Anthropocene geochemistry of metals in sediment cores from the Laurentian Great Lakes

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Geochemical analyses applied to lake sedimentary records can reveal the history of pollution by metals and the effects of remedial efforts. Lakes provide ideal environments for geochemical studies because they have steady deposition of fine grained material suitable for fixation of pollutants. The Laurentian Great Lakes are the most studied system in this field, and they have well-preserved chronological profiles. To date, this important system has been considered in parts for inorganic geochemistry, hampering basin-wide conclusions regarding metal contamination. We filled spatial and temporal gaps in a comprehensive geochemical analysis of 11 sediment cores collected from all five Great Lakes. Hierarchical cluster analysis of all Great Lakes samples divided the metal analytes into five functional groups: (1) carbonate elements; (2) metals and oxides with diverse natural sources, including a subgroup of analytes known to be anthropogenically enriched (Cd, Pb, Sn, Zn, and Sb); (3) common crustal elements; (4) metals related to coal and nuclear power generation; and (5) all of the co-occurring rare earth elements. Two contamination indices (I_{geo} and EF) applied to sedimentary metals indicated that Na, Co, Mn, Cd, Pb, Ta, and Cu were each, at some point during the Anthropocene, the most enriched metal pollutants in Great Lakes sediments. Land uses correlated with the metal analytes, such as increases in contaminant metals with the rise in catchment population and increases in carbonate elements (e.g. Ca) with agriculture. Certain contamination trends were observed basin-wide, such as for the atmospheric pollutant Pb, which followed a rise associated with fossil fuel combustion and a decline following the ban of leaded gasoline. Other trends were lake-specific, such as recent high concentrations of Na in Lake Superior, likely due to road salt applications, and a late-20th-century peak in Ca associated with algal whiting events in Lake Ontario. Some metals exceeded guidelines for sediment quality, in some cases prior to European settlement of the basin, indicating that a paleolimnological context is important for appropriate management of sediment contamination. The Great Lakes are sensitive to environmental changes such as pollution

by metals, and it is clear that while there has been remedial success, results from the uppermost intervals of cores indicate ongoing problems.

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Abstract

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13 well-preserved chronological profiles. To date, this important system has been considered in
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15 contamination. We filled spatial and temporal gaps in a comprehensive geochemical analysis of
16 11 sediment cores collected from all five Great Lakes. Hierarchical cluster analysis of all Great
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18 metals and oxides with diverse natural sources, including a subgroup of analytes known to be
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30 metals exceeded guidelines for sediment quality, in some cases prior to European settlement of
31 the basin, indicating that a paleolimnological context is important for appropriate management of
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33 pollution by metals, and it is clear that while there has been remedial success, results from the
34 uppermost intervals of cores indicate ongoing problems.

Introduction

36 The Laurentian Great Lakes have a complex history of contamination. While Native American
37 influence on the environment of the Great Lakes was likely minimal and localized, such as
38 copper mining effects around Isle Royale, Lake Superior (Pompeani et al., 2015), European
39 westward expansion was marked by overfishing, logging, mining, and the introduction of non-
40 native species. Increasing environmental concentrations of metals in the region in the 1850s
41 correspond with extensive European settlement and with the growth of population and industry,
42 increasing even more rapidly due to the burning of fossil fuels. Contamination of the lakes
43 increased until pollution reached such a critical level that the governments of the United States
44 and Canada felt compelled to act (Sly & Munawar, 1988; Beeton, 2002) with the passing of the
45 Clean Water Act (United States of America, 1972) and the Great Lakes Water Quality
46 Agreement (Canada & United States of America, 1972).

47 In order to assess the historical and continuing environmental impacts of contamination and the
48 efficacy of cleanup efforts, a long-term account of environmental metals is needed. Such
49 assessments have been supported by paleolimnological investigations. Metals are useful for
50 assessing historical pollution in lakes, as they are among the best characterized contaminants for
51 monitoring. Pollutants are mobilized in rivers, move away from their sources, and are
52 incorporated into lacustrine sediments. Several pollutants are also deposited via the atmosphere.
53 The pollutants are preserved due to affinity with sediments, the fact that they do not degrade, and
54 most of them do not mobilize (though there are some exceptions such as aqueous forms of Fe
55 and Mn). This kind of geochemical analysis is useful in systems where the sediment record is
56 minimally disturbed by bioturbation or flow (Alderton, 1985). Heavy metals are among the best
57 characterized contaminants for environmental monitoring (especially Hg and Pb), as they are
58 persistent in the sediments (Heim & Schwarzbauer, 2012). However, a comprehensive study of
59 metals and other inorganic chemicals throughout the entire Great Lakes basin has not been done.
60 Studies to date have been generally limited to a few inorganic contaminants or geographically
61 limited portions of the Great Lakes basin. This report is the first comprehensive geochemical
62 analysis of metals for the whole Great Lakes basin, with a major goal being historical
63 reconstruction of natural conditions, anthropogenic impacts, and remediation.

64 Many paleolimnological studies in the Great Lakes have focused exclusively on the highly toxic
65 element Hg: Kennedy, Ruch & Shimp (1971), Pirrone et al. (1998), Rossmann (2010), and Yin et
66 al. (2016) in Lake Michigan; Kovacik (1972), Walters et al. (1972), Walters, Wolery & Myser
67 (1974), Wolery and Walters (1974), Pirrone et al. (1998) in Lake Erie; and Thomas (1972),
68 Breteler et al. (1984), Pirrone et al. (1998), Marvin et al. (2004) in Lake Ontario. It was generally
69 observed that Hg levels in sediment records increased beginning in the mid-1800s, reached a
70 maximum in the 1970s, and decreased with recent industrial regulations. Several studies have
71 also exclusively tracked historical Pb concentrations as a tracer of leaded gasoline combustion
72 using sediment cores in the Great Lakes: Edgington, Robbins & Karttunen (1974), Robbins &
73 Edgington (1974), and Edgington & Robbins (1976) in Lake Michigan; Ritson et al. (1994) in
74 Lake Erie, Rossmann, Pfeiffer & Filkins (2014) in Lake Michigan; Rossmann, Pfeiffer & Filkins
75 (2014) in Lake Huron; and Graney et al. (1995) throughout the entire Great Lakes Basin.
76 Overarching findings were that Pb concentrations increased in the 20th century but more recently
77 declined due to the legislated transition to Pb-free gasoline.

78 In general, Great Lakes geochemical studies in sediment cores have focused on individual lakes.
79 Nussmann (1965) chose Lake Superior as the first lake for this kind of study because it was
80 viewed as the least anthropogenically impacted lake and thereby represented a baseline for
81 comparison with other lakes. Subsequent studies included Lake Michigan (Shimp, Leland &
82 White, 1970), Lake Ontario (Cronan & Thomas, 1972), Lake Erie (Walters, Wolery & Myser,
83 1974), and eventually Lake Huron (Robbins, 1980). A full review of this previous work is
84 presented by Aliff et al. (Aliff et al. this issue; companion manuscript #44690).

85 We aimed to fill spatial and temporal gaps and to cover a wide range of metals analytes in a
86 comprehensive geochemical analyses of 11 sediment cores from the five Great Lakes. Because
87 of likely lake-specific interests to Great Lakes researchers, we spend time on descriptive
88 interpretations relative to each lake. We further aimed to relate geochemical history to past

89   anthropogenic activities, both detrimental and remedial. This included stratigraphic surrogates
90   for natural deposition due to erosion of soils, and bedrock and human activities such as mining,
91   tailings disposal, and burning of fossil fuels. In performing a basin-wide investigation, we
92   anticipated similarities in widespread stressors such as atmospheric lead deposition (Norton et
93   al., 1990) but that lake-specific trends would correspond with each lake's unique anthropogenic
94   history and physico-chemical characteristics.

95   **Methods**

96   **Coring.** Eleven sediment cores were collected per Reavie et al. (2017; Fig. 1). Three cores were
97   collected from Lake Superior, and two cores were collected from Lakes Huron, Erie, Ontario,
98   and Michigan. Cores were collected from the USEPA's R/V Lake Guardian or the University of
99   Minnesota's R/V Blue Heron using an Ocean Instruments model 750 box corer, from which two
100   6.5-cm internal diameter cylindrical cores were subsampled, or an Ocean Instruments model
101   MC-400 multi-corer (9.4 cm diameter cores). Temporal records ranged from ~100 y to over 300
102   y prior to the coring date.
103
104   **Extrusion and Dating.** For each location, one core was extruded at fine intervals (as fine as 0.25
105   cm in upper intervals to 1 cm intervals at the bottom of the core), depending on estimated
106   accumulation rates and need for temporal resolution. Isotopic dating to develop temporal records
107   for each core follows methods described by Shaw Chraïbi et al. (2014). All cores had
108   exponential ^{210}Pb profiles indicating typical isotopic decay with time, and errors associated with
109   dates ranged from 1–2 yr in the most recent three decades to +/- 10–20 yr around ca. 1850.
110   Because background concentrations of ^{210}Pb were not achieved, the western Lake Erie core
111   dating included supplementary ^{137}Cs analysis to pinpoint the 1963 peak resulting from weapons
112   testing (Appleby, 2002). Complete dating models for these cores are provided in the
113   supplementary materials.
114
115   **Historical stressors.** Spatial and temporal land use patterns around the Great Lakes were
116   collected from historical records going back as far as the late 1700s (Reavie, Cai & Brown,
117   2018). Land uses included were agriculture, population, mining, and forest cover. The level of
118   each land use was summarized within watersheds covering the Great Lakes basin. We selected
119   sub-watersheds around each lake to summarize historical lake-specific stress. These data and full
120   details on their sources are available in a public archive provided by Reavie, Cai & Brown
121   (2018).
122
123   **Chemical Analyses.** Sedimentary analyses for metals and oxides were performed by personnel
124   at the University of Minnesota, Department of Earth Sciences, Analytical Geochemistry
125   Laboratory. Excepting modern instruments, these methods largely follow Malo (1977) for
126   extraction and analysis of metal analytes. For equipment calibration, standard reference materials
127   and sample blanks were assessed every time a new core was being analyzed. For trace metals
128   (As, Ba, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr,
129   Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Tm, U, V, Y, Yb, Zn, Zr) analysis, sediment subsamples
130   were freeze-dried, and 0.25 ± 0.02 g of dry sediment were added to a 50-mL centrifuge tube. To
131   this, 25 mL 0.5 N HCl was added and samples were heated at $80 - 85$ °C in a hot-water bath for
132   30 minutes. Vials were transferred to an ice-water bath and allowed to cool for 5 minutes.

133   Samples were centrifuged at 2000 rpm for 10 minutes and then 10.0 mL of the supernatant was
134   moved to 125-mL acid-washed poly-bottles. Each sample was diluted with 40 ± 0.5 g deionized
135   water. Samples were assessed using inductively coupled plasma mass spectrometry (ICP-MS),
136   which is capable of the determination of a range of metals and several non-metals (B'Hymer,
137   Day & Caruso, 2000; Jarvis & Jarvis 1992). Instrumentation was a Thermo Scientific XSERIES
138   2 ICP-MS (inductively coupled plasma – mass spectrometer) with ESI PC3 Peltier cooled spray
139   chamber, SC-FAST injection loop and SC-4 autosampler. Elements were analyzed using He/H$_2$
140   collision-reaction mode. For quality control, all samples were analyzed three times and flagged if
141   any single analysis of a given analyte varied by 10 % from any other analysis for that analyte. No
142   such discrepancies were noted so analyses as presented are averages of the three analyses.

143   For major metals (Al, Ca, Fe, K, Li, Mg, Mn, Na, P, Si, Ti), HCl-extracted samples were
144   analyzed using a Mira Mist Peek nebulizer paired with a Thermo Scientific iCAP 6500 dual view
145   ICP-OES (inductively coupled plasma - optical emission spectrometer) with the following
146   settings: power 1150 W, nebulizer flow 0.65 L/min, cooling gas 12 L/min, auxiliary gas 0.5
147   L/min, 1 mL/min sample flow rate, 8 sec/replicate and 5 replicates/sample. For analysis of
148   oxides, freeze-dried sediment subsamples (~0.5 g) were processed directly using the same
149   settings as those for major metals. Due to its low detection limit requirement and high cost of
150   analysis, geochemical data for mercury (Hg) were not generated. For quality control, all samples
151   were analyzed twice and flagged if the analyses for a given analyte varied by more than 10 %.
152   No such discrepancies were noted so analyses as presented are averages of the two analyses.

