



Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: [www.elsevier.com/locate/jglr](http://www.elsevier.com/locate/jglr)

## Fossil diatoms, geochemistry, and the Anthropocene paleolimnology of Lake Huron

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### ARTICLE INFO

#### Article history:

Received 8 January 2018

Accepted 21 May 2018

Available online xxxxx

Communicated by Craig Stow

#### Keywords:

Lake Huron

Diatoms

Geochemistry

Stressors

Paleolimnology

Nutrients

### ABSTRACT

Sediment cores from northern (NL) and southern (SL) Lake Huron were analyzed for diatom fossils and sediment geochemistry to investigate human effects on the lake over the last two centuries. Anthropogenic activities drove two major transformations in diatom indicators of lake ecology for the NL around 1972 and 1991 and three transformations for the SL around 1921, 1964, and 1998. The synergistic effects of increased agriculture and decreased forest land coincided with a shift in the SL to a more mesotrophic condition after 1921. Population increase and attendant industry and mining pollution were apparent in sediment contaminants that increased rapidly in the 1930s. Diatom indicators of climate change appeared as early as the 1970s. Mitigation efforts resulted in water quality improvements as indicated by geochemical indicators of contamination and diatom species shifts, but these changes were concurrent with the negative impacts of invasive mussels and climate warming since the 1990s. Until these stressors are alleviated phytoplankton abundance will likely remain at the current low levels. The composition of the diatom flora will continue toward dominance by *Cyclotella sensu lato*, which may have implications on food web characteristics such as feeding strategies of zooplankton. Overall, these paleo-records provide evidence of human impacts, remediation, and future trajectories for lake condition, all of which are important factors for consideration by lake managers.

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### Introduction

Lake Huron provides many beneficial uses including sustained recreational and commercial fishing industries (Brown et al., 1999; Bence and Smith, 1999), and non-consumptive recreation (DiToro and Matystik, 1980; Raphael and Jaworski, 1979). The Lake has had notable problems including heavy metal pollution in Saginaw Bay (Fanslow et al., 1995; Wells et al., 1980) and mining pollution from the Sudbury mining district (Adamo et al., 1996) that threatened beneficial uses. Cultural pollution that occurred due to expanding population in the Lake Huron watersheds in the 1950s–1970s led to dissolved oxygen concentrations low enough to affect fish and benthic invertebrates in Saginaw Bay (Colby et al., 1972; Schaefer et al., 2000). Phosphorus (P) was targeted as the major contributor to algal blooms and lowered oxygen concentrations. Increased P and nitrogen concentrations as well as increases in conductivity, total dissolved solids, and decreases in hypolimnetic oxygen and transparency occurred in the lake in this period (Colby et al., 1972). The Great Lakes Water Quality Agreement (IJC, 1972; amended in 1978) established point source P removal programs and P content reduction for detergents (IJC, 1978) to prevent further degradation of water quality. The agreement acknowledged that biological monitoring was fundamental to charting ecosystem health.

Subsequently, the Environmental Protection Agency established a phytoplankton monitoring program that included monitoring algae for Lake Huron (Makarewicz et al., 1989).

Algal monitoring has been useful for assessment of water and environmental quality of Lake Huron since the 1970s, but prior to 1971 there were few studies (e.g. Fenwick, 1962, 1968; Parkos et al., 1969). Pre-1970 information about Lake Huron's ecology comes primarily from paleolimnological work of Wolin et al. (1988), who examined a sediment core taken from the Goderich depositional basin in 1981. They concluded, based on diatom microfossil succession, that the lake progressed from ultra-oligotrophic to meso-oligotrophic beginning around the 1930s reflecting increased anthropogenic nutrient loading. Vollenweider et al. (1974), based on samples collected primarily in 1967, spatially classified Lake Huron as oligotrophic (offshore) and mesotrophic (inshore). Munawar and Munawar (1986), using samples collected in 1971, showed that Lake Huron had relatively high biomass concentrations for the upper Great Lakes. A decline of high-nutrient species in the upper intervals of the Wolin et al. core suggested decreased phosphorus loading since the early 1970s, a possible early result of remedial action.

