

# A 2014 UPDATE ON THE CHLORIDE HYDROGEOCHEMISTRY IN SENECA LAKE, NEW YORK.

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## **Introduction:**

Seneca Lake is the largest of the 11, elongated, north-south trending, Finger Lakes in central and western New York State (Fig. 1). It has a volume, surface area, watershed area, and maximum depth of 15.5 km<sup>3</sup>, 175 km<sup>2</sup>, 1,621 km<sup>2</sup> (including Keuka watershed), and 188 m, respectively (Mullins et al., 1996). The lake basins were formed by glacial meltwaters eroding and deepening former stream valleys underneath the retreating Pleistocene Ice Sheet cutting into the Paleozoic sedimentary rocks approximately 10,000 years ago. Each basin was subsequently filled with a thick deposit of glacial tills and a thin veneer of pro-glacial lake clays. Basins not completely filled with sediment (e.g., Tully Valley), were subsequently filled with water and slowly accumulating postglacial muds. Seneca Lake is classified as a Class AA water resource by the New York State Department of Environmental Conservation (NYS DEC), except for a few locations along the shore (<http://www.dec.ny.gov/regs/4592.html>, Halfman et al., 2012). It supplies drinking water to approximately 100,000 people in the surrounding communities.

Berg (1963) and Schaffner and Oglesby (1978) noted that chloride concentrations were significantly larger in Seneca Lake, and to a lesser extent in Cayuga Lake, than the other Finger Lakes. Wing et al. (1995) argued that the elevated chloride concentrations required an extra source of chloride beyond the measured fluvial fluxes to the lake. They expanded and substantiated arguments by Berg (1963) and Ahrnsbrak (1975), and hypothesized that the extra source of chloride originated from the Silurian beds of commercial grade rock salt (Halite) some 450 to 600 m below the lake's surface. Measured concentration gradients in the sediment pore waters indicated that chloride diffuses into the lake from the lake floor.

Seismic reflection profiles revealed an extensive thickness of glacial till that filled half of the basin down to the bedrock floor under Seneca Lake. The bedrock floor is deep enough to intersect the Silurian beds of rock salt (Mullins and Hinchey, 1989, and Mullins et al., 1996). The most likely location for this intersection is not well defined, but projected to be located under the northern portion of the lake based on a uniform 1° southerly dip of the bedrock and the depth profile of the basin's bedrock floor. Wing et al. (1995) hypothesized that this connection provided an avenue for brine to migrate from these rock salt beds into these two lakes, and not the other Finger Lakes (Fig. 2).

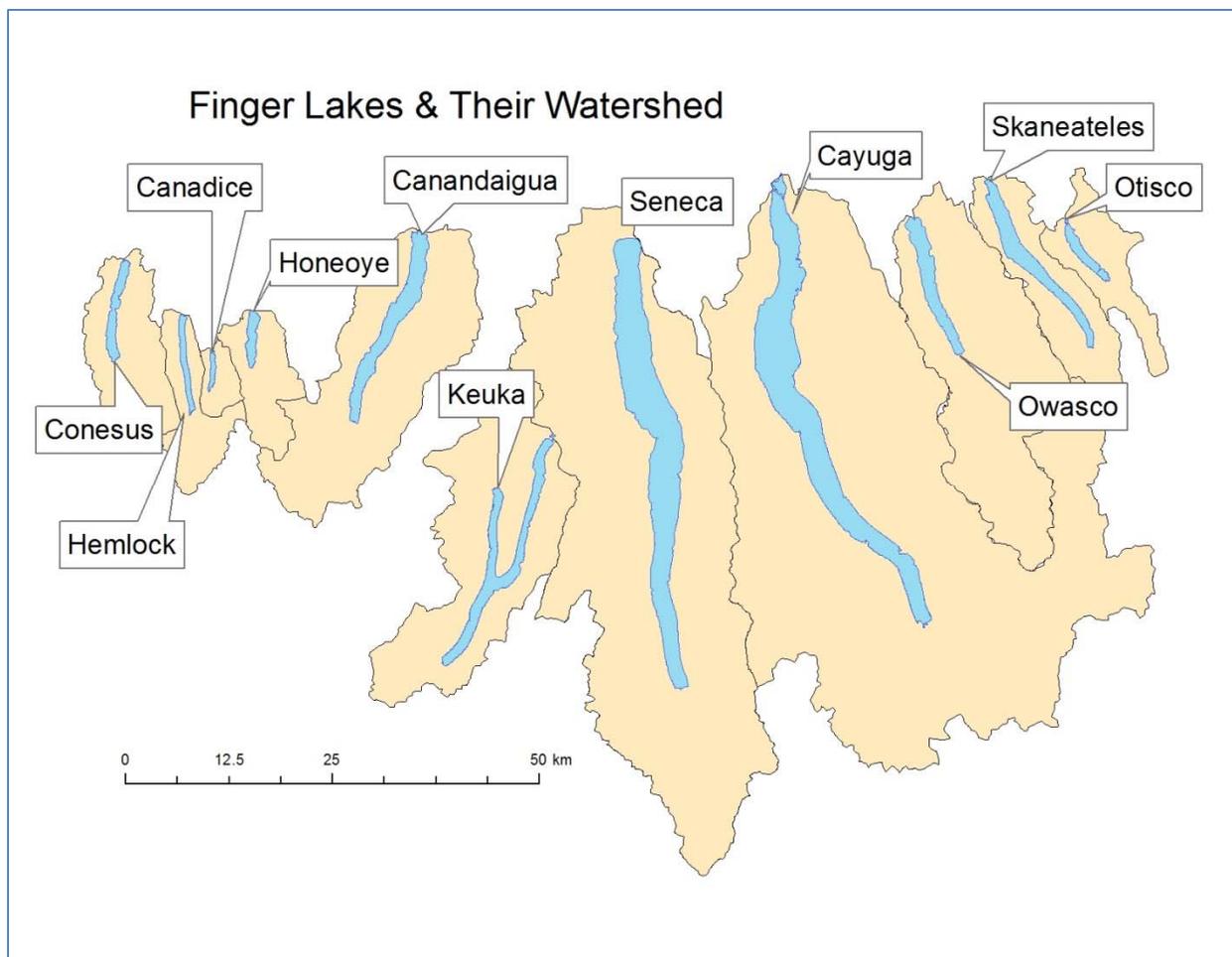


Fig. 1. The Finger Lakes & their watersheds.

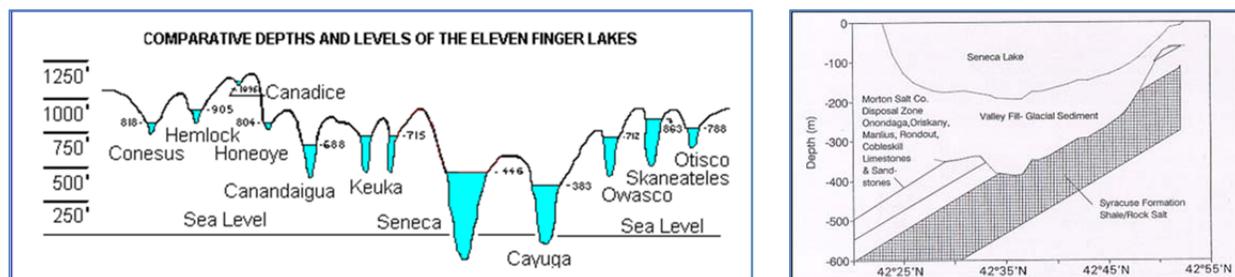


Fig. 2. The depths of the Finger Lakes and connections to the Silurian rock-salts under Seneca Lake (modified from Wing et al., 1995).

Callinan (2001) offered an alternative hypothesis. He noted a decline in sodium concentration since the 1970s to the late 1990s in Seneca Lake and speculated that the decline may reflect changes in analytical accuracy and precision, and/or a decline in the discharge of brine water waste from the salt mines located near Watkins Glen along the southern shores of Seneca and Cayuga Lakes. However, Wing et al. (1995) calculated that the presumed 3,500 kg/day discharge of chloride to Seneca Lake by the mines would only increase chloride concentrations by a few mg/L in Seneca Lake. Thus, an extra groundwater source of chloride was still necessary to explain the larger concentration in Seneca Lake.

Halfman et al. (2006) expanded the major ion investigation of Seneca Lake to include all of the major ions: chloride, sulfate, sodium, potassium, calcium and magnesium. No horizontal spatial-scale trends in major ion concentrations were observed in the well-mixed lake. Vertically, the epilimnion (surface waters) was slightly less saline than the hypolimnion (bottom water). Mass-balance calculations subdivided the major ions into three populations. Chloride, sodium, and to a lesser extent sulfate, were up to four times greater in the lake than the streams ( $\text{Cl}^-$  140 vs. 33 mg/L,  $\text{Na}^+$  80 vs. 20 mg/L,  $\text{SO}_4^{2-}$  40 vs. 30 mg/L, respectively). Thus, these ions required another source to attain the concentration detected in the lake. Conversely, calcium and magnesium were more concentrated in the streams than the lake and required a mechanism to remove a portion of these ions from the lake ( $\text{Ca}^{2+}$  60 vs. 42 mg/L,  $\text{Mg}^{2+}$  17 vs. 11 mg/L, respectively). Finally, the fluvial flux of potassium was at equilibrium with the lake. The mean molar ratio of chloride and sodium for all the analyses was nearly 1:1, suggesting a common Halite ( $\text{NaCl}$ ) source for these two ions. All of these observations were consistent with a substantial groundwater source to explain the elevated concentration detected in the modern lake.

Steady-state conditions are crucial, if Seneca Lake is to remain a potable drinking water supply for nearly 100,000 people in the region. The EPA's total dissolved salt (TDS) drinking water advisory concentration is 500 mg/L, and 250 mg/L for chloride (EPA 822-S-12-001, 2012). The drinking water advisory concentration for sodium is between 30 and 60 mg/L, and the threshold is lowered to 20 mg/L for those on low-salt diets (<500 mg/day) and newborn infants (EPA 822-R-03-006, 2003). NYS DEC regulations use the 250 mg/L limit for chloride and 20 mg/L for sodium as drinking water guidelines (<http://www.dec.ny.gov/regs/4590.html>). Thus, any increase in the current chloride (122/128 mg/L, surface/bottom) and/or sodium concentrations (75/79 mg/L) for the lake would be a concern, as sodium already exceeds its 20 mg/L drinking advisory limit. This report updates the major ion hydrogeochemistry of Seneca Lake focusing on the chloride data collected and discovered since the earlier publications.

## Methods:

Since 2000, surface water samples for major ion analysis were routinely filtered through a 0.45  $\mu\text{m}$  HA Millipore or 0.45  $\mu\text{m}$  glass fiber filters at four lake sites (1-4) located at the northern end of the lake as part of the Finger Lakes Institute's monitoring program of Seneca Lake (Fig. 3). Bottom water samples, approximately 1 to 5 m above the lake floor, weather permitting, were collected at the two deeper, mid-lake sites, 1 & 3, and processed in an identical manner. When funding was available, surface and bottom samples were collected from at least five additional sites that follow a mid-lake transect down the central axis of the lake (one or more full-lake cruises occurred during 1989, 1999, 2011 and 2014). A state-of-the-art SeaBird SBE-25 CTD (conductivity, temperature and depth profiler) water column profile of temperature, specific conductance (proportional to salinity), pH, dissolved oxygen, fluorescence (chlorophyll indicating algal abundance), turbidity, and PAR (light availability) was also collected at each site along with other limnological parameters. The SBE-25 replaced a SeaBird SBE-19 in 2006. Water samples were also collected and analyzed from up to 17 streams in the Seneca Lake watershed focusing on base-flow and not rain/runoff event samples. Sample frequency of each stream varied from once or twice a year in the late spring to weekly samples throughout the year

in selected subwatersheds during the 1999 to 2014 monitoring program depending on the availability of funds.

