate the need to lime the soils.

## Annual Variability in Lake Concentrations

Effler et al. (1989) and Callinan (2001) suggested that waste water from salt mine operations played a significant role in the hydrochemical budget of chloride and sodium. Callinan (2001) noted that chloride concentrations declined from 175 to 130 mg/L from the 1970s to the late 1990s (Fig. 5). Callinan argued that this decline could result from reduced discharge of brine wastes over time. This decline may be important in Cayuga Lake as its chloride and sodium concentrations are ~50% of that in Seneca Lake. However, the salt mines only discharge 3,500 kg of NaCl a day to Seneca Lake, or $1.3 \times 10^6$ kg of chloride each year (Wing et al. 1995). This discharge is less than 1% of the extra, non-fluvial flux required to balance the chloride budget. Similar insignificant quantities are calculated for sodium. The decline in ion concentrations may result from a decline in the advective flux of chloride and sodium from beneath the lake. This scenario is unlikely because declining groundwater inputs would not impact the other ions but the other ions reveal decade-scale variability.

Climatic variability may explain the decade-scale

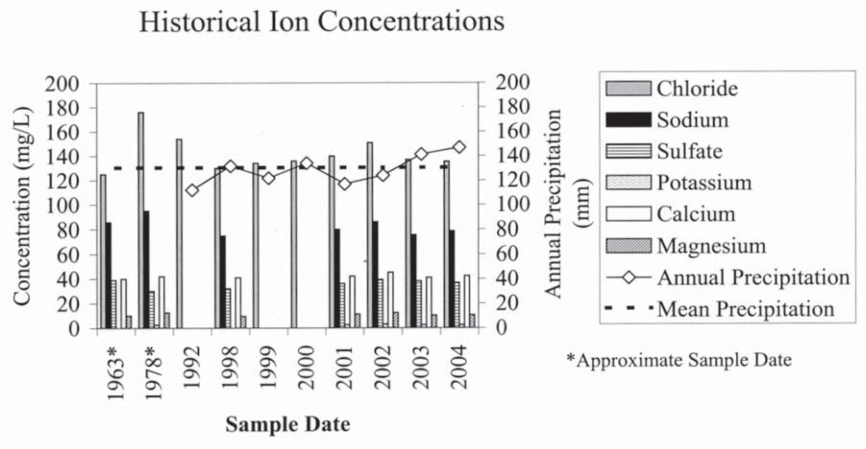


*Figure 5. Major ion concentrations for Seneca Lake over time. Data are from 1963 - Berg (1963), 1978 - Schaffner and Olgelby (1978), 1992 - Wing et al. (1995), 1998 - Callinan (2001), and 2000, 2001, 2002, 2003, and 2004 from this study. The 1963 and 1978 dates are the approximate sample date, and reflect fewer analyses. Annual precipitation totals for each year and the mean annual precipitation for the past century are also shown (New York State Agricultural Experiment Station, Cornell Univ., Geneva, New York, http://www.nysaes.cornell.edu/weather/history).*

variability in salt concentrations in the lake (Fig. 5, Table 3). Covariance between precipitation annual totals and the available (1964 – present) P – E data ($r^2 = 0.81$) suggests that precipitation data is a good proxy for P – E. The ion concentrations, except for sulfate, appear to be inversely correlated to annual precipitation, especially in the last four years of data (Table 3). We hypothesize that years with large precipitation totals dilute the lake concentrations of chloride and sodium, and dilute the stream concentrations of potassium, magnesium and to a lesser degree calcium. Chloride, sodium, and sulfate concentrations decreased by ~20% during a rainfall/runoff event that increased discharge in Wilson Creek by 30% (Kostich and Halfman 2003). Calcium and magnesium concentrations decreased by 5%, and potassium concentrations increased by 5% during this same event. Correlations between precipitation totals and ion concentrations are less obvious in earlier years and perhaps are masked by a smaller number of samples, the uneven distribution or lack of samples through the year, the distribution and type of precipitation events, the impact of rainfall totals in previous years, and other factors. Precipitation data were not plotted for 1963 and 1978 because the sample dates for these data are unknown, however precipitation totals averaged 10 mm above the mean from 1955 through 1960, and averaged 10 mm below the mean from 1960 through 1970. This precipitation trend is inversely proportional to the 1963 to 1978 concentration data.

The year-to-year change in annual precipitation averaged ~20 mm, or ~20% of the average annual precipitation over the past century. If the precipitation decreases by 20 mm for one year to the next, then the fluvial flux of the ion to the lake decreases by ~10% assuming 50% of the precipitation infiltrated into the ground and the remainder enters surface runoff. A simple, steady-state model that used a water residence time of 18 years, a lake volume of 15.54 $km^3$, a surface runoff of 863 x $10^6$ $m^3/yr$, a surface outflow of 760 x $10^6$ $m^3/yr$ and the chloride flux data presented here indicates that a 10% reduction in ion flux to the lake followed by an identical increase the following year can decrease the steady state ion concentration in the lake by a few mg/L. Annual variability may also influence groundwater discharge to the lake but groundwater data are lacking to assess the direction and magnitude of this possibility. We suggest that a variable input of subsurface seeps and/or climatic variability are potential forcing mechanisms for the annual-scale variability in ion concentrations in the lake, and present an interesting topic for further research.

## CONCLUSIONS

Analysis of major ion concentrations ($Cl^-$, $SO_4^{2-}$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $K^+$) in lake and stream samples from the Seneca Lake watershed during the spring, summer and fall months of 2000 through 2004 indicate that groundwater fluxes are important to the major ion hydrogeochemistry of Seneca Lake. Groundwater diffusion and advection augments the fluvial flux of chloride, sodium and, to a lesser degree, sulfate to the lake. Sediment pore water gradients and local sulfur seeps suggests that chloride and sodium probably originate from the Silurian evaporite deposits from beneath the lake, and sulfur from the sulfate-rich Bertie Formation. Calcium and magnesium are unique from chloride, sodium and sulfate in that the excess fluvial flux of calcium, and to a lesser degree magnesium, are removed from the water column as whiting events of low-Mg carbonate and zebra/quagga shell formation. Potassium is conservative in this watershed. Year-to-year variability in major ion concentrations in the lake appear to inversely vary with annual changes in rainfall, and to a lesser degree changes in the direct discharge of mine wastes to the lake, and present an interesting hypothesis for future research.

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