



Long-term trends of Great Lakes major ion chemistry

Steven C. Chapra^a, Alice Dove^{b,*}, Glenn J. Warren^c

^a Civil and Environmental Engineering Department, Tufts University, Medford, MA 02155, USA

^b Water Quality Monitoring and Surveillance, Environment Canada, Burlington, ON, Canada L7R 4A6

^c U.S. EPA Great Lakes National Program Office, 77 W. Jackson Blvd., Chicago, IL 60604, USA

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ABSTRACT

Data from U.S. and Canadian federal monitoring programs are compiled to assess long-term trends of major ions in each of the Laurentian Great Lakes. Time series are developed for the primary cations and anions as well as for specific conductance and alkalinity. When combined with historical estimates, these modern datasets provide a 150-year overview of each lake's chemical makeup. Because of their long residence times, lakes Superior, Michigan and Huron exhibit persistent increases in most ions. For lakes Erie and Ontario, several ions (chloride, sodium, calcium and sulfate), as well as specific conductance, reached peak levels between 1965 and 1975, but then began to decline. The decreases are attributable to different mechanisms: industrial point discharge reductions (sodium, chloride), atmospheric loading declines (sulfate), and the introduction of exotic dreissenid mussels (calcium). Recent data indicate that these ions are now increasing again (chloride, sodium) or have leveled off (calcium, sulfate). The results establish how much the chemical makeup of the Great Lakes has changed due to anthropogenic influences, and underscore the importance of long-term, systematic, water-quality monitoring.

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Introduction

Over 40 years ago, Alfred Beeton documented a variety of significant chemical and biological changes that had occurred in the Laurentian Great Lakes during the preceding century (Beeton, 1965). Aside from its scientific merit, this analysis was instrumental in raising public awareness of the urgent need to improve environmental conditions in the Great Lakes. The resulting political pressure culminated in a massive remediation program aimed primarily at reducing pollutant discharges from municipal and industrial sources (IJC, 1978).

An important feature of Beeton's analysis involved documenting the progressive increase in total dissolved solids as well as the concentrations of several major ions. Although they did not pose a water-quality threat in their own right, Beeton recognized that salts could serve as a general indicator of anthropogenic impacts on the system. This insight was critical because adequate long-term time series for the parameters of interest (e.g., phosphorus) had not yet been compiled in the early 1960s.

By the late 1960s and early 1970s, concern over eutrophication, especially in the lower Great Lakes (lakes Erie and Ontario) led to concerted efforts to reduce phosphorus discharges, to the development of phosphorus loading targets and to the signing of the U.S.–Canada Great Lakes Water Quality Agreement (GLWQA) in 1972. In particular,

the reduction of phosphorus in laundry detergents and upgrades to wastewater treatment plants lead to great improvements in water quality. During the 1970s and 1980s, total phosphorus concentrations and primary productivity were reduced considerably, particularly in lakes Michigan (Barbiero et al., 2002) and Ontario (Johengen et al., 1994; Stevens and Neilson, 1987). As we will subsequently discuss, these same pollution controls likely resulted in reduced concentrations of some major ions in the Great Lakes at the same time.

Starting in about 1989, the introduction and subsequent widespread expansion of the invasive zebra (*Dreissena polymorpha*) and quagga (*Dreissena bugensis*) to each of the Great Lakes, with the exception of Lake Superior, have again profoundly altered the lakes (Higgins and Vander Zanden, 2010). Together with other factors, dreissenid mussels have been implicated in affecting the cycling of nutrients (Hecky et al., 2004), exacerbating the growth of nearshore nuisance cladophora (Auer et al., 2010; Ozersky et al., 2009), accelerating oligotrophication in lakes Michigan (Evans et al., 2010; Fahnenstiel et al., 2010b; Mida et al., 2010), as well as Huron (Evans et al., 2010) and likely Ontario (Dove, 2009), altering lower food webs (Fahnenstiel et al., 2010a; Mills et al., 2003) and lowering prey fish abundances (Environment Canada, U.S. Environmental Protection Agency, 2012). Dreissenids have also been implicated in reducing calcium levels and hence the tendency for whiting events in the lower Great Lakes (Barbiero and Tuchman, 2004; Barbiero et al., 2006), but possible impacts of dreissenids on other ions has not been documented. Indeed, a systematic review of major ions trends has not been conducted since Beeton's (1965) analysis.

* Corresponding author. Tel.: +1 905 336 4449.
E-mail address: Alice.Dove@ec.gc.ca (A. Dove).

Dove (2009) describes long term trends for several major ions for Lake Ontario, and chloride was recently used as a conservative tracer in the Great Lakes to describe long-term trends and elucidate loadings (Chapra et al., 2009). More recently, Winter et al. (2011) examined 30-year trends in Lake Ontario nearshore water quality measured at water treatment plant intakes. However, the only major ion discussed was chloride and the results agreed with those of Chapra et al. (2009).

This is the first comprehensive compilation of major ion chemistry for the Great Lakes in over 40 years. This paper builds on the previous work of Chapra et al. (2009), with an expanded scope to include the other ions that contribute significantly to the lakes' macrochemistry. The current study employs more recent observations to extend Beeton's (1965) historical trends to the present. The major nutrients nitrogen, phosphorus and silica are not included here; these will instead be the focus of a separate analysis.

Beyond their utility as indicators of human impacts, there are several other reasons why it is important to understand and quantify the major ion chemistry of lakes and other freshwater ecosystems. In the broadest sense, the trends of major anions and cations are relevant as they generally constitute the lake's background chemical environment or "macrochemistry". In this sense, they can be of significance individually as well as collectively via their effects on ionic strength, pH and acid neutralizing capacity. For example, pH can affect metal speciation, which in turn can strongly influence toxicity (e.g., Campbell and Stokes, 1985; Di Toro et al., 2001), and invasion of exotic species will occur only if the chemical environment is suitable (e.g., Mellina and Rasmussen, 1994; Strayer, 1991). Sufficient calcium in lakes, together with warm temperatures and photosynthetically-induced pH rises, can lead to calcite precipitation in summer, surface waters (Kelts and Hsü, 1978). Such "whittings", which have been observed in the Great Lakes (Strong and Eadie, 1978), have a profound impact on water quality as they diminish water clarity (Weidemann et al., 1985). In addition, calcite precipitation can influence eutrophication via its impact on light penetration (Homa and Chapra, 2011) as well as nutrient scavenging (Murphy et al., 1983; Otsuki and Wetzel, 1972).

The observed trends of major ion concentrations will necessarily reflect to a great degree the underlying hydrology of the system and the biogeochemistry of each lake's watershed. The physical characteristics of the Great Lakes are provided in Table 1. As recommended by Quinn (1992), the lake volumes correspond to average rather than base surface elevations. The upper Great Lakes (lakes Superior, Michigan and Huron) are characterized by larger drainage areas, greater lake volumes and surface areas, and longer residence times compared with the lower Great Lakes (lakes Erie and Ontario). These characteristics have a strong influence on how each lake responds to inputs of major ions.