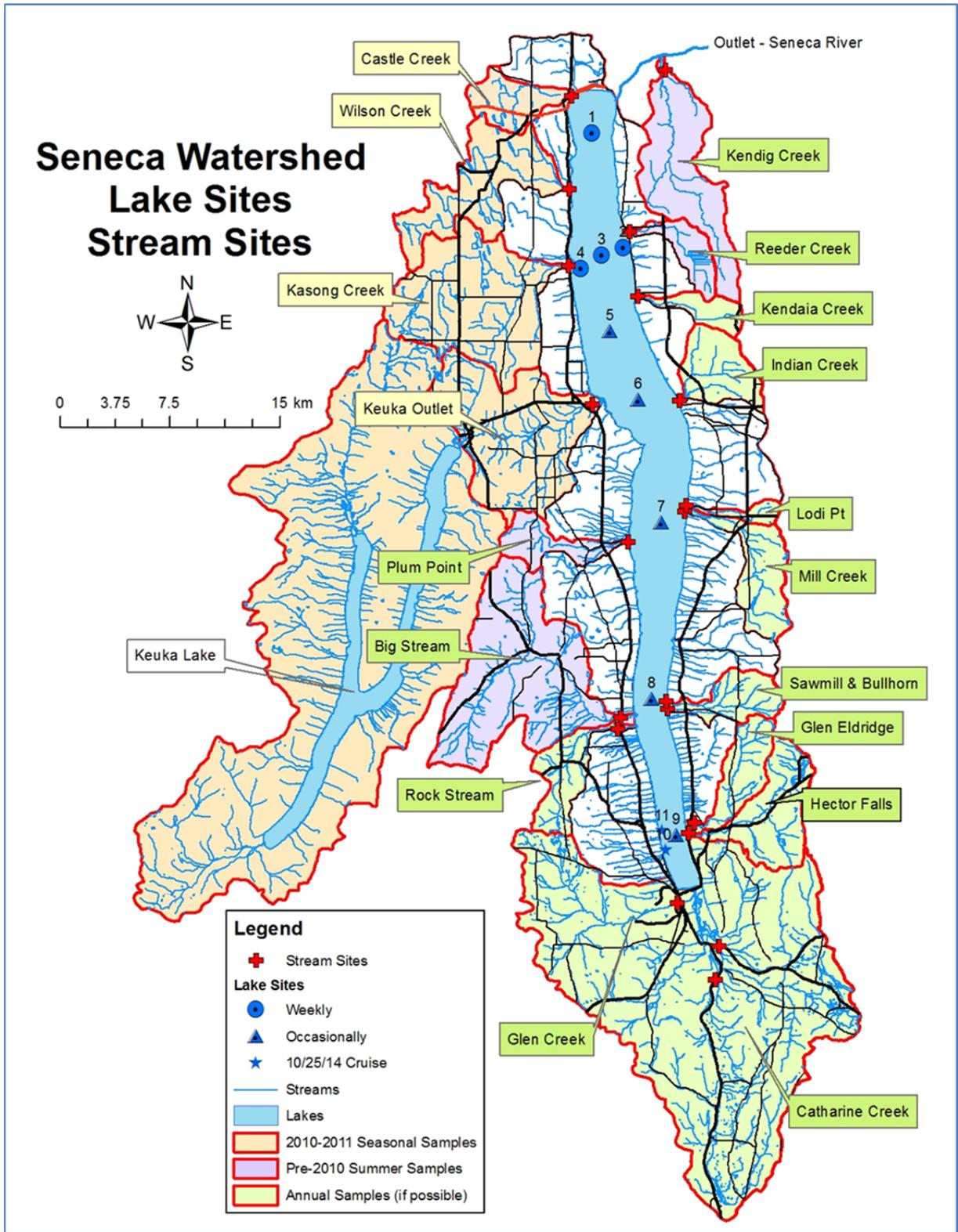


Fig. 3. Lake and stream site locations in the Seneca Lake watershed.

The filtrate was saved in pre-rinsed Nalgene bottles and typically stored at 4°C until analysis for major anions (chloride, sulfate) and cations (sodium, potassium, magnesium and calcium) by Ion Chromatograph (IC, Dionex DX-120). The IC protocol uses a standard anion column (AS14) and bicarbonate eluent for anions, and a standard cation column (CS12A) and methane-sulfonic acid eluent for the cations. The accuracy, measured by the mean difference between the result from analyzing samples and their known concentrations during each run, typically averaged less than 1 mg/L, and precision, measured by the standard deviation of three or more runs of the same sample, averaged 0.2 mg/L. Before 2000, and on subsequent checks in the field, chloride was analyzed by a silver nitrate titration using a potassium chromate indicator (LaMotte PSC-DR). All water samples were analyzed for total alkalinity (primarily bicarbonate ion,  $\text{HCO}_3^-$ ) by titration with sulfuric acid using a phenolphthalein and bromocresol green/methyl red indicator in the field (LaMotte WAT-MP-DR). Both titration techniques revealed an average precision of 4 mg/L. The average difference in the anion/cation charge balance was 0.5 meq/L, approximately 10% of the total charge, and deviations were probably due to the less precise alkalinity data.

In addition to the work on Seneca Lake, monthly surface and bottom water samples and CTD casts were also collected from a minimum of two sites during the May to October field season in Honeoye, Canandaigua, Keuka, Cayuga, Owasco, Skaneateles and Otisco Lakes starting in 2005 (Fig. 1). These samples were processed in an identical manner. This dataset was augmented with data from the literature (Berg, 1963, Schaffner and Ogelby, 1978, Wing et al., 1995, Callinan, 2001, Halfman et al., 2006), and are all graphically presented below.

Century-scale chloride data were also discovered for Seneca, Cayuga, Hemlock & Canadice, and Skaneateles Lakes. These data are reproduced with permissions from the Hemlock Water Quality Laboratory for the City of Rochester, Oneonta County Water Authority for the City of Syracuse, and Glenn Jolly, USGS, Reston (Jolly, 2005, Jolly, 2006, Jolly, 2012, Sukerfort & Halfman, 2005, 2006, Sukerfort et al., 2006). All of these lakes supply water to neighboring communities, e.g., Geneva, Ithaca, Rochester & Syracuse, and water providers measure chloride and other potential contaminants in the water to ensure the conveyance of potable drinking water. The century-scale data are a challenge to find as they are typically buried within water quality reports that may or may not have been archived, and reporting regulations changed over time. I am grateful for the hard work by Glenn Jolly, who dug through Cornell's archives for the Seneca Lake, Cayuga Lake, Fall Creek and Keuka Outlet data. I am also grateful to the Hemlock Water Quality Laboratory and the Oneonta County Water Authority for their data that they gave to me and/or my students (e.g., Sukerforth).

## Results & Discussion:

**Lake Concentrations:** The salinity of Seneca Lake is still dominated by chloride, sodium and bicarbonate ions (Table 1. Fig. 4). The mean major ion concentrations in the lake, averaging the 2000 through 2013 data, are 128 for Cl (as Cl), 77 for Na (as Na) and 105 mg/L for bicarbonate (as CaCO<sub>3</sub>) for a total dissolved solids concentration of 390 mg/L. These chloride and sodium concentrations equate to 1.98 million and 1.19 million metric tons of Cl and Na, respectively, dissolved in Seneca Lake (assuming a lake volume of 15.5 km<sup>3</sup>). A significant event must happen to change the concentration of chloride or sodium in Seneca Lake. For example, instantaneously adding 100,000 metric tons of chloride to the entire, well-mixed, lake will only increase the chloride concentration from 128 to 135 mg/L (Table 2). Over 1 million tons must be added to increase the lake's concentration to 190 mg/L. Conversely, adding 50 cm of rain to the lake will only decrease the epilimnetic chloride concentration of 128 to 125 mg/L assuming an epilimnetic thickness of 30 meters, a lake surface area of 175 km<sup>2</sup> and no inputs from streams. The epilimnetic chloride concentrations decrease to 120 mg/L, assuming 40% of the precipitation over land enters stream runoff and eventually the lake, and this event-based runoff dilutes the stream mean major ion concentrations by 40%. However, these percentages require additional verification to more accurately represent these parameters in the Seneca Lake watershed. Please note: These relatively sudden changes, when not sustained over time, will only impact the lake concentration for a few decades because concentrations will exponentially return back to its original equilibrium concentration in time (50 to 100 years in Seneca Lake).

**Table 1. Mean major ion concentrations in the Seneca Lake watershed (2000-2013 data).**

Lake Sites	Chloride (mg/L)			Sulfate (mg/L)			Sodium (mg/L)			Potassium (mg/L)			Calcium (mg/L)			Magnesium (mg/L)		
	Average	StDev	N	Average	StDev	N	Average	StDev	N	Average	StDev	N	Average	StDev	N	Average	StDev	N
Site 1S	128.0	7.5	242	34.4	3.5	240	77.0	4.4	243	3.6	1.4	242	38.8	3.3	242	11.1	1.0	242
Site 2S	127.4	7.5	224	34.4	3.0	222	76.5	4.3	222	3.6	1.4	222	39.0	3.0	221	11.1	1.0	221
Site 3S	126.9	7.0	223	34.3	2.9	221	76.1	4.8	224	3.6	2.0	224	38.9	3.0	223	11.1	1.3	223
Site 4S	127.7	7.9	233	34.6	3.3	231	76.6	4.6	231	3.5	1.6	232	39.1	3.1	231	11.1	1.0	230
Site 1B	128.2	7.3	239	34.5	3.2	237	77.0	4.6	238	3.7	1.4	237	39.7	3.1	237	11.1	1.0	237
Site 3B	130.2	7.2	225	35.0	3.0	223	78.4	4.5	223	3.6	1.4	224	40.7	2.5	222	11.1	1.0	222
<b>Stream Sites</b>																		
Glen	14.6	3.3	7	21.0	16.0	7	11.7	2.7	7	1.9	0.5	7	38.0	3.9	7	9.1	3.2	7
Rock Stream	35.0	13.8	13	20.4	16.4	13	21.3	8.3	12	3.0	1.4	12	40.2	19.0	12	13.1	11.0	12
Big Stream	39.6	11.1	43	23.3	9.5	43	23.1	6.2	41	2.8	1.0	41	48.9	7.4	41	13.2	3.5	41
Plum Pt.	77.1	31.7	43	39.3	12.5	43	39.6	16.5	40	3.5	1.5	40	56.6	14.1	40	16.4	3.8	40
Keuka	33.8	12.9	124	26.5	7.7	124	19.8	6.8	122	3.5	1.5	122	42.1	11.8	122	13.0	5.5	122
Kashong	45.7	11.8	118	33.9	9.4	118	23.4	6.1	113	4.5	2.3	114	71.6	20.4	112	24.8	8.9	113
Wilson	55.3	17.6	110	36.0	13.1	110	28.6	8.0	109	5.3	1.7	108	82.4	17.9	110	25.8	6.1	110
Castle	148.0	113.2	71	35.5	12.0	72	80.8	50.7	71	4.6	1.5	72	79.7	19.3	72	23.8	6.7	72
Kendig	38.1	9.8	40	41.5	12.0	40	21.5	11.1	38	3.2	1.1	38	70.2	20.5	38	21.5	7.5	38
Reeder	45.0	20.2	52	41.2	12.4	52	31.9	12.6	52	3.7	3.7	52	81.9	20.7	52	17.0	5.5	52
Kendaia	36.1	19.7	11	35.9	17.9	11	23.5	13.0	11	3.3	1.8	11	70.8	20.8	11	14.8	5.3	11
Indian	35.2	17.3	11	40.7	19.7	11	16.5	5.2	11	2.8	1.2	11	72.8	10.3	11	17.8	5.6	11
Lodi Pt.	48.5	23.5	3	29.1	17.4	3	34.0	4.9	3	4.1	1.0	3	66.4	38.6	3	19.5	4.3	3
Mill Cr	7.6	2.3	8	17.6	8.4	8	8.8	2.3	6	1.9	0.8	7	31.0	17.7	7	8.2	4.7	7
Bullhorn	40.4	11.9	9	31.8	17.3	9	22.3	5.8	9	3.0	1.5	9	62.9	9.1	9	13.1	4.7	9
Sawmill	18.1	13.1	13	23.3	14.2	13	13.9	7.4	11	2.5	1.6	11	53.4	26.2	11	11.5	6.0	11
Glen Eld.	12.3	4.0	12	21.0	14.0	12	8.5	2.3	11	1.9	1.0	11	44.7	12.8	11	9.4	3.8	11
Hector Falls	18.2	3.3	11	15.1	12.2	11	12.8	3.1	11	1.9	1.2	11	43.3	5.6	11	9.9	3.3	11
Catharine	29.4	10.1	17	13.9	2.7	17	22.1	5.2	17	3.8	1.2	17	49.7	11.5	17	12.8	3.6	17
<b>Average Lake</b>																		
Average Lake	128.1	7.4	231.0	34.5	3.1	229.0	76.9	4.5	230.2	3.6	1.5	230.2	39.4	3.0	229.3	11.1	1.1	229.2
St Dev Lake	1.1	0.3	8.2	0.3	0.2	8.2	0.8	0.2	8.8	0.0	0.2	8.2	0.7	0.3	8.8	0.0	0.1	8.8
Maximum Lake	130.2	7.9	242.0	35.0	3.5	240.0	78.4	4.8	243.0	3.7	2.0	242.0	40.7	3.3	242.0	11.1	1.3	242.0
Minimum Lake	126.9	7.0	223.0	34.3	2.9	221.0	76.1	4.3	222.0	3.5	1.4	222.0	38.8	2.5	221.0	11.1	1.0	221.0
<b>Average Stream</b>																		
Average Stream	40.9	18.4	37.7	28.8	12.9	37.7	24.4	9.4	36.6	3.2	1.4	36.7	58.2	16.2	36.7	15.5	5.4	36.7
St Dev Streams	30.8	24.1	40.0	9.2	4.2	40.0	16.0	10.7	39.3	1.0	0.7	39.3	16.2	8.1	39.3	5.4	2.0	39.4
Maximum Streams	148.0	113.2	124.0	41.5	19.7	124.0	80.8	50.7	122.0	5.3	3.7	122.0	82.4	38.6	122.0	25.8	11.0	122.0
Minimum Streams	7.6	2.3	3.0	13.9	2.7	3.0	8.5	2.3	3.0	1.9	0.5	3.0	31.0	3.9	3.0	8.2	3.2	3.0

