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Chloride hydrogeochemistry of the finger lakes in Central and Western New York, USA

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ABSTRACT

Road deicing salts have impacted the hydrogeochemistry of lakes throughout the snow-belt region of the globe. This paper advances our understanding of the historical change in salt concentrations in, and sources to, the Finger Lakes of western and central New York state, and compares the results to other lakes across the globe. Surface water samples from Honeoye, Canandaigua, Keuka, Seneca, Cayuga, Owasco, Skaneateles and Otisco lakes were analyzed for chloride (Cl) concentrations, and augmented with published and unpublished decade, and for the first time, century-scale Cl data for these lakes and Hemlock Lake. A mass-balance model estimated the Cl flux required to match the measured Cl concentrations in each lake. Cl concentration and flux trends defined two groups of lakes. Group 1: A mid-1900′s peak in Cl concentrations was detected in Seneca and Cayuga lakes, that resulted from a short but significant spike of Cl, most likely from salt mine wastes during pre-Environmental Protection Agency times. Group 2: Hemlock, Honeoye, Canandaigua, Keuka, Owasco, Skaneateles and Otisco lakes, revealed smaller yet increasing concentrations and fluxes over time that were interpreted to reflect increasing use of road deicing salts in their watersheds and supported by correlations to their state and federal road lengths, percentage of impervious surfaces, water residence times in each watershed and the production of road salt in the US, but not to their trophic status, nor their percentage of agricultural land. Estimated Cl inputs from municipal wastewater treatment facilities, individual septic systems and the atmosphere (precipitation) were also insignificant in the Finger Lakes region. These results help clarify the processes responsible for increasing Chloride concentrations in lakes globally.

1. Introduction

Since pioneering road salt use during the late 1930 s in New Hampshire, USA, the use of road deicing salts has spread throughout the snow belt regions (areas influenced by snowfall) of the globe, and, as a result, increased the salinity of adjacent streams, lakes, and even the Laurentian Great Lakes (e.g., Mairs, 1967, Sutcliffe and Carrick, 1983, Smith et al., 1987, Siver et al., 1996, Robinson et al., 2003, Thunqvist, 2003, Kaushal et al., 2005, Novotny et al., 2008, Chapra et al., 2009, Daley et al., 2009, Bonte and Zwolsman, 2010, Steele and Aitkenhead-Perterson, 2011, Muller and Gachter, 2012, Corsi et al., 2015, Rogola et al., 2015, Dugan et al., 2017a; b, Zuidema et al., 2018, Dugan et al., 2020, Yao et al., 2020, Dixon et al., 2022, Dugan et al., 2023). Modeling of salt application rates, road density and runoff for lakes across the USA indicated that lakes in Minnesota, Wisconsin, Michigan, New York, Ohio, Indiana, Pennsylvania, and New England are most susceptible to increased salinities (Solomon et al., 2023). The rise in salinity has also impacted aquatic biota (e.g., Richburg et al., 2001, Twiari and Rachlin, 2018, Hintz and Relyea, 2019, Arnott et al., 2020). Chloride's increased impact on human health, aquatic biota, and infrastructure (e.g., lead and copper pipe corrosion) has initiated a reversal in Cl concentrations in some lakes achieved by reduced road deicing salt technologies and/or use of alternative deicing materials (e.g., Sutherland et al., 2018).

Decade-scale increases in Cl concentrations in lakes or streams are typically attributed to increased use of road deicing salts in the watershed. Some authors investigated other human-induced sources of Cl, including municipal wastewater treatment facilities (MWWTFs), septic systems, agricultural fertilizers (e.g., potash and other fertilizers), livestock waste, and atmospheric deposition (Kelly et al., 2010; Heisig, 2000; Stets et al., 2020; Overbo et al., 2021; Rossi et al., 2022). MWWTFs and septic systems influence Cl concentrations primarily through the use of water softeners, because they typically replace Calcium with Sodium (the Sodium from NaCl crystals) using a cation

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exchange process, to consumers supplied with ‘hard’ water. More sophisticated statistics were used to untangle the relative contributions of multiple sources (e.g., Rossi et al., 2022). The diversity in the Finger Lakes and their watersheds provide an ideal natural laboratory to assess the relative impact of all these sources of Cl in a rural setting.

The eleven Finger Lakes of western and central New York are critical to the health, well-being and economy of the rural region. The lakes contain 8.1 trillion gallons (30.8 km^3) of water and their watersheds span a 2630 $mile^2$ area (4970 km^2, Fig. 1, Table 1). These lakes are a source of Class-AA drinking water, i.e., water suitable for drinking, culinary or food processing purposes; primary and secondary contact recreation; and fishing (6 CRR-NY 701.5, 2021), to 1.5 million residents in the surrounding communities including neighboring Syracuse and Rochester, and for the billion-dollar agricultural-winery-tourism based economy in this rural region. These lakes also provide an ideal natural laboratory to investigate watershed-lake hydrogeochemical processes and interactions, like the source of Cl to these lakes, as these lakes offer a range of maximum depths (9 to 186 m), maximum widths (0.6 – 5.6 km), lengths (5 – 61 km), surface areas (3 to 175 km^2), volumes (0.035 – 15.54 km^3), watershed areas (32 – 1870 km^2), water residence times (0.8 – 18.1 years), state & federal road lengths (0 to 1410 km) and densities (length/watershed area, 0.00 to 9.2 km/km^2), land use activities (agriculture: 9 – 50%, forests: 31 - 77%, urban: 3 – 6%, wetlands: 2 – 6%), percent impervious surfaces (0.5 – 1.1%), and trophic levels (ultra-oligotrophic to eutrophic, e.g., Bloomfield, 1978, Callinan, 2001, Halfman, 2017, Clinkhammer et al., 2019, Table 1).

In New York state, road deicing salts have impacted numerous watersheds. Studies detailed a decadal increase in chloride concentrations over time in nearby streams, lakes and groundwater systems, and some compared the results to deicing salt spreading rates, manufacturing wastes, and estimated inputs from municipal wastewater treatment facilities and septic systems (e.g., Effler et al., 1986, Heisig, 2000, Godwin et al., 2003, Kelly et al., 2010, Kelting et al., 2012, Sutherland et al., 2018). A combination of salt mine wastes, salt mine collapse, and/or groundwater seepage from the underlying Silurian Salina and other evaporite beds are also proposed sources of Cl to Seneca, Cayuga and neighboring areas (e.g., Ahrnsbrak, 1975, Schnaffer and Oglesby, 1978, Effler et al., 1986, Effler et al., 1989, Wing et al., 1995, Kappel, 1996, Callinan, 2001, Halfman et al., 2006, Shaw et al., 2011, Yager, 2013). Mining these rock salt beds support a segment of the local economy as well (Lilek, 2017). For example, the American Rock Salt Mine, Mount Morris, NY, just west of the Finger Lakes produces $\sim$5 million metric tons of road salt each year.

Earlier publications on the salinity and Cl concentrations of the

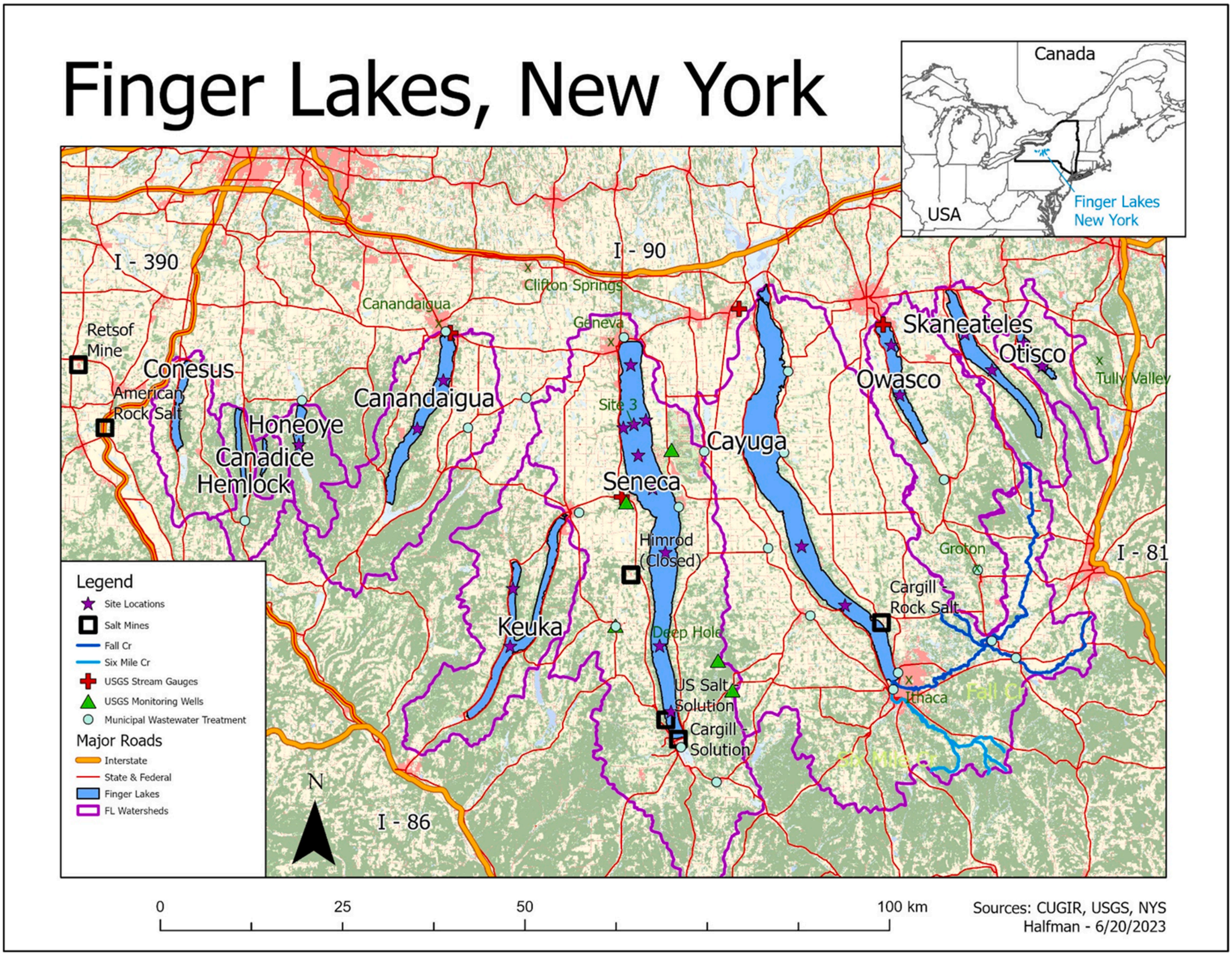

Fig. 1. A map of Finger Lakes and surrounding land use. The location of sample sites, major roads, active and abandoned salt mines, Fall & Six Mile Creeks, USGS Outlet flow and groundwater monitoring wells, and municipal wastewater treatment facilities that discharge into Finger Lake watersheds (NYS WWTP Map, 2023) are also shown.

Table 1
Finger Lakes Statistics.