153   Here, we present geochemical data as concentrations relative to sediment dry weight (ppm). Not
154   presenting accumulation rate data was partly for the sake of brevity, but we noted that profiles of
155   metal accumulation rates were similar to those for concentrations, so we do not anticipate that
156   the presentation of accumulation rates would have a notable effect on major trends. Further, as
157   detailed by Engstrom & Wright (1984), there are several reason to preferentially choose
158   concentrations. Most notably in our case, several metals (such as Fe) are highly mobile in Great
159   Lakes sediments, so calculated accumulation rates would falsely represent the actual
160   accumulation at the time of deposition. Despite caution on the use of these data, we present our
161   calculated accumulation rates as supplementary materials.

162   **Mapping.** The land use map (Fig. 1) was compiled using ArcGIS 10.4. The map has a spatial
163   resolution of 30 meters. The US Land Use data was accessed through the mrlc.gov, the Multi-
164   Resolution Land Characteristics Consortium. The data are part of the National Land Cover
165   Database and the raster file was downloaded on May 14, 2019. The Canadian Land Use data
166   were accessed through the open.canada.ca website, a project of Open Canada. The maps were
167   produced by Agriculture and Agrifood Canada and TIFF files were downloaded on May 14,
168   2019. Classifications for both countries were combined which involved simplifying and
169   combining land-cover classifications for each country.

170   **Data Analysis.** The following analyses were performed in R (R Core Team, 2018): cluster
171   analysis, principal components analysis (PCA) and plotting of analyte temporal profiles. All
172   analyses were done entirely in base R except for PCA which was plotted with the package
173   maptools in order to minimize overlap of the analyte labels (Bivand & Lewin-Koh, 2017).

174 Hierarchical cluster analysis of the Great Lakes geochemical dataset focused on determining
175 relationships among analytes (metallic elements and oxides). The cluster analysis used an
176 unweighted pair group method with arithmetic mean by taking Euclidean distances of the
177 correlation matrix. Ultimately, clustering was used to identify groups of analytes that exhibited
178 similar trends in the last 150–200 years across all Great Lakes cores. A preliminary detrended
179 correspondence analysis (DCA) indicated a first-axis gradient less than one standard deviation
180 unit (i.e. low overall environmental variability), so PCA (a linear method) was chosen over other
181 ordination methods. PCA using singular value decomposition of the centered and scaled data
182 matrix allowed us to further illustrate relationships among these groups and to trace the temporal
183 trajectories of each sediment core over time relative to the analyte scores. Analyte concentrations
184 were scaled in order to avoid placing emphasis on analytes with naturally higher values.

185 Two indices were applied to determine the extent and threat of anthropogenic contamination in
186 the sediment records: the geoaccumulation index (I_{geo}) and enrichment factor (EF). I_{geo} is a
187 measure used to compare present day contaminant concentrations with pre-impact background
188 levels in order to better quantify anthropogenic impacts (Stoffers et al., 1986). For a select set of
189 contaminant elements, I_{geo} was calculated according to the following formula from Müller
190 (1969): $I_{geo} = log_2(C_n/1.5B_n)$

191 Eq. 1

192 where C_n is the concentration of a given element n in ppm in a sediment interval that is
193 considered anthropogenically influenced (above the baseline intervals) and B_n is the average
194 concentration in ppm of the element in the pre-impact intervals of the sediment core. The 1.5
195 multiplication factor was introduced by Stoffers et al. (1986) to include variation in background
196 values, which could be attributed to natural variations in sediment properties. Pre-impact
197 (background) intervals for each core were selected based on plots of historical stressors (Reavie,
198 Cai & Brown, 2018; Fig. 2). A lake was considered impacted based on a horizon of increased
199 population, increased agricultural acreage, or increase in mining activity.

200 EF is a measure of sediment contamination relative to baseline (i.e. pre-impact) conditions
201 adjusted for sediment composition. It minimizes contaminant variability associated with clay-
202 rich mud/sand ratios by normalizing the contaminant content with respect to a reference element
203 that acts as a proxy for the clay content of the sediment (Abrahim & Parker, 2007). EFs were
204 calculated according to the following equation adapted from Weiss et al. (1999):

$$EF = \frac{\left(\dfrac{Contaminant\ ppm}{Al\ ppm}\right)_{sediment}}{\left(\dfrac{Contaminant\ ppm}{Al\ ppm}\right)_{background}}$$

205

206 Eq. 2

207 Where *sediment* is the sediment layer in the post-impact interval of interest and *background* is
208 the sediment interval considered pre-impact. The Al concentration is used in this case as a

209 reference element, as it is conservative and a major constituent of clay minerals. Aluminum has
210 previously been used as a reference element in the Great Lakes by Kemp and Thomas (1976) and
211 Kemp et al. (1976).

212 Within each core, I_{geo} and EF values were averaged within each decade following the temporal
213 horizon representing the "impact" period. Lake Erie's western core was excluded from these
214 analyses because the core only went back to 1930, which was after the start date of significant
215 human impacts. Sodium concentrations were not included for Lake Huron South or Lake
216 Michigan South as initial Na values were zero in both of these cores, hence there was no way to
217 quantify enrichment relative to baseline.

218 Historical stressors of agriculture area, forested area, mining stress, new mining sites, overall and
219 urban population were summarized for 60 watersheds of the Laurentian Great Lakes basin from
220 early 1800 to 2010 (Reavie, Cai & Brown 2018). The relationships between metal concentrations
221 and historical stressors of drainage watersheds were analyzed by checking Pearson's correlation.
222 The annual data of historical stressors were summarized as the sum, area weighted average and
223 lake water volume weighted data, then linearly interpolated to sediment interval dates. Data from
224 the 11 sediment cores were combined for analysis against stressors. Pearson correlation analyses
225 were performed in R 3.5.1 using the function rcorr in the Hmisc package (Harrell, 2019).

Contamination and toxicity guidelines

227 Sediment contamination guidelines help managers assess risk to biota and other water uses. In
228 the Great Lakes region, Ontario set guidelines using the screening level concentration (SLC)
229 approach. The SLC approach uses field data to examine the relationships between benthic
230 organisms and contaminant levels. The SLC represents the concentration that 95% of species can
231 tolerate. For metal contaminants, the Ontario guidelines have two levels: the lowest effect level,
232 which indicates sediment that is clean to moderately polluted, and the severe effect level, which
233 indicates heavy pollution that is likely to negatively impact the health of benthic organisms
234 (Persaud, Jaagumagi & Hayton, 1993). Another set of contamination guidelines in use are the
235 Effects Low Range (ER-L) and the Effect Medium Range (ER-M) developed by NOAA in
236 marine systems. ER-L values represent the lower 10th percentile for biological impact and the
237 median was represented by the ER-M. These guidelines are not used as official standards or
238 criteria but can be used to help managerial decision making (Long & Morgan, 1990; Long et al.,
239 1995). Yet another approach for calculating sediment guidelines is the apparent effects threshold
240 (AET), which reports the sediment concentration of a contaminant above which significant
241 biological effects always occur in benthic organisms. Apparent effects threshold-low (AET-L)
242 and apparent effects threshold-high (AET-H) values were based on data from Puget Sound
243 (Barrick et al., 1988). For our purposes, we used the Ontario guidelines when available, followed
244 by the ER-L and ER-M values, and we used AET values when neither of the other sets of
245 guidelines was available for a given metal contaminant. Even with all three of these guidelines,
246 only a small subset of the metals had relevant guidelines.

247 **Results**

248 **Cluster Analysis:** The dendrogram formed by hierarchical cluster analysis of all Great Lakes
249 samples (Fig. 3) divided the analytes into five functional groups.

250 • Group 1 contains only Ca, Mg and their oxides. Calcium and Mg are common carbonate
251   elements (Callender, 1969; Kemp et al., 1976) that come from terrigenous clay minerals and
252   they are also associated with carbon cycling in lakes (Sgro & Reavie, 2017). Microorganism
253   respiration creates CO_2, which dissolves Ca from its carbonate minerals. Peaks can represent
254   historical algae blooms and other spikes in primary productivity (Yuan, 2017).
255 • Group 2 contains analytes with diverse natural sources, though some are considered
256   anthropogenic pollutants. For instance, sediment Na may be related to road salt input and
257   P_2O_5 (phosphorous pentoxide) may come from fertilizer applications (Chambers et al.,
258   2016). Many Group 2 elements are also known to be strongly associated with Fe and Mn
259   oxides, which they sorb to strongly, especially Pb, Cu, Zn, Ni, Cd, and Co (Stone &
260   Marsalek, 1996). Group 2 is further subdivided into Group 2a, a set of analytes known to be
261   highly enriched in the Great Lakes (Cd, Pb, Sn, Zn, and Sb; Robbins, 1980; Yuan, 2017).
262   Group 2a elements are also all atmospheric and specifically enriched due to smelting of Pb
263   and Cu (Crecel & Johnson, 1974; Warren, 1981; Galloway et al., 1982; Christensen &
264   Osuna, 1989; Biegalski & Hopke, 2004; Yohn et al., 2004; Shotyk, Krachler & Chen, 2005;
265   Norton et al., 2007; Ettler et al., 2010).
266 • Group 3 analytes are mostly common crustal elements with sources such as soil dust, runoff,
267   and coastal erosion. Sr, K, and Fe are also related to mining inputs. Iron is mobile in
268   sediments and can concentrate just below the sediment/water interface due to redox-related
269   migration, a phenomenon that is visible as a rust colored sediment layer in Lake Superior
270   cores (Shaw Chraïbi et al., 2014).
271 • Group 4 contains analytes which are widely distributed but are magnified by anthropogenic
272   inputs. U and Cs are both associated with nuclear power and weapons testing (Alloway,
273   2013; Reavie et al., 2005). Ru and U are associated with coal combustion (Campbell et al.,
274   2005; Alloway, 2013). Cr is associated with steel production and leather tanning (Reavie et
275   al., 2005).
276 • Group 5 is the largest and most diverse group containing all of the rare earth elements. Some
277   other elements included are Ba, which is used as a drilling fluid (Moore, 1991), and Th,
278   which is a byproduct of uranium mining (ASTDR, 1990). Otherwise, most of these elements
279   are not known to be directly anthropogenically sourced though they may be increased due to
280   erosion.

281 **PCA**

282 Based on PCA (Fig. 4), 51% of the variance in the geochemical data is explained by the first two
283 axes, which we present visually. The first, second, and third axes described 38.5%, 12.8%, and
284 8.2% of the variance, respectively. The five groups of analytes identified by cluster analysis are
285 clearly segmented along the first axis. We infer this primary gradient to largely represent the
286 bedrock and soil conditions in the vicinity of the sediment cores, indicating that natural setting is

287 the strongest determinant of geochemical condition across the Great Lakes basin. The second
288 axis appears to be a measure of contamination and temporal changes within cores, with more
289 anthropogenically enriched analytes (e.g. Zn, Cd, Sn, Sb, Pb; Group 2a) having higher axis 2
290 values. Figure 4b explores the temporal trajectories of sample scores. While not clearly apparent
291 for all cores, there is a general pattern of positive movement along axis 2 from the oldest to most
292 recent samples, indicating movements toward the contaminant Group 2a. Additional PCA score
293 trajectory data are used in conjunction with each lake's results (below).

Geochemical Profiles

295 Figures 5 through 11 present the geochemical profiles of each grouped cluster of analytes. These
296 results are mainly used for lake-specific interpretations, but some basin-wide observations in
297 historical trends are notable. Carbonate-related analytes were variable or monotonous since
298 ~1850 (Fig. 5), but Lake Ontario had a distinct peak in Ca and CaO centered around the 1970s.
299 Concentrations of Group 2a (Fig. 6; heavy metal contaminants) increased starting in the early
300 1900s, peaking around 1970. The Lake Ontario cores have the largest increases in these Group
301 2a elements followed by Lake Michigan. Concentrations of the Group 2 analytes (Fig. 7)
302 followed erratic profiles, however there are a few exceptions. Manganese, MnO, and As
303 concentrations have near-surface peaks likely related to redox conditions in the sediment. All
304 cores increase in Na concentrations from presettlement times, accelerating quickly beginning
305 around a 20-year period from the 1950s-70s with surface peaks in many cores. The rise in Na
306 began much earlier in the 20th century in western Lake Superior.