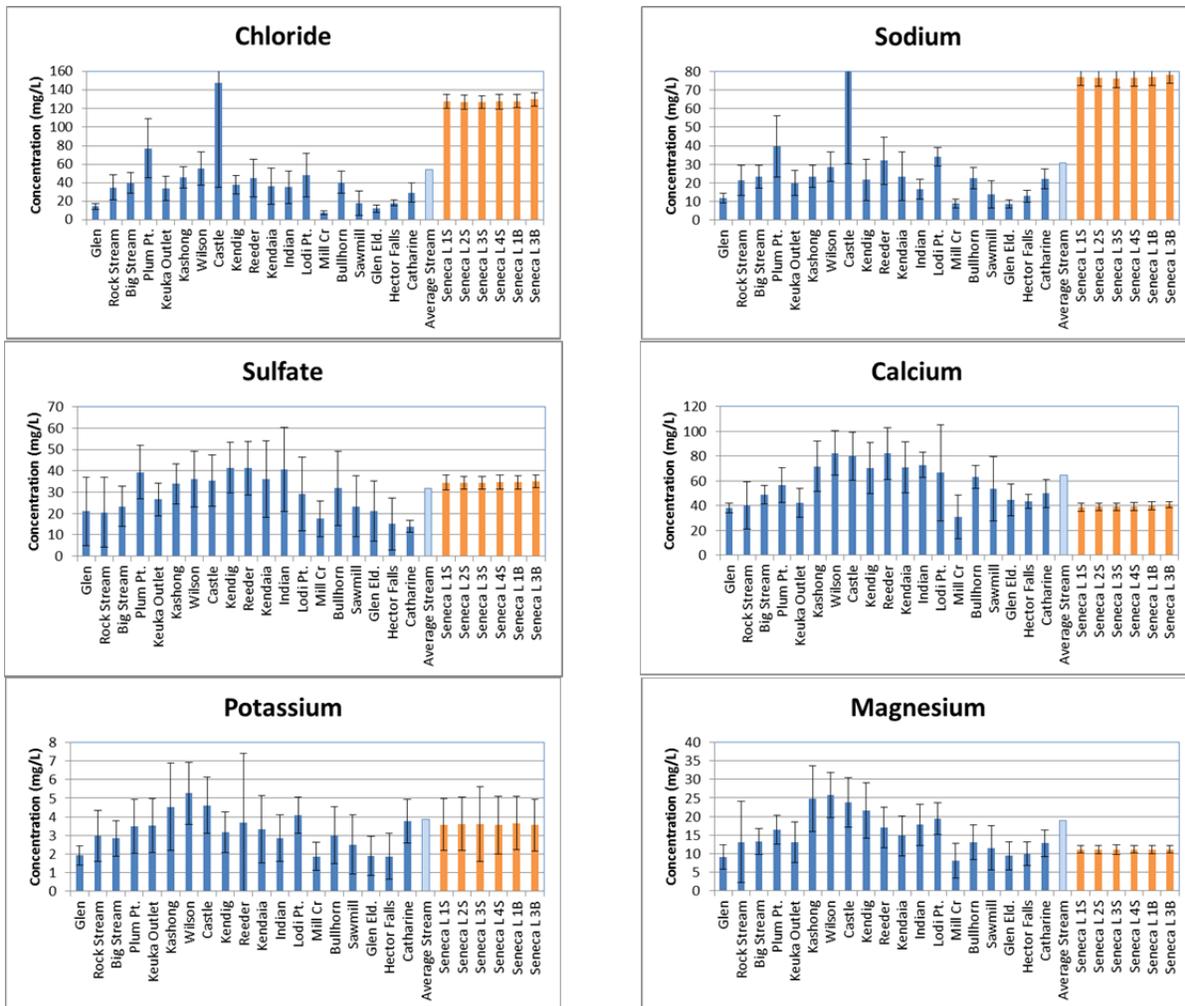


Fig. 4. Mean major ion concentrations in the Seneca Lake watershed (2000-2013 data). The lake samples are highlighted in orange, stream samples in blue and the mean stream value in light blue. The error bars are the 1  $\sigma$  deviation about the mean for each site.

Calcium (as Ca, 39 mg/L), sulfate (as SO<sub>4</sub>, 34 mg/L), magnesium (as Mg, 11 mg/L) provide the bulk of the remaining major ions in the lake with minor amounts of potassium (as K, 4 mg/L). The total dissolved solids (TDS) concentration in Seneca Lake of 390 mg/L is larger than the mean TDS of 235 mg/L for other Finger Lakes (240 mg/L), but all are below the drinking water advisory level of 500 mg/L and 100 times less saline than sea water (35,000 mg/L). These concentrations are typically slightly smaller than those reported in Wing et al. (1995) and Halfman et al. (2006).

Samples from a recent full-lake cruise on October 25, 2014 were also run for sodium, chloride and specific conductance at both Halfman's research lab and a commercial lab, Community Science Institute, Inc. (Table 3, see appendix). Each lab reported slightly different values, with the CSI lab results slightly larger than Halfman's lab. The mean difference between the two labs was 7 mg/L for Cl, 5 ppm for Na, and 22  $\mu$ S/cm for specific conductance. The differences may reflect different analytical techniques. The on-site specific conductance data measured by a hand-held probe (Oakton CON 410 Series) aboard the ship was 11  $\mu$ S/cm smaller

**Table 2. Chloride concentrations after inputs of chloride and rainfall.**

Entire Lake Chloride Concentrations with One Time Slug of Chloride							
Original & Resulting Lake Concentration (mg/L)							
Cl Load (tons)	100	120	128	140	160	180	200
1,000	100	120	128	140	160	180	200
10,000	101	121	129	141	161	181	201
100,000	106	126	134	146	166	186	206
1,000,000	165	185	193	205	225	245	265

Epilimnion Chloride Concentrations with One Time Slug of Chloride							
Original & Resulting Lake Concentration (mg/L)							
Cl Load (tons)	100	120	128	140	160	180	200
1000	100	120	128	140	160	180	200
10000	102	122	130	142	162	182	202
100000	119	139	147	159	179	199	219
1000000	290	310	318	330	350	370	390

Epilimnion Chloride Concentrations with Rain							
Original & Resulting Lake Concentration (mg/L)							
Rain (cm)	100	120	128	140	160	180	200
10	100	120	128	140	159	179	199
20	99	119	127	139	159	179	199
30	99	119	127	139	158	178	198
40	99	118	126	138	158	178	197
50	98	118	126	138	157	177	197
60	98	118	125	137	157	176	196

Epilimnion Chloride Concentrations with Rain and Runoff							
Original & Resulting Lake Concentration (mg/L)							
Rain (cm)	100	120	128	140	160	180	200
10	99	119	127	138	158	178	198
20	98	117	125	137	156	176	195
30	97	116	124	135	154	174	193
40	96	115	122	134	153	172	190
50	95	114	121	132	151	170	188
60	94	112	120	131	149	168	186

than that measured by the CTD. A CTD value was estimated by averaging all data within the upper 10 m and lowest 10 m in each cast for comparison to the surface and bottom water samples. This methodology may have induced the reported difference. Please note: These differences are small, are focused on a small range of data, and most importantly, are always proportional. The best correction is between Halfman's on-site specific conductance results and the CTD ( $r^2 = 0.99$ ). Thus, any conclusions based on one data set should be mimicked by data from the other lab. This report focuses on the IC results from Halfman's lab due to its known precision and accuracy and more importantly, for comparison to Halfman's earlier data from Seneca and the neighboring Finger Lakes.

Mean chloride, sodium and to a lesser extent sulfate concentrations in Seneca Lake were three or more times larger than those from Honeoye, Canandaigua, Keuka, Cayuga, Owasco, Skaneateles and Otisco Lakes (Table

4, Fig. 5). The other major ions reveal similar concentrations between all the sampled Finger Lakes. This pattern is consistent with the earlier results and still suggests that Seneca Lake has a unique additional source for its chloride and sodium ion concentrations.

**Table 4. Mean major ion concentrations in the Finger Lakes region (2005-2013 data).**

	Chloride	Sulfate	Sodium	Potassium	Magnesium	Calcium	Alkaninty
Lake	Cl mg/L	SO4 mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	CaCO3 mg/L
Seneca	126.4	32.7	75.7	4.4	11.4	38.3	105.0
Honeoye	19.5	9.0	14.9	3.1	7.3	23.1	99.6
Canandaigua	31.6	19.2	21.1	3.9	11.9	39.0	140.4
Keuka	23.2	18.9	15.7	3.8	10.1	30.2	111.5
Cayuga	40.8	27.0	26.9	4.4	11.4	40.9	130.8
Owasco	17.1	10.9	13.9	3.5	9.2	40.0	146.4
Skaneateles	13.7	12.8	10.5	2.9	8.0	35.6	125.3
Otisco	29.6	12.8	20.9	3.5	11.3	42.0	147.3

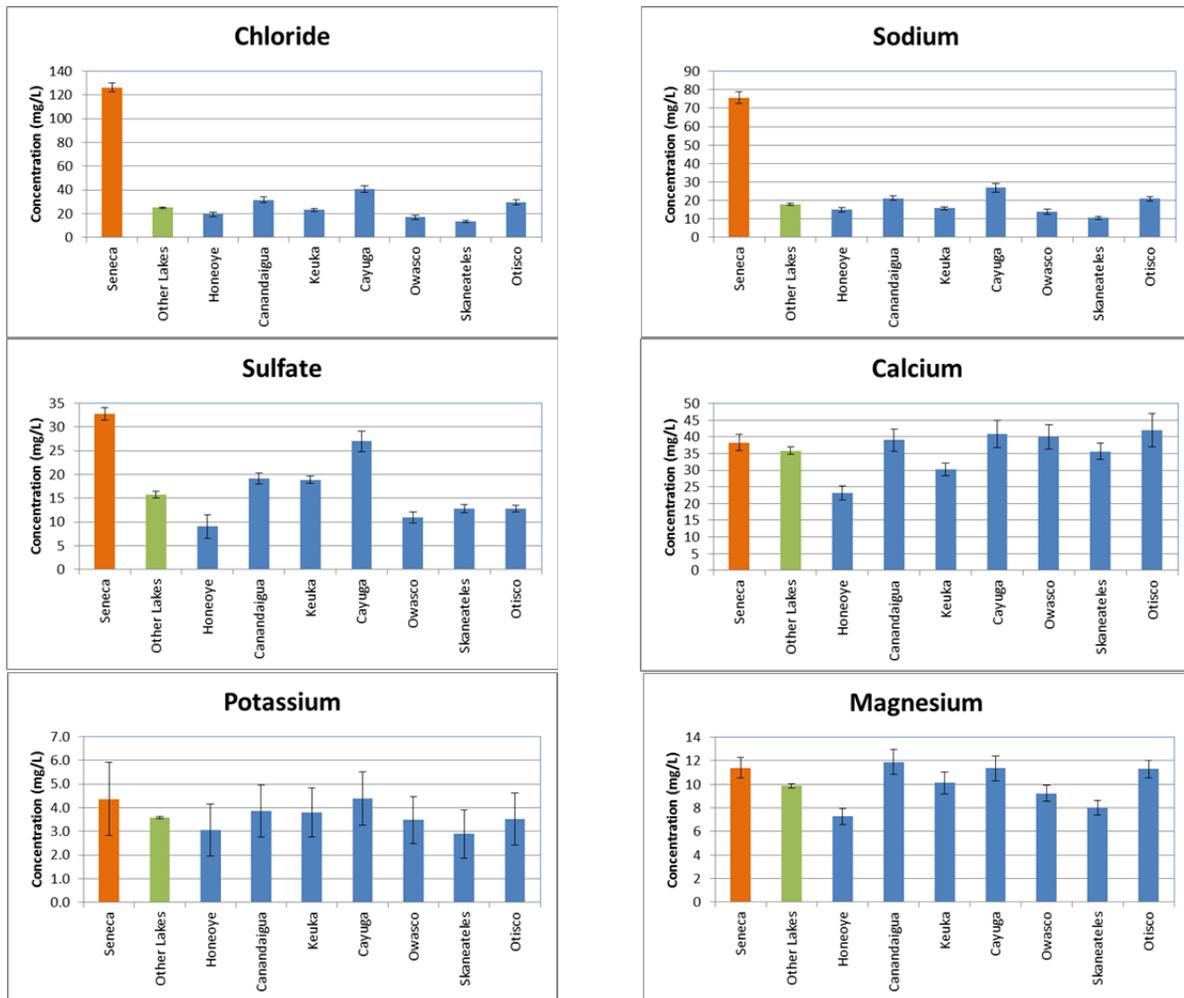


Fig. 5. Mean major ion concentrations in the eight easternmost Finger Lakes (2005-2013 data). Seneca Lake is highlighted in orange, and the mean concentration for all the other Finger Lakes is highlighted in green. The error bars are the 1  $\sigma$  deviation about the mean for each lake.