Several observations are notable in the lake since the Wolin et al. (1988) study. Makarewicz and Bertram (1991) reported a preponderance of oligotrophic and mesotrophic indicator species, and found that algal biomass and trophic status had changed little from 1972 to 1982–1985 in Lake Huron. However, structural and functional changes

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resulting from consequences of human activities and interventions especially over the past 25 years are impacting the lake. Climate change in the form of atmospheric warming (Nicholls, 1998; Saros et al., 2012; Reavie et al., 2016), reduction in total phosphorus (TP) concentrations (Dodds et al., 2010; Dolan and Chapra, 2012; Warner and Lesht, 2015), and introduction of invasive species, particularly dreissenids and *Bythotrephes* (Gobin et al., 2015; Nicholls and Hopkins, 1993; Vanderploeg et al., 1993) have all been implicated individually or as synergistic stressors responsible for perturbations of Lake Huron's ecology. These perturbations, occurring over different time scales, altered spatial distributions of nutrients (Hecky et al., 2004; Nalepa et al., 2009), resulted in lower primary productivity and chlorophyll *a* (Warner and Lesht, 2015), reduced spring algal biovolume, and reduced numbers of larger diatom species (Reavie et al., 2014).

Reavie et al. (2016, 2017) revealed physical and chemical processes associated with climate change were likely driving phytoplankton assemblages in all of the Great Lakes. Recent elevated abundances of the *Cyclotella comensis* complex in Lake Huron's sedimentary record are thought to be due to its benefiting from longer ice-out periods and stronger water column stratification. Ascribing such drivers to changes in the base of the lake's food web is made cautiously due to the multitude of concurrent stressors. Hence, more details of Huron's paleolimnology are needed to better clarify how and why the pelagic system is changing.

Recently, two other paleolimnological studies using the same methods we present in this study have been conducted in Lakes Erie (Sgro and Reavie, 2018) and Superior (Shaw Chraibi et al., 2014). The most striking commonality between these cores is the presence of a dramatic diatom assemblage shift between the 1980s and 1990s. Again, the synergistic effects of climate change, mitigation efforts, and invasive species are implicated in these changes that seem to have occurred nearly simultaneously throughout the Great Lakes Basin.

This study is a paleolimnological investigation of the diatom record of Lake Huron integrated with geochemistry and human history records. We aimed to provide an update to previous paleolimnological work and place the more recent ecology of Lake Huron in a longer historical context. We hypothesized that structural changes in fossil diatom assemblages, a surrogate for past phytoplankton communities and water quality, reflected anthropogenic stressors and remedial activities such as nutrient abatement. We examined paleoecological trends alongside catchment stressor data to discern the important stressors that have and are contributing to changes in water and primary producer quality. We expected that geochemical data would reflect atmospheric and catchment-delivered pollutants, but that more recent sediments should indicate reductions in contamination (e.g. reduced lead since its removal from gasoline). We further hypothesized that multiple synergistic stressors drive pelagic conditions in the lake and that recent trajectories of changes may support lake management by estimating future conditions.

## Methods

Permanent diatom slides, sediment archives and all data from this study are maintained at the Natural Resources Research Institute, Duluth, Minnesota (contact author E. Reavie).

### Lake Huron

Lake Huron is dimictic and has an area of 59,600 km<sup>2</sup> within a 131,300 km<sup>2</sup> drainage basin (Fig. 1). It is of glacial origin and contains many islands, shoals, and troughs. Its two largest inflows are from Lake Michigan through the Straits of Mackinac and Lake Superior through the Saint Mary's River and the major outflow is through the St. Clair River. The maximum depth is 229 m and the mean depth is 59 m. Eight water masses can be identified based on physical and chemical characteristics: Central Lake Huron, Southern Lake Huron, Georgian

Bay proper, Straits of Mackinac, North Channel/St. Mary's River inflow, North Channel proper, nearshore zone of Georgian Bay, and the mouth of Saginaw Bay/nearshore zone of Southern Lake Huron (IJC, 1977; Moll, 1985). The pelagic region of the Lake has been divided into two zones based on unique water quality and phytoplankton (Cai and Reavie, 2018), the northern lake (NL) and southern lake (SL).