307 Group 3 analytes (Fig. 8), representing terrigenous sediment inputs, also show few consistent
308 patterns over time. However, Sr and SrO peaked in Lake Ontario between 1979 and 1984. Al
309 concentrations decreased over time in Lake Huron North. Several cores had near-surface peaks
310 in Fe likely related to redox activity in the sediments. Throughout the period of analyses the
311 composition of instrumental calibration standards changed, preventing accurate measurement of
312 Li or Ti in certain cores, so they were not part of multivariate analyses; they are plotted with this
313 group due to similar profiles. Lithium concentrations increased over time for Lake Huron North
314 and decreased for Superior West, Michigan South, and Huron South. Lake Superior West and the
315 Lake Superior mid-lake "Isle Royale" core had very similar Ti profiles, with jagged peaks in the
316 1980s and 1990s and then decreases to surface intervals.

317 The concentrations of Group 4 analytes associated with coal ash and nuclear power generation
318 (Fig. 9) are mostly stable over time, though K_2O densities decreased in Lakes Ontario and
319 Michigan. Cr had a spike in Lake Michigan North in 1867 and Lake Ontario West in 1928.

320 Figure 10 represents Group 5's rare earth and associated element concentrations over time. Many
321 of the profiles are monotonous and erratic, but there appears to be a slight downward trend over
322 time, and there is a distinctive dip in each of these elements in the Michigan South core in 1933.
323 Lake Ontario cores and the Lake Michigan south core had recent peaks in Ba and BaO.

324 Lake Superior

325 Lake Superior samples are mainly associated with the Group 3 (siliciclastic, watershed-derived)
326 analytes (Fe, Sr, K, Na$_2$O, Si), though the Isle Royale core is specifically influenced by Group 2
327 analytes such as Mn, P, and their oxides (Figs. 4,7,8). The core sample scores track positively
328 along PC2, with Superior West as the least enriched with Group 2 metals and Isle Royale as the
329 most enriched. Upward migrations along PC2 (Fig. 4) reflect increases in Group 2a contaminants
330 such as Pb and Cd during the mid-20th century, with declines in these metals after the 1950s (Fig.
331 6). Of all the cores in this study, Lake Superior West had the tightest sample score distribution,
332 indicating the smallest quantitative change in geochemical characteristics over time.

333 A gradual rise in Na concentration (Fig. 7) is evident in the 20th century through the uppermost
334 sediments in all Superior cores, though the western core, which is closest to the urban centers of
335 Duluth and Superior, has the earliest and most substantial rise, especially after the 1950s. Lake
336 Superior cores had a distinct peak in metals just below the sediment surface denoted by peaks in
337 Mn, As (Fig. 7) and Fe (Fig. 8) corresponding with a known horizon formed by the migration of
338 redox-induced mobilization of metals (Li et al., 2012). Several Group 3 (Fig. 8) and Group 5
339 (Fig. 10) analytes gradually declined in concentration over the last ~100 years.

340 Cu in Superior East began to increase in concentration around 1922 from less than 100 ppm,
341 peaking around 1958 at 456 ppm and decreasing to ~220 ppm by the 1970s, after which it has
342 remained stable. The installation of new mines in Lake Superior's catchment peaked between
343 1900 and 1920 (Fig. 2; Kerfoot et al. 1999), well before this notable rise in Cu. Superior West
344 had peaks in Ni and Cu in 1980.

345 Lake Michigan

346 The Lake Michigan cores were both associated with the Group 1 (carbonate) analytes (Ca, Mg,
347 CaO, MgO) though the Lake Michigan South core had a dip in all of these analyte concentrations
348 beginning around 1948 and ending around 1993 when the analytes increased to well over historic
349 levels (Figs. 4 and 5). Both cores tracked positively along PC2 over time. The northern core had
350 stronger increases along PC2 over time and the Lake Michigan South core had less net change
351 (Fig. 4). Upward migrations along PC2 reflect increases in Group 2a contaminants such as Sn
352 and Pb during the mid-20th century, with declines in these metals after the 1960s (Fig. 6). Group
353 2a analyte concentrations in the south core of Lake Michigan were second only to Lake Ontario,
354 indicating substantial enrichment in contaminants in closer proximity to urban centers such as
355 Chicago. The rise in Na was more subtle in Michigan compared to other lakes (Fig. 7), though
356 the southern core demonstrated a distinct horizon of first Na detection around 1940. The Lake
357 Michigan South core experienced dips in Group 5 analytes (especially the rare earth elements)
358 around 1933 potentially representing a large sedimentation event that would have diluted
359 sediment metals (Fig. 10). Both cores experienced a less extreme dip in these analytes around
360 1968. In recent decades both cores have had drops in Group 2a contaminants, though Pb and Sn
361 are now higher in Michigan South than any other Great Lakes core (Fig. 6). There have been
362 drops in the Group 1 carbonate elements to around pre-impact levels (Fig. 5). In Michigan North,
363 there have been recent increases in Group 5 elements (Fig. 10) and the Group 4 elements Cr, Rb,
364 and K$_2$O (Fig. 10).

365   Lake Huron

366   Lake Huron South was primarily associated with Group 1 (carbonate) analytes (Fig. 4), having
367   the highest stable concentrations of all of these elements and the highest concentrations of Mg
368   and MgO, both historically and in modern times (Fig. 5). Huron North was associated primarily
369   with the terrestrial analytes of Group 3 and had the highest stable concentrations of Al, K, and Si,
370   though Al concentrations decreased steadily over time (Figs. 4 and 8). Both cores tracked
371   positively along PC2 over time, though they both had relatively tight distributions of sample
372   scores (Fig. 4). These increases reflect increasing concentrations of Group 2a concentrations
373   such as Sn and Pb, which both peaked in the 1990s (Fig. 6). Lake Huron cores had peaks in
374   many Group 2 elements (Fig. 7), corresponding with a horizon likely formed by the migration of
375   redox-induced mobilization of metals (e.g. Mn, As, Fe; Fig. 8). Lake Huron South historically
376   had Na concentrations below detection limits until the most recent decade, when Na increased to
377   130 ppm by 2012 (Fig. 7). Prior to the 1970s, the northern location contained Na concentrations
378   around 110 ppm, after which Na levels increased. Lake Huron South had a peak in Nb around
379   1968 (Fig. 8). The Lake Huron South core has gradually decreased in Group 5 (rare earth)
380   analyte concentrations in recent times (Fig. 10). Around 1983, the Lake Huron North core had a
381   notable dip in all of the Group 5 analytes (Fig. 10) along with Sr and SrO (Fig. 8).

382   Lake Erie

383   Lake Erie's central basin was primarily associated with the terrestrial analytes of Group 3,
384   especially Fe and SiO_2 (Figs. 4 and 8). Lake Erie's western basin has been associated with
385   analytes between the carbonates of Group 1 and the terrestrial elements of Group 3 such as Mg,
386   Zr, and SiO_2. Both cores moved up PC2 slightly over time (Fig. 4), representing increases in
387   Group 2a (contaminant) analytes (Fig. 6). Unlike other lakes, historical trends in carbonate-
388   related analytes show a gradual decline but are otherwise unremarkable (Fig. 5). These increases
389   were smaller than those of Lakes Michigan and Ontario but larger than those of Superior and
390   Huron. The central core had a peak in many elements including Sn, Sb, Cu, Mo, Na, Co, and Nb
391   in the 1880s (Figs. 6, 7, and 8). A gradual rise in Na concentration (Fig. 7) is evident in the 20th
392   century through the uppermost sediments in both Erie cores, though the central core, which is
393   adjacent to the urban center of Cleveland, began its rise before the 1950s. There was a hump in
394   As concentrations in the Erie West core in the late 1960s (Fig. 7). For Group 2 analytes, Ni and
395   Cu both had peaks in the 1960s (Fig. 7). Fig. 9 reveals a rise and fall of Cr during the mid-20th
396   century as well as a fairly persistent rise in U and K_2O in western Erie. As for other lakes, a
397   gradual decline in rare earth elements is apparent for Lake Erie over the last ~100 years (Fig. 10).

398   Lake Ontario

399   Lake Ontario East was historically associated with the soil derived analytes of Group 3 (Figs. 4,
400   8), specifically Si. Lake Ontario West was historically related to the rare earth analytes of Group
401   5 (e.g. Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy; Figs. 4, 10). Lake Ontario had the highest increases
402   in PC2, the dimension associated with pollutants (Fig. 4) related to the cores having the highest
403   peaks in all Group 2a analytes (Zn, Cd, Sn, Sb, and Pb; Fig. 6). Lake Ontario West had a peak in
404   Cr around 1928 (Fig. 9). The Lake Ontario west core also had a peak in P concentrations in the

405   late 1940s (Fig. 7). Notable Ca and CaO peaks occurred from ~1960 through ~1990 (Fig. 5), and
406   there was a hump in As concentrations in the late 1960s (Fig. 7). The highest Na concentrations
407   occurred near the surfaces of the cores (Fig. 7). Lake Ontario also had peaks around 1980 in
408   several other elements including Sr and Ba (Figs. 8 and 10), while most of the other rare earth
409   elements exhibited a decline in the last few decades (Fig. 10). In the late 1960s and early 1970s,
410   the Ontario East core had elevated levels of Ti (Fig. 8). Cores had a distinct peak in metals just
411   below the sediment surface denoted by peaks in Mn, As (Fig. 7) and Fe (Fig. 8).

412   **Historical contaminant enrichment**

413   Pre-post-impact transition dates were defined as follows using historical stressor data (Fig. 2):
414   Lake Superior = 1900 due to a clear horizon of new mining; Lake Michigan = 1880 due to an
415   increase in agriculture and mining; Huron = 1880 due to an agricultural increase; Erie = 1880
416   due to increases in agriculture and to correspond with dates confirmed by Yuan (2017); and
417   Ontario = 1900 due to increases in agricultural land and decreases in forest land.

418   For the purposes of calculating these two indices, Group 2 and 2a elements (determined by
419   cluster analysis and PCA) were considered the contaminant elements of interest. I_{geo} and EF
420   values were placed on a heatmap (Fig. 11), highlighting the contaminant element that had the
421   maximum value for each of the indices in a given decade. The contamination indices I_{geo} and EF
422   showed similar temporal trends to one another though there were some differences. I_{geo} indices
423   never achieved more than a "heavily" contaminated ranking (most were considered
424   uncontaminated or moderately contaminated), whereas EF had several cases indicating
425   "extreme" enrichment of contaminant elements, especially for Co.

426   In Lake Superior, Na was the most common, dominant contaminant since the beginning of the
427   20th century, well before road salt was in common use. The most contaminated decade in Lake
428   Superior was the 1950s with an I_{geo} of 0.2 and a 3.6 EF value with Co being the most enriched
429   element. The 1980s (I_{geo} of 0.2, EF of 2.1), 2000s (I_{geo} of 0.2, EF of 2.6), and 2010s (I_{geo} of 0.3,
430   EF of 1.7) were also contaminated, with Na being the maximum value except for EF in 2010,
431   which was dominated by Mn.

432   In Lake Michigan, sediments have been enriched with Group 2 elements consistently since the
433   1940s, being dominated by Cd in most decadal intervals. The highest I_{geo} (0.9) and EF (4.1)
434   values were in the 1990s with Co being dominant in both cores. After that, Pb, Cd and Mn were
435   the dominant contaminants.

436   In Lake Huron, Co was a leading contaminant in the 1890s, 1900s, 1960s, and 2010s, with
437   maximum I_{geo} (0.8) and EF (35.2) values in the 1960s. Cd and Pb were the other leading
438   contaminants in this lake beginning in 1910 all the way up until the 2000s.

439   Lake Erie I_{geo} and EF values were strongly influenced by Ta and Cd, though the highest values in
440   recent times were Na, with an average I_{geo} of 0.1 (minimal contamination) and 2.7 EF (moderate
441   enrichment).

442   Lake Ontario had the highest enrichment in the 2000s with an I_{geo} of 1.1 (extremely
443   contaminated) and a moderate EF of 8.8 attributed to high Co. Ontario also had high enrichment
444   of Mn, Cd, and Cu.

Contamination and toxicity guidelines

446   In Group 2a, there were guidelines for Zn, Cd, Sb, and Pb. For Zn, no cores were ever above the
447   severe effect level, though lowest effect level exceedances were common. Lake Ontario, Lake
448   Erie Central, and Lake Superior Isle Royale exceeded lowest effect level in pre-impact
449   sediments. For Cd, Lake Michigan South and Lake Superior Isle Royale were above the lowest
450   effect level pre-impact, but no sediments exceeded the severe effect level. Sb did not have levels
451   defined by the Ontario guidelines, so AET-L and AET-H levels were used. None of the cores
452   were above either of these levels at any point. No cores had Pb levels above ER-M at any point,
453   though every core except Lake Superior West exceeded ER-L at some point. Though levels have
454   declined with time, all but Superior West and Huron South remain above ER-L for Pb.