Within Seneca Lake, surface lake concentrations revealed minimal ( $< 1$  mg/L) spatial variability, especially within the northern end of the lake (Fig. 4). The occasional entire lake cruises also revealed similar uniformity over the lake's surface and thus indicates that the epilimnion is well-mixed by waves and surface currents. Base flow stream inputs are also quickly homogenized into the lake. Lake concentrations were consistently measured as close as 10 to 100 m from the stream mouth, except during the largest flood events, and highlights the relatively small inputs by streams compared to the quantity of ions in and volume of the lake. The data also revealed slightly larger concentrations with increasing depth in the water column with a maximum increase in chloride and sodium concentrations between the surface and bottom water samples of 15 and 10 mg/L, respectively, at the deepest sites (7 & 8) offshore of Lodi Point. Chloride, sodium and sulfate explained 85 to 90% of the increase in concentrations along the deepest lake floor. The lake-wide surface uniformity and slightly elevated concentrations at the deepest depths is consistent with the earlier results. Samples collected offshore of the US Salt outfalls near Watkins Glen on the 10/25/2014 cruise did not reveal any significant spatial changes. In conclusion, input of saline or fresh water to Seneca Lake is apparently quickly

mixed throughout the lake. Significant “issues” along the southern shores will impact lake water at the northern end. It implies that we all share the same lake.

Seneca Lake CTD specific conductance (proportional to salinity) profiles from 10/25/2014 revealed a similar uniformity across the epilimnion (Fig. 6). Vertically, two notable increases in salinity were detected, an increase in salinity from the well-mixed epilimnion to the hypolimnion, and another increase in salinity from the lower hypolimnion to the lake floor at only at the deepest sites offshore of Lodi Point (Sites 7 & 8). Please Note: Internal seiche activity forced the shallower thermocline depths, and boundary between the epilimnion and hypolimnion, towards the southern end of the lake.

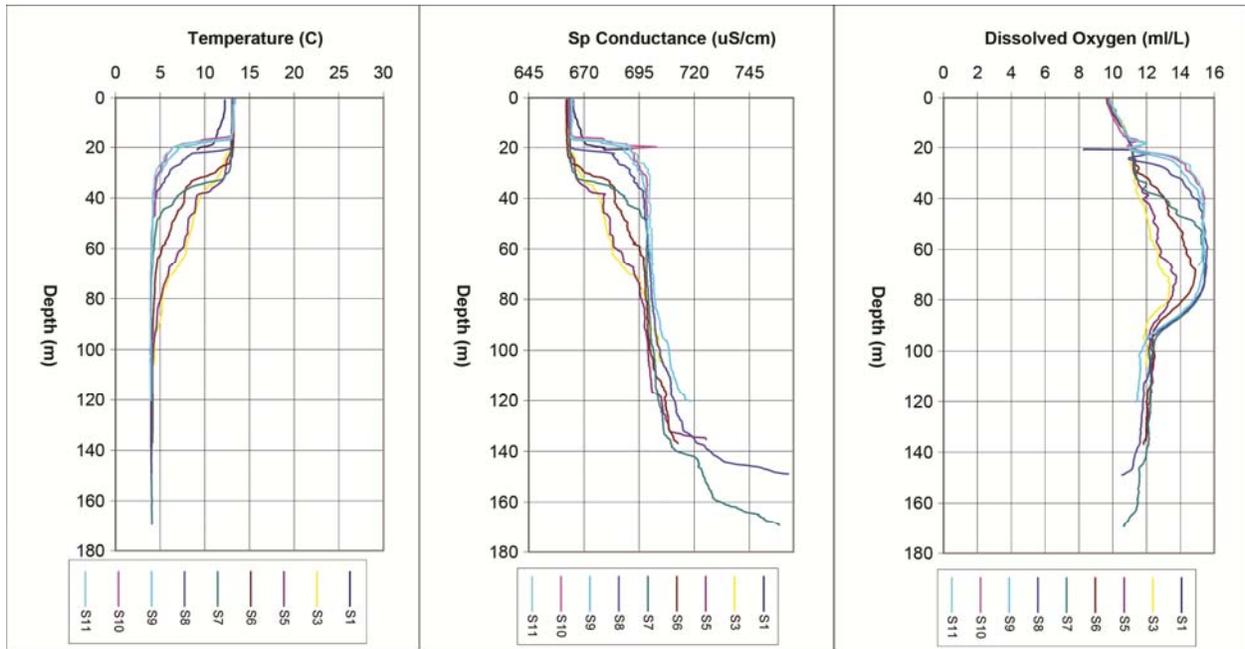


Fig. 6. CTD temperature, specific conductance, and dissolved oxygen profiles from the 10/25/2014 full-lake cruise.

A systematic seasonal decrease in epilimnetic (surface water) salinities by approximately 50  $\mu\text{S}/\text{cm}$  ( $\sim 20$  mg/L) occurred each year during the stratified summer seasons. The CTD profiles revealed uniform concentrations with water depth during the isothermal spring. With the onset of thermal stratification, the epilimnion salinity increasingly decreased through the summer season (Fig. 7). This concentration difference would dissipate during the breakdown of the thermal stratification in the fall. The epilimnetic decrease in salinity during summer stratification is interpreted to reflect the dilution of the epilimnion by less saline rainfall and surface runoff. The seasonal decrease is consistent with adding  $\sim 50$  cm of rain to the lake. However, other unknown factors may come into play because the year-to-year decrease does not correlate with seasonal or annual rainfall totals from Geneva, NY assuming Geneva rainfall is representative of the entire watershed. Specific conductance in the hypolimnion remained relatively constant each year, except in the deepest portions of the lake. This uniformity is counter to earlier statements made by Wing and his coauthors (1995), but is consistent with the data presented in their manuscript. Subsequent mixing due to the fall – spring overturn yields a salinity somewhere between the end of summer epilimnion and hypolimnion concentrations. It is proportionally closer to the hypolimnion salinity because the hypolimnion is approximately

twice as large as the typical epilimnion (~10 vs 5 km<sup>3</sup>, respectively). Finally, the observed multiyear decrease and uniformity is counter to a significant source of salts from the lake floor.

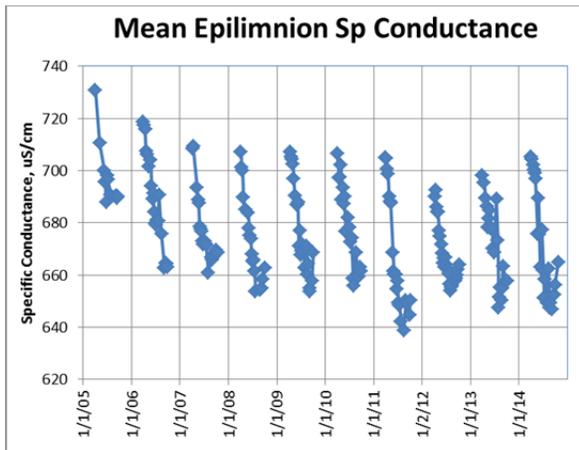


Fig. 7. Daily mean epilimnetic specific conductance data (2005-2014 data).

very small (0.0002 g/cm<sup>3</sup>). In comparison, the change in density from the epilimnion to the hypolimnion due to a temperature difference of 18°C (early summer) is ten times larger, 0.002 g/cm<sup>3</sup>.

A number of mechanisms can create the increase in salinity near the lake floor. The accumulation of ions could be from the natural biogeochemical decomposition of organic matter at or near the sediment-water interface, and is consistent with the observed slight decrease in dissolved oxygen concentrations and increase in bicarbonate species. The ions could also result from the accumulation of occasional inputs of saline water to the lake, either through natural seeps or human-induced inputs. Its greater density and gravity would transport and maintain the layer at the deepest depths in the lake over time. It is impossible to estimate the volume of this layer without more accurate bathymetric maps of the lake floor. However, I suspect that the amount of chloride in this layer was too small in this layer to reflect the quantity of groundwater chloride required to achieve the hypothesized groundwater flux of chloride to the lake (Wing et al., 1995, Halfman et al., 2006). Also, the available specific conductance profiles have not revealed increasing salinities in either the epilimnion or hypolimnion over time. Perhaps groundwater inputs have recently ceased.

**Stream Concentrations:** Stream mean major ion concentrations were dominated by bicarbonate (180 mg/L as CaCO<sub>3</sub>), calcium (64 mg/L as Ca), chloride (62 mg/L as Cl), sulfate (36 mg/L as SO<sub>4</sub>), sodium (35 mg/L as Na), magnesium (21 mg/L as Mg), and finally potassium (4 mg/L as K). The stream concentrations were more variable between streams (± 24.1 mg/L for Cl) and over time in any one stream than the lake sites (± 7.4 mg/L for Cl, Table 1, Fig. 4). For example, subwatershed mean chloride concentrations were largest in Castle (148 mg/L) and Plum Point (77 mg/L) Creeks and smallest in Mill Creek (7 mg/L) with no systematic change across the watershed. Sodium concentrations paralleled the chloride trends.

In a comparison of Castle, Wilson, Kashong, Plum Point, Big Stream and Catharine Creeks, the watershed road density correlated to their mean chloride concentrations ( $r^2 = 0.9$ ). Presumably streams with more roads per unit area received more road de-icing salts. Castle Creek drains the City of Geneva. Its large chloride concentrations and large variability in concentrations is interpreted to reflect its urban subwatershed. Plum Point drains an abandoned salt mine (Morton-Himrod Site) which had, when active, working salt piles and brine ponds. It also drains the watershed with the second largest road density. Both issues probably contributed to its larger chloride concentrations.

Calcium, magnesium, alkalinity, and sulfate concentrations were progressively larger towards the northern end of the Seneca Lake watershed. The trend parallels the distribution of limestone bedrock in the watershed and more importantly, more limestone in the glacial tills and soils underlying these watersheds.

Temporal variability in the major ion concentrations in each stream is large as well. For example, the range in chloride concentrations was up to 600 mg/L in Castle Creek, but was under 100 mg/L in the other creeks with adequate data. The variability was mostly attributed to sampling during and just after the application of road de-icing salts and storm events. De-icing salts enter the streams after the snow and ice melts. In contrast, storm events and the associated surface runoff would dilute the base-flow/groundwater contributions of the major ion population.

The differences between the lake and streams concentrations in Seneca Lake still differentiate the major ions into three groups: (1) chloride, sodium and sulfate, (2) calcium and magnesium, and (3) potassium. The concentration of chloride, sodium, and to a lesser extent sulfate are much larger in the lake than the streams. Whereas as calcium and magnesium concentrations are much smaller in the lake than the streams, and potassium concentrations are relatively uniform, i.e., means are within 1 standard deviation, across the watershed. To quantify these differences and investigate the potential additional sources and sinks for the first two groups of ions beyond the modern day fluvial inputs, ion flux and mass balance calculations were performed (after Harte, 1988, Halfman et al., 2006). The mass balance calculations assumed equilibrium, steady-state conditions, i.e., the stream and lake concentrations, fluxes of each ion into and out of the lake, and fluxes of water into and out of the lake, were constant over time.

### **Ion Fluxes:**

Fluxes for each ion from each subwatershed were calculated using the following equation:

$$\text{Fluvial Flux } In_{ion} = SC_{ion} \times Q_{inflow}$$

Where:

*Fluvial Flux  $In_{ion}$*  is flux of each ion to the lake by each subwatershed (mtons/year),  
 *$SC_{ion}$*  is the mean stream concentration of each ion in each subwatershed (mg/L), and  
 *$Q_{inflow}$*  is the annual runoff of water from each subwatershed to the lake ( $m^3$ /year).