Finger Lake	Maximum Depth[1] (m)	Length[1] (km)	Maximum Width[1] (km)	Surface Area[1] (km^2)	Watershed Area[1] (km^2)	Volume[1] (km^3)	Residence Time[2] (y)	Length Federal & State Roads (km)	Agr, For, Urban Land Use (%)NLCD (2019)	Impervious Surfaces (%)NLCD (2019)	Historical Trophic Status[2] (code[3]); Most Recent[4]
Conesus	18	125.6	1.3	13.6	180.5	0.157	1.4 - 2.5	111.2	40, 42.9, 6.2	0.39	Eutrophic (5) Now Mesotrophic
Hemlock	29	10.8	0.8	7.2	96	0.106	2.0 - 2.5	707.0	21.9, 62.8, 4.9	0.53	Oligo-Mesotrophic (2) Now Eutrophic
Canadice	27	5.1	0.6	2.6	32	0.043	2.0 - 4.5	0.0	9.2, 76.7, 2.9	0.40	Oligo-Mesotrophic (2) Now Mesotrophic
Honeoye	9	6.6	1.4	7.1	95	0.035	0.8 - 1.5	341.1	11.6, 73.4, 3.7	0.46	Eutrophic (5)
Canandaigua	84	24.9	2.4	42.3	477	1.64	7.4 - 10.0	1182.9	34.7, 47.1, 5.7	0.64	Oligotrophic (1) Mesotrophic
Keuka	57	31.6	3.3	47.0	405	1.434	6.0 - 8.0	989.4	31.9, 50.5, 5.3	0.54	Oligo-Mesotrophic (2) Mesotrophic
Seneca	186	56.6	5.2	175.4	1181	15.54	12.0 – 23.0	976.0	40, 38.2, 6.3	1.07	Oligo-Mesotrophic (2) Mesotrophic
Cayuga	132	61.4	5.6	172.1	1145	9.379	8.5 - 10.0	1175.6	50.3, 30.6, 6	0.98	Oligo-Mesotrophic (2) Mesotrophic
Owasco	52	17.9	2.1	26.7	470	0.781	1.5 - 3.1	1326.9	48.8, 35.4, 4.5	0.50	Mesotrophic (3)
Skaneateles	84	24.2	3.3	35.9	154	1.563	8.5 - 17.7	1410.8	36.4, 36.9, 5.6	0.72	Oligotrophic (1)
Otisco	20	8.7	1.2	7.6	94	0.078	1.0 - 1.9	691.9	43.6, 40.9, 4.5	0.54	Eutrophic (5)

[1]Mullins et al., (1996), [2]Callinan (2001), Halfman (2017), [3]In parentheses is the trophic status code used in the correlations, [4]Clinkhammer et al. (2019)

Finger Lakes focused on the impact by local salt mine wastes and groundwater inputs to Seneca and Cayuga lakes, and not road salt. Ahrnsbrak (1975) investigated saline plumes from salt mine waste entering the southern end of Seneca. Berg (1963) and Schaffner and Oglesby (1978)) noted elevated concentrations of Cl in Seneca and Cayuga compared to the neighboring Finger Lakes, and speculated that it required an extra source of Cl beyond fluvial fluxes to the lake. Groundwater sources flowing through the Silurian-age salt beds below the lake's floor were hypothesized to augment the fluvial sources of Cl to Seneca based on steady-state, mass-balance models (Wing et al., 1995). The analysis of stream and lake major ion concentrations, sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-), in the Seneca watershed supported and expanded on Wing's hypothesis (Halfman et al., 2006).

Halfman et al. (2006) also noted the following: Chloride and sodium concentrations in Seneca Lake were significantly higher than the remaining eight eastern Finger Lakes. The molar ratio of Na to Cl in Seneca was 0.9, suggesting a common source for these two ions assuming some absorption of sodium onto soil particles and other electronegative surfaces (e.g., Rhodes et al., 2001). The other major ion (K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-}) concentrations in the eight eastern Finger Lakes were more uniform, and the variability between lakes reflected the composition of the tills and bedrock, i.e., the percentage of carbonate in the glacial tills and bedrock of each watershed that paralleled the calcium and alkalinity concentrations in the lake. The concentration of the major ions in the streams to Seneca were similar to the neighboring Finger Lakes, and thus stream inputs were probably the primary source of these ions to the neighboring lakes. Steady-state, mass-balance models indicated that the fluvial fluxes of Na and Cl were insufficient to support their concentrations in Seneca even after adding published chloride and sodium fluxes from salt mine wastes, and that the missing salts probably originated from saline groundwater sources (Halfman et al., 2006). In support, Seneca is the only Finger Lake where the bedrock floor intersected the underlying Salina formation (Silurian-age) evaporites (Wing et al., 1995; Mullins et al., 1996).

Callinan (2001) summarized an alternative hypothesis for Seneca and Cayuga. A suspected 1970 to 1990 decline in the chloride and sodium concentrations in these two lakes, based on only a few historical data points, suggested non-equilibrium conditions. They speculated that the decline followed an earlier and significant input of salt mines wastes. For Cayuga, a mixed-model demonstrated that decreasing Cl concentrations since 1970 was the result of an abrupt reduction in pre-1970 s loading from salt mining activity and not groundwater sources (Effler et al., 1989). Longer term, e.g., century-scale data, are required to resolve these differences. Finally, none of these local papers referenced above in the preceding paragraphs discussed in detail Cl concentrations in and/or sources to the neighboring Finger Lakes.

In this paper, we refine and expand our understanding of the Cl hydrogeochemistry in the Finger Lakes using our multi-decadal Cl data augmented by decade- to century-scale data from published and unpublished sources. We endeavored to answer the following questions:

1. What is the historical change in chloride concentrations in these lakes?
2. What processes, e.g., salt mine wastes, road deicing salts, saline groundwater inputs, and/or other potential sources, caused the historical change in chloride concentrations?
3. What watershed characteristics, e.g., road lengths, impervious surfaces, water residence times, trophic status, municipal and septic wastewater treatment, and/or agricultural land use, that were deemed significant for other lakes and streams nationally and internationally, are also important in the rural setting of the Finger Lakes?

We plan to show how human activities have influenced the Cl hydrochemistry of these lakes over the past century in this rural setting, and how these finding may expand the list of parameters influencing Cl concentrations in lakes throughout the globe.

2. Methods

2.1. Field Work

In Seneca, surface (< 1 m) and bottom (within a few meters of the lake floor) water samples for Cl and other analysis, along with equipment blank and field duplicate samples, were collected from four offshore sites located at its northern end from 1996 through 2022 (Fig. 1). These were augmented by surface water samples from 5 additional sites along the length of the lake on one or more cruises in 1998, 1999, 2010, 2011, and 2014 through 2016. SeaBird (SBE-19 from 1994 to 2006; SBE-25 from 2007 to 2022) CTD profiles of temperature, specific conductance (proportional to salinity), and other limnological parameters were also collected at each site. Weekly surveys during the late spring and early fall were augmented with weekly to monthly summer samples after 1998. A CTD cast was also collected annually from the deepest point in the lake from 2017 to 2020.

In Honeoye, Canandaigua, Keuka, Cayuga, Owasco, Skaneateles and Otisco lakes, surface and bottom water samples, field blanks and duplicates, CTD profiles and the other routine limnological parameters detailed above were collected monthly from a minimum of two mid-lake sites during the May to October field season from 2005 through 2022 (Fig. 1). This data was augmented with pre-2005 samples collected from the shoreline a few times each summer. Every water sample was filtered through a 0.45 μm HA Millipore filter in the lab and stored until analysis. The April and May samples should have been influenced by the spring flush of chloride from winter deicing activities, as the lakes were still or just becoming stratified from the winter season.

2.2. Analytical Work

Throughout the study Cl was determined in the lab and/or the field on selected samples by a silver nitrate titration using a potassium chromate indicator (LaMotte PSC-DR field kit). Total alkalinity, a measure of all the titratable pH influencing ions (e.g., bicarbonate, carbonate, sulfate, and hydroxide ions, and in these lakes primarily bicarbonate), was determined on all samples in the field by an acid-base titration (LaMotte WAT-MP-DR field kit). Multiple triplicate analyses using selected field duplicates for both ‘field kits’ revealed an average precision of 4 ppm.

To increase the precision and usefulness of the research, major ion (Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}) analyses were performed on the 2007 through 2015 samples using an Ion Chromatograph (IC, Dionex DX-120). The subsequent, 2015 through 2022, samples were analyzed for Cl using a PerfectION Cl combination ion probe. The accuracy of the Ion Chromatrograph, determined by measuring standards and blanks during each run, typically deviated from the standard concentration by less than 1 ppm; and, precision, measured by multiple triplicate analyses of selected field duplicates, averaged 0.2 ppm. 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 shipboard alkalinity data. Routine triplicate analyses of selected field duplicates by the PerfectION Cl Probe yielded a mean standard deviation of 0.2 ppm.

A comparison of the Cl titration to the PerfectION Cl Probe results (202 samples), Cl titrations to the Ion Chromatograph results (77 samples), and Cl Probe to the IC results (58 samples), when more than one method analyzed any given sample, consistently revealed strongly positive and significant correlations ($r^2 = 0.97, 0.96, 0.99$, p-values < 0.0001), slopes of 1.01, 0.91 and 0.92, and intercepts of 0, 0 and 0, gleaned from the best-fit linear trend lines and regression analyses. The best-fit trend lines also revealed a mean deviation of each analysis from the respective trend line of 2.5, 2.5 and 2.5 ppm, respectively. It indicates that all three analytical techniques yielded consistent results, i.e., were within the precision of the employed techniques, and more importantly, these errors were significantly smaller than the historical range in Cl concentrations detected in these lakes (2 to 200 ppm). A matrix of sample dates, number years of data, mean of annual averages, range in annual averages, and mean of the concentration ranges from each individual year by chloride source and location (lake/stream) is in Table 2.

2.3. Historical Data

Decade-scale data were gathered from published and unpublished sources (Berg, 1963; Schaffner and Ogelby, 1978; Wing et al., 1995; Callinan, 2001; Halfman et al., 2006; Halfman, 2014; NYS DEC Finger Lakes HUB, 2022; Community Science Institute, 2023, Upstate Freshwater Institute, UFI, 2023). Century-scale Cl data was provided with permission for Hemlock (unpublished data, Hemlock Water Quality Laboratory, City of Rochester), Skaneateles (unpublished data, Onondaga County Water Authority, City of Syracuse), and Seneca and Cayuga lakes (Jolly, 2023). Additional century-scale data was gathered for Fall and Six Mile Creeks that flow into the southern end of Cayuga (Jolly, 2023). In general, these multiple datasets tracked each other well. The range in the mean annual Cl concentration from the available data sources averaged 8.2 ppm when data from different sources overlapped. The largest differences were biased by a few isolated and potentially anomalous data (> 20 ppm difference for some DEC & UFI data), especially in Cayuga, Keuka, Owasco and Otisco lakes (Here ‘DEC’ combines data from Callinan, 2001 and NYS DEC Finger Lakes HUB, 2022). The Finger Lakes are fortunate because century-scale water quality data are available, as these long-term datasets are less common elsewhere.

2.4. Cl Modeling

The flux (mass/time) of chloride to each lake over the past century was determined using STELLA Professional 3.1 software package (Fig. 2). The model for each lake utilized (1) lake’s hydrology, i.e., the input (stream and precipitation) and output (evaporation and surface outflow) of water, and steady-state water volumes; and, (2) the lake Cl geochemistry, i.e., the total Cl flux to the lake (mass/time, combining all sources), the output of Cl from the lake (flow via the outlet), the mass of Cl in the lake, and the resultant time-variable Cl concentration in the lake. The model used the Euler method of integration in ¼ year steps, and assumed a 1900 starting Cl concentration of 40 ppm for Seneca, 20 ppm for Cayuga, and 2 ppm for the other Finger Lakes, a concentration slightly smaller than the earliest concentration reported for each lake. STELLA’s “STEP” function facilitated changes to the Cl flux (total chloride input, Fig. 2) at specific years during the model run. The amount and timing of the changes were adjusted repeatedly until the difference between the annual modelled Cl concentrations with the annual mean measured and historical concentrations were minimized, i.e., typically less than 10 ppm each year of the study, a cutoff similar to the precision of the analytical techniques (Table 3). The differences between the modelled and measured concentrations were typically biased by a few isolated and potentially anomalous data points from the literature. The models used the equilibrium hydrological data determined below (2e).

2.5. Lake Hydrology

Mean annual evaporation, precipitation, surface inflow and outflow rates, and water residence times for each lake were calculated to use in the model. Only Seneca and Owasco had sufficient data to calculate all the hydrologic variables. For evaporation, 30-minute meteorological and twice-daily water column temperature data were downloaded from the Finger Lake Institute’s buoys deployed seasonally since 2006 and

Table 2
Chloride Source Data Matrix by Source & Lake/Stream.