Methods

Along with the parameters originally reported by Beeton (TDS, calcium, chloride, sulfate, sodium/potassium), we also include magnesium. While Beeton reported sodium and potassium collectively, we have compiled independent measurements of each parameter.

Beyond these individual ionic species, we have also included two aggregate parameters: specific conductance and alkalinity.

The data can be divided into two categories: historical (prior to the mid-1960s) and modern (after the mid-1960s). Historical data are taken primarily from Beeton (1965) with additional measurements drawn from a variety of other sources (Bartone and Schelske, 1982; O'Connor and Mueller, 1970; Schelske, 1985a,b; Schindler, 1988; ULRG, 1977a,b; Weiler, 1978, 1981).

Beginning in the late 1960s, much more systematic data collection efforts were instituted under the auspices of Environment Canada (EC) and, in 1983, by the U.S. Environmental Protection Agency's Great Lakes National Program Office (GLNPO). Because they involved more rigorous quality control, these "modern" data sets exhibit considerably less uncertainty than the historical data. Hence, they provide a better basis for separating long-term, emerging trends from interannual natural variability.

Both EC and GLNPO conduct ship-based cruises to collect water quality samples on the Great Lakes. Methods for EC's Great Lakes Surveillance Program are described in Dove et al. (2009). Sampling and analytical procedures for GLNPO's Open Lake Water Quality Surveys are provided in GLNPO (2010). Briefly, EC conducts monitoring in each of the Great Lakes except Lake Michigan, which is located entirely within the United States. Each lake is generally monitored every second year, with multiple cruises conducted during that year. All regions (nearshore, offshore and major embayments) are monitored for the EC program. GLNPO conducts one spring and one summer cruise on all waters except Georgian Bay, with stations located more along the central long axis of each lake.

Open-lake, spring, surface water cruise-median values from the modern programs are presented to extend the historical trends to the modern period. Open-lake (offshore) waters best indicate long-term trends because, in contrast to shallower nearshore waters, they are less influenced by local pollutant discharges. In Lake Superior, open-lake stations comprise those with depths of at least 150 m; in lakes Michigan, Huron and Ontario, the cutoff depths are 60, 50 and 100 m, respectively. Beyond omitting near-shore zones, the major embayments (i.e., Georgian Bay, Green Bay, Saginaw Bay and Lake Huron's North Channel) are excluded from analysis here.

Because its offshore waters exhibit a persistent west-to-east gradient, a somewhat different approach is adopted for Lake Erie. As we are examining dissolved ions that are for the most part conservative, the eastern basin concentration represents the best indicator of the integrated effect of the entire lake's loadings. Consequently, the analysis is limited, in both the GLNPO and EC data sets, to deep-water (>30 m) stations in the lake's eastern basin.

Restricting the modern data to spring, unstratified periods (April and early May) is done to minimize the impact of biological activity on the levels of constituents. In particular, biotic effects can reduce calcium from the epilimnion during the summer stratified period. It should be noted that although the trend analysis focuses on spring conditions, the summer data are also used to assess biotic effects on constituents such as calcium by comparing winter/early spring concentrations with summer surface concentrations.

Table 1

Physical characteristics of the Great Lakes. The residence times are calculated as the ratio of volume to outflow.

Basin	Elevation (m)	Drainage area (km ²)	Surface area (km ²)	Volume (km ³)	Mean depth (m)	Maximum depth (m)	Outflow (km ³ /yr)	Residence time (yr)
Superior	183	127,687	82,103	12,115	147.6	406	67.4	179.8
Michigan	176	115,804	59,600	4947	83.0	282	44.9 ^a	110.2
Huron	176	131,313	59,750	3567	59.7	229	167.2	21.3
Erie	173	62,263	25,220	499	19.8	64	187.7	2.7
Ontario	74	64,030	18,960	1651	87.1	244	220.3	7.5

^a Includes the outflow via both Straits of Mackinac and Chicago Diversion.

For each ion, yearly medians are determined separately for both EC and GLNPO data. The resulting values are then plotted versus time and linear regression is used to generate a best fit line for each ion for each lake,

$$c(t) = c(1970) + \text{rate}(t-1970) \quad (1)$$

where $c(t)$ = concentration (mg L^{-1}) at time t (yr), and rate = linear rate of change ($\text{mg L}^{-1} \text{yr}^{-1}$). Although some modern data were collected earlier, 1970 is chosen as the base year (i.e., the intercept) of Eq. (1) as the best reference point prior to the implementation of major water-quality controls and the approximate onset of systematic water quality monitoring by the Canadian federal government.

In addition to the trends of the individual ions, charge balances were computed for the beginning and the end of the modern data record. Because not all lakes were monitored in all years, the best fit lines were extended to 1970 and 2009, where necessary.

In order to place the recent data in a longer context, the historical and modern data sets for some of the major ions (chloride, sodium, calcium and sulfate) are also plotted together. Laboratory methods have improved over time; in general, colorimetric and nephelometric methods were replaced by atomic absorption methods, and these have in turn been replaced by ion chromatography. Method comparisons have been conducted as laboratory methods changed, interagency comparisons have been conducted (e.g., Esterby and Bertram, 1993), and there is greater confidence in the accuracy of more recent measurements.

Wherever possible, best-fit lines are superimposed to aid visualization of the underlying long-term trends. Because of their high uncertainty, the fits of the historical data rely heavily on the original trend lines drawn by Beeton (1965). These historic lines are sampled at ten-year intervals and then combined with the more recent EC and GLNPO data to create long-term trend lines with linear fits or smoothing splines (de Boer, 2001, 2008).

To more definitively establish the Lake Erie calcium trend, we also compiled data collected by EC as part of the Niagara River Upstream-Downstream Program (Niagara River Secretariat, 2007). At Niagara-on-the-Lake, sampling has been conducted approximately biweekly since 1975, providing a consistent, long-term, year-round and high-frequency data set that is well correlated with the eastern Lake Erie measurements.

Historical total dissolved solids (TDS) data have been compiled (Beeton, 1965; Weiler, 1978), but measurements for specific conductance and alkalinity are not available for the same period. Further, direct TDS measurements based on gravimetric methods are no longer routinely made by either EC or GLNPO. In the absence of direct measurements, calculations based on the individual constituents provide a means to estimate long-term trends of such aggregate variables.

We do not sum the concentrations of the individual dissolved constituents to estimate dissolved solids concentrations because a portion of the bicarbonate ion is volatilized as carbon dioxide during drying (Hem, 1985). Instead, we relate specific conductance to dissolved solids for the period when both measures were available, and use specific conductance to estimate dissolved solids when direct measurements are not available. Beeton's (1965) historical TDS trends are therefore extended linearly to 1965 when the modern data set provides measurements of specific conductance. The average ratio of (historical) TDS to (modern) specific conductance is calculated for each lake (Table 2).