Mean ion concentrations were used, recognizing this value will be high because it is primarily base-flow data. For any subwatershed without major ion data, the average of the mean

concentrations from the two nearest neighboring subwatersheds was used to preserve the spatial variability in the major ion concentrations observed across the entire watershed. The stream flow for each subwatershed was assumed proportional to the total inflow to the lake ( $863 \times 10^6 \text{ m}^3/\text{yr}$ ) by subwatershed area. The total flux for each ion to the lake was therefore the sum of the individual fluxes from each subwatershed (Table 5).

The flux of any ion from the lake was calculated:

$$\text{Flux Out}_{ion} = LC_{ion} \times Q_{outflow}$$

Where:

$\text{Flux Out}_{ion}$  is the flux of each ion out of the lake (mtons/year),

$LC_{ion}$  is the mean lake concentration for each ion (mg/L), and

$Q_{outflow}$  is the annual flow of water through the outlet ( $760 \times 10^6 \text{ m}^3/\text{year}$ ).

The unknown or extra flux to balance the mass budget was calculated:

$$\text{Extra Flux}_{ion} = \text{Fluvial Flux In}_{ion} - \text{Flux Out}_{ion}$$

Where:

$\text{Extra Flux}_{ion}$  is the required flux of each ion to balance the budget (mtons/year).

Finally, the theoretical lake concentration based on these fluxes were calculated:

$$\text{Lake Conc} = (\text{Flux}_{ion} / Q_{out}) \times 1 \times 10^6$$

Where:

$\text{Lake Conc}$  is the theoretical ion concentration in the lake (mg/L),

$\text{Flux}_{ion}$  is the total/partial flux of each ion to the lake (mtons/year), and

$Q_{out}$  is the annual outflow of water through the outlet ( $760 \times 10^6 \text{ m}^3/\text{year}$ ).

**Table 5. Fluxes of chloride and sodium in the Seneca Lake watershed.**

	Chloride	Sulfate	Sodium	Potassium	Calcium	Magnesium
Measured Mean Lake Concentration (mg/L)	128.0	34.4	76.9	3.7	39.3	11.1
Measured Mean Stream Concentration (mg/L)	54.4	31.9	30.7	3.9	64.4	18.9
<b>Total Influx - Sum Individual Stream Inputs (metric tons/yr)</b> assumes Q = 863 million m <sup>3</sup> /yr						
Total Influx	33,765	21,776	20,333	3,038	45,048	12,723
<b>Total Efflux Out (metric tons/yr)</b> assumes Q = 760 million m <sup>3</sup> /yr Winf et al., 1995						
Total Efflux	97,306	26,164	58,453	2,791	29,887	8,439
Annual Unaccounted Influx/Efflux (metric tons/yr)	(63,541)	(4,387)	(38,120)	247	15,161	4,284
Mean Annual Combined Mine Waste (metric tons/yr)	9,204		5,968			
Unaccounted Flux after including fluvial and mine inputs	(54,337)		(32,152)			
<b>Estimated Lake Concentrations (mg/L)</b>						
a- Stream Input Alone	44.4	28.7	26.8	4.0	59.3	16.7
b- With 3,500 kg/day Cl Mine Waste*	46.1		27.8			
c- With 26,000 kg/day Cl Mine Waste*	56.9		34.9			
*Sodium calculation assumes molar 1:1 ratio with Cl						
<b>Mean Annual Combined Mine Wastes (metric tons/yr)</b>						
Cargill Waste Stream Avg Cl: 7,550 kg/day, Oct 97 - May 14						
US Salt Waste Stream Avg Cl: 18,450 kg/day, Oct 99 - May 14 Pipes 1&2						
Combined Cl: 26,000 kg/day						

Theoretical lake concentrations were first calculated assuming the only ion source was from the fluvial fluxes. This was done to compare the theoretical concentrations to the actual lake concentrations, and determine which ion requires an additional source to the lake, which ion required a sink from the lake and which ion is in equilibrium with the lake. These steady-state,

equilibrium calculations assumed a discharge of water into ( $863 \times 10^6 \text{ m}^3/\text{yr}$ ) and out of ( $760 \times 10^6 \text{ m}^3/\text{yr}$ ) the lake used by Wing et al. (1995) and again by Halfman et al. (2006). Please note: The recent discharge data out the outlet measured by the USGS Gauge 04232739 at Seneca Falls are smaller than the outflow used previously and used in this report. The mean annual discharge measured at Seneca Falls from 2006 to 2013 was  $592 \times 10^6 \text{ m}^3/\text{year}$ , with a range from  $407 \times 10^6$  to  $973 \times 10^6 \text{ m}^3/\text{yr}$ . Continuous stream discharge data were also not available for any subwatershed, except for the Keuka Outlet, a stream influenced by precipitation/runoff and the outlet gates for Keuka Lake. Finally the lake's bathymetry, thus lake volume, is poorly constrained because the available bathymetric data are old. Despite these issues, I doubt if the theoretical concentration results will significantly change from those presented here because the theoretical concentrations are based on the ratio between inflow and outflow, and this ratio will probably not significantly change.

The present day fluvial fluxes support a steady-state, theoretical, chloride concentration of 44 mg/L and sodium concentration of 27 mg/L. These concentrations are similar to the measured concentration of chloride and sodium in the other Finger Lakes. It suggests that the fluvial inputs measured in this watershed are sufficient to explain the concentration of these two ions in the other Finger Lakes. The small differences between the other lakes could result from different road densities and road salt inputs, or a slightly different evaporation to inflow ratio. A weak correlation is found between the road density and mean chloride concentration in the Finger Lakes after excluding Keuka Lake ( $r^2 = 0.4$ ). The Finger Lake residence times and watershed to lake surface area ratios vary between lakes as well but only water residence times weakly correlates to chloride concentrations ( $r^2 = 0.3$ ); watershed to lake surfaces areas do not correlate ( $r^2 = 0.0$ ).

The flux of chloride and sodium to the lake is also influenced by mine wastes. The mean annual discharge of chloride and sodium from the two salt mines near Watkins Glen are available on the EPA ICS web site (Cargill Salt Inc., NPES NY0002241 and US Salt LLC – Watkins Glen Refinery, NPES NY0002330). The web sites tabulate monthly maximum and/or average concentration, flow and/or loading data starting in the late 1990s. The sodium flux from the mines were calculated from the chloride numbers assuming a 1:1 molar ratio with chloride (Table 5).

The mine fluxes were added to the fluvial fluxes for chloride and sodium to determine the contribution to another theoretical lake concentration. Please note: these calculations overestimated the chloride and sodium contribution from the salt mines because some of the mine waste water started as lake water thus the mine waste effluent included existing ions that were already in the lake and new ions from the mine operations. If the lake chloride is excluded from these calculations, then the mine loads should be reduced to 80% of the reported values, and the theoretical concentrations due to the combined fluvial and mine waste inputs should be reduced to 95% of the reported values. The difference in the percentage from 80 to 95% reflects the addition of a constant fluvial flux to a reduced mine waste flux. Unfortunately, the majority of the EPA ICS data lacked concentration and flow data. Therefore, this reduction was not included in this report.

The theoretical chloride concentration for Seneca Lake increased from 44 to 57 mg/L and sodium increased from 27 to 35 mg/L after adding the mean annual EPA ICS reported flux of

chloride and sodium from the two salt mines. Even these concentrations are significantly below the current concentrations measured in Seneca Lake (128 and 77 mg/L, respectively). Clearly, the lake must have a significant extra source of chloride and sodium, presumably from a groundwater source, as reported by Wing et al. (1995) and later substantiated by Halfman et al. (2006). Alternatively, some other process could be at work in Seneca Lake.

The theoretical calculations also highlight the following: (1) the lake gains an extra 54,000 metric tons of chloride, 32,000 metric tons of sodium and 4,400 metric tons of sulfate each year from another, non-fluvial, source (or sources) to attain their measured concentrations in the lake; (2) carbonate precipitation removes 22,000 metric tons of calcium and 6,100 metric tons of magnesium each year from the water column to attain the measured concentrations in the lake; and (3) the lake is at equilibrium with the measured fluvial inputs of potassium. This grouping is identical to the earlier publications. However the additional data typically increased the concentrations and the fluvial and mine waste fluxes reported earlier (Halfman et al., 2006).

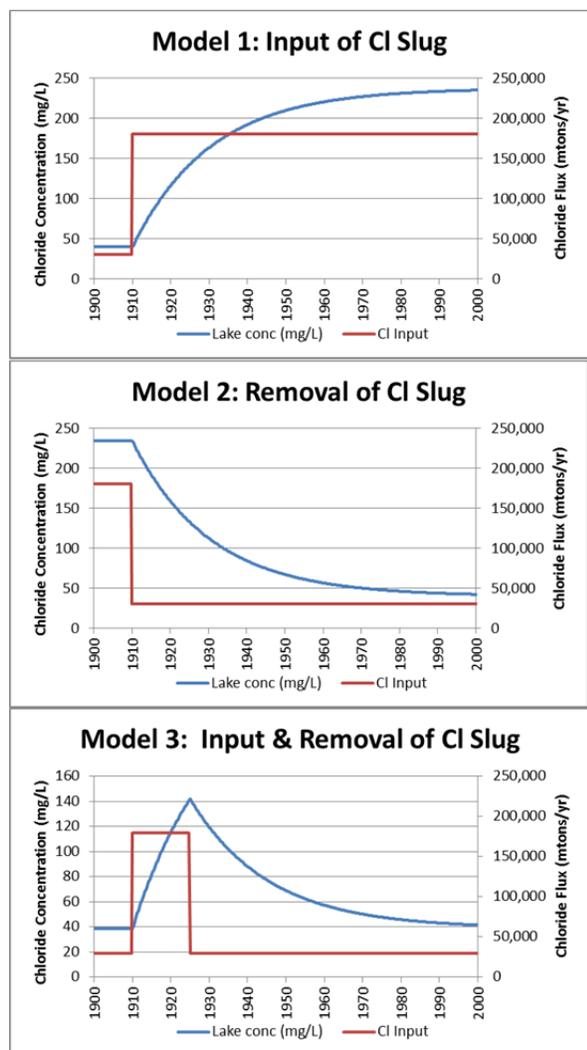


Fig. 8. Modeling Seneca Lake chloride concentrations with three different inputs of chloride.

These theoretical calculations are only valid in steady-state systems, i.e., the ions in the lake must be at equilibrium. This means that the ion inputs and output must be equal and the lake concentrations cannot vary. Three models will help explain this concept (Fig. 8). These models used the assumed hydrology for Seneca Lake to investigate the addition or removal of chloride in a stepwise manner.

Model 1: If the annual flux of chloride to the lake increased in 1910 by five times the original input of ~30,000 mtons/yr to a total influx of 180,000 mtons/yr, then the chloride concentration in the lake would exponentially increase from a concentration of 40 mg/L to a steady-state, equilibrium concentration of 240 mg/L. The right-hand, nearly horizontal portion of the lake concentration curve reveals its approaching to a steady-state concentration. More importantly, the concentration increase is not instantaneous. It takes over 100 years (or greater than five times the water residence time) to exponentially achieve the equilibrium concentration in this lake.

Model 2: If the annual flux of chloride decreased from ~180,000 mtons/yr in 1910 by 150,000 mtons/yr to the 30,000 mtons/yr “original input” of chloride used in the first example, then the chloride concentration in the lake would exponentially decrease from 240 to

a steady-state concentration of 40 mg/L, and more importantly, the freshening would take time, over 100 years in this lake.

Model 3: If the original chloride influx of 30,000 mtons/yr was instantaneously increased in 1910 by five times the original input, but this extra annual input only persisted for 10 years and not for the remaining run as the earlier two models, then chloride concentrations would increase exponentially from 40 mg/L to a peak of 140 mg/L in 1925, and then return to the original concentration of 40 mg/L about 100 years later. Notice, the lake never reaches equilibrium concentrations with the extra input of chloride because the total flux of chloride was reduced before it could reach equilibrium. The model eventually attained equilibrium concentrations near the end of the model run.

These three models suggest that the present day chloride concentration in Seneca Lake could be explained by a one-time addition of a large slug of chloride many years ago, an amount larger than the current fluvial, mine waste and other inputs to the lake. The current lake's concentration could then be influenced by the equilibrium-striving decrease in lake concentrations from the addition of this slug as well as the fluvial and mine waste inputs. The critical factors are the relative quantities of a slug and fluxes to and from the lake as well as the lake's residence time and initial concentration. Thus, it is critical to know the history of chloride in the basin. Was chloride in Seneca Lake at steady-state, i.e., in equilibrium over time? The answer is yes, if the lake had constant chloride concentrations over time. The answer is no, if the concentrations changed over time.