Lake - Stream	Cl Source	Range Sample Dates	Number Years with Data (n)	Mean Annual Averages (ppm)	Range in Annual Averages (ppm)	Mean Individual Years Range (ppm)
Hemlock	Hemlock Plant	1919 - 2013	41	17.6	33.0	n.a.
Honeoye	IC Data	2007 - 2021	9	19.8	7.9	1.9
	Ion Probe	2007 - 2021	8	27.3	8.6	3.8
	Lake Titrations	2005 - 2006	2	29.7	2.4	10.5
	Lab Titrations	2005 - 2021	10	22.1	18.1	9.3
	DEC	1978 - 2020	7	24.1	21.2	6.3
Canandaigua	IC Data	2007 - 2015	9	32.3	10.4	2.2
	Ion Probe	2015 - 2021	7	47.8	21.4	6.7
	Lake Titrations	2005 - 2006	2	19.2	3.6	2.3
	Lab Titrations	2005 - 2021	9	34.7	30.4	3.9
	DEC	1963 - 2019	8	32.3	47.2	3.6
Keuka	IC Data	2008 - 2015	8	24.0	5.0	2.5
	Ion Probe	2015 - 2021	7	32.2	7.0	1.7
	Lake Titrations	2005 - 2006	2	12.0	5.5	12.2
	Lab Titrations	2015 - 2021	8	24.4	23.4	6.7
	Jolly	1971 - 2014	10	20.9	24.3	3.4
	DEC	1978 - 2021	7	27.5	29.9	6.1
Seneca	IC Data	2008 - 2015	8	124.2	10.6	9.7
	Ion Probe	2015 - 2021	7	128.4	11.4	9.9
	Lake Titrations	1996 - 2021	22	125.2	28.6	15.2
	Lab Titrations	2014 - 2021	8	127.7	17.5	9.9
	Jolly	1908 - 2014	44	121.5	128.0	22.9
	DEC	1963 - 2020	11	132.0	63.6	43.5
	US Salt	1972 - 1980	9	181.5	21.3	13.7
Cayuga	IC Data	2008 - 2015	8	40.9	1.9	3.9
	Ion Probe	2015 - 2021	7	52.3	18.1	5.8
	Lake Titrations	2005 - 2006	2	30.9	1.3	7.0
	Lab Titrations	2005 - 2021	10	43.4	25.7	5.8
	Jolly	1903 - 2022	55	62.2	83.6	17.9
	DEC	1964 - 2020	11	67.9	61.0	16.1
	CSI	2007 - 2022	15	46.3	12.3	14.8
	UFI	1998 - 2013	6	41.3	5.0	8.0
Owasco	IC Data	2008 - 2015	8	17.4	3.0	3.4
	Ion Probe	2015 - 2021	6	19.0	5.9	5.4
	Lake Titrations	2005 - 2006	2	24.4	6.8	1.0
	Lab Titrations	2014 - 2021	8	18.2	14.0	9.3
	DEC	1963 - 2020	9	18.8	19.9	6.3
	UFI	2001 - 2003	3	23.1	2.7	2.9
Skaneateles	IC Data	2008 - 2015	8	14.2	3.5	1.6
	Ion Probe	2015 - 2021	7	15.2	9.1	2.5
	Lake Titrations	2005 - 2006	2	22.4	6.8	1.2
	Lab Titrations	2014 - 2021	8	14.3	9.3	7.8
	OWCA	1908 - 2021	41	12.0	25.6	n.a.
	DEC	1963 - 2020	8	14.3	18.2	2.0
	UFI	2001 - 2003	3	13.9	0.7	2.1
Otisco	IC Data	2008 - 2015	8	30.7	6.9	1.5
	Ion Probe	2016 - 2018	3	39.9	5.0	6.1
	Lab Titrations	2014 - 2019	6	31.9	11.7	14.0
	DEC	1963 - 2020	8	29.6	41.5	7.8
	UFI	2001 - 2003	3	37.0	4.0	2.4
Fall Creek	Jolly	1903 - 2014	27	16.5	38.4	12.4
	CSI	2002 - 2022	21	22.9	11.1	41.8
Six Mile Creek	Jolly	1906 - 2013	35	15.3	72.3	3.8
	CSI	2004 - 2022	19	25.4	31.3	58.9

2014 in Seneca and Owasco (FLI Seneca Buoy, 2022; FLI Owasco Buoy, 2022). Monthly mean, April through October, surface water temperature, humidity, air temperature, barometric pressure, wind speed, and approximations for the winter months estimated a mean annual linear evaporation rate of 0.77 ± 0.16 m/y for Seneca and 0.81 ± 0.10 m/y for Owasco (Harrold et al., 1986). A mean annual linear precipitation rate from the 35 meteorological stations within the Finger Lake watersheds with > 10 years of historical data was 1.01 ± 0.13 m/y (CLIMOD2, 2022). Linear evaporation from and precipitation to the surface of each lake were converted to volumes/time by multiplying them by the surface area of each lake. Mean daily discharge data from Seneca (USGS 04232730, since 2006) and Owasco (USGS 04235440, since 2000) were downloaded to calculate calendar-year (not water-year) means (USGS National Water Information System, 2023). The calendar-year averages were 616 ± 63 km^3/y and 304 ± 186 km^3/y, respectively. Surface runoff (S) to each lake was estimated from the evaporation (E), precipitation (P), and outflow (O) data from each lake, and assumed the lakes were at equilibrium over the past century on annual time frames (i.

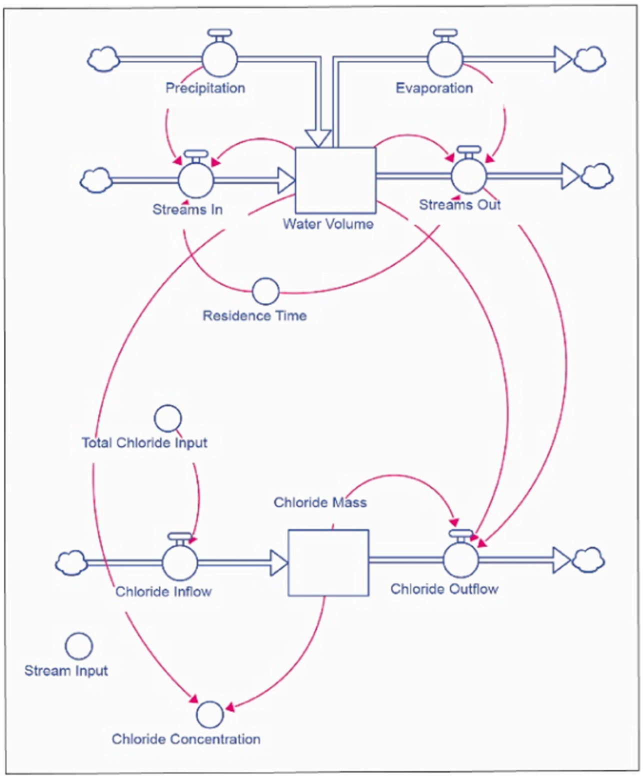

Fig. 2. Inputs, outputs and reservoirs for a representative STELLA mass-balance model.

Table 3
Finger Lake 2020 Modelled Chloride Concentration and Flux Results.

Finger Lake	2020 Modelled Concentration (ppm)	2020 Modelled Total Flux (mtons/y)	Mean Annual Range (ppm)*	Mean Annual Difference (ppm)**
Hemlock	34.8	1660	n.a.	2.0
Honeoye	30.8	900	5.3	6.8
Canandaigua	53.2	11,800	6.4	8.4
Keuka	36.6	7700	7.0	6.7
Seneca	121.5	68,000	10.2	9.9
Cayuga	49.6	44,000	15.8	4.9
Owasco	19.9	5800	6.6	7.8
Skaneateles	20.1	2200	5.9	2.5
Otisco	40.9	1300	8	3.8
Average	45.3	15,929	8.2	5.9

[*] Mean range between mean annual measured concentrations from different sources.
[**] *Mean difference between mean annual measured and modelled concentrations*

e., S = O + E – P).

Annual groundwater flow out of these lakes was assumed negligible compared to the other inputs and outputs in the hydrologic budget. In support, mean annual water tables in the five USGS monitoring wells throughout the Seneca watershed (USGS Site 422710076462901 at Burdett, 422902076475801 at Reynoldsville, 423145076582601 at Dundee, 424024076574801 at Dresden, 424347076530202 at Romulus, Fig. 1) were 45 to 400 m above mean (and flood-stage) lake levels, indicating that groundwater flows into, and not out of the lake. Groundwater inputs were not estimated due to the limited number of wells in a 1181 km^2 watershed, but were also assumed negligible. Resultant water residence times (RT), based on the lake volumes (V, Table 1, Mullins et al., 1996), and estimated mean annual evaporation and outflow rates (i.e., RT = V/[E + O]), were 21.8 years for Seneca and 2.5 years for Owasco, both within their published ranges (Table 1, Callinan, 2001).

For the other lakes, a mean annual evaporation rate was estimated using the average linear E for Seneca and Owasco, 0.79 m/y, and each lake's surface area. A mean annual precipitation rate was estimated using the Finger Lakes linear P average, 1.01 m/y, and each lake's surface area. A slight spatial gradient existed in the precipitation data, i.e., lakes in the west experienced 0.93 m/y, the central Finger Lakes, 0.87 m/y, and the east 1.06 m/y. To test the sensitivity of precipitation variability in the model, we decreased the precipitation input by 1 standard deviation, and the resultant model's 2020 Cl concentration and flux changed by less than 1%. The mean equilibrium annual outflow (O) and inflow (I) were estimated from each lake's volume (Table 1), residence time (mean of the published ranges, Table 1), and evaporation and precipitation rates estimated above (i.e., O = V/RT – E, I = V/RT – P). Groundwater input and output was assumed negligible as above. The hydrologic data used in the STELLA models are found in Table 4.

Outflows and lake volumes were double checked where field data were available. A twenty-year average of mean daily, calendar-year, outflow data from Canandaigua and Keuka (Canandaigua, USGS 04232482 and Keuka USGS 04232482) were within 3% of the calculated values used here (USGS National Water Information System, 2023). Lake volumes were also estimated for each lake using crowd-sourced echo-sounder data (Navionics, 2023). Surface areas at up to 10 depths in each lake, surfaces defined where each depth intersects the lake floor, were calculated using GIS, and water volumes interpolated between each depth. These estimated volumes were within 2% of the published values used here.

2.6. *Statistical Analyses*

Means, standard deviations and graphs were performed in MS-Excel. Best-fit linear trendlines (r^2 values), and regression analyses (p-values at the 95% confidence level) were also determined in Excel, to visually compare and quantitatively assess the significance of any correlation between Cl fluxes and concentrations to potential Cl sources in the region. An insignificant fit in this paper assumed a p-value above 0.10.

3. Results

3.1. *Chloride Concentrations & Fluxes*

The historical Cl concentration trends divide the lakes into two groups. Group 1, Seneca and Cayuga, revealed a decade-scale peak in Cl concentration in the late 1960 s and early 1970 s (Fig. 3). Specifically, Cl concentrations in Seneca and Cayuga lakes increased from below 40 ppm in 1900 to ~115 and 65 ppm, respectively, by the late-1950's to early 1960's. Concentrations then rapidly doubled to peaks of ~195 in Seneca and 110 ppm in Cayuga around 1970. Chloride concentrations then exponentially decreased to ~120 and 50 ppm, respectively, by the present. Chloride concentrations in these lakes were not at equilibrium over the past century, and thus invalidated earlier steady-state, mass-balance models in the literature that assumed steady-state conditions for lake Cl concentrations.