Results

Modern data

The statistics for the linear fits are summarized in Table 3 and classified based on P-values for the slope (i.e., rate in Eq. (1)) as strong ($<1 \times 10^{-4}$), moderate (1×10^{-4} to 0.05), or weak (>0.05). This classification is also depicted in the accompanying graphs using heavy solid

Table 2

TDS and specific conductances for the Great Lakes. The ratio is used to convert modern specific conductance data to TDS so that both measures can be displayed on the same plot (Fig. 6).

The TDS for 1965 comes from Beeton (1965).

Lake	TDS (mg L^{-1})	Estimated spec cond circa 1965 ($\mu\text{S cm}^{-1}$)	Ratio (mg L^{-1}) ($\mu\text{S cm}^{-1}$) ⁻¹	Measured spec cond circa 2009 ($\mu\text{S cm}^{-1}$)	Estimated TDS circa 2009 (mg L^{-1})
Superior	56	97	0.58	102.3	59
Michigan	154	269	0.57	297.0	169
Huron	114	203	0.56	216.2	121
Erie	195	315	0.62	272.6	169
Ontario	199	342	0.58	305.3	177

(strong fits), dashed (moderate), and dotted (weak) lines. Note that because they are clearly curvilinear, the chloride and sodium trends for the lower lakes are represented graphically with smoothing splines (de Boer, 2001, 2008).

Chloride and sodium

The modern chloride (Fig. 1a) and sodium (Fig. 1b) measurements for lakes Michigan and Huron indicate strong upward trends whereas Lake Superior manifests a moderately significant upward trend. Starting in the early 1970s, first Lake Erie and then Lake Ontario showed dramatic decreases in chloride and sodium concentrations. However, they are now increasing again, albeit at a somewhat slower rate. The 6-to-10-year lag in Lake Ontario's response relative to Lake Erie is consistent with Lake Ontario's 7.5 year residence time and suggests that a significant component of the Lake Ontario trend is induced by the Lake Erie signal. As would be expected for non-reactive ions, concentrations increase with distance downstream in the Great Lakes basin.

Calcium and sulfate

The trends of calcium are depicted in Fig. 2a. There is a strong but gradual positive trend for Lake Superior. Otherwise the calcium concentrations in the upper lakes are relatively constant, with Lake Huron values intermediate between lakes Superior and Michigan. In contrast, the levels in both Lake Erie and Lake Ontario have dropped significantly over the past 40 years, so that the calcium concentration in Lake Michigan now exceeds that in lakes Erie and Ontario. Although the Lake Erie data exhibit considerable variability, there is a suggestion that the calcium decline accelerated in the early 1990s, with minimum values reached in the mid-1990s. The acceleration may be connected with the dreissenid mussel invasion in the early 1990s as discussed later in this paper. For Lake Ontario, after peaking in the early 1970s, the rate of decrease has been more constant, with a minimum reached in about 2000 and little change since that time.

As depicted in Fig. 2b, the trends of sulfate are qualitatively similar to those for calcium; that is, increases in the upper lakes and decreases in the lower lakes. Although a statistically significant trend is not evident for Lake Huron, linearly increasing trends are evident for lakes Superior (strong) and Michigan (moderate). Unfortunately, there are no sulfate data for Lake Michigan since 1992, and so it is not known if the linear trend observed between 1976 and 1992 continues to the present. In contrast, the levels in both Lake Erie (moderate) and Lake Ontario (strong) have declined over the past 40 years. We will explore these trends in more detail when we integrate the modern sulfate data with historical data later in this paper.

Magnesium and potassium

The modern data for magnesium and potassium are displayed in Figs. 3a and b, respectively. Lake Superior exhibits the lowest concentrations. The highest magnesium levels occur in Lake Michigan, whereas potassium concentrations rise as the waters move through lakes Erie

Table 3

Summary statistics for linear fits of Great Lakes chemical data from 1965 to 2009. Strong fits are indicated by bold-face and shading (P-value < 1×10^{-4}), and moderate fits by bold-face (<0.05). Note that the statistic $s_{y/x}$ is the standard error of the estimate (i.e., the root-mean-squared error of the residuals, adjusted for the two estimated coefficients).

Lake	Statistic	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Na (mg L ⁻¹)	K (mg L ⁻¹)	Cl (mg L ⁻¹)	SO ₄ (mgSO ₄ L ⁻¹)	Spec. conduct. (μS cm ⁻¹)	Alkalinity (mgCaCO ₃ L ⁻¹)
Superior	n	22	21	21	19	34	20	33	33
	c(1970)	12.98	2.62	1.25	0.484	1.17	2.61	97.3	41.1
	c(2009)	13.62	2.83	1.44	0.505	1.42	3.85	102.3	41.9
	rate	0.0162	0.0053	0.0048	0.00053	0.0064	0.0319	0.128	0.020
	r ²	0.680	0.445	0.736	0.064	0.353	0.671	0.104	0.051
	$s_{y/x}$	0.149	0.081	0.040	0.0270	0.106	0.290	4.66	1.00
	P-value	2.3×10⁻⁶	9.6×10⁻⁴	6.5×10⁻⁷	0.294	2.1×10⁻⁴	1.0×10⁻⁵	0.068	0.207
Michigan	n	16	15	16	13	25	13	25	25
	c(1970)	35.13	11.09	4.45	1.096	6.53	20.46	272.18	110.4
	c(2009)	35.95	11.28	6.26	1.406	12.05	24.01	296.99	107.9
	rate	0.0209	0.0048	0.0464	0.00795	0.1414	0.0910	0.6363	0.062
	r ²	0.017	0.015	0.703	0.389	0.963	0.680	0.816	0.093
	$s_{y/x}$	1.344	0.319	0.255	0.0525	0.207	0.306	2.271	1.46
	P-value	0.630	0.658	4.9×10⁻⁵	0.023	5.2×10⁻¹⁸	5.2×10⁻⁴	6.3×10⁻¹⁰	0.138
Huron	n	32	31	31	29	43	29	42	44
	c(1970)	26.45	6.84	2.99	0.809	4.99	15.60	204.8	77.0
	c(2009)	26.40	7.46	3.86	0.939	6.58	15.83	215.9	78.5
	rate	0.0014	0.0158	0.0222	0.00334	0.0408	0.0062	0.284	0.039
	r ²	0.000	0.311	0.632	0.293	0.812	0.024	0.136	0.048
	$s_{y/x}$	0.955	0.237	0.170	0.0500	0.207	0.379	7.73	1.84
	P-value	0.937	1.1×10⁻³	9.1×10⁻⁸	2.4×10⁻³	1.8×10⁻¹⁶	0.423	0.016	0.154
East Erie	n	26	26	26	24	36	24	40	35
	c(1970)	37.52	7.75	9.56	1.235	20.64	24.80	309.22	94.7
	c(2009)	32.11	8.89	8.58	1.431	14.58	22.81	274.06	88.9
	rate	0.1389	0.0292	0.0250	0.00503	0.1553	0.0511	0.9018	0.149
	r ²	0.560	0.525	0.081	0.296	0.340	0.322	0.467	0.259
	$s_{y/x}$	1.465	0.331	1.006	0.0909	2.494	0.878	13.329	3.01
	P-value	1.1×10⁻⁵	2.9×10⁻⁵	0.160	6.0×10⁻³	1.9×10⁻⁴	3.8×10⁻³	1.2×10⁻⁶	1.8×10⁻³
Ontario	n	36	36	36	34	48	35	52	47
	c(1970)	42.03	7.91	12.74	1.407	28.30	28.58	337.82	95.96
	c(2009)	33.55	8.61	11.56	1.501	19.56	25.54	305.32	90.08
	rate	0.2173	0.0179	0.0305	0.00241	0.2243	0.0781	0.8334	0.1507
	r ²	0.893	0.568	0.302	0.151	0.763	0.434	0.430	0.301
	$s_{y/x}$	0.741	0.153	0.456	0.0535	1.314	0.826	11.450	2.371
	P-value	4.6×10⁻¹⁸	1.1×10⁻⁷	5.1×10⁻⁴	0.023	5.3×10⁻¹⁶	1.7×10⁻⁵	1.3×10⁻⁷	6.5×10⁻⁵