### **Decade-Scale Chloride Concentration Trends:**

Chloride concentrations do change in Seneca Lake on decade- and century-scale time scales. On the decade-scale, annual mean chloride concentrations decreased from 1992 to today (Fig. 9). Annual averages were used to remove any seasonal trends. It was not a uniform decrease over time. Annual mean chloride concentrations remained between 130 and 140 mg/L from 1992 to 2001, rose to 150 mg/L in 2002 and decreased since to 125 mg/L in 2013 with a noticeable dip to 117 mg/L in 2006. The annual mean epilimnetic CTD specific conductance data also consistently decreased from 698  $\mu\text{S}/\text{cm}$  in 2005 to 672  $\mu\text{S}/\text{cm}$  in 2014, earlier data are not available. The potential drivers for this decade-scale decrease in salinity are numerous and include increased rainfall, decreased road salt application and associated fluvial fluxes, increased removal of chloride by the outlet, decreased loading by the salt mines, decreased salt production by the salt mines, and/or some other unknown factor.

Annual precipitation measured by the Cornell's New York State Agricultural Experiment Station in Geneva, NY, revealed variable annual and seasonal precipitation accumulations since 1901 (Fig. 10). The annual precipitation pattern does not correlate with the chloride data ( $r^2 < 0.01$ ). No correlation is detected when using annual precipitation data from the Penn Yan Airport either ( $r^2 = 0.02$ ). However, perhaps these two weather stations are not representative of precipitation totals over the entire lake, as annual rainfall at these two sites does not co-vary as well. Thus, more work is necessary to quantify rainfall patterns and totals over the Finger Lakes region.

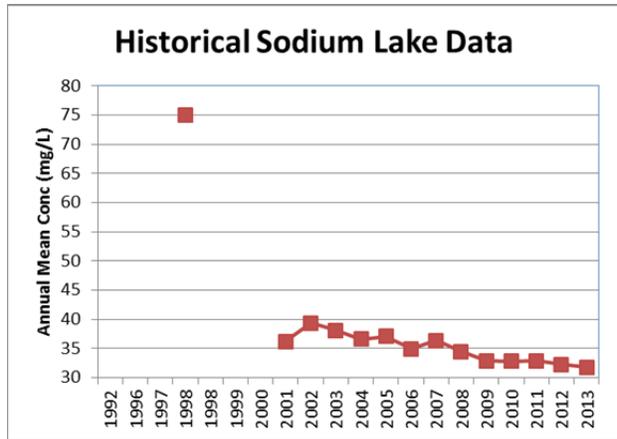
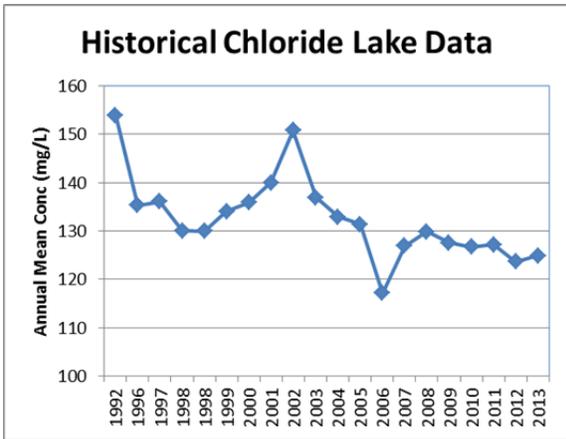


Fig. 9. Annual mean chloride and sodium concentrations in Seneca Lake since 1990.

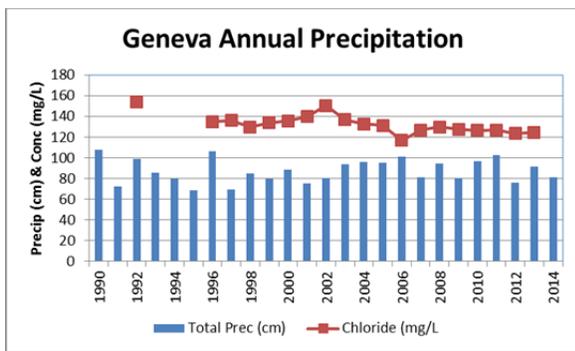


Fig. 10. Annual mean precipitation totals from Agricultural Experiment Station in Geneva, NY.

tonnages supplied to municipalities throughout the northeast and a parallel increase in stream chloride concentrations throughout the northeast during the 1960s and 1990s (e.g., Goodwin et al., 2003, Robinson et al., 2003). It indicates that fluvial sources of chloride increased over time to Seneca Lake, presumably by the increased use of road salts. This hypothesized increase in fluvial fluxes however, are counter to the decade-scale decrease in chloride concentrations in Seneca Lake.

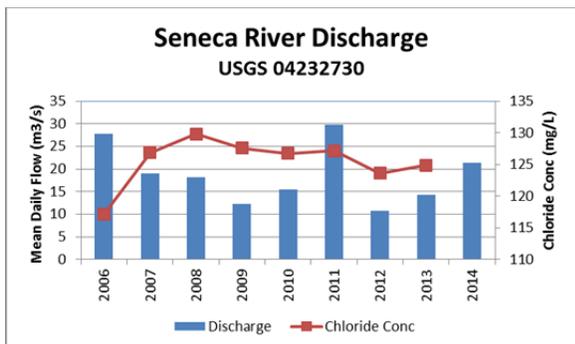


Fig. 11. Annual mean daily outflow discharge from Seneca Lake.

as the calculated fluxes equal the concentration times the discharge ( $r^2 = 0.9$ ). The annual discharges themselves however, do not correlate to the mean annual lake chloride concentrations

Unpublished historical chloride concentrations for Fall Creek, which flows into Cayuga Lake, and Keuka Outlet, which flows into Seneca Lake, increased from < 10 mg/L before 1960, to 10 & 20 mg/L in the 1980s and to 20 & 30 mg/L after the 1990s (Jolly, 2012). A parallel increase in chloride concentration over the past 15 years was also detected in other streams in the Seneca watershed and other Finger Lakes (see subsequent discussion, Fig. 14). These trends are consistent with the known, two-step, increase in road de-icing salt

The outlet removes, on average,  $592 \times 10^6$  m<sup>3</sup>/year of lake water. Thus, 75,800 metric tons of chloride and 45,500 metric tons of sodium are removed, on average, by the outlet each year (Fig. 11). The range in the chloride flux from the lake was 40,000 to 120,000 metric tons/yr for chloride and 25,000 to 71,000 metric tons/yr for sodium using the measured annual variability in the outflow and the annual mean chloride and sodium concentrations in the lake. The annual chloride fluxes out of the lake do correlate to the chloride concentrations in the lake, as expected,

( $r^2 = 0.1$ ). Thus, the outlet removes the chloride available in the lake but does not appear to control the chloride concentration.

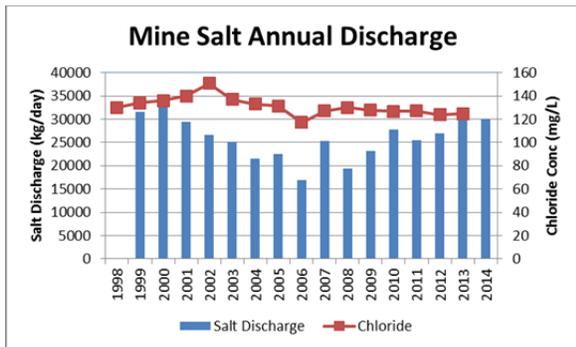


Fig. 12. Annual mean salt-mine discharge of waste chloride and sodium to the lake from the two salt mines near Watkins Glen.

The combined chloride loading from the two salt mines near Watkins Glen decreased from 1999 through 2006 from approximately 34,000 kg/day to 17,000 kg/day, and then returned to 1999 loads (30,000 kg/day) by 2014 (Fig. 12, EPA ICS web site). This pattern however does not directly co-vary with the chloride data ( $r^2 < 0.1$ ) but reveals a weak correlation when the salt loads are compared to the following year's chloride data ( $r^2 = 0.3$ ). The lag is expected because the modeled change in the lake's concentration happens after a change in the inputs or outputs, but the delay should be a few more years in this lake.

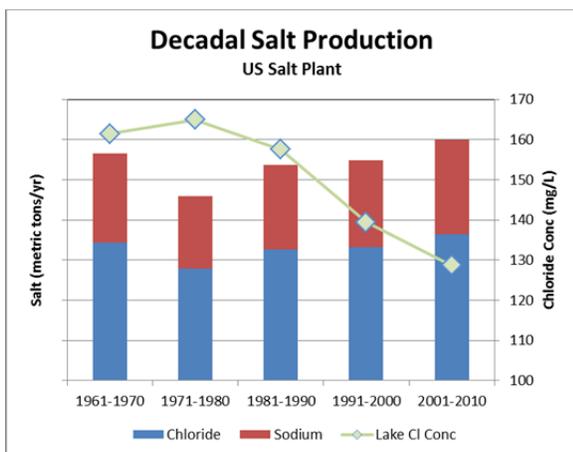


Fig. 13. Decadal mean mine production data from US Salt, Watkins Glen. The units for salt production are omitted due to their proprietary nature.

Finally, salt production may influence the input of salt to the lake (Fig. 13). A presumed increased in fluid pressures applied to the salt caverns for additional salt production may induce more salt seepage into the lake from the bedrock. However, decadal salt production data from US Salt at Watkins Glen starting in the 1960s negatively correlates to the decadal average salt concentration in the lake ( $r^2 = 0.5$ ). Unfortunately, Cargill was unwilling to provide salt production data.

Thus, the observed 20-year decline in chloride concentrations does not correlate to the available annual rainfall totals, fluvial records of road salt loads, Seneca River outflow, salt mine waste discharge rates, and the available salt mine production data. Perhaps a number of these processes combined to generate the observed decrease in chloride concentrations in the lake. Unfortunately, these signals are too short to isolate the specific contributions of each. The decrease in chloride concentrations over the past few decades however, indicates a more important conclusion. The chloride concentrations in the lake and chloride inputs and outputs are not at equilibrium, i.e., not at steady-state in this watershed as previously assumed.

This suggests two non-steady state possibilities to explain the long-term changes in chloride concentrations in the lake. The lake may be becoming fresher with time after a large amount of salt was added a few decades earlier despite the increase in fluvial sources, and/or the seepage of salt from the ground may have decreased over time. If either are true, then the decade-scale correlations are probably not critical because the record would be dictated by

another, more influential control. Long-term, century-scale records are required to investigate these possible mechanisms.

### Century-Scale Chloride Concentration Trends:

Two groups of chloride trends are evident in the available long-term data. Data from Hemlock, Canadice, Canandaigua, Keuka, Owasco, Skaneateles and Otisco Lakes revealed increasing chloride concentrations over time (Fig. 14). The three longest data sets in this group revealed a small (a few mg/L) increase in the 1960s. All of the data sets note a second, more pronounced, increase by 10 to 20 mg/L in the mid to late 1990s. The concentrations have not significantly changed since 2005. These increases are interpreted to mimic the increased use of road de-icing salts in the Finger Lakes region in the 1960s and another larger increase in the 1990s, as discussed above. The increased fluvial fluxes therefore increase chloride concentrations in all the Finger Lakes, except Cayuga and Seneca Lakes.

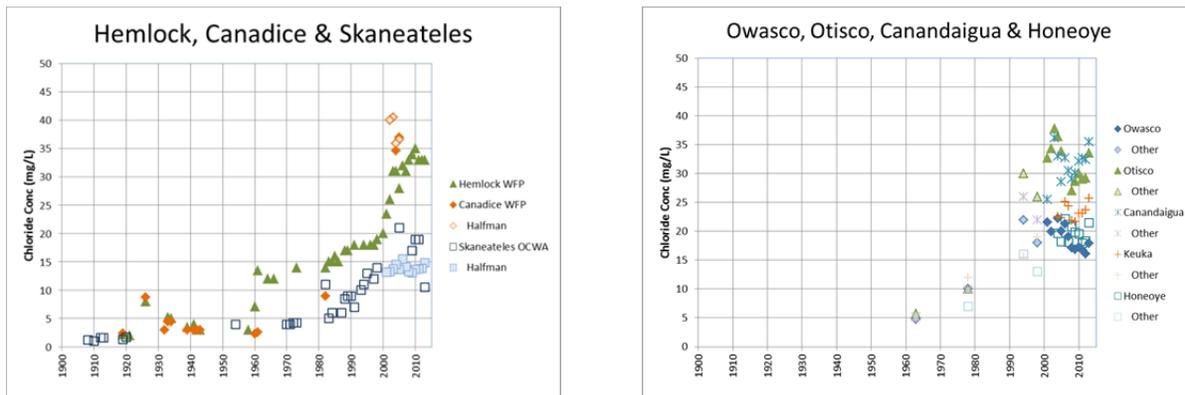


Fig. 14. Available annually-averaged century-scale chloride data from Hemlock, Canadice, Canandaigua, Keuka, Owasco, Skaneateles and Otisco Lakes (refs in text).