455   In Group 2, there were guidelines for Mn, As, Ni, and Cu. For Mn, Lake Ontario East was at the
456   severe effect level pre-impact. Lake Ontario West, Lake Michigan North, Lake Superior Isle
457   Royale, and Lake Superior West were all at the lowest Mn effect level pre-impact. All lakes
458   exceeded the severe effect level for Mn in recent sediments. For As, Lake Ontario West was
459   above severe effect level pre-impact, and all cores except Huron North and Michigan South were
460   above lowest effect level in pre-impact sediments. Both Ontario cores and Lake Huron South
461   were above severe effect level for As in recent sediments. All cores in this study exceeded the
462   lowest effect level for Ni in pre-impact sediments; Ontario West was above severe effect levels
463   pre-impact. In recent sediments, both Ontario cores and Huron North were above Ni severe
464   effect levels. For Cu, all core pre-impact sediments exceeded the lowest effect range; Lake
465   Superior Isle Royale exceeded the severe effects level. In recent sediments, both Lake Ontario
466   cores, Lake Superior Isle Royale, and Lake Superior East were above severe effects level for Cu.

467   Contaminant guidelines existed for Cr in Group 4. In pre-impact sediments, all cores were above
468   the lowest effects level for Cr, while Michigan North and Superior Isle Royale were above
469   severe effect levels. In recent sediments Erie, Ontario West, and Superior Isle Royale were above
470   the severe effects level.

Metal and Stressor Correlations

472   Several metals and oxides were strongly related to stressors. Group 1 (carbonate-related)
473   analytes were strongly positively correlated with agricultural area and population while having
474   negative correlations with mining stress and forestry (Table 1). Group 2a elements, the well-
475   known atmospheric contaminants (Norton et al., 2007; Ettler et al., 2010), had strong positive
476   relationships with population and weaker, negative correlations with mine stress. Pb had a
477   positive correlation with forestry. The remaining Group 2 elements had few correlations with
478   stressors, though some (Na, Mo, Ni, As, Mn, and MnO) had some affinity with population. Nb
479   was negatively correlated with forestry, and Cu was negatively correlated with agricultural area.
480   Group 3 (common crustal) analytes were largely negatively correlated with agricultural area and
481   population and several were positively correlated with forestry and mine stress. Some Group 4

482 analytes (a complicated set of potentially anthropogenic pollutants) were positively correlated
483 with agricultural area (K_2O, Rb, Cs) and population (Cr, U, Rb, Cs), while Rb and Cs had strong
484 negative correlations with forestry and mine stress. Group 5, the widespread rare earth analytes,
485 had mainly negative correlations with agricultural area and, to a lesser extent, forestry and
486 population. TiO_2, Er, Tm, Tb, Lu, Y, and Dy had weak but significant correlations with mine
487 stress.

Discussion

489 Natural, lake-specific physicochemical conditions and unique anthropogenic histories likewise
490 necessitate lake-specific interpretations for geochemistry and contaminant history in the Great
491 Lakes. However, certain patterns in ubiquitous metals and key pollutants were observed
492 throughout the basin, reflecting widespread anthropogenic effects. One example is the up-core
493 reduction in all rare earth elements (Group 5; Fig. 10), which may represent a long-term dilution
494 of natural elements as human development intensified and the flux of other materials (organic
495 and inorganic) increased. The most prevalent basin-wide pollutants were Pb, Cd, Co, and Na.
496 Historical lead pollution is largely related to combustion of leaded gasoline, and since enactment
497 of removal regulations in the 1970s the concentration of Pb has declined in all of the sediment
498 cores (Yuan, 2017). Such long-term trends in this widely scattered, toxic pollutant have been
499 observed worldwide in sedimentary records (e.g. Farmer et al., 1996; Heyvaert et al., 2000).
500 According to Sherman et al. (2015), after leaded gasoline was banned sources of Pb are likely
501 atmospheric deposition from coal and oil combustion, metal mining and processing, battery
502 recycling, and oil refining. Despite continued atmospheric releases, the gasoline ban clearly
503 reduced atmospheric deposition of Pb to aquatic systems in North America. The other related
504 (Group 2a) elements – Cd, Sn, Zn, and Sb – follow patterns in historical Pb, as these atmospheric
505 pollutants volatilize at high temperatures and are frequently associated with smelting and fossil
506 fuels (Norton et al., 2007; Ettler et al., 2010). Cobalt is also an atmospheric contaminant, and one
507 often associated with forest fires (ASTDR, 2004), so it is not surprising it is found at
508 enriched concentrations throughout the Great Lakes basin sediments. Cobalt has not been mined
509 within the Great Lakes basin, but it is likely a byproduct of other mining activities due to its
510 presence in many rock types (Carr & Turekian, 1961).

511 In the metal-stressor correlations (Table 1 and Fig. 2), there is clearly decoupling between
512 agricultural area and population, and especially mines and populations. Landscape mine stress
513 poorly represents itself in these deep lake cores, and instead we get erosional signals (such as
514 seen in Group 3 analytes) during early settlement periods. In terms of sediment geochemistry,
515 human population and sometimes agriculture are good tracers while mine stress is not, probably
516 because actual mine waste is apparently not providing a useful signal in these deep lake cores,
517 the one exception being records from Cu from Lake Superior, described below.

518 Salt pollution is also revealed as a prevailing phenomenon in the Great Lakes. In the United
519 States, annual rock salt used for road deicing was 163,000 tons in 1940, increasing to more than
520 23 million tons in 2005 (Novotny, Murphy & Stefan, 2008). In Minnesota, rock salt use
521 increased from 60,000 to 900,000 tons in the same time period. This rock salt has led to
522 increased salinity in lakes near major roadways of urban watersheds. Sodium is unsurprisingly

523 found at higher concentrations near the surfaces of cores as a result of its prevailing use as a
524 deicing agent (NaCl) on roads since the late 1940s. The use of rock salt can be attributed to Na
525 and Cl tracing each other in sedimentary and water quality datasets, and while increasing
526 lakewater Cl concentrations have been linked concurrently with industrial inputs (Sonzogni et al.
527 1983), concurrence with sedimentary Na trends clarifies the importance of road salt. Lake
528 Superior and Lake Michigan Cl concentrations have continued rising and are currently at
529 maximum recorded levels. In Lakes Huron, Erie, and Ontario Cl concentrations peaked between
530 1965 and 1975 and then decreased, though recent data indicate Cl levels are increasing again
531 (Chapra, Dove & Rockwell, 2009). Na levels in Lake Superior began to increase decades before
532 road salt usage began in the 1940s, possibly because Na is a component of the silicate rocks that
533 comprise the majority of its disturbed watershed (Chapra, Dove & Warren, 2012). In addition to
534 road applications rising, Na values may also represent increases in runoff, weathering, and
535 dissolution of these rocks and soils.

536 While most of the analytes considered in this manuscript tend to be stable in sedimentary
537 records, some are subject to post depositional mobility, which may obscure our ability to use
538 them for historical interpretations. For example, subsurface peaks in Mn, As (Fig. 6) and Fe (Fig.
539 7) observed across the Great Lakes likely correspond with a typical horizon formed by the
540 migration of redox-induced mobilization of these metals (Li et al., 2012). While geochemically
541 interesting, uncertainty should be applied when making historical interpretations from profiles of
542 these mobile metals. Many metals are mobilized by these oxides, which may further complicate
543 interpretation (Presley, Trefry & Shokes, 1980).

544 Expressing a Great Lakes basin-wide interpretation of historical geochemistry is challenging
545 because of strong physical, chemical, and historical anthropogenic differences among the lakes,
546 so it is worthwhile summarizing geochemical histories that are specific to each lake.
547
548 **Lake Superior:**

549 Lake Superior's confined distribution of sample scores according to the PCA (Fig. 4) probably
550 relates to its low sediment accumulation rate and the lowest lake water ion concentrations
551 (Chapra, Dove & Warren, 2012). Due to its relatively small human population (Fig. 2), Lake
552 Superior has not received nutrient and industrial pollutant loads observed in other lakes
553 (O'Beirne et al., 2015). Nriagu et al. (1995) estimated that around 60–80% of anthropogenic
554 inputs to this lake are atmospheric. However, the bedrock in Lake Superior watershed is metal
555 rich, and between 1850 and 1929 the Keweenaw district was the 2nd largest producer of Cu in the
556 world. Even prior to Euro-American settlement, Cu mining activities by Native American
557 communities had detectable effects on lake geochemistry (Pompeani et al., 2015). For much of
558 the Anthropocene (1850–1968), several hundred million metric tons of mine tailings were
559 dumped into the lake (Kerfoot, Lauster & Robbins, 1994), an event that is clearly present in the
560 geochemical profile of the eastern core, where Cu concentration peaked in 1958, lagging behind
561 the largest period of mine openings, showing the long term impact of mining on this system. The
562 highest population density around Lake Superior is in the St. Louis River drainage, which is the
563 2nd largest inflow to Lake Superior (O'Beirne et al., 2015), just upgradient from the western core
564 location (Fig. 1). The proximity to the urban centers of Duluth and Superior explains the high Na

565 levels, which are probably mostly related to road salt use (Anderson, Estabrooks & McDonnell,
566 2000). Iron mining in Lake Superior and disposal of mining waste directly to the lake (Minnesota
567 Historical Society, 2012) lead to increases in water and sediment Fe concentrations that make for
568 distinct iron-laden layers in sedimentary records. Due to redox drivers, Fe and related mobile
569 metals are maintained near the tops of sediment profiles and therefore do not match up with
570 historical records of waste disposal.

Lake Michigan:

572 In terms of 20th-century contamination (largely Group 2a analytes; Fig. 6), Lake Michigan was
573 similarly impacted to Lake Ontario, which is considered to be the most impacted of the Great
574 Lakes (Allan et al., 2013). Industrial contamination is attributed to the influences of the major
575 cities of Chicago and Milwaukee and their industrialized surroundings. Lake Michigan's
576 southern basin has limited river inflows and so inorganic contaminants to the lake tend to be
577 atmospheric inputs from urban centers (Winchester & Nifong, 1971). Rossmann, Pfeiffer &
578 Filkins (2014) found Pb concentrations in Lake Michigan sediments rose after 1850 due to coal
579 and gas combustion, rose more with industrial activity around WWII, and lowered after the
580 Clean Air Act of 1970 and the phase-out of leaded gasoline. These trends largely match our
581 long-term trends for Pb in our sediment cores. The distinct dip in Group 5 analytes in Lake
582 Michigan South around 1933 (Fig. 10) is difficult to explain but is probably a result of a
583 substantial depositional event resulting in dilution of these ubiquitous rare earth materials. It is
584 countered by very high concentrations of SiO_2. The feature also aligns with the timing of the
585 Dust Bowl and may represent a large deposition of sediment from a dust storm in the Great
586 Plains (Cook, Miller & Seager, 2008).

587 In addition to Pb, the last century of sediments in Lake Michigan are defined by Cd and Co
588 enrichment. Cd and Co are both sourced into the environment through mining and smelting
589 emissions, the electroplating industry, and other industrial sources (Jaagumagi, 1993; Jeong &
590 McDowell, 2003).

Lake Huron:

592 Lake Huron had similar long-term trends in Group 2a contaminants as the rest of the Great Lakes
593 basin, in many ways revealing a similar atmospheric contamination signature as Lake Superior.
594 The Lake Huron North core contains higher contaminant concentrations despite being adjacent to
595 lower human populations than the southern core (Fig. 1). This may be due to the influence of the
596 Sudbury mining district located just upgradient. Cadmium is one of the key pollutants in the
597 lake, which is also sourced from the Sudbury area (Bagatto and Alikhan, 1987). Cobalt was also
598 a major contaminant in this lake, and according to ASTDR (2004) 76% of atmospheric Co input
599 into Lake Huron was from natural sources and 24% was from anthropogenic sources.
600 Anthropogenic sources include fossil fuel combustion, vehicular exhaust, copper and nickel
601 mining and smelting, and Co-containing phosphate fertilizers. An example of a likely natural
602 source of Co pollution was the "Fletcher Road Fire" in 1968 in Crawford and Kalkaska Counties
603 in northern Michigan that burned 4,216 acres of trees (Michigan Department of State Police,
604 2012). This event corresponds with the Co peak in the Lake Huron South core along with peaks

605 in Ni, Cu, and Mo. Reasons for the dip in Group 5 analytes around 1983 (Fig. 10) are unknown,
606 as is the decline in Al over time (Fig. 8); no erosional signals (e.g. SiO₂) suggest a dilution effect.