The modelled Cl fluxes to the Group 1 Lakes increased from 30,000 to 73,000 mtons/y in Seneca, and from 30,000 to 60,000 mtons/y in Cayuga from 1900 to the 950's – 1960's (Modelled Cl Flux, Fig. 3). Then, modelled fluxes significantly and abruptly spiked to 243,000 mtons/y in Seneca and 105,000 mtons/y in Cayuga for ~10 years. This spike was quickly followed by an equally large and abrupt decrease in the modelled Cl flux, by 185,000 mtons in Seneca and 75,000 mtons in Cayuga, in the early to mid-1970's in both lakes. Subsequently, the Cl flux to Seneca increased from a low of 58,000 after the spike (1972) to 68,000 mtons/y by 2020. The flux to Cayuga increased from a low of 30,000 after the spike (1967) to 44,000 mtons/y by 2020 (Fig. 3).

The Group 2 Lakes, Honeoye, Canandaigua, Keuka, Owasco,

Table 4
Finger Lake Hydrology.

Finger Lake	Evaporation from Lake Surface (10^6 m^3/yr)	Outflow (10^6 m^3/yr)	Precipitation to Lake Surface (10^6 m^3/yr)	Inflow (10^6 m^3/yr)	Water Residence Times (y)
Conesus	10.67	67.83	14.14	64.36	2
Hemlock	5.33	47.67	7.07	45.93	2
Canadice	2.29	11.15	3.03	10.41	3.2
Honeoye	5.33	10.58	7.07	8.84	2.2
Canandaigua	32.00	156.50	42.42	146.09	8.7
Keuka	35.81	169.04	47.47	157.39	7
Seneca	134.76	578.08	176.75	542.62	21.8
Cayuga	131.06	856.21	173.72	813.54	9.5
Owasco	20.57	291.83	27.27	285.13	2.5
Skaneateles	27.43	91.88	36.36	82.95	13.1
Otisco	6.10	45.90	8.08	43.92	1.5

Skaneateles, Otisco, and Hemlock, revealed smaller 2020 Cl concentrations, ranging from 20 to 53 ppm, and fluxes, ranging from 900 to 12,000 mtons/y, than Group 1 (Fig. 4, Table 2). The temporal trend was also different. Unlike the decade-long, mid-century spike impacting the Group 1 Lakes, the Group 2 Lake fluxes steadily increased in small (250 to 5000 mton) and discrete steps over the past century from ~2 ppm in 1900 to 20 or 50 ppm by 2020. For Hemlock and Skaneateles, the two lakes with century-scale data, the first two steps in Cl concentration occurred in the 1950′s and the 1980′s. The timing of these steps was pinpointed by the increase in chloride fluxes input into each mass-balance model. The largest Cl concentration step occurred between 2000 and 2010 in all but Owasco, and another large increase occurred within 2015 in Honeoye, Canandaigua and Keuka.

Century-scale Cl concentration data were also compiled from Fall and Six Mile Creeks, streams that drain into the southern end of Cayuga Lake (Community Science Institute, 2023; Jolly, 2023, Fig. 5). Chloride concentrations in these two creeks increased over time in multiple steps from 2 ppm starting in 1900 through 1955 to a mean of ~30 ppm from 2005 to 2020 (Fig. 5). Variability exists in the stream concentrations, especially during the past 20 years. We attribute the variability to the timing and location of samples, e.g., base vs. event flow, summer vs. winter season, and upstream vs. downstream sample site locations in relation to Ithaca located at the terminus of these streams (Fig. 1). Mean concentrations for each step were multiplied by the watershed's annual surface inflow to estimate the time-variable fluvial Cl flux to Seneca and Cayuga (Stream Cl Flux, Fig. 3). The timing for each step was determined by notable concentration increases in the streams, and guided by chloride concentration trends in the Group 2 Lakes (Fig. 4).

3.2. Specific Conductance and Major Ion Data

Specific conductance profiles (proportional to salinity) measured by CTD, and major ion (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-) concentrations measured by the Ion Chromatograph from representative Group 1 (Seneca) and Group 2 (Canandaigua and Owasco) Lakes were investigated to assess their consistency with the Cl results presented here. Representative CTD profiles from 2021 revealed seasonal changes in the epilimnion specific conductance data minimal change in the hypolimnion (Fig. 6). July 13, 2020, CTD profiles collected from the deep hole was included to observe the change in specific conductance to the lake floor. Mean annual surface-water (0–10 m) specific conductance data from Seneca 2005 – 2022 CTD data systematically decreased each season by ~40 µS/cm (Fig. 7). The decrease in specific conductance is consistent with a ~5 pm decrease in Cl from 2005 - 2022 (Fig. 3), and a ~3 ppm decrease in Na from 2005 through 2013 (Fig. 8, Table 5). The mean annual concentrations for other major ions (K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, HCO_3^-), revealed smaller decreases from 2008 through 2013. Both the specific conductance, and Cl and Na major ion data are consistent with Seneca Lake becoming less saline over the past 20 years.

Canandaigua and Owasco lakes were chosen to represent two Group 2 Lakes, as they are the two endmember systems in this Group, i.e., Cl concentrations increased the most in Canandaigua (from 2 to 53 ppm) and the least in Owasco (from 2 to 20 ppm) over the last century. Mean annual surface-water specific conductance data increased by 60 µS/cm in Canandaigua, but revealed multiple smaller (~10 µS/cm) fluctuations in Owasco from 2005 through 2020 with no consistent decade-scale trend (Fig. 7). The 2008 – 2013 major ion data revealed a Cl increase of ~7 ppm and Na increase of ~2 ppm in Canandaigua, but both ion concentrations were nearly constant over time in Owasco (Fig. 8). The other major ions revealed smaller or minimal changes in both lakes. Thus, the Canandaigua major ion and specific conductance data were consistent with increased Cl concentrations over the past 20 years. The minimal change in Owasco's major ion and specific conductance data is consistent with its low end-member status for Group 2 Lakes, and with the observed minimal variability in the Cl concentrations over the same time frame (Fig. 4).

Within the epilimnion (stratified surface water) in all three lakes, specific conductance revealed an annual 20 to 40 µS/cm decrease in salinity each stratified season (Fig. 6). Even though the Cl and Na decreased through the summer season, presumably due to their dilution by less saline precipitation and stream inputs to the epilimnion, the magnitude of their change is too small to explain the change in specific conductance assuming specific conductance to ppm conversions derived by Chen and Millero (1986). Of the remaining major ions, Calcium consistently revealed the largest concentration decrease during the stratified season in all three lakes. Its concentration typically returned to its seasonal starting concentration over the winter. We hypothesize that calcium was removed from the water column by the precipitation of calcium carbonate through the occasional epilimnetic whiting events during intense warm-water, algal blooms, and/or the stratified season growth of Dreissenid mussels (calcium carbonate uptake for zebra and quagga mussel shells, e.g., Kelts and Hsu, 1978). The winter decrease probably reflects the mixing of the calcium enriched hypolimnetic (bottom) waters with the epilimnion during overturn, and/or the dissolution of these carbonates when exposed to cold water and/or respiration exceeded photosynthesis (e.g., wintertime and/or in the hypolimnion), as variations in both photosynthesis/respiration and water temperature impact carbonate solubility (e.g., Stumm and Morgan, 1970).

4. Discussion

4.1. Mine Waste & Saline Groundwater to Group 1 Lakes

The century-scale Cl concentration and flux data for the first time clearly reveal that Seneca and Cayuga were subject to significant and time variable Cl inputs, highlighted by a significant spike in concentrations during the mid-1900 s. We hypothesize that the spike resulted from a significant mid-1900′s input of mine wastes. In support, mining activity started in the Seneca and Cayuga watersheds soon after its discovery in 1882 (Salt Mines and Brine Wells, 2023). Effler et al. (1989) concluded that the 1950′s to 1970 peak flux to Cayuga probably resulted

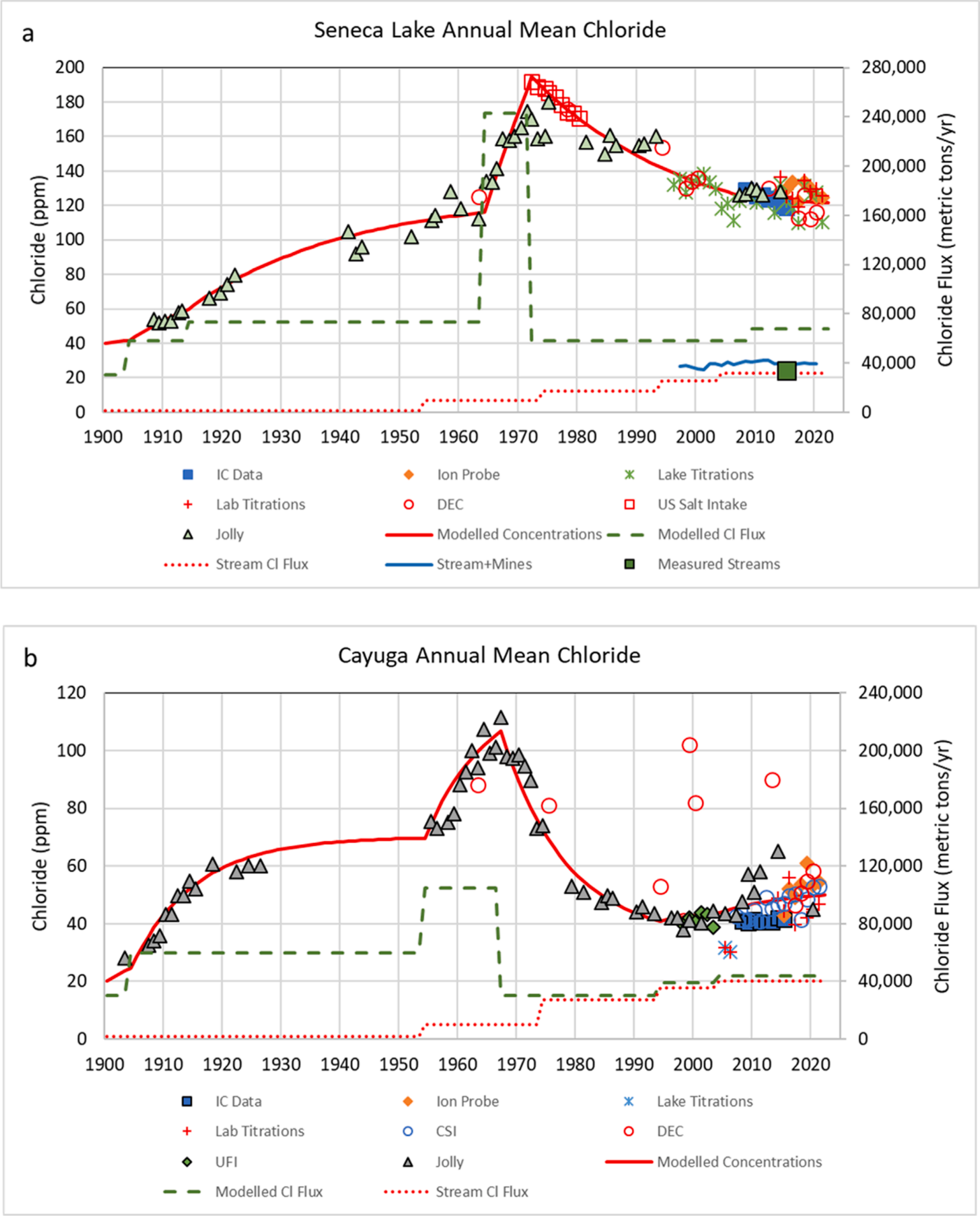

Fig. 3. Mean annual chloride concentrations from different methodologies (Ion Chromatograph (IC), Ion Probe, Lake or Field Titrations) and/or historical sources (CSI, DEC, UFI, Jolly, US Salt) for the Group 1 Lakes, (a) Seneca and (b) Cayuga. Superimposed on this annual data is the modelled Cl fluxes (green dashed), modelled concentrations (red thick solid) along with permitted solution mine wastes (blue thin solid) and estimated stream Cl inputs to Seneca, based on measured Seneca (square) and Cayuga stream (red dotted) data. The stream + mines in the Seneca plot added the estimated annual stream inputs to the EPA reported Cl fluxes (EPA ECHO, 2023).