and Ontario. Although the magnesium trend is not statistically evident for Lake Michigan and the potassium trend is weak for Lake Superior, both ions appear to be rising in all lakes, with the strongest linear increases observed for magnesium in the lower lakes. The potassium data exhibit greater within-lake variability than the other ions examined. Similar to sulfate, there are no potassium data since 1992 for Lake Michigan, so it is not known if the high rate of increase suggested by the earlier data continues to the present.

Specific conductance and alkalinity

Reflecting the integrated effect of the dynamics of the major ions, the plot of specific conductance (Fig. 4a) indicates no discernable trend for Lake Superior, a moderate upward trend for Lake Huron, and a strong upward trend for Lake Michigan. In contrast, lakes Erie and Ontario exhibit strong decreasing trends. In addition, it appears that Lake Erie's conductance leveled off in the mid-1990s and may now be increasing again.

The alkalinity of the upper lakes has not changed measurably during the modern period (Fig. 4b), while the long-term trends in the lower lakes appear to be decreasing. Alkalinity is lowest in Lake Superior, and highest in Lake Michigan, and roughly equivalent in lakes

Erie and Ontario. The data suggest that Lake Erie alkalinity increased until 1990, dropped sharply at that time and rebounded again to the present, although current values remain lower than the maximum observed during the 1980s. The Lake Ontario data appear to mimic Lake Erie data, with some dampening of the variations as expected because of its longer residence time.

Charge balance

The charge balances for 1970 and 2009 are summarized in Table 4. All balances are well within the criterion of ± 0.2 meq/L for anion sums in the range 0–3 meq/L established by APHA (2012). Aside from providing a quality assurance check for the chemical analyses, the charge balances also document the changes that have occurred over the past 40 years. In particular, the results generally indicate how salts have increased in the upper Great Lakes whereas the salt content of the lower lakes have generally decreased. For the latter, the ion balance indicates that the drop is attributable to the combined impact of input reductions (for sodium, chloride and sulfate) and the introduction of dreissenid mussel filtration and primary production reductions (for calcium).

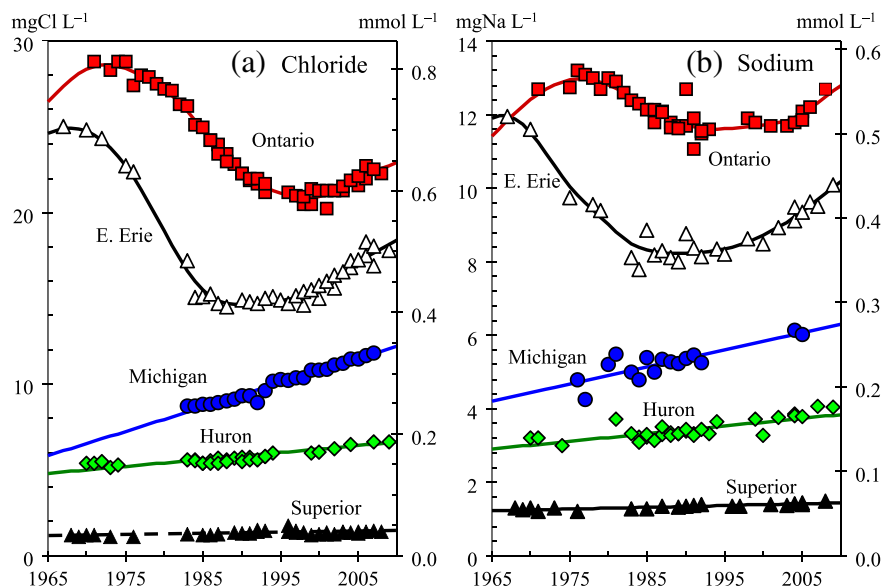


Fig. 1. Modern trends of (a) chloride and (b) sodium concentration for the Great Lakes.

Historical closure

The historical data can be plotted together with the modern data for four of the major ions (Fig. 5). There is no major discontinuity for any ion at the late 1960s junction, indicating consistency between the historic and the modern data sets.

Put into context with the historical data, the rises of most ions appear more pronounced than the modern data indicate alone. Historical values were highest in the lower lakes, although calcium was perhaps historically highest in Lake Michigan. The 1910 values of chloride and sodium in Lake Michigan are suggestive of some possible anthropogenic impact at that time.

The patterns for chloride (Fig. 5a) and sodium (Fig. 5b) show that concentrations in Lake Superior have been relatively constant over the longer term whereas lakes Michigan and Huron show persistent and significant upward trends. The lower lakes exhibit exponential increases up to about 1970 and subsequent declines to minimum

concentrations in the 1990s. Since the turn of the current century, concentrations are rising again.

There is strong evidence of slow but significant increases in calcium (Fig. 5c) and sulfate (Fig. 5d) in the upper Great Lakes, with Lake Huron values again intermediate between lakes Superior and Michigan. In the lower lakes, the trends are curvilinear. While not as definitive as for chloride and sodium, the data suggest increases in both lower lakes to peak values in the 1960s and 1970s, followed by gradual declines. The most recent information suggests that concentrations of both ions may be increasing again.