Lake Erie:

608 The Lake Erie basin has consistently had the highest population and an amount of agricultural
609 land in the catchment that is comparable to the much larger Lake Michigan (Figs. 1 & 2). As for
610 most of the Great Lakes basin, Lake Erie's geochemical record contains contaminant tracers of
611 industrial growth during World War II and the Korean conflict (Förstner, 1976). Peaks of Zn,
612 Cd, Sn, and Pb around 1949 and later declining by 1978 track higher atmospheric levels resulting
613 from combustion of fossil fuels, particularly the trend for the fuel additive Pb. Enrichment of Cd
614 in the central basin of Lake Erie in the late 1940s relates to the growth of the Cleveland
615 electroplating industry (Förstner, 1976). Declines of these metal pollutants are related to the
616 stringent regulations passed in the 1970s, the ban of leaded gasoline and improvement in
617 municipal sewage (Yuan, 2017). Antimony peaked earlier, around 1938, which is earlier than
618 Walters, Wolery & Myser (1974), who found increases in Sb between 1948 and 1953 that they
619 attributed to industrial and diffuse sources. Despite reductions in contaminant metals, persistent
620 urbanization of Lake Erie's catchment has maintained increasing concentrations of sediment Na.
621 Kemp et al. (1976) found that approximately 60% of the heavy metal and nutrient loading to
622 Lake Erie sediments was deposited in the Eastern Basin despite being sourced farther upstream
623 in the vicinities of Detroit and Cleveland, suggesting the contaminants were transported long
624 distances. Closer geochemical investigation of Lake Erie's eastern basin is warranted.
625

Lake Ontario:

627 The Great Lakes Environmental Assessment and Mapping Project ranked Lake Ontario the most
628 stressed of the five Great Lakes (Allan et al., 2013), a ranking that is geochemically supported by
629 modern PCA scores being the most strongly associated with Group 2a contaminants (Fig. 3).
630 Sedimentary contaminants were particularly high in our cores from Lake Ontario. Major sources
631 of nutrients and toxic chemicals to Lake Ontario include cities along the Oswego, Genesee, and
632 Niagara Rivers and metro drainages near Toronto, Kingston, and Ottawa (see the developed area
633 in Fig. 1). There was also direct discharge of industrial and municipal waste from toxic waste
634 dumps (e.g. Hyde Park and Love Canal) into the Niagara River (Estepp & Reavie, 2015). The
635 Niagara River is the single largest tributary to Lake Ontario and is a major source for Cr, Cd, V,
636 As, and a lesser but significant source of Pb, Cu, Ni, corresponding with especially high peaks of
637 these metals in Lake Ontario (Thomas, 1983). In 1987, Canada and the United States signed a
638 Niagara River Declaration of Intent aiming to reduce pollution, which corresponds to decreasing
639 levels of these and other heavy metals in this system (Figs. 6, 7, 8, 10; Murphy, Bhavsar &
640 Gandhi, 2012). In addition to being heavily urbanized and industrialized, Lake Ontario is the
641 farthest downstream in our study so it may also be integrating stressor information about the
642 entire Great Lakes basin.

643 In Group 1 (Fig. 4), which contains carbonate minerals, Lake Ontario's historical association
644 with carbonates is emphasized. Fluctuations in Ca compounds in this system are probably related

645 to "whiting events," calcite precipitation during high primary productivity (algal blooms) during
646 the summer months in the lake. Hodell et al. (1998) found an exponential rise in sediment
647 carbonate after 1930, which peaked in the early 1980s, related to P loading that supported
648 increased algal biomass. Though recycling of sedimentary P can make it an unreliable paleo-
649 indicator (Anderson, Rippey & Gibson, 1993), the exponential rise in P concentrations in the late
650 1940s was likely due to increases in phosphate detergents in urban areas (Estepp & Reavie,
651 2015). Stratigraphic declines in Ca and CaO in Lake Ontario in the mid-1980s likely reflect a
652 decline in open-water calcite formation, a delayed response to P reduction measures that began
653 in the late 1970s (Barbiero, Tuchman & Millard, 2006). Later, Ca uptake by invasive dreissenid
654 mussels, which were first detected in Lake Erie in 1988, probably further contributed to the
655 decline in Ca concentrations in these deepwater sediment core locations.

656 **Sediment Contamination Guidelines**

657 No literature could be found that suggested there is environmental concern regarding sediment
658 metals in the deepest, pelagic regions of the Great Lakes. However, exceedances of sediment
659 contamination guidelines were common, especially in Lake Ontario. Sometimes these
660 exceedances occurred in pre-industrial sediments, so it is worth considering the natural or
661 "baseline" context acquired from long-term sediment records to confirm whether contamination
662 is a result of human activities and to determine appropriate remedial measures. Most of the
663 guideline exceedances are from long-buried sediments, so environmental threat may be minimal
664 assuming these deep sediments are never dredged. With all of these caveats considered, our
665 examination of surface sediment metals suggests Pb in all lakes, Cu in Lakes Ontario and
666 Superior, and Cr in Lakes Erie and Ontario may be problematic in that these high concentrations
667 of contaminant metals are available to benthic biota and so may contribute to food web
668 bioaccumulation. As and Mn values in recent sediments are also above the extreme effect level
669 in all lakes but this may be due to redox-induced mobilization as discussed above.

670 # Conclusions

671 Using paleolimnological methods, we were able to construct a history of metals pollution
672 throughout the Great Lakes basin. Certain trends are observed basin-wide, such as for
673 atmospheric pollutants including Pb, which follows trends related to the use and ban of leaded
674 gasoline. Other trends are lake-specific, such as high levels of Na in Lake Superior due to road
675 salt applications and strong evidence of substantial whiting events in Lake Ontario. The Great
676 Lakes are sensitive to environmental changes such as pollution by metals, and it is clear that,
677 while there has been remedial success, results from the uppermost intervals of cores indicate
678 ongoing enrichment of contaminants. The impact of certain management practices, such as the
679 banning of leaded gasoline and improvement of municipal sewage, is visible in the cores and
680 demonstrates the efficacy of these practices. Certain analytes, especially Na, are still increasing
681 in sedimentary records indicating they may require further management. For future studies,
682 mineralogical contents of the cores should be considered so that elements can be more accurately
683 characterized to natural sources. Further, extension of coring efforts to nearshore areas would
684 allow for better identification of the sources of remaining contaminants of concern.

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Pearson correlations of stressors against downcore analyte data.

Analytes are grouped as determined by cluster analysis (Fig. 3). Coloring applies to positive (red) and negative (blue) relationships and asterisks reflect three levels of P-value.

Group	Analyte	Ag. Area		Forestry		Mine stress		Population	
1	Ca	0.37	***	-0.25	**	-0.28	***	0.4	***
	CaO	0.32	***	-0.19	**	-0.23	**	0.36	***
	Mg	0.42	***	-0.31	***	-0.24	**	0.28	***
	MgO	0.32	***	-0.23	**	-0.17	**	0.16	*
2a	Cd	0.01		0.09		-0.16	*	0.52	***
	Pb	-0.03		0.29	***	-0.16	*	0.37	***
	Sn	0.25	**	-0.04		-0.22	**	0.63	***
	Zn	0.1		-0.05		-0.24	**	0.55	***
	Sb	0.1		0.05		-0.13	*	0.46	***
2	Na	-0.01		-0.09		-0.12		0.2	**
	Ta	-0.03		0.07		0.03		-0.03	
	Nb	-0.1		-0.17	**	0.04		-0.03	
	Cu	-0.29	***	0.16	*	-0.04		-0.04	
	Mo	-0.06		-0.11		-0.08		0.17	*
	Co	0		0		-0.01		-0.01	
	Ni	0.05		-0.04		-0.04		0.16	*
	P	-0.13		0.03		0.01		-0.09	
	P_2O_5	-0.08		0.14	*	-0.1		0.06	
	As	-0.14	*	0.01		-0.17	*	0.14	*
	Mn	-0.11		0.1		-0.1		0.23	**
	MnO	-0.13		0.1		-0.1		0.21	**
3	SiO_2	0.14	*	-0.1		0.17	*	-0.17	*
	Zr	-0.51	***	-0.11		0.42	***	-0.36	***
	Hf	-0.43	***	-0.11		0.39	***	-0.33	***
	Sr	-0.49	***	0.15	*	-0.15	*	-0.22	**
	SrO	-0.34	***	0.27	***	-0.18	**	-0.14	*
	K	-0.58	***	0.63	***	0.27	***	-0.59	***
	Na_2O	-0.68	***	0.46	***	0.33	***	-0.63	***
	Al	-0.5	***	0.2	**	0.23	**	-0.45	***
	Fe	-0.07		-0.14	*	-0.09		-0.05	
	Si	-0.3	***	0.2	**	0.08		-0.32	***
	Li	0.15		0.78	***	-0.12		0.04	
	Ti	-0.8	***	0.54	***	0.05		-0.58	***
4	Cr	-0.04		-0.04		-0.19	**	0.3	***
	K_2O	0.4	***	-0.07		-0.11		0.08	
	U	0		-0.21	**	-0.16	*	0.26	**
	Rb	0.22	**	-0.32	***	-0.3	***	0.18	**
	Cs	0.25	**	-0.31	***	-0.35	***	0.32	***
	Fe_2O_3	-0.44	***	-0.02		0.04		-0.2	**

	Ba	-0.3	***	0.19	**	0.09		-0.12	
	BaO	-0.32	***	0.19	**	0.06		-0.12	
	TiO$_2$	-0.45	***	-0.3	***	0.25	**	-0.22	**
	Er	-0.38	***	-0.24	**	0.18	**	-0.18	**
	Tm	-0.38	***	-0.3	***	0.13	*	-0.17	*
	Yb	-0.33	***	-0.28	***	0.19	**	-0.15	*
	Lu	-0.35	***	-0.29	***	0.17	**	-0.16	*
	Y	-0.39	***	-0.2	**	0.15	*	-0.2	**
	Dy	-0.4	***	-0.22	**	0.16	*	-0.18	**
5	Tb	-0.45	***	-0.26	***	0.06		-0.19	**
	Ho	-0.45	***	-0.27	***	0.11		-0.2	**
	Th	-0.42	***	0.1		-0.12		-0.25	**
	Gd	-0.43	***	-0.16	*	0.09		-0.2	**
	Sm	-0.41	***	-0.14	*	0.01		-0.19	**
	Eu	-0.39	***	-0.17	**	0.04		-0.19	**
	La	-0.38	***	0.04		-0.05		-0.18	**
	Ce	-0.4	***	-0.04		-0.01		-0.16	*
	Pr	-0.48	***	-0.08		-0.09		-0.23	**
	Nd	-0.42	***	-0.05		-0.01		-0.21	**
	Ga	-0.17	*	-0.03		-0.1		-0.07	
	Al$_2$O$_3$	-0.14	*	-0.1		-0.06		-0.12	
	Sc	-0.22	**	-0.24	**	0.01		-0.08	
	V	-0.13		-0.4	***	-0.18	**	0.09	

*	P<0.05
**	P<0.01
***	Bonferroni correction for P=0.05

Figure 1

Land use map of the Great Lakes basin watershed.