Curiously, Hemlock, Candice, Canandaigua and Otisco Lakes had larger concentrations than Skaneateles and Owasco Lakes since the 1990s, a circumstance that might be related to road density and bedrock composition. Road density weakly correlates ( $r^2 = 0.4$ ) to recent chloride concentrations, if Keuka Lake is excluded from the analysis. Weathering of some rock types would liberate more chloride and sodium than others. Carbonates (and interbedded sulfates and halides) comprise up to 5% percent the bedrock underlying Skaneateles, Canandaigua, Owasco and Otisco watersheds, and none underlies Hemlock and Candice watersheds. The bedrock variability does not parallel the chloride trends. The small concentrations in Skaneateles Lake may reflect a strong history of water quality protection in this watershed, as the lake is one of a handful of water bodies across the US with a filtration exception for public drinking water use. However, Owasco Lake has a similar low chloride concentration but is less regulated in its watershed protection. A tally of the actual salt tonnage applied in the individual watersheds over time would help answer this curiosity but it is beyond the scope of this report. Please note: Luckily, the Finger Lakes have not attained chloride concentrations as large as those observed in some of the urban waterways of the northeast, that has prompted the creation “salt-free” or “salt-reduction” roadway zones that fall within the watersheds of critical water supplies for major metropolitan areas.

Chloride concentrations in Seneca and Cayuga Lakes were consistently larger than the other Finger Lakes throughout the past century, and the rise in chloride concentrations started significantly earlier than what was observed in the other Finger Lakes, as well (Fig. 15). In Seneca, and to a lesser extent in Cayuga lake, chloride concentrations steadily increased from 40 mg/L in the early 1900s to a pronounced peak starting at 1965 that lasted for 5 to 10 years. Chloride concentrations declined afterwards as noted in the decade-scale data. Some scatter is observed in the raw data, especially during the 1965 to 1975 concentration peak, but the century-scale trend is unique. The decline since 1975 is notable because the concentration declined in both lakes despite likely increased fluvial inputs of chloride over time.

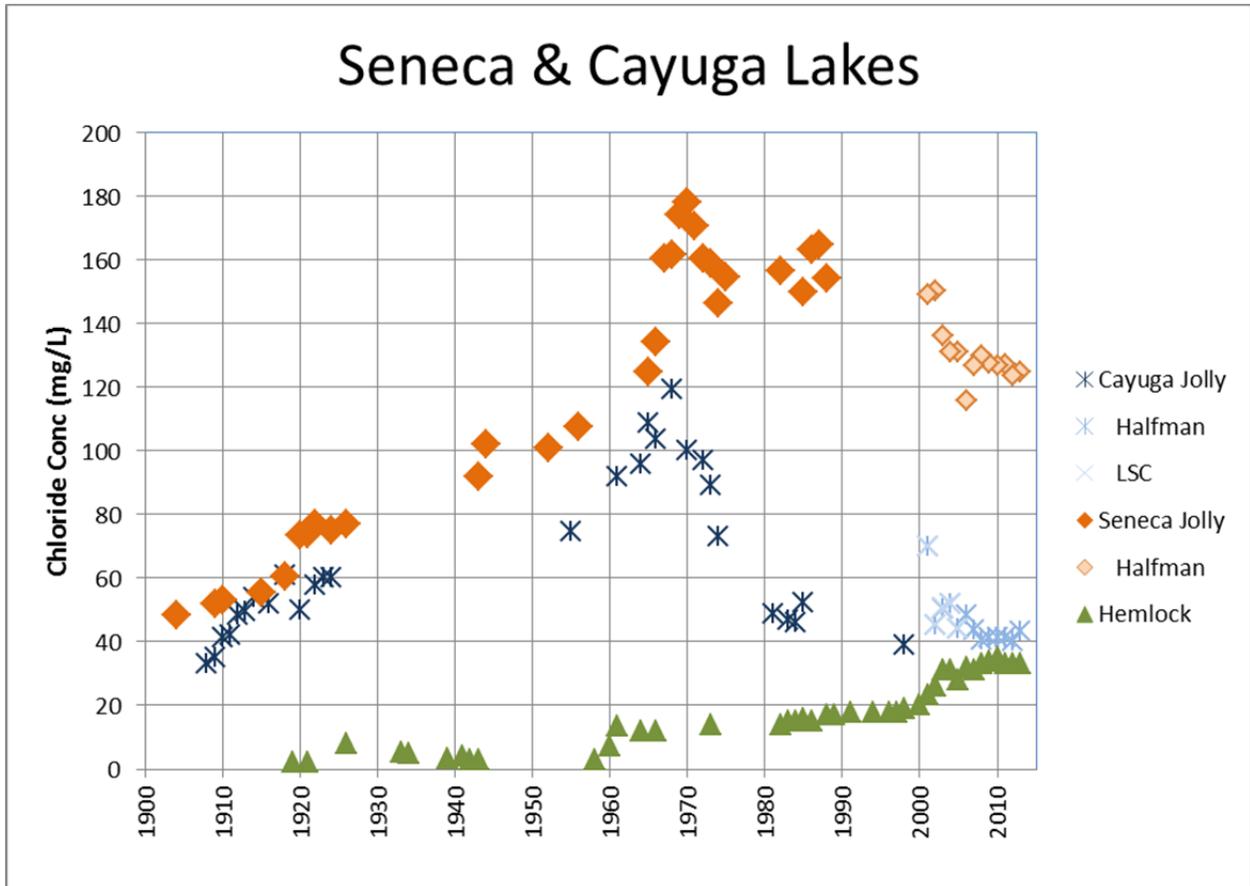


Fig. 15. Available annually-averaged century-scale chloride data from Seneca and Cayuga Lakes (Jolly, 2005, 2006, Hemlock Water Filtration Plant, Cornell's Lake Source Cooling (LSC) Data, Halfman et al., 2006).

Effler et al. (1989) wrote that their complete-mixed model of the decrease in Cayuga chloride concentrations since the 1965 to 1975 peak is consistent with an abrupt decrease in salt mine wastes input into the lake at that time, and subsequent freshening of the lake since as the lake regained equilibrium to the entering fluvial and mine waste fluxes. The 1970s timing corresponds with a major change in the disposal methods for salt tailings from the Cargill Rock-Salt Plant in the Cayuga watershed. This change significantly decreased chloride disposal into the lake. Now, chloride concentrations in Cayuga Lake are similar to the saltier members of other Finger Lakes, and suggest that the chloride in Cayuga Lake reached equilibrium from its 1960s slug and has now returned to steady-state conditions as predicted by Effler. Presumably chloride in Cayuga Lake is currently supported by fluvial and mine waste inputs. It also implies

that mining practices probably controlled the pre-1960 elevated chloride concentrations. Thus, Cayuga Lake may never have received any groundwater inputs over the past century. Maybe Cayuga Lake is not deep enough to intersect the Silurian rock salts underneath the basin as previously postulated which eliminates an avenue for groundwater inputs.

Seneca Lake chloride concentrations were consistently larger than any other Finger Lake during the past century (Fig. 5). The earliest chloride concentrations measured in Seneca Lake were 48 and 49 mg/L in 1904, a concentration near but slightly larger than those of the other modern day Finger Lakes. These early 1900s Seneca Lake concentrations were significantly larger than the early 1900s data reported for Skaneateles and Hemlock Lakes. Chloride concentrations clearly varied over time in Seneca Lake as well, increasing from the early 1900s to a concentration peak from 1965 to 1975, and declining since.

The changes were modeled for the Seneca Lake Watershed Management Plan: Characterization and Evaluation report using a non-steady state, mass balance approach (Fig. 16, Halfman et al., 2012). The model assumed a constant inflow of water ( $863 \times 10^6 \text{ m}^3/\text{yr}$ ), a constant evaporation rate ( $103 \times 10^6 \text{ m}^3/\text{yr}$ ) and a constant surface water outflow ( $760 \times 10^6 \text{ m}^3/\text{yr}$ ) as before. It also assumed an initial input of chloride ( $30,000 \text{ mtons/yr}$ ) to attain an assumed pre-1900 chloride concentration of  $40 \text{ mg/L}$  in the lake. The model did not attempt to differentiate one chloride source from another. Rather it lumped all sources together into one to determine the total quantity of chloride, in units of the initial input ( $30,000 \text{ mton/yr}$ ), that must be added to, or removed from, the lake to mimic the concentration distribution over time.

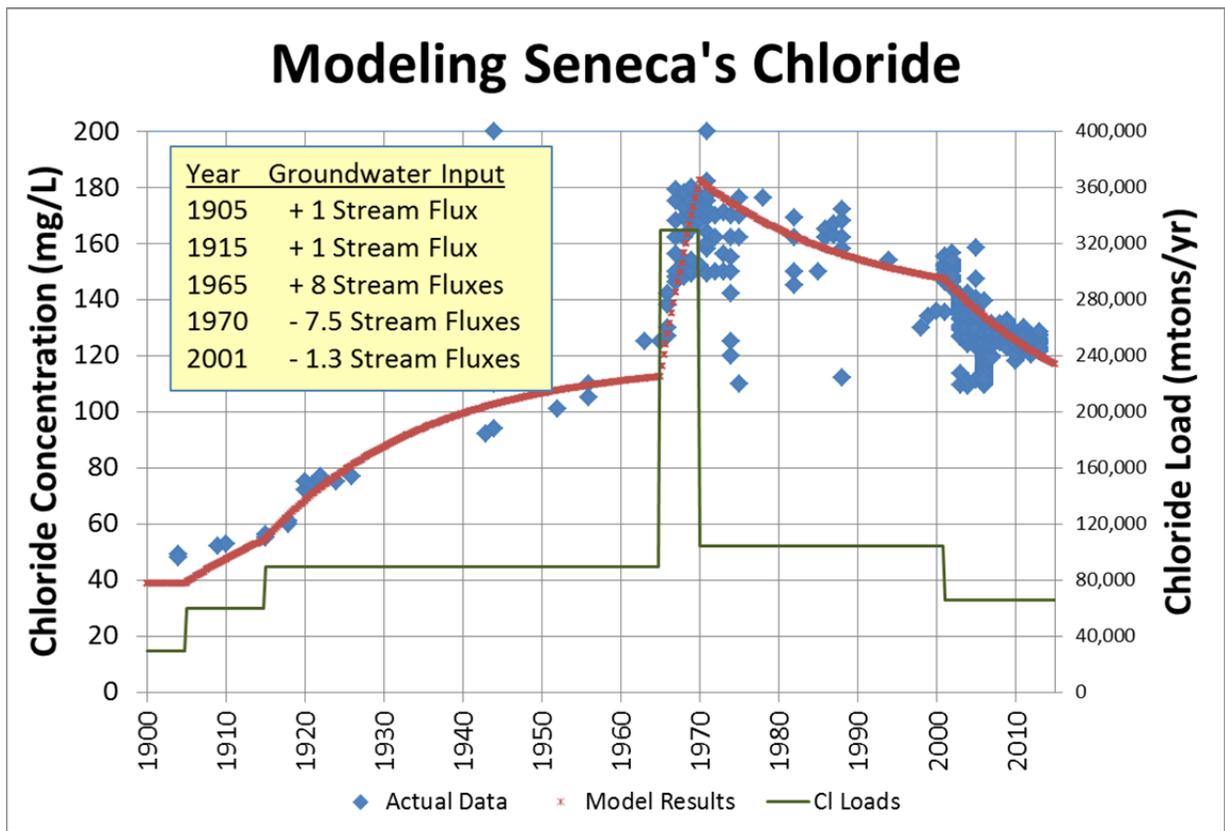


Fig. 16. Modelling changes in the total chloride flux to attain the historical record of chloride concentrations in Seneca Lake (updated from Halfman et al., 2012).