Historic values of specific conductance, estimated from TDS measurements as described previously, are shown along with the modern data in Fig. 6. The Lake Superior data suggest no change over time, with a weak upward trend implied in the modern data. In contrast, conductance in lakes Michigan and Huron has risen measurably since the late nineteenth century. Lake Michigan exhibits a steady increase of about $0.64 \mu\text{S cm}^{-1} \text{ yr}^{-1}$ whereas Lake Huron is also rising,

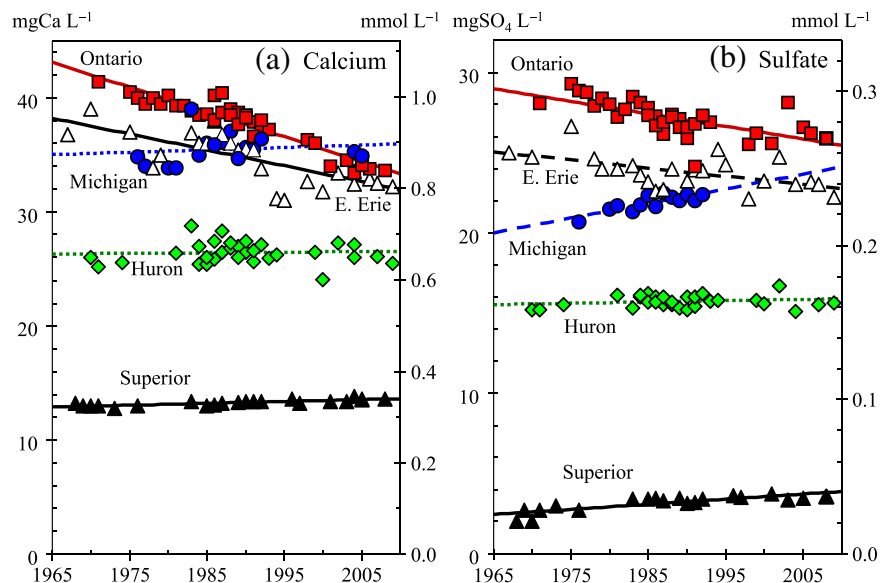


Fig. 2. Modern trends of (a) calcium and (b) sulfate concentration for the Great Lakes.

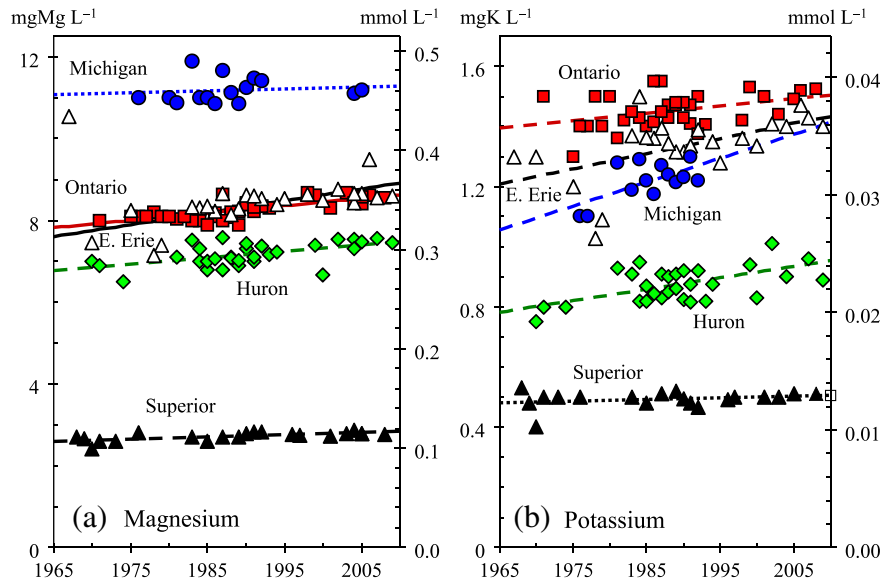


Fig. 3. Modern trends of (a) magnesium and (b) potassium concentration for the Great Lakes.

but at a slower rate of approximately $0.28 \mu\text{S cm}^{-1} \text{ yr}^{-1}$. Both lower lakes manifest the N-shaped pattern of increase, decrease and rebound.

Discussion

The number of people inhabiting the Great Lakes watersheds has greatly increased over time, from approximately 10.5 million people in the early 1900s to approximately 54 million in 2000. Growing concern and mounting evidence of environmental damage to the lakes gave rise in the 1960s and 1970s to major pollution control initiatives, embodied by the signing of the bi-national (U.S.–Canada) Great Lakes Water Quality Agreement in 1972 and its amendment in 1978. Large-scale pollution controls were implemented in both countries, targeted mainly toward industrial processes and sewage treatment. The resulting decrease of pollutant loading to the Great Lakes was perhaps most famously responsible for the dramatic decline in total phosphorus observed during the 1970s and 1980s (Chapra, 1980; Lesht et al., 1991; Stevens and Neilson, 1987).

The major ion loadings to the Great Lakes were doubtlessly diminished by these pollution controls. In this way, the ion loadings likely declined during the 1970s and 1980s. Recent population growth and human development in the lower lakes' watersheds, and continuing adjustment of the lower Great Lakes to historic loads to the upper Great Lakes, account in large part for the rebounds that have occurred beginning in the early 2000s. In addition, as described next, these trends have also been influenced by other factors such as air-pollution control and the introduction of invasive species.

Chloride and sodium

The rising trends of chloride in the upper Great Lakes are primarily the result of increases of industrial discharges and road salt runoff that started in the early twentieth century (O'Connor and Mueller, 1970). Although major industrial load reductions occurred between 1965 and 1980, their impact on the chloride concentrations in the upper Great Lakes is difficult to perceive because of their slow response times for conservative constituents (Chapra et al., 2009). The

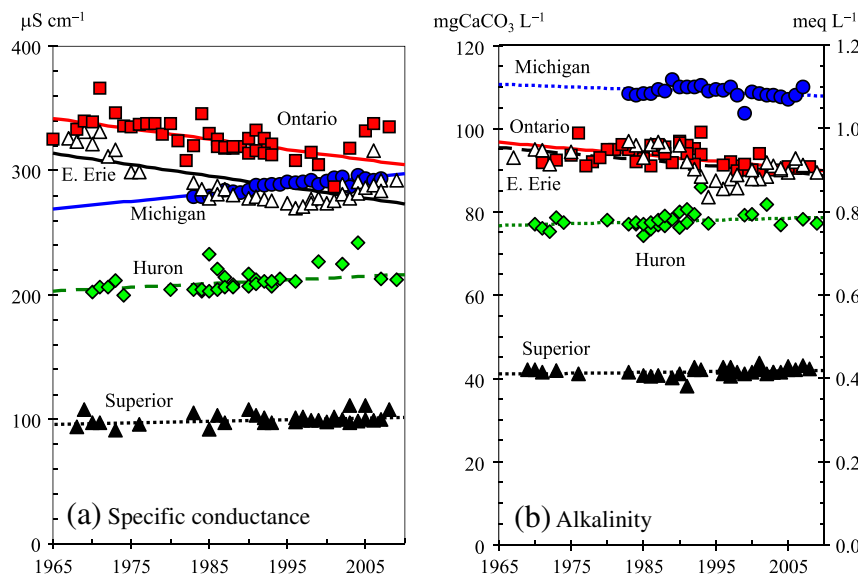


Fig. 4. Modern trends of (a) specific conductance and (b) alkalinity for the Great Lakes.

Table 4

Charge balances for the Great Lakes for 1970 and 2009 with values in meq/L. Both the difference (Σ cations – Σ anions) and the error [$(\Sigma$ cations – Σ anions) / (Σ cations + Σ anions) \times 100%] are indicated.