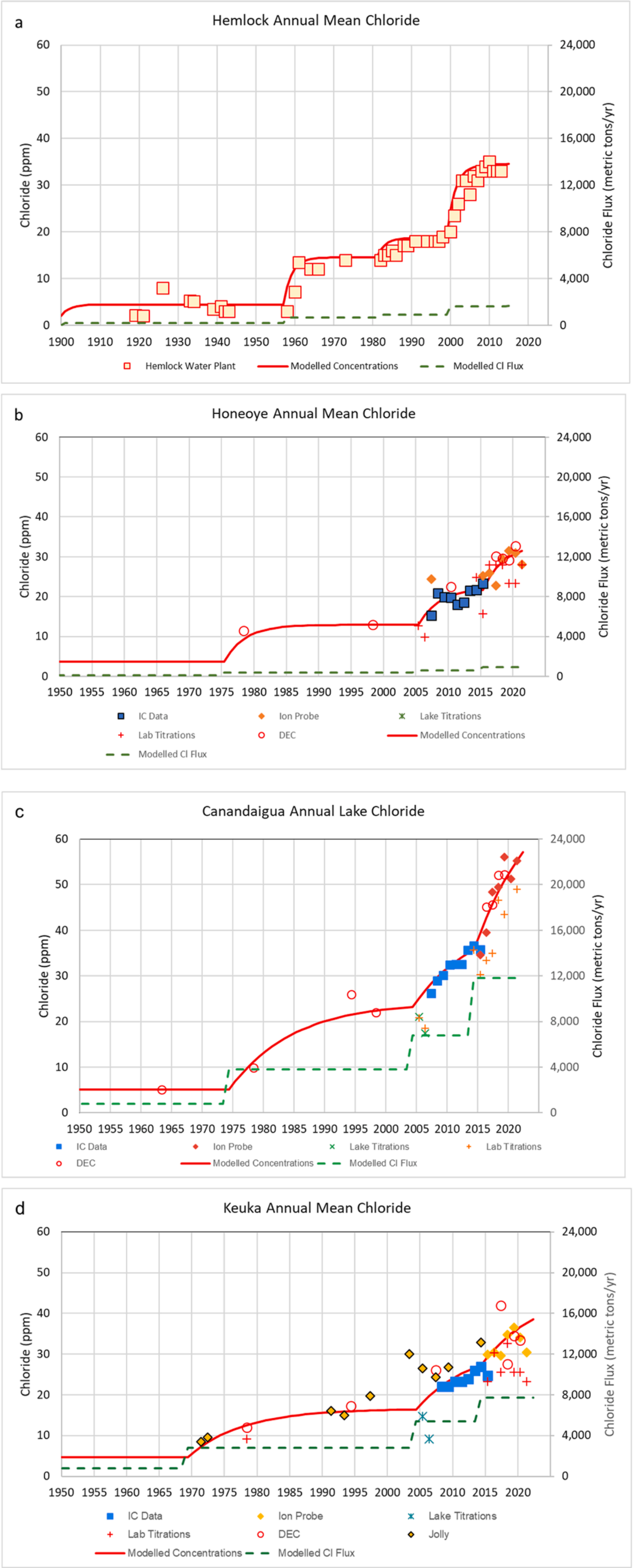

Fig. 4. Mean annual chloride concentrations from different methodologies (Ion Chromatograph (IC), Ion Probe, Lake or Field Titrations) and/or historical sources (Hemlock Water Plant, Onondaga County Water Plant (OWCA), DEC, UFI, Jolly) for the Group 2 Lakes, (a) Hemlock, (b) Honeoye, (c) Canandaigua, (d) Keuka, (e) Owasco, (f) Skaneateles, and (g) Otisco. Superimposed on these annual data are the modelled Cl fluxes (green dashed), and modelled concentrations (red thick solid).

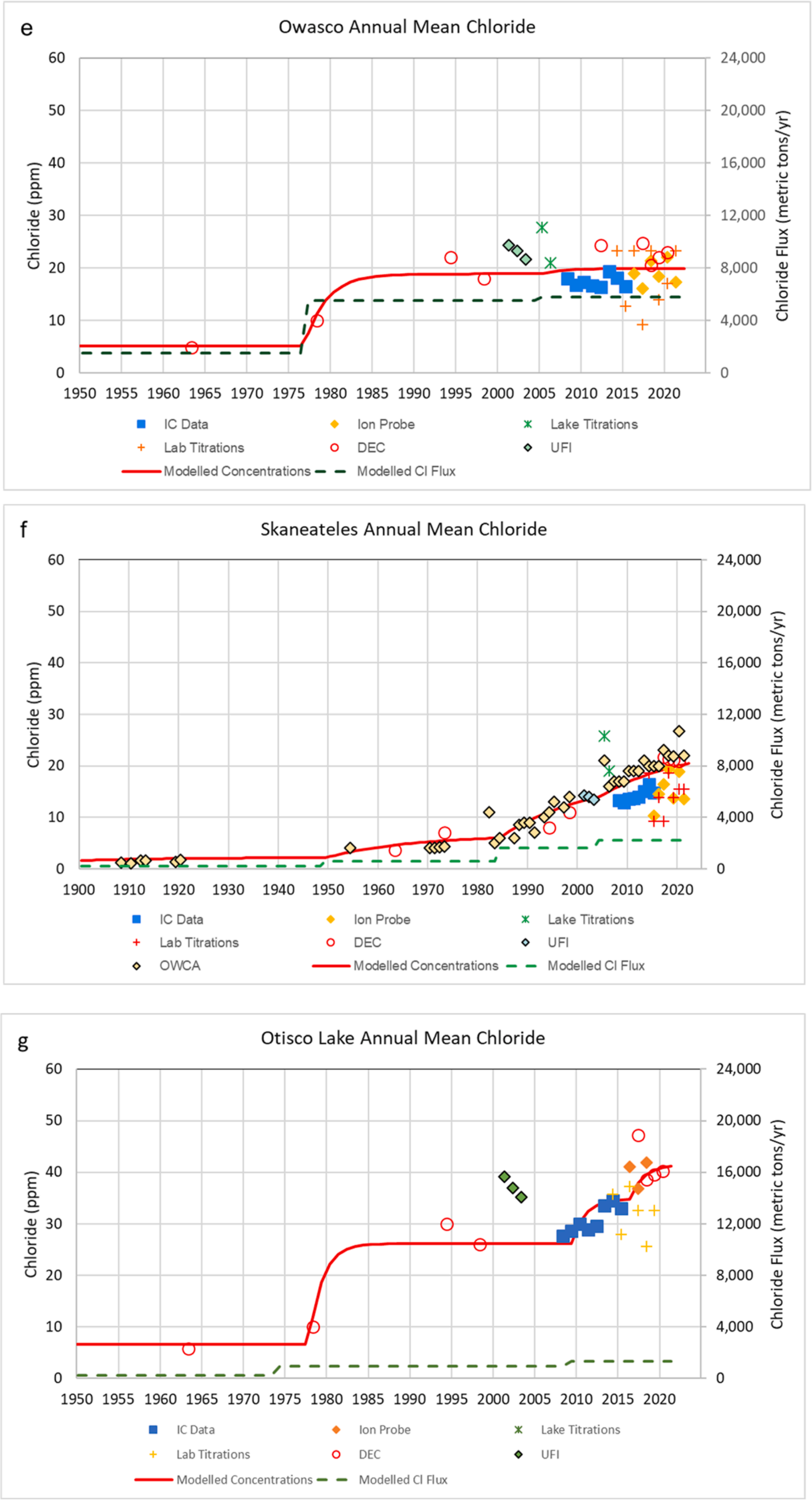

Fig. 4. (*continued*).

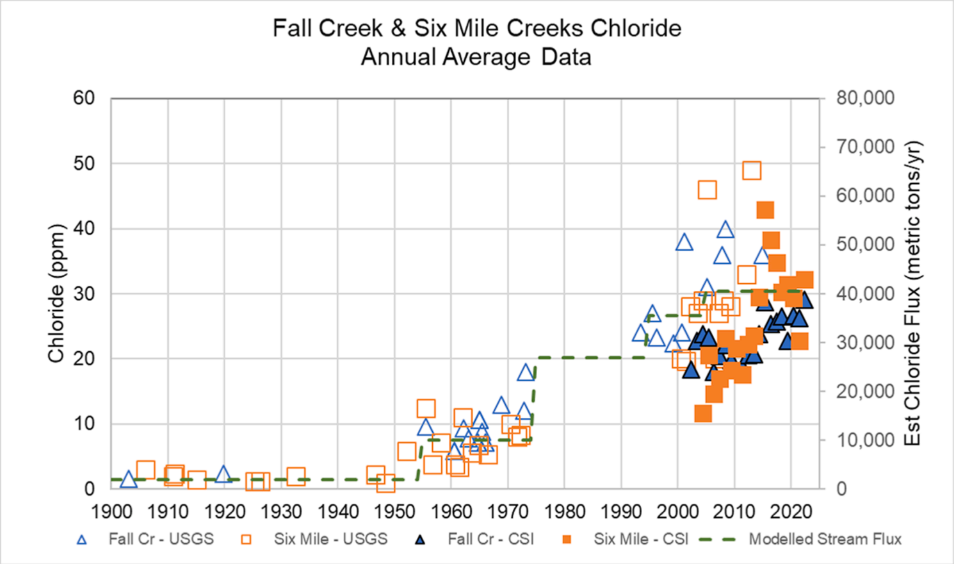

Fig. 5. Chloride (Cl) concentrations for Fall and Six Mile Creeks that enter the southern end of Cayuga and estimated stream Cl flux (dashed) to the lake. (USGS – Jolly, 2023; CSI – Community Science Institute, 2023).

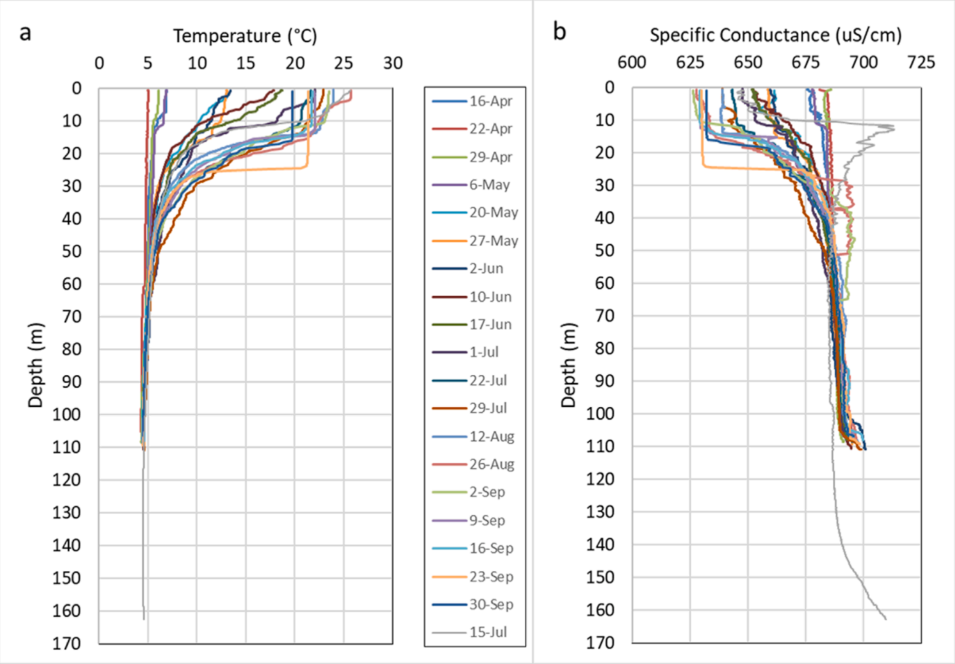

Fig. 6. Weekly CTD (a) temperature and (b) specific conductance profiles from Site 3 on Seneca Lake in 2021. The July 15, 2020 (grey) profile is from the deepest depth in the lake to show the deepest hypolimnion.

from a pre-Environmental Protection Agency (EPA) disposal of fines from rock salt mining activities at the Cargill Salt - Lansing Mine. Since then, fines disposal at Cargill was restricted to onsite methods, and the Cl concentrations in the lake exponentially decreased until a slight, two-step rise in 1995 and 2004.