Each lake's catchment is depicted and the 11 sediment core locations are shown. United States land use data is taken from the National Land Cover Database and Canadian land use data is taken from the open.canada.ca website. The classifications for each country were simplified and combined. The Canadian data does not separate development by intensity so all of the Canadian developed land is coded as medium intensity.
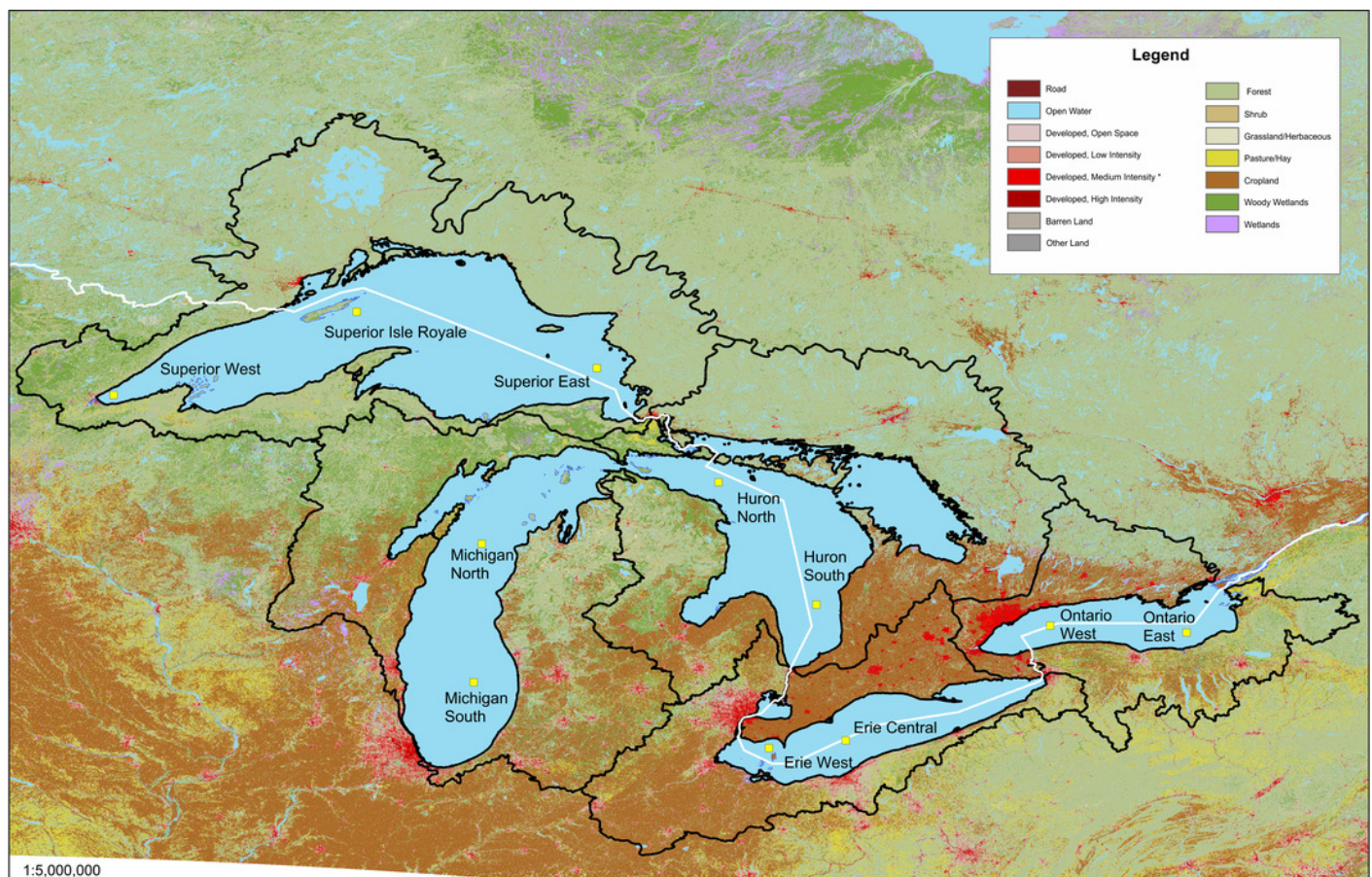
Figure 2

Plots of historical watershed stressors in the Great Lakes.

Data are compiled from Reavie, Cai & Brown (2018).
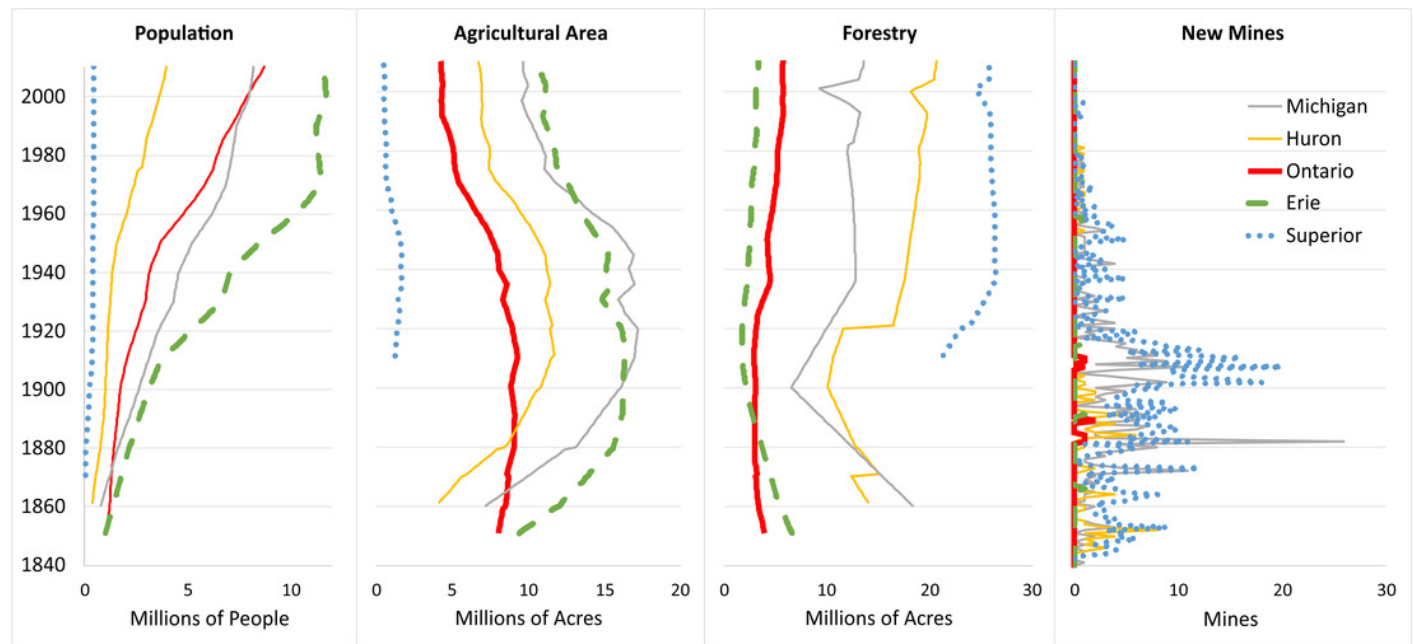
Figure 3

Dendrogram of cluster analysis for 60 analytes in the Great Lakes sediment cores.

Li and Ti are excluded from this analysis due to missing values. Five groups were defined based on the dendrogram and were numbered based on their positions in the PCA (Fig. 4).
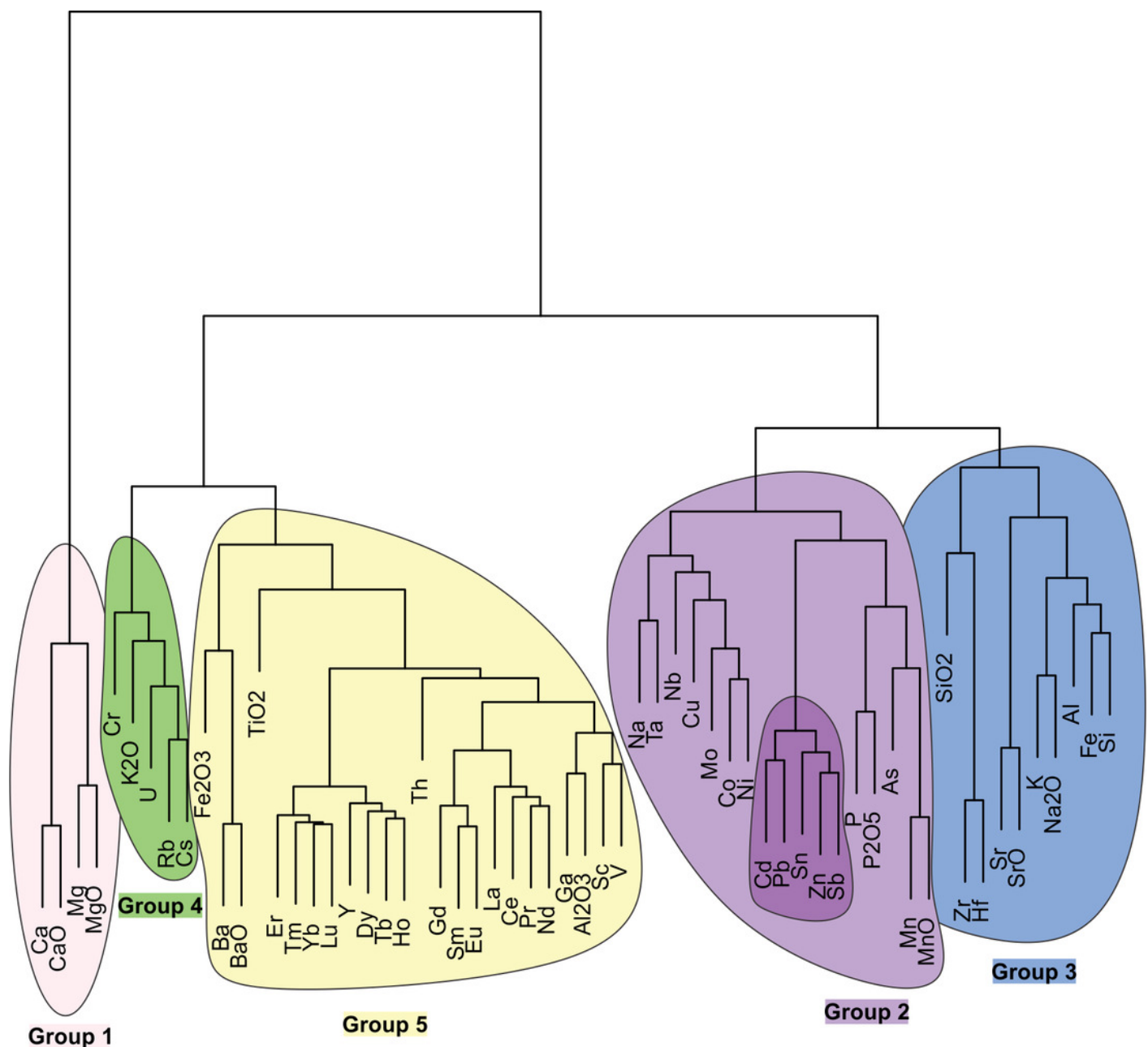
Figure 4

First two axes of a principal components analysis of all sediment sample metals geochemistry.

(A) Analyte scores with the five groups (as identified by cluster analysis; Fig. 3) outlined and filled in with different color. (B) Sample score trajectories for each core. Grey shapes in the background represent the groups shown in Panel (A).

PCA

A

Group 1
CaO
Ca
Mg
MgO

Group 2
MnO Mn P2O5
As
Mo Ni
P
Co Na
Ta

Group 2a
Zn
Sn Cd Sb
Pb

Group 4
SrO Cr
Cs
Cu Sr

Group 5
Ba BaO
Ga
Rb
U Fe2O3 La Al2O3
V Sc Ce
Th Pr Nd Sm
Gd Eu
Y Dy Tb
Er Ho
Yb Tm
Lu

Group 3
K2O
Fe
Nb
Si K
Al
Na2O
SiO2
Hf
TiO2

B

- Erie Central
- Erie West
- Huron North
- Huron South
- Michigan North
- Michigan South
- Ontario East
- Ontario West
- Superior Isle Royale
- Superior East
- Superior West

2008
2013
2012
2008
1672
1651
2012
2011
2012
2012
2011
1800
1716
2012
1870
1722
1814
1874
1930
1707
2009
1820

PC2

PC1

Figure 5

Analytes defined as Group 1 by cluster analysis.

These analytes are common carbonates from terrigenous clay minerals and carbon cycling in lakes.
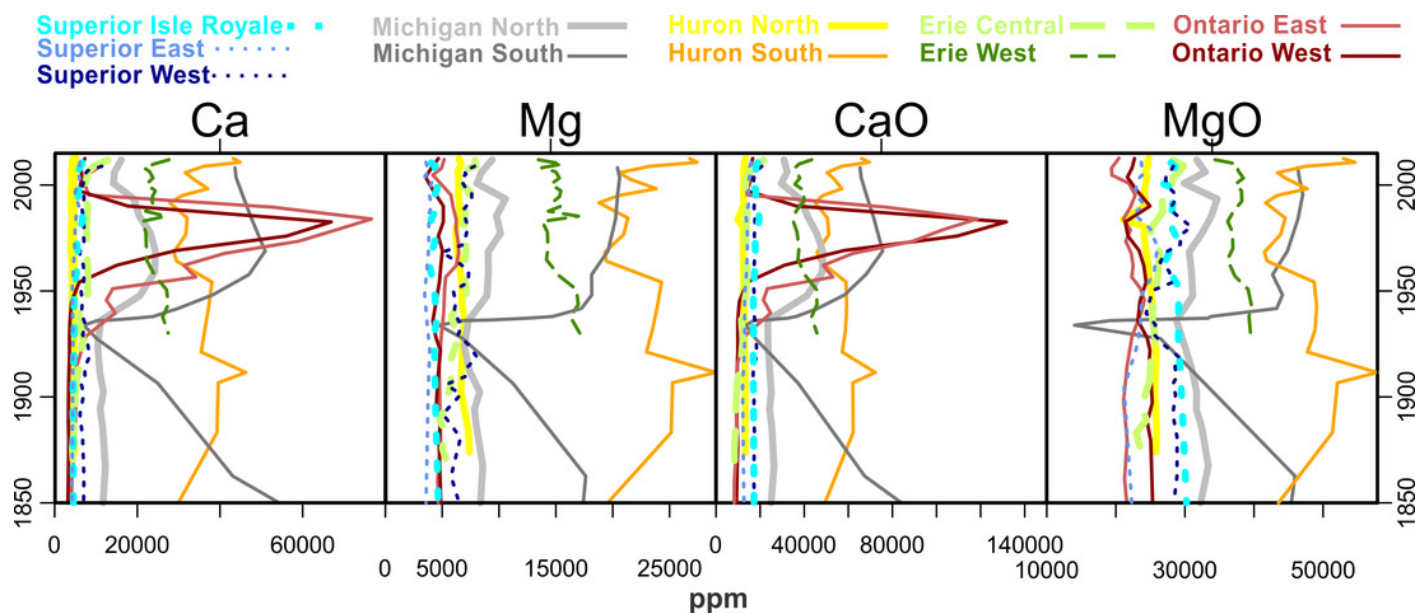
Figure 6

Analytes defined as group 2a by cluster analysis.