	Superior		Michigan		Huron		East Erie		Ontario	
	1970	2009	1970	2009	1970	2009	1970	2009	1970	2009
Calcium	0.648	0.680	1.753	1.794	1.320	1.317	1.872	1.602	2.097	1.674
Magnesium	0.216	0.233	0.913	0.928	0.563	0.614	0.638	0.732	0.651	0.708
Sodium	0.054	0.063	0.194	0.272	0.130	0.168	0.416	0.373	0.554	0.503
Potassium	0.012	0.013	0.028	0.036	0.021	0.024	0.032	0.037	0.036	0.038
Σ anions	0.930	0.988	2.887	3.030	2.034	2.123	2.958	2.744	3.338	2.924
Chloride	0.033	0.040	0.184	0.340	0.141	0.186	0.582	0.411	0.798	0.552
Sulfate	0.054	0.080	0.426	0.500	0.325	0.330	0.516	0.475	0.595	0.532
Nitrate	0.020	0.027	0.018	0.024	0.018	0.026	0.011	0.021	0.017	0.032
Bicarbonate	0.818	0.834	2.186	2.140	1.527	1.563	1.883	1.758	1.898	1.789
Carbonate	0.003	0.004	0.021	0.018	0.013	0.009	0.011	0.019	0.020	0.012
Σ cations	0.929	0.985	2.836	3.022	2.024	2.113	3.003	2.685	3.329	2.917
Difference	0.001	0.003	0.051	0.009	0.010	0.010	–0.046	0.058	0.009	0.007
Error	0.06%	0.15%	0.90%	0.14%	0.25%	0.23%	–0.76%	1.08%	0.14%	0.12%

industrial reductions have in fact slowed the rate of increase in each of these lakes. However, such improvements are confounded by their continuing adjustment to pre-1970 increases in non-industrial chloride inputs such as road salt. The net result is that despite significant industrial load reductions, the concentrations in these lakes should continue to rise for decades into the future (Chapra et al., 2009).

The characteristic “N-shaped” pattern of increase, decrease, and rebound for chloride that is seen for the lower Great Lakes can be ascribed to the pattern of century-long deterioration of water-quality followed by improvements due to the post-1970 load reductions. The current increases are attributable to the system’s continued adjustment to the lagged response of the upper lakes, uncontrolled diffuse sources, and possibly to new point sources (Chapra et al., 2009).

The modern trends for sodium are strikingly similar to those for chloride. The correspondence between these ions suggests that much of their dynamics are driven by loadings of their salt, sodium chloride. This hypothesis is reinforced by the fact that some of the major anthropogenic salt inputs to the system (e.g., road salt) are predominantly in the form of sodium chloride (Environment Canada, Health Canada, 2001). Due to the high correspondence between road salt usage and human population (Morin and Perchanok, 2003) and the projected population increase in the Great Lakes basin (Manson, 2005), road salt usage will likely continue to increase, and the trends of sodium and chloride are likely to continue to reflect each other well into the future.

Further insight can be developed by examining the molar ratio of chloride to sodium, which should be unity if sodium chloride is the predominant source of both ions. As indicated by Fig. 7, the actual situation is a bit more complex. Lake Superior differs from the other lakes in having a Cl/Na ratio that is much lower than 1. This is not unexpected as Lake Superior has been the least impacted by human development. Hence, its levels should be primarily dictated by diffuse sources such as direct precipitation and natural runoff.

Based on the data collected at 23 locations around the Great Lakes (USGS, 2008), the Cl/Na ratio for wet deposition is about 0.76, which is consistent with global average values for continental (i.e., non-coastal) precipitation in North America (Berner and Berner, 1987). Hence, precipitation would tend to lower the Cl/Na ratio below unity. However, because the actual concentrations of the ions in rainwater are much lower than the in-lake concentrations, the influence of precipitation to the lakes is negligible.

The more likely explanation for Lake Superior’s low Cl/Na ratio is that sodium is a major component of the silicate rocks that comprise most of its watershed. In contrast, the chloride content of such rocks is minimal. Hence, the long-term weathering and dissolution of these silicates should result in greater runoff of sodium relative to chloride.

In contrast to Lake Superior, the other lakes all have Cl/Na ratios greater than unity, suggesting that they may have significant sources

of chloride in addition to sodium chloride. For example, chloride can be introduced with other cations as ferric chloride (steel pickling process, wastewater treatment), potassium chloride (potash fertilizer), and calcium chloride (snow and ice control).

Calcium

The reason for the halting of the calcium declines in the lower Great Lakes, is less straightforward than for sodium and chloride. Closer inspection of the calcium trends in Lake Erie suggests that there was a major drop between 1990 and 1995 with levels stabilizing thereafter. In addition, since 2000 the Lake Ontario calcium levels also appear to be constant. Although the Lake Erie data exhibit considerable variability, there is a suggestion that the decline accelerated in the early 1990s following the dreissenid mussel invasion as noted previously by Barbiero et al. (2006). The post-1995 data appear to be rising again.

For Lake Ontario, after peaking in the early 1970s, the decrease has been smoother with a minimum reached in about 2000 with no discernable upward trend thereafter. The downward trend in Lake Ontario calcium concentrations has been noted elsewhere (Barbiero et al., 2006) and has been attributed to uptake by dreissenid mussels. While the mussels may have had a significant impact, Fig. 2a suggests that calcium in the lower lakes began decreasing prior to the introduction of the mussels in the late 1980s. In particular, the Lake Ontario data indicate a persistent downward trend starting in the mid-1970s. This implies that factors other than dreissenids may have also contributed to the reductions. A reduction in primary production in Lake Ontario due to the continued reduction in nutrient concentrations and other factors (as summarized by Mills et al., 2003) may also be reducing calcite levels in the lake.

Based on the patterns of chloride and sodium, a rise in Ontario’s calcium concentration is anticipated. Using chloride as a conservative tracer, a lag of 6 to 10 years between lakes Erie and Ontario is expected. Therefore, we hypothesize that we may later confirm that calcium levels increased in Lake Ontario starting in the early 2000s.