In Seneca, newspaper reports and anonymous communications from mine personnel indicated that the mid-1960′s to 1970′s spike in Cl concentrations was, in part, due to the improper disposal of fines by the, now abandoned, Morton Salt Mine at Himrod, NY (e.g., The Geneva Times, 1973, The Geneva Times, 1980). US Salt LLC – Watkins Glen Refinery, and perhaps other solution mines, also added saline waste water to the lake for normal solution mining processing, and a cavern's saline water to store liquid and gaseous hydrocarbons in their abandoned salt caverns during this time. The storage of petroleum products displaced saline water originally in the caverns, and this salty water was disposed directly into Seneca at that time (e.g., EIA, 2023, anonymous communication). Since the 1970′s and the onset of the EPA, the wastes entering the lake significantly decreased as these point-sources became regulated.

Century-scale Cl estimated flux data from Fall and Six Mile Creeks, streams that drain into the southern end of Cayuga Lake, enabled a comparison to the modelled Cl fluxes to Cayuga and Seneca lakes. The estimated fluvial flux to Seneca Lake is similar to an estimated stream Cl flux into Seneca based on the 2008–2013 seasonal, spring through summer, stream Cl concentrations (mass/volume) and discharges (volume/time) from the 19 largest sub-basins flowing into the lake

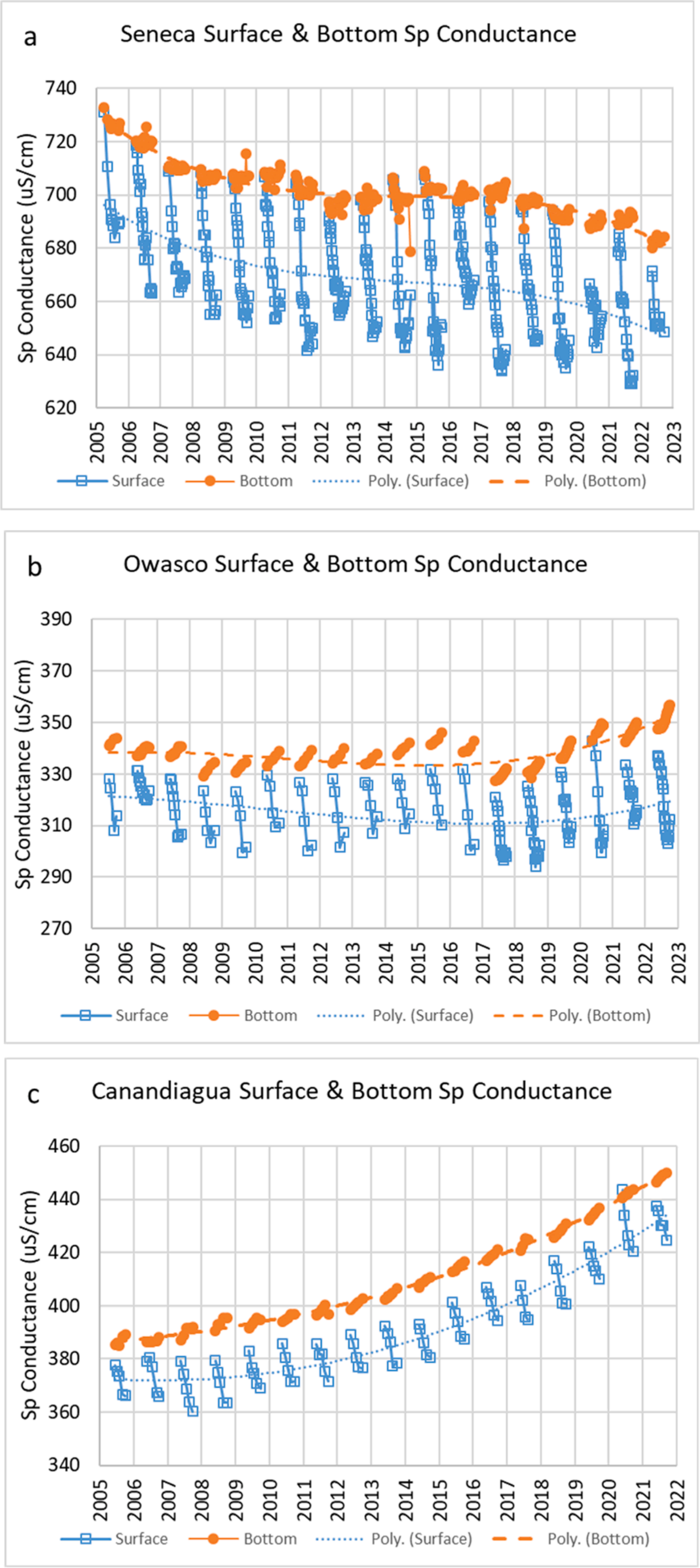

Fig. 7. Mean surface (blue squares) and bottom (orange dots, a few meters above lake floor) water (10-m depth interval) CTD specific conductance data from (a) Seneca, (b) Owasco and (c) Canandaigua since 2005.

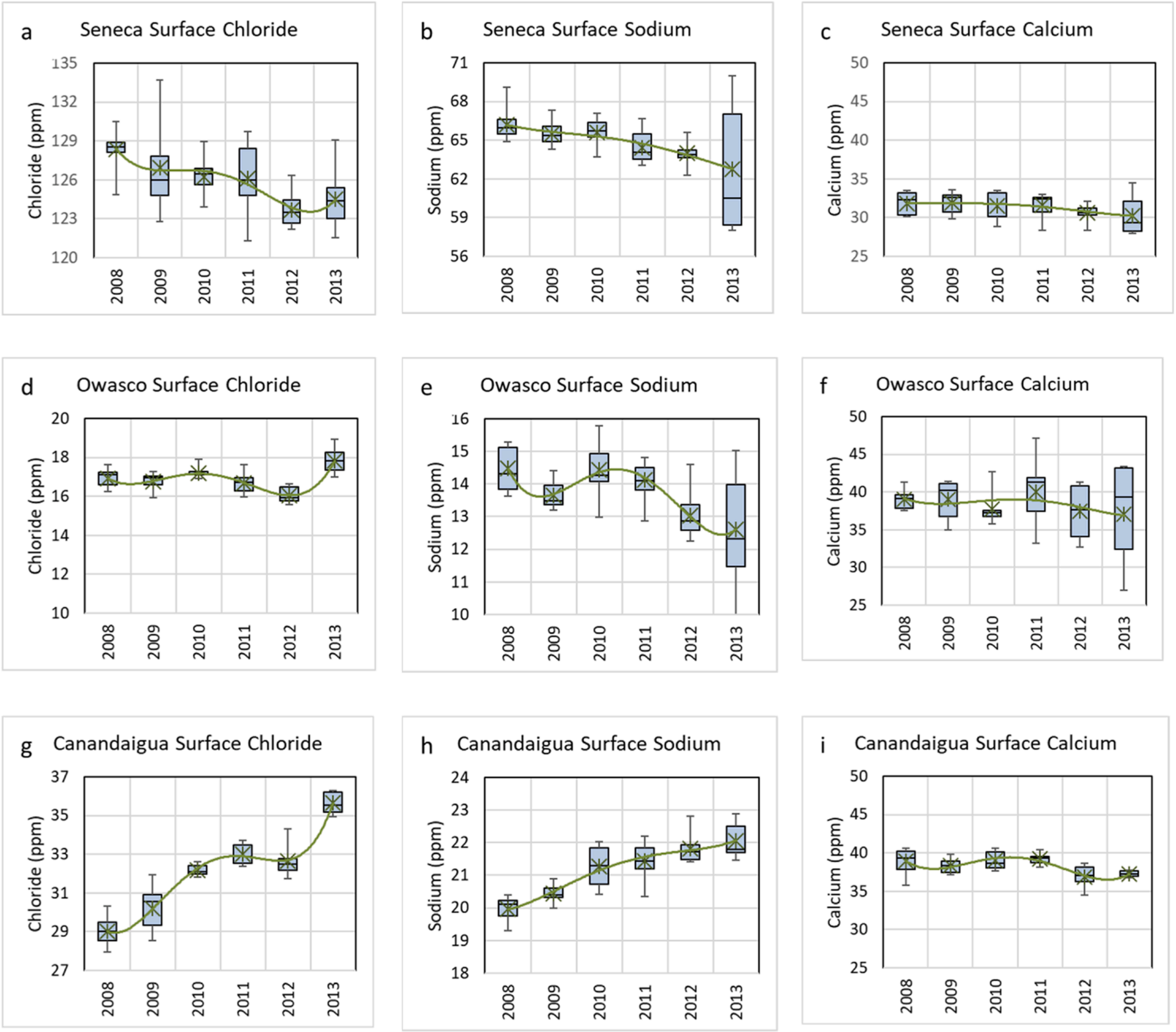

Fig. 8. Box and whisker plots of the 2008 – 2013 annual (a, d, g) chloride, (b, e, h) sodium and (c, f, i) calcium concentrations from (a, b, c) Seneca, (d, e, f) Owasco and (g, h, i) Canandaigua. The blue box depicts the annual 1st and 3rd quartiles, the whiskers depict the annual minimum and maximum values, and the green cross depicts the annual mean. Annual mean concentrations for all the major ions and specific conductance are in Table 5.

(Measured Streams, Fig. 3, Halfman et al., 2006; Halfman, 2014).

For Cayuga Lake, pre-1975 Fall and Six Mile Creeks derived fluvial Cl flux falls short by 30,000 to 60,000 mtons/y of the modelled Cl flux (streams supply < 1%), but is consistent with the modelled flux (streams supply > 90%) after the 1960 to 1970′s mine-waste induced spike (Stream Cl Flux, Modelled Cl Flux, Fig. 3). Therefore, we hypothesize that the stream inputs were augmented by undocumented mine wastes and perhaps saline groundwater flow into the lake before the spike, but data are unavailable to confirm or refute either scenario. A groundwater source is possible as the bedrock floor of Cayuga Lake was the second deepest of the Finger Lakes, and approached the Silurian rock salts below (Mullins et al., 1996). The post-spike consistency in the Fall and Six Mile Creek stream and modelled fluxes (Fig. 3), suggests that fluvial sources alone (e.g., road deicing salts) was the primary source of Cl to the lake since 1975. It also suggests that the two, post-1990, small steps in Cl fluxes to Cayuga reflect increases in road deicing salt use. We infer that fluvial sources were also the pre-spike Cl source, and ground water inputs were not required to balance the Cl budget, as its challenging to turn groundwater sources on and off.

We used the Fall and Six Mile Creek chloride data for a similar fluvial Cl flux comparison at Seneca Lake by multiplying the Fall and Six Mile Creeks Cl annual mean concentrations times the Seneca watershed annual inflow. The estimated fluvial Cl flux estimates were up to 70,000 mton/y short of the pre- (streams supply < 15%) and post-spike (streams supply 30 to 45%) modelled Cl flux to the lake (Stream Cl Flux, Fig. 3). These differences become larger if the smallest published water residence time (12.0 y instead of 21.8 y) was used in the Seneca Lake model. The early 1900′s gap in modelled and stream fluxes were potentially resolved by unregulated mine wastes at that time as the solution mining industry was initiated in 1882. Pre-1950′s mine waste data are unavailable to substantiate this claim.

Since 1992, the quantity of solution mining wastes dumped into Seneca Lake is published (EPA ECHO, 2022). Two solution mines were operational during this time frame, US Salt LLC-Watkins Glen Refinery

Table 5
Annual Mean Surface Water Major Ion and Specific Conductance Data (Halfman, 2014).