### Sediment core collection and analysis

Sediment cores were collected from the NL (Lat. 45.60°, Long. –83.42°; cored July 24, 2012) from 0 to 34 cm sediment depth and from the SL (Lat. 43.89°, Long. –82.06°; cored July 25, 2012) from 0 to 36 cm depth (Fig. 1). The NL core site was selected as an area of likely high sedimentation rate within the Cockburn Basin and the SL site was selected to correspond with a core collected previously for paleolimnological studies by Wolin et al. (1988; within the Goderich Basin). Sgro and Reavie (2018) provide details on core collection and analysis procedures for diatoms, geochemistry, and sediment dating. Many of the following methods descriptions and explanations in the results section are closely paraphrased from Sgro and Reavie (2018), and we mention this here to alleviate plagiarism concerns.

### Geochemistry

Sediment cores were analyzed by gamma spectrometry for <sup>210</sup>Pb activity to determine age (Appleby 2001). Supported <sup>210</sup>Pb was measured as <sup>214</sup>Pb, a short-lived intermediary in the radioactive decay sequence from <sup>226</sup>Ra to <sup>210</sup>Pb.

Analyses for trace metals and oxides were performed to provide stratigraphic surrogates for natural deposition due to erosion of soils and bedrock and human activities such as mining, tailings disposal, and burning of fossil fuels. Trace metal concentration analysis followed Sgro and Reavie (2018).

We used sediment total organic carbon (TOC), TOC mass accumulation rate, total nitrogen and their isotopes to track productivity. TOC and TOC accumulation rate are measures of biological activity in the lake and its catchment area with increasing values providing evidence for increasing productivity (Hodell and Schelske, 1998; Jellison et al., 1996). TOC concentrations can be affected by sediment particle size, so mass accumulation rates are more reliable than TOC percentages for measuring TOC preservation (Meyers, 2003). We also measured the stable isotope of organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ , corrected for the Suess effect), and the stable isotope of TN ( $\delta^{15}\text{N}$ ) in the sediment. These isotopes respond to primary productivity in the water column. Increased values of these isotopes in the sediment are a marker for increased primary productivity (McKenzie, 1985; Meyers, 1994, 1997, 2003; O'Beirne et al., 2015). However,  $\delta^{15}\text{N}$  values in the sediment can be increased due to fertilizer runoff from farms or from sewage in the watershed (Teranes and Bernasconi, 2000), or decreased from nitrogen fixing cyanobacteria (Fogel and Cifuentes, 1993), which may confound our interpretation. We distinguished algal material in the sediment by atomic ratio of organic carbon to nitrogen ratios ( $\text{C}_{\text{org}}:\text{TN}$ ). Algal material in the sediment is distinguished from aquatic or terrigenous C3 and C4 plants by typically having  $\text{C}_{\text{org}}:\text{TN}$  ratios between 4 and 10 with vascular plants having ratios  $\geq 20$  (Meyers, 1994, 1997, 2003; O'Beirne et al., 2015). See Sgro and Reavie (2018) for details of the productivity proxy methods.

### Data analysis

Stratigraphically constrained cluster analysis (CONISS) with chord distance was used to characterize stratigraphic zones in both the diatom and chemistry data based on chord distance matrices using all species data. CONISS considers only stratigraphically adjacent clusters for merging (Grimm, 1987). Broken stick analysis (Bennett, 1996) using the bstick function in R package rioja (version 0.09-9, Juggins, 2015) in R version 3.0.1 (R Core Team, 2013) identified the minimum number of

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