In order to gain more insight into the Lake Erie calcium trends, we have supplemented the EC and GLNPO open-lake data with calcium concentrations measured by EC in the Niagara River at Niagara-on-the-Lake (NOTL). As shown in Fig. 8, the Niagara River data are generally consistent with the open-lake measurements. However, because they provide a more continuous and high-frequency time series, the river concentrations allow us to more definitively identify the onset and duration of the decline. Thus, the major reduction began between the summer of 1989 and the winter of 1989/90 and persisted until about 1994. Subsequent data suggest that concentrations may now be increasing slowly. This

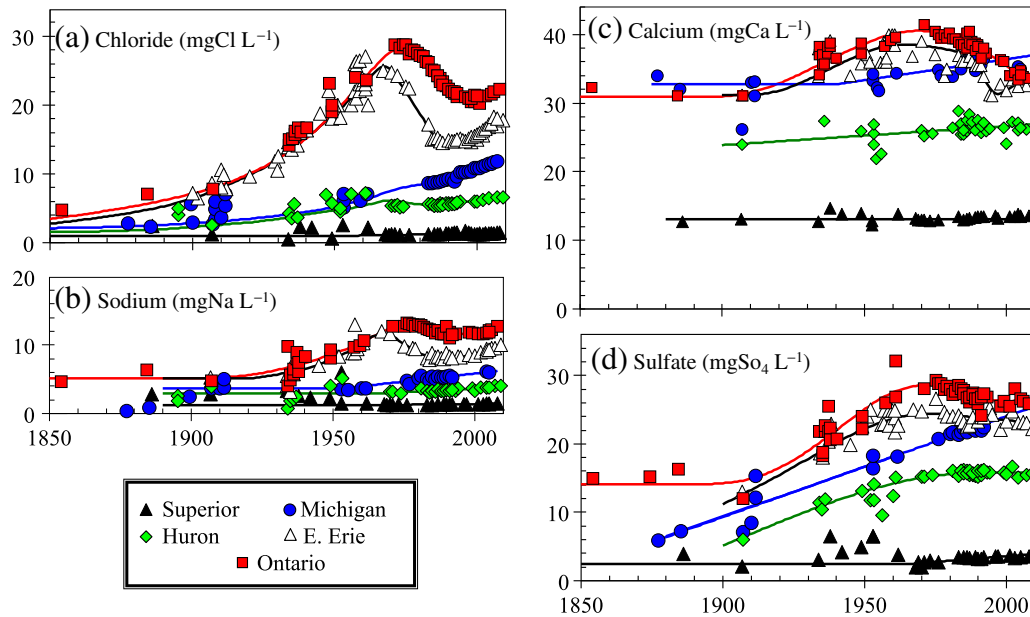


Fig. 5. Long-term trends of major ions for the Great Lakes.

represents strong circumstantial evidence of the intense impact of the mussel invasion on Lake Erie's calcium levels in the early 1990s.

Beyond the concentration trends, the difference between each year's winter and summer values provides an estimate of calcite precipitation in the lower lakes. We calculate that the difference for Lake Erie averaged 1.68 mg L^{-1} prior to 1989 and 1.35 mg L^{-1} after 1994. These values can be converted to equivalent calcite concentrations of 4.2 and $3.4 \text{ mg CaCO}_3 \text{ L}^{-1}$, respectively.

Even more dramatic trends are evident for Lake Ontario. Fig. 9, which shows spring (whole water column) and summer (surface) values, indicates that the summer concentration (generally measured in August) is less than the spring value (generally measured in late March or early April) but that the difference appears to be decreasing with time. Based on the linear fits in Fig. 9, the spring–summer difference dropped from about 3.3 mg L^{-1} in 1970 to 1.0 mg L^{-1} in 2005. If the difference is attributed to calcite precipitation, these observations correspond to a reduction of about $5.75 \text{ mg CaCO}_3 \text{ L}^{-1}$. Although some of the generated calcite would settle out of the epilimnion, the impact on water clarity would nevertheless be considerable owing to calcite's propensity to scatter light (Homa and Chapra, 2011; Peng and Effler, 2005; Weidemann et al., 1985). As suggested previously

by Barbiero et al. (2006) and Dove (2009), this is undoubtedly one of the reasons for the remarkable increase in water clarity that has been observed in Lake Ontario over this period.

Sulfate

Sulfate trends reflect the increase in fossil-fuel usage and subsequent air-pollution controls (Likens and Bormann, 1974; Schindler, 1988). The upper lakes, with their long residence times, are still equilibrating to the increased loading from many decades ago. The lower lakes, which are more temporally responsive, are currently showing improvement due to air-pollution controls (Holland et al., 1999; Husain et al., 1998; Lehmann et al., 2007; Malm et al., 2002). Some effect of acid-rain leaching from watersheds may play a role here; as acid rain worsened and subsequently improved, sulfate in runoff may have increased and then reduced correspondingly.

The early sulfate record for Lake Michigan is probably suspect; we believe that Lake Michigan values were likely constant until about 1900, at which time they increased in a fashion similar to that seen for Lake Ontario. It is not plausible that the steep increase implied by the historical data for Lake Michigan could have occurred prior to 1900, when fossil-fuel combustion and the population in the Lake Michigan watershed were still relatively low (Government of Canada, United States Environmental Protection Agency, 1995).

Although the sulfate trends (Fig. 5d) appear qualitatively similar to the other major ions, there are some significant differences that

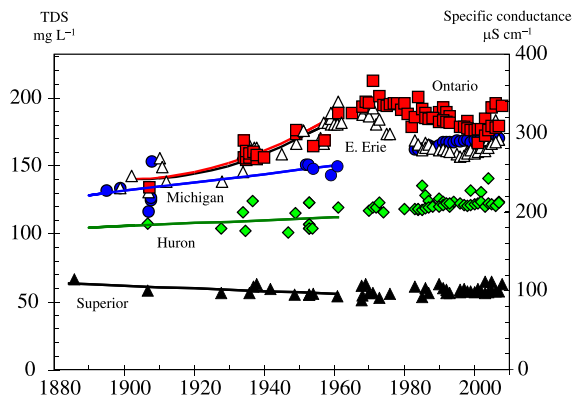


Fig. 6. Long-term trends of TDS/specific conductance for the Great Lakes. The lines were originally developed by Beeton (1965) to depict the underlying trends of historical TDS data.

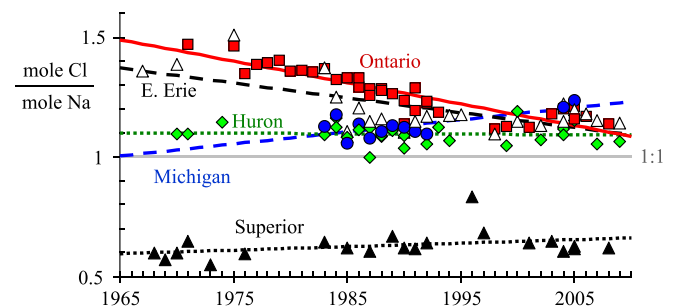


Fig. 7. Molar ratios of chloride to sodium for the Great Lakes.

bear mention. Whereas Lake Superior's sulfate levels have been rising mildly since the early 1970s (recall Fig. 2b), the levels have risen significantly in Lake Michigan. Unfortunately, sulfate levels are unavailable for Lake Michigan after 1992. Hence, it is unclear whether concentrations have continued to rise since that time.

Although not quite as dramatic, Lake Huron also exhibited a considerable increase during the first half of the twentieth century. Because sulfate measurements in Lake Huron have extended to the present, Fig. 5d suggests that the trend has leveled off.

The sulfate trends in the lower lakes again suggest a build-up during the early twentieth century with peaks in the early 1970s and subsequent declines into the 1990s. As with calcium, future measurements will bear watching to establish if sulfate levels are now stable or are beginning to rise.