These analytes are recognized as distinct heavy metal contaminants in the Great Lakes system and are all known atmospheric contaminants. Arrows represent lowest and severe effect level values according to Ontario Sediment Quality Guidelines. For Pb no values were available using Ontario guidelines so ER-L (open triangle) and ER-M (closed triangle) values (US toxicity guidelines) are shown. For Sb neither of the two other indices had guidelines so AET-L (open square) and AER-M (black square) values (USEPA guidelines from Puget Sound, Washington) were used.
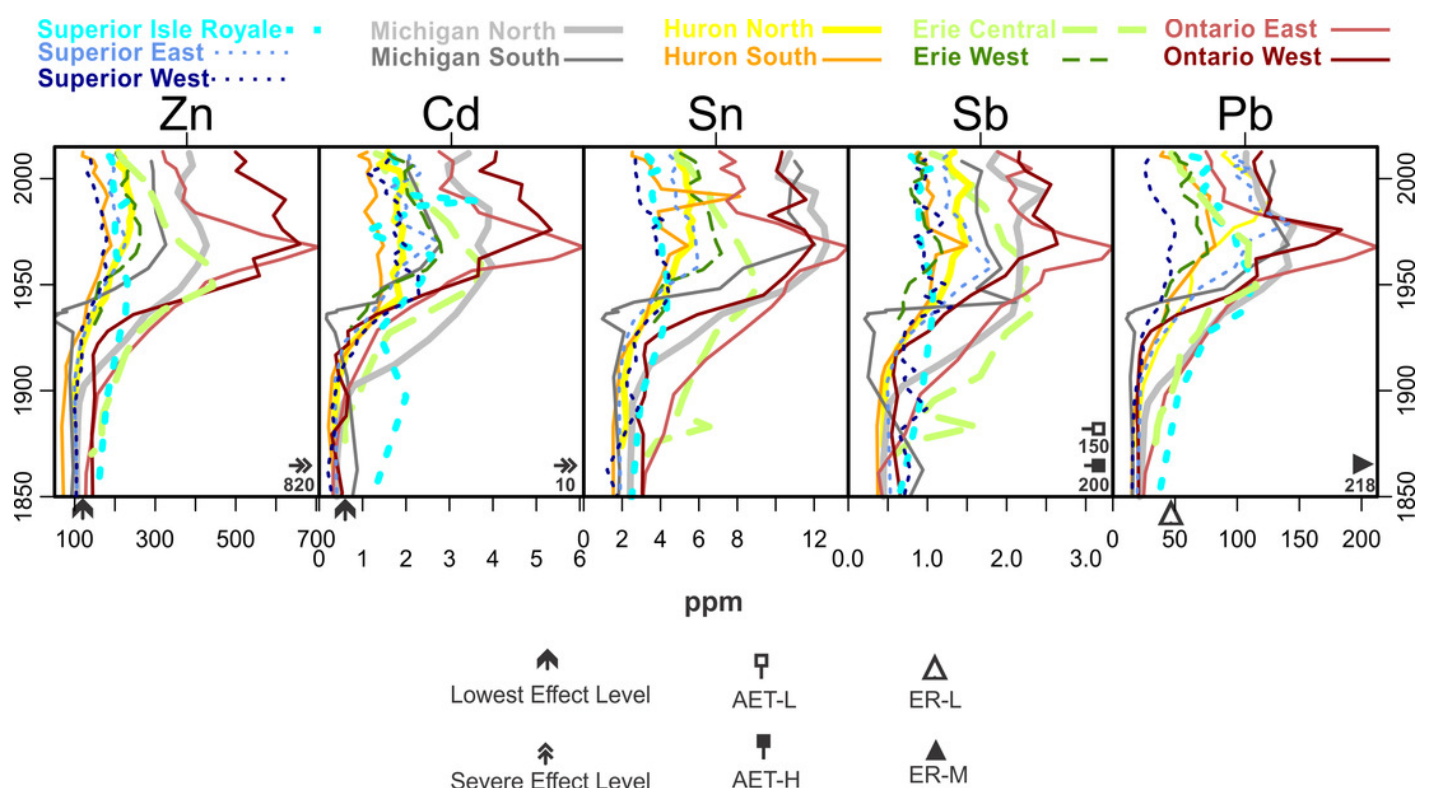
Figure 7

Analytes defined as Group 2 by cluster analysis.

Analytes from diverse natural sources, though some are considered anthropogenic pollutants. Arrows represent lowest and severe effect level values according to Ontario Sediment Quality Guidelines.

Superior Isle Royale ·   **Michigan North** —   **Huron North** —   **Erie Central** – –   **Ontario East** —
Superior East ····   **Michigan South** —   **Huron South** —   **Erie West** – –   **Ontario West** —
Superior West ·····

Mn   As   MnO   P2O5

P   Ni   Cu   Mo

Na   Co   Ta

ppm

↑ Lowest Effect Level   ⇑ Severe Effect Level
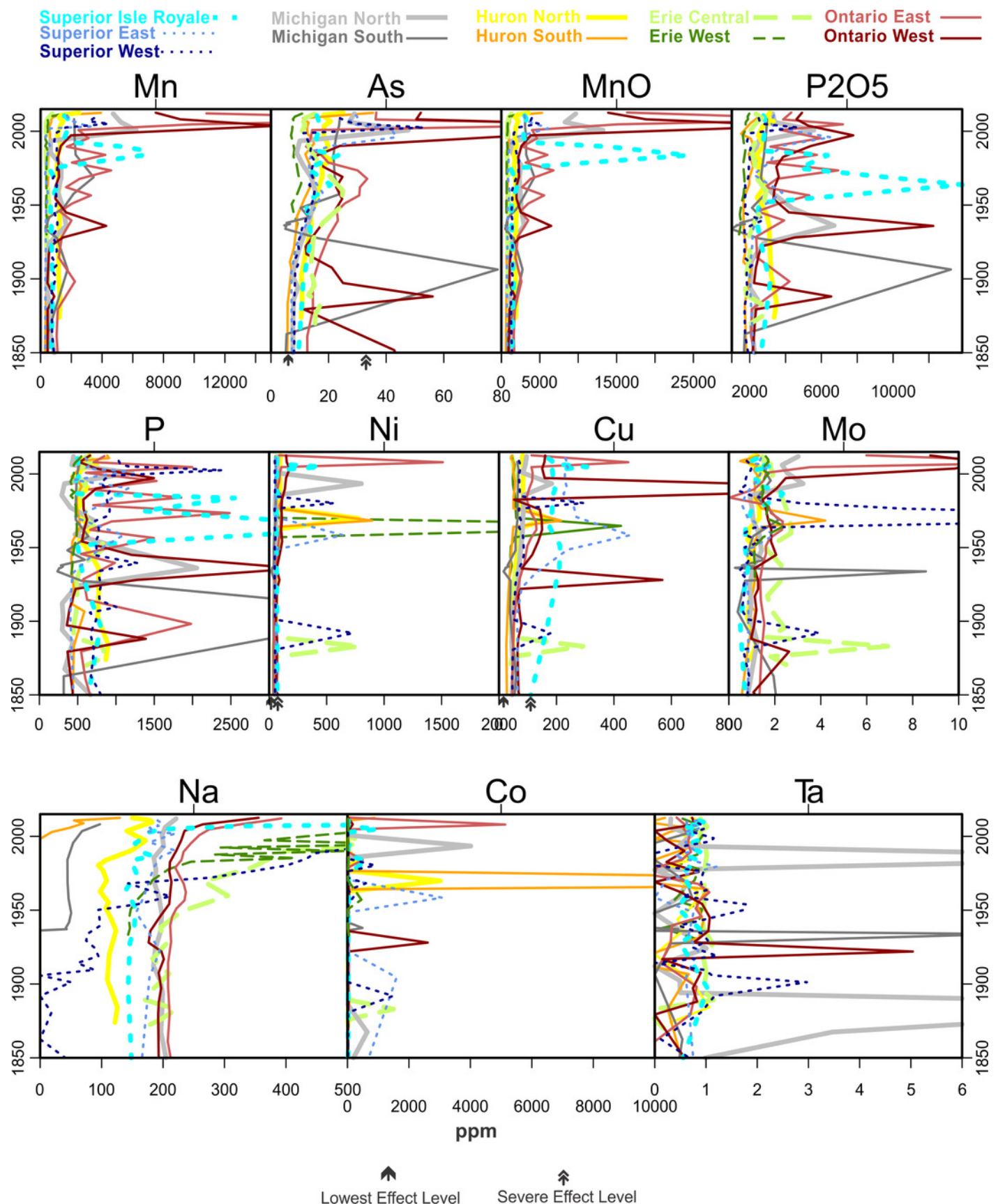
Figure 8

Analytes defined as Group 3 by cluster analysis.

Common crustal analytes with lake sources such as soil dust, runoff, and coastal erosion. Li and Ti had too many NA values to be part of the PCA or cluster analyses but were grouped with Group 3 elements based on similar profiles.
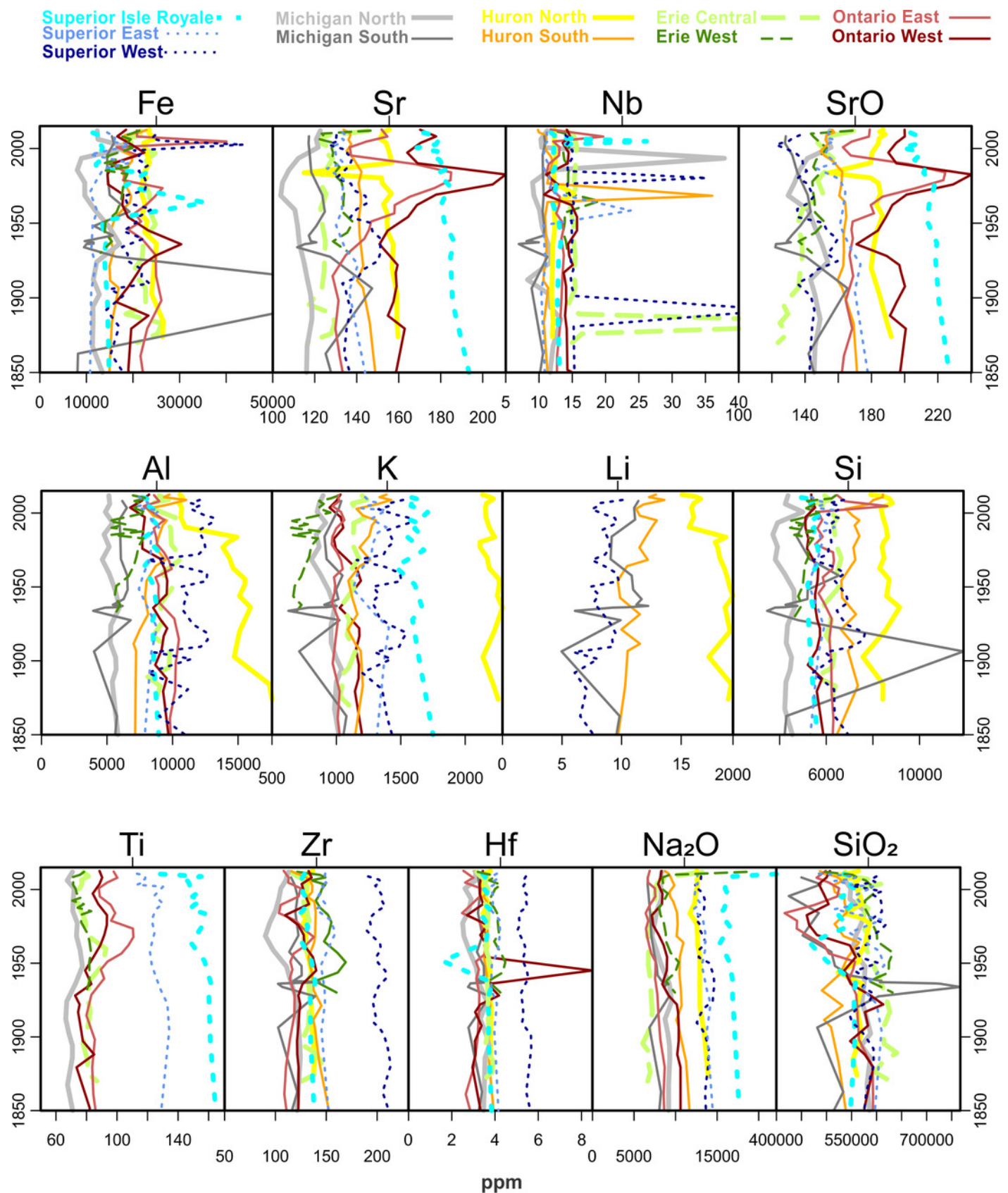
Figure 9

Analytes defined as Group 4 by cluster analysis.