The model indicates that increasing the influx of chloride by 1 initial unit (increase by 30,000 mtons/yr) in 1905, by another 1 initial unit in 1915, then once again by 8 additional units in 1965, provides enough chloride to attain the peak concentrations in the 1970s. At this time, some ~ 350,000 mtons of chloride were added to the lake each year. Then, the model decreased the input of chloride by 7.5 units in 1970, and another 1.3 units in 2001, to achieve the observed decrease in chloride concentrations since the 1965 to 1975 peak to today. Over the entire century, the net increase in the total chloride fluxes from 1900 loads was 36,000 mtons/yr. Most of the changes in chloride fluxes never attained equilibrium concentrations, especially since 1965. Regardless, this model has shown that the input of chloride to the lake increased above the initial input of 30,000 mtons/yr until the mid-century peak in chloride concentrations, and this excess was subsequently and almost completely turned off by 2001. It also revealed that chloride in Seneca Lake should eventually return to equilibrium concentration of 85 mg/L by 2085 assuming nothing modulates chloride inputs and/or outputs in the future from the current fluvial and mine waste inputs, and outlet outputs. The decline since 1970 can explain the recent decade-scale decrease in chloride concentrations.

### **Chloride Sources:**

The model unfortunately could not differentiate the sources for the chloride or the relative proportion of one source to another because critical numbers are lacking. The existing data only indicate that fluvial, mine wastes, mine accidents, and perhaps groundwater sources have all played an important role in the history of chloride in Seneca Lake. A few points in time are worth mentioning though.

Today's concentration in the lake reflects its attempt to reach equilibrium concentrations from the large slug of chloride that entered the lake back in the 1960s, along with the current inputs from the streams and mines. The overprint of the mid-century chloride slug on subsequent chloride concentrations in the lake, and the decreasing salinities since the 1970s also precludes any attempts to look for any correlations between potential forcing functions and the past 50 years of chloride concentrations in the lake as attempted earlier in this report.

The next period of time worth noting is the early 1900s. The historical records from Fall Creek, Keuka Outlet, and other Finger Lakes outlined above indicate that fluvial sources to Seneca Lake, were smaller in the early 1900s than today. The 1900 fluvial flux to Seneca Lake is estimated at 15,000 mtons/yr, assuming the present-day hydrologic budget in Seneca Lake and a fluvial supported equilibrium concentration of 20 mg/L, which was the earliest concentration detected in Hemlock Lake and the largest in the available historical lake data. Combining the estimated 1900 fluvial fluxes with a mine waste identical to today's discharge (~9,000 mtons/yr), results in an input of chloride that is still insufficient to attain a combined input of 35,000 mtons/yr during the early 1900s. Perhaps mine wastes were larger back then. Reliable data are not publically available to investigate this possibility. Perhaps groundwater inputs were active back then. As earlier authors stated, Seneca Lake's depth, deeper than any of the other Finger Lakes, provides an avenue for saline groundwater to enter the lake from the rock salt formations.

Another significant point in time is the 1965 to 1975 peak in chloride concentrations. Brine pool leaks, injection of saline wastes into leaky fractured bedrock (carbonates, sandstones and shales), dust from piles of rock salt and other issues at the abandoned hard-rock Morton-Himrod mine located in the Plum Point subwatershed influenced the 1965 to 1975 chloride peak detected in the lake. According to newspaper articles, the opening of the Himrod mine in the late 1960s came with a number of mine waste “issues” that resulted in the leakage of an estimated 1.1 million tons of salt into the lake. The concentration spike is consistent with the chloride record if it leaked over a span of a few years. Specific details follow: The mine started construction in 1969. By 1973 a news report stated neighbors complained of salt disposal down Plum Point Creek beginning in the fall of 1972, most likely due to brine pool breaches. The mine shut down in 1979 after extracting 4,000 tons of salt a day from the ground. Saline water still flows down Plum Point Creek, as mentioned above, probably a legacy issue from the abandoned mine but also from a high density of roads and de-icing salts. The 1.1 million ton leakage of salt is similar to the modeled input to generate the 1965 to 1975 peak, if discharged into the lake over a period of a few years. Unfortunately, the timing of the mine “issues” post-date the rise in chloride concentrations in the lake by a few years so the event does not explain the entire peak but rather sustained the peak for a few years. Thus, some other unknown source must have combined with the Himrod mine accidents to create the chloride peak. Was it a modulation of mine wastes and/or groundwater inputs and/or something else? Data are lacking to answer this important question.

Groundwater inputs may still be a significant source of chloride to Seneca Lake. Earthquakes could have opened and closed the abundant fractures in the local bedrock and provide avenues for groundwater flow during discrete intervals of time in the lake’s geologic history. The shale-rich bedrock in the region is full of fractures (Jacobi, 2002). This is especially true at depths shallower than 1,000 meters. Natural gas companies will not “frack” the Marcellus Shale shallower than 1,000 meters because the unit was already naturally fractured and released its gas. These fractures could have opened and closed as the region experienced the occasional earthquake and associated ground movements. Earthquakes have occurred in the region, as strong as 5.8 on the Richter Scale, especially along the St Lawrence Seaway but also within the central and western portion of New York. The solution cavities used by the mining companies typically eroded into the non-salt bedrock above and below and interbedded within the salt layers. These cavity wall breaches into interbedded and neighboring bedrock could have provided an avenue for groundwater flow.

Alternatively, pressures from the solution mining processes at the Cargill and US Salt mines near Watkins Glen may have also induced saline groundwater flow into the lake. The onset of mining practices in the late 1800s may have increased the formation pressures to stimulate groundwater flow into the lake, i.e., sufficiently pressurize the unit so groundwater could flow uphill and overcome gravity. Thus, the rise and fall of mining pressures may have modulated the chloride concentration in the lake. However, a gentle 1° southerly dip of the bedrock, the density of the brine, and a southward location of the mines from where the bedrock intersects the lake, creates a difficult hurdle for this groundwater flow. As a general rule, groundwater always flows downhill under the force of gravity unless additional pressures push the water to overcome gravity. The available 50-year production data from US Salt also negatively correlates to the chloride concentrations. Yet, artesian systems and saline springs are found in the region, e.g., Tully Valley, Clifton Springs, Geneva, and other locations in New York

State. The possibility that mining pressure has induced the flow of chloride into the lake has implications for the current proposal to store liquid propane and natural gas in the abandoned salt cavities. I would highly recommend a pressure test of the abandoned salt cavities and check for any rise in the chloride and/or sodium concentrations throughout the lake before they are used to store liquid propane and natural gas. Alternatively, any leakage from the current storage of natural gas in abandoned salt cavities on the US Salt property should be made public to ferret out or put to rest these concerns.

## **Conclusions:**

Decade and century-scale records of salt content in the majority of the Finger Lakes dictate a two-part, step-wise increase in the fluvial inputs of chloride to the lakes, during the 1960s and 1990s. The increase in chloride concentrations parallels the documented increase in fluvial chloride concentrations across the northeast and in two local streams from the increased use of road de-icing salts to keep roadways ice-free. The historical chloride concentration pattern for and source of chloride ions to Seneca and Cayuga Lakes were different. Cayuga Lake was influenced by extra mine wastes discharged into the lake up to and during the 1970s. Its chloride concentrations have decreased since, to the early 2000s as the lake moved towards equilibrium concentrations after the 1970s pulse. The present day chloride content in Cayuga Lake is presumably supported by the present-day fluvial and mine waste inputs.

The century-scale history of chloride in Seneca Lake revealed chloride concentrations of ~40 mg/L at the turn of the 20<sup>th</sup> century, smaller than any other time in the lake's history, but larger than nearly all of the other Finger Lakes. The history also revealed much larger concentrations during a mid-century peak of 180 mg/L only to subsequently decline to the present day concentrations of 125 mg/L. The earliest recorded concentrations are much larger than those found in other lakes, and indicate that fluvial sources alone were insufficient to support Seneca's chloride concentrations at the turn of the 20<sup>th</sup> century. Either significantly larger mine wastes than today's inputs and/or a significant groundwater flux is/are required to reach these earliest concentrations.

Models indicate that significant increase in the annual chloride loads were required during 1905 and again in 1915 to attain the slow historical rise in concentrations from 1900 to 1965. The fluvial sources were insufficient at that time and must have been augmented by mine wastes larger than present day inputs and/or groundwater inputs. A slug of chloride leaked into Seneca Lake from the now abandoned Morton-Himrod mine probably sustained the mid-century chloride peak but its release was a few years after the chloride rise and thus cannot be the sole cause of the peak. Since the late 1800s, solution mining operations at the southern end of the lake have discharge chloride-rich brines into Seneca Lake. The loads from reliable sources are unknown until the late 1990s, but the reported loads and the recent fluvial fluxes are still insufficient to attain or even modulate the record of concentrations in the lake. However, the recent concentrations do not require groundwater inputs to attain the present day concentration in the lake, as hypothesized by previous authors. The elevated concentration observed today can be attributed to the time lag to reach equilibrium from the input of the 1970s slug of chloride.

It follows that Seneca Lake has had a multifaceted chloride history. Sources include the streams, mine wastes, former mine issues, and groundwater. Stream inputs have limited data throughout the century and still need to be estimated from century-scale records from neighboring lakes to fill in the gaps. Reliable mine waste reports were only available since the late 1990s. Earlier reliable records would help answer questions in the total chloride input to the lake over the past century. The former Himrod mine “issues” are unfortunate, but provide a glimpse into what might happen if another slug of chloride enters the lake. Finally, groundwater inputs are the biggest unknown. They were postulated to make up the present day gap in chloride inputs, but recent evidence presented here suggests groundwater inputs are probably not required today. This does not preclude significant groundwater inputs during the past. Once these source questions are sorted out, the next generation of models will probably glean additional insights into the chloride history of Seneca Lake.

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Appendix:

Table 3. Results from the 10/25/2014 full-lake cruise.

Sites	Chloride (Cl mg/L)		Sulfate (SO4 mg/L)		Sodium (Na mg/L)		Potassium (K mg/L)		Magnesium (Mg mg/L)		Calcium (Ca mg/L)	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	122.3	121.2	31.6	31.5	75.7	75.2	5.4	5.3	10.5	10.5	36.2	36.5
3	121.6	126.9	31.5	32.4	75.0	77.7	5.4	5.5	10.5	10.6	36.5	38.0
5	122.9	129.2	31.5	32.6	75.0	78.9	5.4	5.5	10.5	10.7	36.6	38.4
6	122.2	128.1	31.5	32.5	74.9	78.3	5.3	5.5	10.6	10.6	36.7	38.3
7	121.6	137.6	31.3	33.2	74.9	84.5	5.4	5.7	10.6	10.8	37.1	39.6
8	121.4	135.8	31.2	33.0	75.1	83.8	5.4	5.7	10.6	10.8	37.2	39.4
9	121.1	127.4	31.1	32.0	75.0	78.9	5.4	5.5	10.6	10.7	37.0	38.8
10	120.8	124.1	31.1	31.7	74.7	76.6	5.6	5.6	10.6	10.7	37.1	38.5
11	121.4	125.7	31.1	32.3	75.1	76.8	5.5	5.6	10.7	10.6	37.4	38.5
Average	121.7	128.4	31.3	32.4	75.0	79.0	5.4	5.5	10.6	10.7	36.9	38.4

Data Comparison between Labs

Sites	Chloride (Cl mg/L)		Chloride CSI		Sites	Sodium (Na mg/L)		Sodium CSI	
	Surface	Bottom	Surface	Bottom		Surface	Bottom	Surface	Bottom
1	122.3	121.2	128	131	1	75.7	75.2	80	79
3	121.6	126.9	130	133	3	75.0	77.7	78	81
5	122.9	129.2	130	131	5	75.0	78.9	76	83
6	122.2	128.1	129	132	6	74.9	78.3	83	79
7	121.6	137.6	132	146	7	74.9	84.5	81	90
8	121.4	135.8	127	139	8	75.1	83.8	78	91
9	121.1	127.4	129	136	9	75.0	78.9	80	86
10	120.8	124.1	130	131	10	74.7	76.6	83	83
11	121.4	125.7	129	132	11	75.1	76.8	80	81
Average	121.7	128.4	129	135	Average	75.0	79.0	80	84

Sites	Sp Cond (uS/cm)		Sp Cond CSI		Sites	Sp Cond (uS/cm)		Sp Cond CTD	
	Surface	Bottom	Surface	Bottom		Surface	Bottom	Surface	Bottom
1	675.0	684.0	654	669	1	675.0	684.0	666	673
3	666.0	719.0	662	680	3	666.0	719.0	662	705
5	669.0	730.0	660	692	5	669.0	730.0	663	712
6	671.0	728.0	662	690	6	671.0	728.0	662	710
7	668.0	760.0	665	728	7	668.0	760.0	663	747
8	677.0	763.0	667	720	8	677.0	763.0	664	741
9	670.0	730.0	668	667	9	670.0	730.0	664	714
10	671.0	704.0	655	680	10	671.0	704.0	663	698
11	668.0	716.0	666	683	11	668.0	716.0	665	701
Average	670.6	726.0	662	690	Average	670.6	726.0	663.5	711.1

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