Magnesium

A large portion of the system's magnesium comes from the erosion of limestone in the Lake Michigan basin. Hence, the highest levels occur in that lake. In contrast, Lake Superior exhibits the lowest concentrations and, as suggested by historical data (Weiler, 1978), levels have been relatively constant over the past century. Lake Huron, which receives comparable levels of inflow from lakes Superior and Michigan, has an intermediate concentration ($\sim 7 \text{ mg L}^{-1}$). Due primarily to the high dolomite content of the bluffs along the north shore of Lake Erie (Kemp and Dell, 1976; Kemp et al., 1976), lakes Erie and Ontario have slightly higher levels, on the order of 8 mg L^{-1} .

Potassium

Similar to sodium, potassium is a dominant ion in the Earth's crust, but it is present at lower concentrations in surface waters because it is readily incorporated into clay minerals. Of all the ions presented here, the modern potassium record demonstrates the most straightforward long-term trends, with gradual linear increases in all the lakes, and higher concentrations downstream in the basin. This implies that loadings of potassium have not fluctuated as dramatically as other ions, and that diffuse sources (such as the contribution of KCl as a constituent of fertilizer and road salt) may comprise the dominant anthropogenic potassium loads to the system.

TDS and specific conductance

Although Beeton (1965) sketched a slight decrease in TDS for Lake Superior, he noted that the trend was not significant due to the high uncertainty of the early data. Based on the entire data record, we concur with Beeton's (1965) conclusion that the TDS of Lake Superior has not changed greatly over the past century. However, as noted elsewhere (Chapra et al., 2009), because of its extremely long residence time ($\sim 180 \text{ yr}$), the apparent lack of a trend should not necessarily be construed as evidence that Lake Superior's dissolved inorganic solids levels have not been elevated somewhat due to human activities. As for the

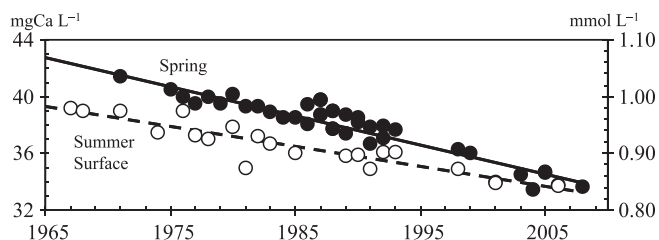


Fig. 9. Trends of spring, water column (filled squares; solid line) and summer, surface (open squares; dashed line) calcium concentrations for Lake Ontario.

other lakes, conductance in lakes Michigan and Huron has risen measurably since the late nineteenth century and lakes Erie and Ontario manifest the N-shaped pattern of increase, decrease and rebound.

Conclusions

To summarize, Lake Superior shows the lowest concentrations of many ions. This is to be expected, as it is the Great Lake least impacted by human influences (Government of Canada, United States Environmental Protection Agency, 1995). However, the long-term record presented here demonstrates strong upward trends of calcium, sodium and sulfate. These findings indicate that anthropogenic water-quality impacts have indeed occurred. It should be noted that such increasing trends for Lake Superior have also been observed for non-salts such as nitrogen (Bennett, 1986; McDonald et al., 2010; Sterner et al., 2007).

Lake Michigan shows the highest concentrations and the highest rates of increase for many ions. Of the six ions described in Table 3, three of them (sodium, potassium and sulfate) show the highest rate of increase occurring in Lake Michigan. Unlike the lower Great Lakes, where some constituents have shown periods of improvement, the trends in Lake Michigan tend to reflect unceasing linear increases over the period of record.

Concentrations of most ions in Lake Huron are intermediate between lakes Superior and Michigan, representing the nearly equivalent influence of these two lakes on its water quality (Chapra and Sonzogni, 1979; Schelske, 1985b). Because the water quality in Lake Superior is much more stable, the direction of trends observed for Lake Huron tends to follow that of Lake Michigan.

Water quality is the most variable in Lake Erie due to its short water residence time and high watershed loads (Chapra et al., 2009; Dolan and McGunagle, 2005). Recall that only deep stations from the eastern basin are considered here; this helps greatly to reduce the scatter in the ion plots and elucidate longer-term trends. Because Lake Erie receives waters from the upper Great Lakes as well as its own loads, ion concentrations tend to be greater than those observed in the upstream waters.

In general, the highest concentrations of many ions are observed in Lake Ontario, a natural consequence of its most downstream position in the basin, but also the result of high anthropogenic ion loads from its watershed (Doerr et al., 1994; Effler, 1987; Effler and Matthews, 2003).

The very long residence times of the upper Great Lakes mean that water quality impacts in these lakes can continue to occur and impact the downstream lakes, long after the causes of the impacts have been abated. In this way, the concentrations of chloride, sodium, sulfate and calcium are increasing in lakes Superior, Michigan and Huron, even while the concentrations are varying or declining (in the case of calcium) in the lower lakes. Using the example of chloride, Chapra et al. (2009) previously demonstrated that the concentrations can be expected to increase in Lake Ontario to unprecedented levels over the next few decades due to the influence of previous loads to the upper lakes, even though those loads may have subsequently declined.

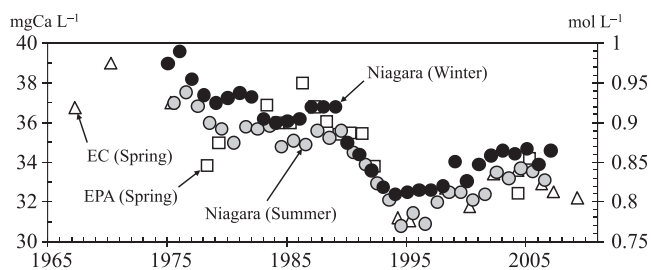


Fig. 8. Winter and summer calcium concentrations for the Niagara River at NOTL along with spring, open-water measurements for eastern Lake Erie.

In the lower Great Lakes, the shorter residence times result in trends that are more dynamic and responsive to watershed and upstream loads. For several major ions (e.g., chloride, sodium and possibly sulfate), an oblique N-shaped trend is observed as lake concentrations increased, decreased and rebounded. We believe that the N-shaped trends observed in the lower Great Lakes reflect the broad patterns of urban development and industrialization (as concentrations increased), the implementation of significant source controls (when concentrations decreased), followed by the system's adjustment to (still-increasing) upstream loads and possibly new sources that are fuelled by the population growth and accelerated development in the lower lakes' watersheds.

The trends documented in this paper could not have been established without the systematic regular monitoring programs conducted by both Canada and the United States governments. It will be essential, moving forward, that these important long-term monitoring programs continue in the face of increasing resource pressures and despite any perceived lack of immediate utility. Well-run, accessible environmental monitoring programs provide contextual information for shorter-term research initiatives as well as contributing important scientific advances and crucial information to guide environmental policy (Lovett et al., 2007; Magnuson, 1990; Stow et al., 1998). The long-term data sets utilized here comprise some of the most comprehensive, systematic and detailed information that is available for such a large freshwater system. The usefulness of these data sets for retrospective assessment of ecosystem response to anthropogenic stresses, to important environmental policy, or to global climate change, cannot be underestimated.

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