Seneca	2008			2009			2010			2011			2012			2013		
Chloride (ppm)	128.4	±	1.5	126.9	±	3.4	126.3	±	1.2	126.1	±	2.4	123.6	±	1.1	124.5	±	2.0
Sulfate (ppm)	57.7	±	0.7	56.2	±	1.4	55.9	±	0.7	55.9	±	1.0	55.0	±	0.4	55.0	±	1.4
Sodium (ppm)	66.2	±	1.1	65.5	±	0.8	65.6	±	1.0	64.4	±	1.1	64.0	±	0.8	62.7	±	4.8
Potassium (ppm)	22.7	±	0.4	23.3	±	0.5	22.6	±	0.9	22.2	±	0.5	21.3	±	0.5	21.0	±	3.2
Magnesium (ppm)	10.0	±	0.5	9.9	±	0.4	9.6	±	0.4	9.7	±	0.3	10.0	±	1.2	8.9	±	0.6
Calcium (ppm)	31.9	±	1.4	31.9	±	1.2	31.5	±	1.6	31.6	±	1.4	30.7	±	0.8	30.2	±	2.6
Sp Conductance (µS/cm)	675	±	17	674	±	19	676	±	18	669	±	23	669	±	11	671	±	18
Owasco																		
Chloride (ppm)	16.9	±	0.5	16.8	±	0.4	17.2	±	0.2	16.7	±	0.4	16.1	±	0.4	17.8	±	0.6
Sulfate (ppm)	12.1	±	0.3	11.7	±	0.3	11.0	±	0.1	10.3	±	0.3	10.1	±	0.5	10.3	±	0.4
Sodium (ppm)	14.5	±	0.7	13.7	±	0.4	14.4	±	0.8	14.1	±	0.5	13.0	±	0.7	12.6	±	1.6
Potassium (ppm)	4.3	±	0.9	3.6	±	0.6	3.7	±	0.8	4.2	±	0.5	2.5	±	0.5	2.3	±	0.7
Magnesium (ppm)	9.3	±	0.1	9.1	±	0.2	9.5	±	0.2	9.4	±	0.1	9.2	±	0.4	8.1	±	0.8
Calcium (ppm)	39.0	±	1.4	39.0	±	2.5	37.7	±	1.9	40.0	±	3.4	37.4	±	3.5	37.0	±	6.4
Sp Conductance (µS/cm)	312	±	8	311	±	11	318	±	9	313	±	12	315	±	11	318	±	8
Canandaigua																		
Chloride (ppm)	29.0	±	0.7	30.2	±	1.1	32.2	±	0.3	33.0	±	0.6	32.7	±	0.8	35.6	±	0.5
Sulfate (ppm)	20.2	±	0.5	19.7	±	0.3	19.0	±	0.3	18.6	±	0.3	18.0	±	0.4	17.5	±	0.3
Sodium (ppm)	20.0	±	0.4	20.4	±	0.3	21.3	±	0.7	21.4	±	0.6	21.8	±	0.5	22.1	±	0.6
Potassium (ppm)	4.7	±	0.8	3.7	±	0.7	4.6	±	0.6	4.2	±	1.2	3.1	±	0.4	3.2	±	0.0
Magnesium (ppm)	12.0	±	0.3	11.8	±	0.2	12.0	±	0.2	12.0	±	0.3	12.4	±	0.6	11.1	±	0.1
Calcium (ppm)	38.9	±	1.6	38.3	±	0.9	39.0	±	1.3	39.2	±	0.8	36.9	±	1.5	37.3	±	0.4
Sp Conductance (µS/cm)	371	±	7	375	±	6	377	±	6	379	±	6	382	±	5	385	±	7

(NYDES NY0002330) and Cargill Salt Inc. (NYDES NY0002241), and both are located at the southern end of the lake. After adding their annual wastes to Seneca's estimated Cl fluvial inputs (Streams+Mines, Fig. 3), the resultant Cl flux is still ~20,000 mtons/y short (streams supply 55 to 70%) of the modelled Cl flux to the lake over the past 30 years. The deficit suggests that Seneca must gain additional Cl and other salts from other sources. We hypothesize that the extra source is saline groundwater as postulated earlier by Wing et al. (1995) and supported by Halfman (2006).

In support, saline seeps are observed in the Finger Lakes region. For example, subsurface seeps and mud boils discharging brackish and very turbid water are observed at Tully Valley, a "filled Finger Lake", about 100 km east of Seneca and 20 km south of Syracuse, NY (Kappel, 2014). Kappel et al. (1996) reported mud boil brine concentrations up to 50, 000 ppm of total dissolved solids at a mean discharge of 0.003 m^3/s, and brines in monitoring wells revealed a total dissolved solid concentration over 100,000 ppm. The source of these salts was the underlying Salina formation (Silurian age) rock salts. Salt springs are also found near Onondaga Lake, probably originating from the Salina formation in the shallow/surficial bedrock under Syracuse. Sulfurous springs are found near the cities of Geneva, Clifton Springs and Canandaigua, presumed originating from the Bertie Formation evaporites overlying the Salina rock salts. The stratified-season uniformity in the hypolimnetic specific conductance data suggest that the groundwater probably inputs directly into the epilimnion of the lake or during the non-sampled winter months (e.g., Fig. 6). Recent Cl, sulfate and other data from the Belhurst Hole, an isolated, lake-floor depression in the northern part of Seneca, routinely revealed Cl concentrations up to 550 ppm that may balance the major ion hydrogeochemistry in the lake (Loubsky-Lonergan et al., 2019, David Finkelstein, personal communication, 2023). In the deepest basin of the lake, lake-floor increases in salinity detected in the deepest basin of the lake can be explained by the permitted disposal of salt mine wastes (Fig. 6). Thus, it suggests that groundwater only impacts the lake at specific locations, like the Belhurst Hole, and not over the entire lake floor, but clearly more work is required to substantiate this hypothesis.

Salt mine and saline groundwater inputs to the Group 1 Lakes therefore add another potential Cl source to the list gleaned from the literature, especially in lakes underlain by rock salts and other evaporites, e.g., Michigan, Pennsylvania, Texas, Louisiana, Mississippi (USGS Bedrock Maps, 2023). In Europe, Permian evaporites are found underlying the Barents Sea, Northern Caspian, the German and North Sea basins, and Triassic rift basins (Evenick, 2021). To our knowledge, only a few researchers attribute chloride concentrations in a lake to groundwater seepage and underlying evaporites. Onondaga Lake and Ichkeul Lake, northern Tunisia, are two examples (Kappel, 2014; Ouchir et al., 2022). It suggests a potential avenue of future research.

Besides resolving the extent and magnitude of the 1960–1970's Cl spike, the modelling effort also revealed the decade-scale time frame required to increase the Cl concentration in each lake, and to subsequently and naturally flush the Cl from the lake; the former highlighted by the time required for Cl concentrations to reach equilibrium after an increase in the Cl flux, and the latter highlighted by the time required for the exponential decay of Cl since the 1960–1970′s peak in Cl concentration. Seneca took ~50 years, and Cayuga ~35 years to recover, or 2 to 4 times the water residence time in each lake. The time delay is an important outcome when water quality regulators are trying to clean up past mistakes from removing a contaminant input, and must instead wait out their careers to finally observe the impact of the cleanup, or to the dismay of environmental activists who want to see immediate, i.e., next year results. This delay emphasizes the importance of not allowing huge contaminant spikes to be discharged into a lake in the first place, i.e., EPA point-source regulations, and re-emphasize the importance of century-scale monitoring data to resolve the decline that was only suspected in the earlier decade-scale Cl data previously available for the Finger Lakes.

4.2. *Road Deicing Salts to Group 2 Lakes*

Our road deicing salt hypothesis as the Cl source to the Group 2 Lakes is consistent with specific conductance and major ion data detailed above, and causal factors controlling the Cl fluxes to, and concentrations in these lakes. For example, the total length of the State and Federal roads in each Group 2 watershed was proportional to the 2020 modelled Cl fluxes ($r^2 = 0.83$, p-value 0.03) and 2020 Cl concentrations ($r^2 = 0.66$, p-value 0.10) (Fig. 9, Table 6). Owasco and Skaneateles were the exceptions, as both watersheds revealed significantly more highway miles than required by their modelled Cl fluxes and concentrations. We hypothesize that these two watersheds used smaller road salt application rates per km of road, perhaps to 'protect' their drinking water supplies, but road deicing salt spreading rate data are not available for confirmation from these and any other Finger Lake watershed. Inclusion of Seneca and Cayuga in the road length comparison yields a much smaller correlation ($r^2 < 0.04$, p-value 0.60 for flux and $r^2 = 0.04$, p-value 0.89 for concentrations), but this discrepancy is resolved as their mine waste

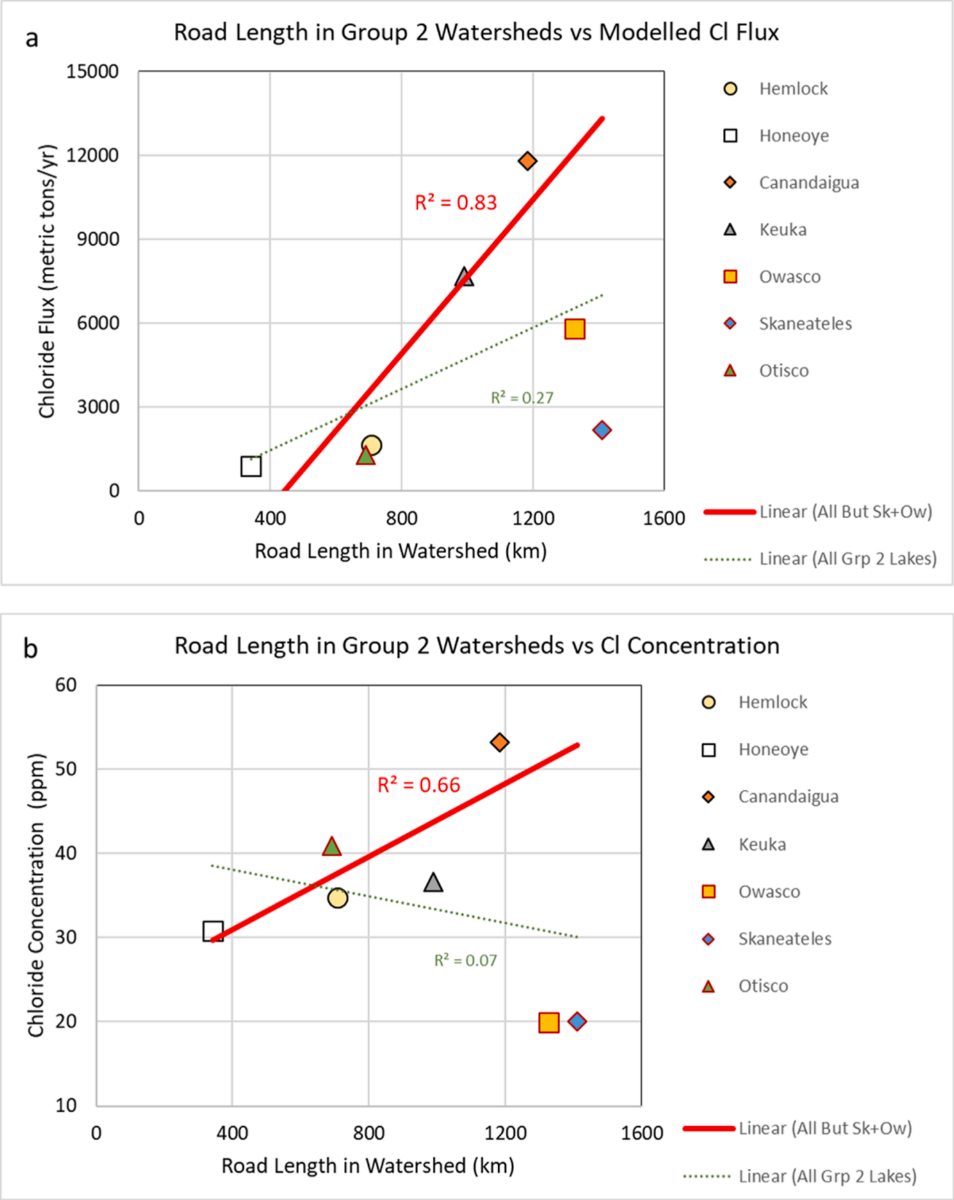

Fig. 9. Comparison of road lengths to the modeled (a) Cl flux and (b) Cl concentration in each Group 2, 'road salt' lake. Skaneateles (Sk) and Owasco (Ow) were excluded from the best-fit line (red solid), due to their presumed reduced road salt usage in their watersheds. Minimal correlation was revealed (green dotted) when these two lakes are included with the other Group 2 Lakes.

histories overshadow any road salt inputs. The Cl fluxes and concentrations in the Group 2 Lakes increase to the present day, and suggests that alternative deicing salts materials and processes have not yet but perhaps should be implemented in these watersheds to protect their drinking water sources. As noted above, once the road salt Cl input is stopped or significantly reduced, our models indicate that 2 to 4 water residence times are required to naturally 'flush' the accumulated Cl from the lakes.