These analytes are considered widely distributed but magnified by anthropogenic inputs. Arrows represent lowest and severe effect level values according to Ontario Sediment Quality Guidelines.
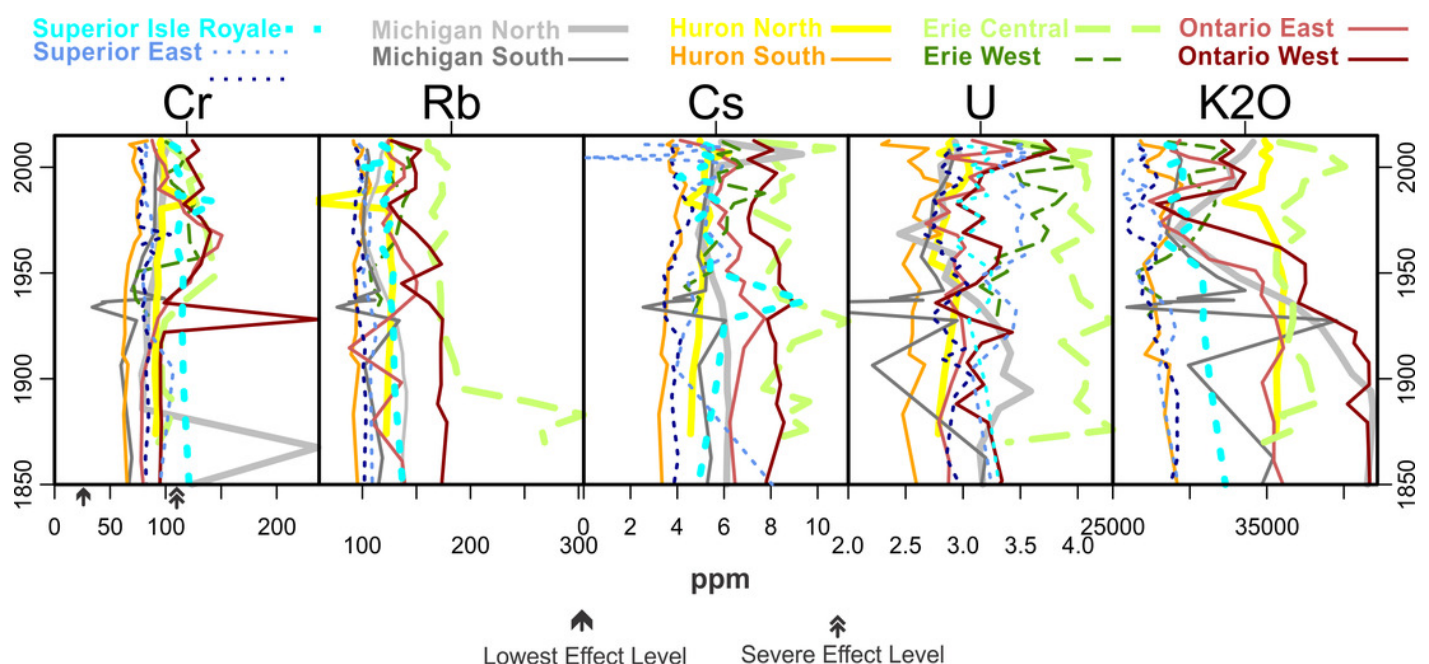
Figure 10

Analytes defined as Group 5 by cluster analysis.

This is the largest and most diverse group which contains all the rare earth elements.
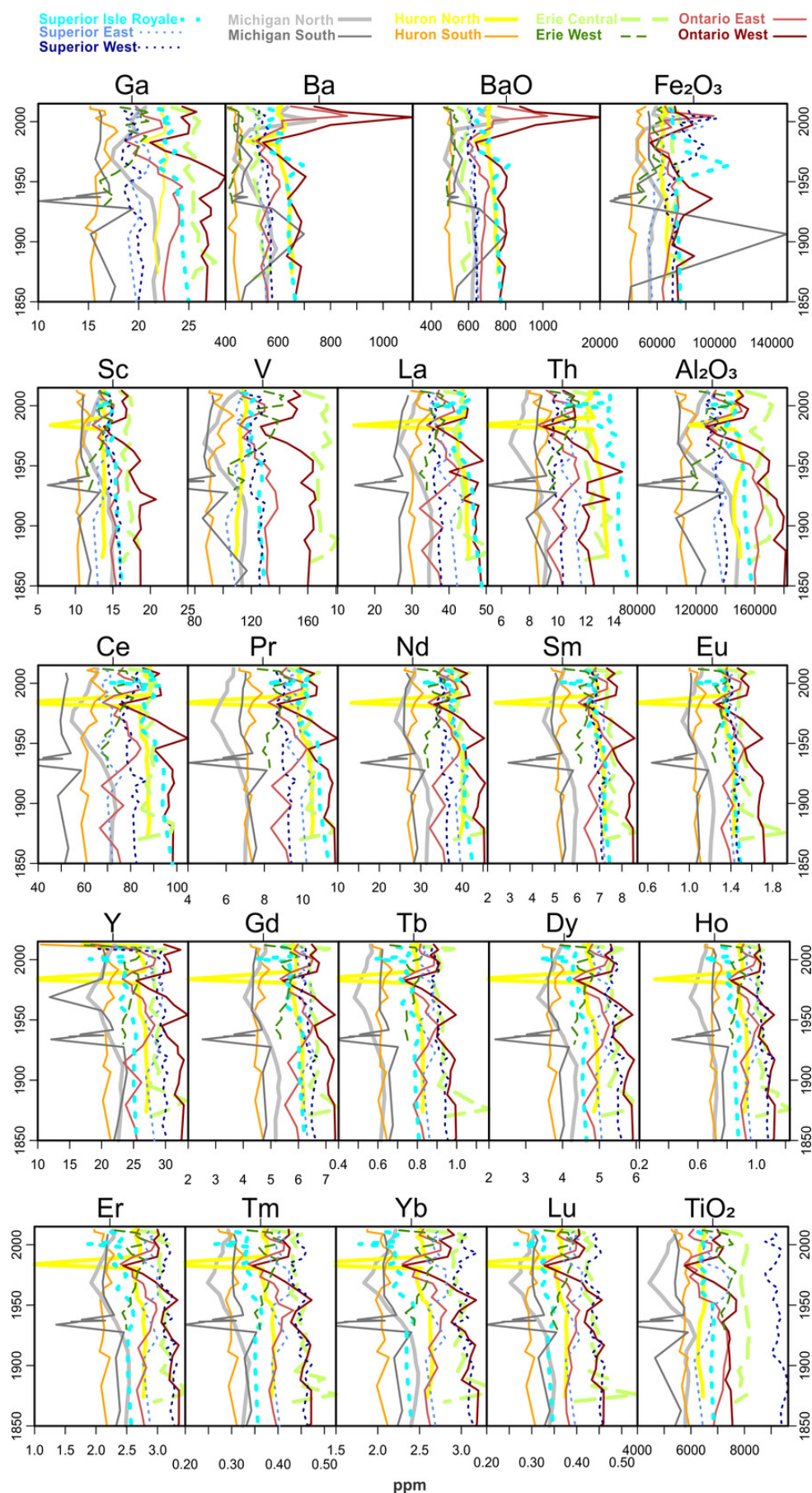
Figure 11

I_{geo} and EF heat map for each of the five lakes.

The numbers represent overall contamination values (Equations 1 and 2) averaged for each of the "Group 2" contaminant elements of interest in the decade shown. The elements listed represent the element with the highest contamination values for the interval.

	Superior				Michigan				Huron				Erie				Ontario			
	I_{geo} Avg	I_{geo} Max	EF Avg	EF Max	I_{geo} Avg	I_{geo} Max	EF Avg	EF Max	I_{geo} Avg	I_{geo} Max	EF Avg	EF Max	I_{geo} Avg	I_{geo} Max	EF Avg	EF Max	I_{geo} Avg	I_{geo} Max	EF Avg	EF Max
2010	0.3	Na	1.7	Mn	0.5	Pb	3.5	Cd	0.5	Co	3.0	Co	0.1	Na	2.7	Na	0.8	Mn	4.0	Mn
2000	0.2	Na	2.6	Na	0.7	Pb	3.2	Mn	0.2	Pb	1.9	Pb	-0.2	Ta	1.3	Na	1.1	Co	8.8	Co
1990	-0.1	Na	1.8	Na	0.9	Co	4.1	Co	0.3	Pb	2.2	Pb	0.0	Co	1.6	Co	0.5	Cu	3.0	Cu
1980	0.2	Na	2.1	Na	0.5	Cd	3.1	Cd	0.1	Co	1.7	Co	-0.2	Ta	0.5	Ta	0.1	Co	3.1	Co
1970	-0.1	Na	1.7	Na	0.2	Cd	2.8	Cd	0.3	Pb	1.8	Pb	-0.1	Cd	1.2	Cd	0.4	Cd	3.2	Cd
1960	0.1	Na	1.8	Mo	0.6	Mn	3.2	Cd	0.8	Co	35.2	Co	0.0	Cd	1.3	Cd	0.5	Cd	2.8	Cd
1950	0.2	Co	3.6	Co	0.5	Cd	2.7	Cd	0.1	Cd	1.4	Cd	0.4	Ta	1.8	Cd	0.4	Cd	2.4	Cd
1940	-0.1	Cd	1.9	Cd	0.3	Cd	2.0	Cd	0.1	Cd	1.4	Cd	0.3	Ta	1.6	Cd	0.2	Cd	2.1	Cd
1930	-0.4	Na	1.0	Na	-0.3	Co	1.9	Co	0.0	Cd	1.2	Cd	0.1	Ta	1.4	Cd	0.2	Mn	0.1	Mn
1920	-0.5	Na	0.8	Na	-0.3	Cd	1.4	Cd	-0.3	Cd	1.0	Pb	-0.1	Ta	1.1	Ta	-0.2	Co	-0.2	Co
1910	-0.7	Na	1.1	Na	-0.5	Cd	1.3	Cd	-0.4	Pb	0.8	Pb	-0.4	Sb	0.9	Sb	-1.1	Pb	0.7	Pb
1900	-0.5	Co	2.2	Co	-0.3	As	2.0	As	-0.1	Co	5.1	Co	-0.5	Sb	0.7	Sb	-0.9	Ta	0.5	Sn
1890					-0.9	Pb	0.9	Pb	0.7	Co	15.4	Co	-0.3	Ta	0.8	Ta				
1880					-0.6	Ta	1.6	Ta	-0.4	Ta	0.8	Co	0.1	Co	3.8	Co				

I_{geo} <0 Uncontaminated
0< I_{geo} <1 Uncontaminated to moderately contaminated
1< I_{geo} <2 Moderately contaminated
2< I_{geo} <3 Moderately to heavily contaminated
3< I_{geo} <4 Heavily contaminated
4< I_{geo} <5 Heavily to extremely contaminated
I_{geo} >5 Extremely contaminated

EF <2 Deficiency to minimal enrichment
2< EF <5 Moderate enrichment
5< EF <20 Significant enrichment
20< EF <40 Very high enrichment
EF >40 Extremely high enrichment