The Group 2 Cl fluxes increased in multiple, small (250 to 5000 mton) and discrete steps over the past century. The timing of the steps paralleled those found in other streams and lakes across N. America (e.g., Smith et al., 1987, Godwin et al., 2003, Robinson et al., 2003, Kaushal et al., 2005, Chapra et al., 2009, Daley et al., 2009, Kelting et al., 2012, Corsi et al., 2015, Dugan et al., 2017, Zuidema et al., 2018, Dugan et al., 2020, Dixon et al., 2022, Dugan et al., 2023). Specifically, steps in multiple lakes were detected at one or more of the following decades, the 1950 s, 1980 s, 1990 s, 2000 s, and 2010 s. The most common decade for a stepped increase was during the 1990 s and 2000 s, and consistent with the timing of the largest step increase in the Finger Lakes. The differences between locations probably reflect the variable timing of increased use of road deicing salts. In support, a tally of road deicing salt consumption in the US from 1940 through 2014 reveals increasing consumption over time with significant steps in 1960 – 1970, and again in 1995 – 2000 (American Geosciences Institute, 2017). The coincident timing adds additional support to the road deicing salt hypothesis.

Detailed stream analyses in the Seneca watershed provided additional support for the road deicing salt hypothesis (Halfman, 2014). Extrapolation of the nineteen, first-order, mean stream concentrations to the entire Seneca watershed estimated an equilibrium, mass-balance concentration of 45 ppm in the lake, which is within the range of concentrations for the Group 2 Lakes. Total road lengths in each Seneca sub-basin were also proportional to their mean stream concentrations, and Cl stream concentrations were largest in the

Table 6
Watershed Characteristics (r^2, and p-values) vs Group 2 Cl Fluxes and Concentrations.

Parameter	Road Lengths	Water Residence Times	Agricultural Land Use	Trophic Status	Impervious Surfaces
Fluxes					
All but Sk & Ow, r^2	0.83	0.97	0.13	0.55	0.70
p-value	0.03	0.002	0.54	0.04	0.08
All Group 2 Lakes, r^2	0.27	0.14	0.09	0.49	0.88
p-value	0.23	0.40	0.50	0.08	0.56
Concentrations					
All but Sk & Ow, r^2	0.66	0.46	0.42	0.52	0.88
p-value	0.10	0.21	0.24	0.36	0.02
All Group 2 Lakes, r^2	0.07	0.00	0.01	0.16	0.00
p-value	0.57	0.90	0.80	0.93	0.94

Note: Sk = Skaneateles, Ow = Owasco.

occasional late winter and early spring stream sample, especially after snow events.

The available data substantiates that road deicing salts are the primary source of Cl to Group 2 Finger Lakes, and since 1990 s, Cayuga Lake. A hypthesis consistent with many lakes and streams throughout the snow-belt regions of the western hemisphere.

4.3. Other Potential Cl Sources to the Finger Lakes

Besides road lengths, other factors influencing the input of Cl to freshwater lakes include water residence times, impervious surfaces (NLCD, 2019), trophic status, and agricultural land use (NLCD, 2019). These parameters were compared to the Group 2 Lake 2020 Cl flux and concentration data. Water residence times correlated with the 2020 Cl fluxes, but less well to Cl concentrations after excluding Skaneateles and Owasco from the comparisons (Table 6). It suggests that the increased exposure time for water in lakes with larger residence times enabled more evaporation and concentrated larger Cl concentrations. The reason Cl flux is proportional to water residence times is less intuitive. A larger residence times would equate to proportionally smaller stream inflows and/or larger volumes (RT = V/I), assuming a fixed lake volume. Thus, larger residence times require larger Cl fluxes to balance the potential decrease caused by smaller stream flows. This relationship is demonstrated by a positive linear relationship (not shown) between 2020 Cl concentrations and fluxes to the watershed areas (a proxy for stream inflow). Finally, impervious surfaces also positively correlated to the 2020 Cl fluxes and concentrations (after excluding Skaneateles and Owasco), a result consistent with the lengths of major roads. This result was unexpected because the range in the percentage of impervious surfaces is very small, yet it adds support to the road deicing salt hypothesis.

In contrast, trophic status weakly and inversely correlated to 2020 Cl fluxes, but did not correlate to 2020 Cl concentrations. Trophic status was coded from 1 through 5 for the oligotrophic, meso-oligotrophic, mesotrophic, meso-eutrophic and eutrophic historical classifications (Table 1). We used the historical classifications rather than the most recent because the chloride changes were during historical times. The percentage of agricultural land use in each watershed also did not correlate to the 2020 Cl fluxes or concentrations (Table 6). It suggests that potash and other chloride bearing fertilizers are not a significant Cl source in these rural, agriculturally-rich, watersheds. We recommend assembling a detailed fertilizer inventory to substantiate this claim. Perhaps agricultural contributions are hidden within other fluvial supplied sources, e.g., road deicing salts, and thus are challenging to isolate with the available data.

Three additional potential Cl sources for lakes, atmospheric (precipitation) deposition, municipal wastewater treatment facilities (MWWTFs) and individual septic systems, were investigated with the available data. Mean annual Cl concentrations in precipitation (atmosphere) averaged 0.053 ± 0.006 ppm (2018 – 2021 data, Site: NY67, Ithaca, NY, National Atmospheric Deposition Program, 2023), yielding a flux of 0.03 to 0.9 mtons/y to the Finger Lakes (the range depends on the lake's surface area) or 0.2 to 3.1 mtons/y to the Finger Lake watersheds (assuming a 50% runoff/infiltration ratio). The direct contribution to each lake's surface was < 1% of the total flux to each lake, and deemed insignificant for these lakes.

The input of Cl from MWWTFs was estimated in three ways. (1) The input of Chlorine (Cl_2) residuals from MWWTFs, that reported the value within the Finger Lakes region, averaged 2.5 ± 0.8 mton/y from 2015 through 2022, and less than 1% of the total Cl flux to these lakes (EPA ECHO, 2023). Unfortunately, data on chloride (Cl) concentrations in MWWTF effluents are not reported. (2) Instead, we investigated mean base flow Cl concentrations and stream discharge data from at least dozen sample dates each year between April through October in 2006–2007 & 2011–2013 just upstream and downstream of the Groton MWWTF along the Owasco Inlet to estimate the flux of Cl to the lake from this source. The nonwinter sample dates and base flow selections maximizes the contributions from the facility compared to winter-time deicing salt runoff and/or Cl dilution during a precipitation event. The mean increase in Cl concentration between sites and the mean stream discharge at the downstream site was 16.2 ± 12 mg/L and 0.8 ± 0.8 m^3/s, respectively. Thus, this MWWTF contributes 213 ± 123 mtons/y of Cl to Owasco Lake. Assuming the entire Cl increase between these two sample sites is due to the facility and not from other sources, like road salt, along the ~3 km length of stream, these estimates are only 3% of the annual fluvial flux to Owasco Lake, and thus deemed insignificant. (3) Finally, measured Cl concentrations from 4 different MWWTFs outfalls in the Cayuga watershed averaged 100 ± 23 ppm (based on 132 outflow samples, that ranged in Cl concentration from 17 to 279 ppm, and collected from 2007 – 2020, Community Science Institute Database, 2023). These MWWTF contributions are also < 1% of the total Cl flux to the lake, thus deemed insignificant.

The input from 600 septic systems along Owasco Lake was estimated at ~15 mtons/y, or < 1% of the total Cl flux to the lake (Owasco Lake Watershed 9E Plan, 2022). We assumed that all of the Ca available in the water (~40 ppm) was converted to Cl by water softeners, and each septic system discharged 120 gallons/day/bedroom (Building Code standards). Effluent loads by non-lakeshore septic systems to the watershed would be similarly small. The density of septic systems is similar along the other Finger Lakes, thus septic systems are deemed an insignificant source in the rural Finger Lakes region. Road salt dominance is consistent with the publications that investigate multiple Cl sources (e.g., Overbo et al., 2021). Like the mine wastes for Group 1 Lakes, we conclude that road deicing salts is the primary Cl source to Group 2 Lakes in this rural region.

5. Conclusions

We investigated three questions for the Finger Lakes region: (1) the historical change in chloride concentrations, (2) the probable source of chloride that caused these changes, and (3) the impact of various watershed characteristics deemed important elsewhere across the globe on the flux to and concentration of chloride in the Finger Lakes of central and western New York State, USA.

Decade to century-scale Cl concentration data and modelled Cl fluxes for nine Finger Lakes in rural central and western New York State revealed two groups of lakes. Group 1 Lakes, Seneca and Cayuga, both experienced a decade-long spike in Cl concentrations and fluxes during the mid-1900′s. We hypothesize that the spike resulted from the input of substantial salt mine wastes before the establishment of the Environmental Protection Agency. A deficit between the modelled total Cl flux required to attain the lake concentrations and an estimated Cl fluvial flux to Seneca Lake using century-scale Cl data from Fall and Six Mile Creeks indicates that Seneca must gain saline groundwater and salt mine wastes to balance the modelled Cl flux to the lake. In contrast, fluvial sources (e.g., road deicing salts) supported the modelled Cl flux to Cayuga Lake after its mid-1900′s spike. A salt mine source or groundwater seepage from evaporite beds is rarely invoked as a source of Cl to lakes across the globe, but perhaps should be investigated in the future, especially in areas underlain by rock salts and other evaporites.

Group 2 Lakes, Hemlock, Honeoye, Canandaigua, Keuka, Owasco, Skaneateles and Otisco, revealed smaller and stepped increases in Cl concentrations and fluxes over time. These trends were interpreted as increased road deicing salt use in their watersheds. A road deicing salt hypothesis was supported by the correlation of the 2020 Cl fluxes and concentrations to total road lengths, impervious surfaces, water residence times in each watershed, its consistency with available specific conductance and major ion concentrations trends, and the step’s timing with similar increases in Cl concentrations in other N. American lakes. Two lakes, Skaneateles and Owasco, were exceptions, and their data suggest lower road salt application rates are used in these watersheds than the others in the area, presumably to ‘protect’ their drinking water supplies. The Group 2 Cl concentration and flux trends increase to the present day, and suggest that alternative deicing salts materials and processes have not yet been, but perhaps should be implemented in these watersheds.

Other potential predictors for elevated Cl concentrations, e.g., percent agricultural land use, trophic status, municipal wastewater treatment facilities, individual septic systems, and atmospheric deposition, were insignificant compared to the inputs by road deicing salts in this rural setting.

CRediT authorship contribution statement

Horvath MaryBridget: Formal analysis. **Halfman John:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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