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Anthropogenic influences on the sedimentary geochemical record in western Lake Superior (1800–present)

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ABSTRACT

The sediments of western Lake Superior hold a record of environmental changes that have accompanied the settlement and urbanization of the surrounding watershed. Organic carbon concentrations are low (1.5%) with little variation in stable isotope composition (−26.5 ± 0.5‰) prior to 1900. Organic carbon and nitrogen concentrations begin to rise after 1900, as increased anthropogenic disturbance led to enhanced inputs of terrigenous matter as well as nutrients (i.e., nitrogen and phosphorus) from the watershed. An episode of enhanced aquatic productivity from 1900 to 1970 is recorded in the sediments by the ^{13}C-enrichment of bulk organic carbon as well as the observed correlation between the bulk and aquatic molecular δ^{13}C records, coinciding with the major developmental period of the Duluth-Superior harbor region. Decreasing organic carbon accumulation after 1925, prior to regulatory implementation of municipal discharges to the lake, is likely due to the construction of hydropower dams along the St. Louis River and a decrease in forest harvest within the immediate watershed. Recentshort-lived decreases in the accumulation rate of organic matter can be attributed to the implementation and operation of water treatment plants, but the ^{13}C-enrichment observed in the last ~ decade remains enigmatic, though we hypothesize that it may be attributable to climate change impacts on primary production.

Introduction

Lakes are intimately connected with their surrounding environment, making them sensitive indicators of perturbations within their watersheds. Organic geochemical proxies preserved in lake sediments can provide a history of ecosystem change (e.g., carbon cycling). These proxies enable us to gauge the historical impacts of regional development and subsequent regulations within lake systems while providing insight to guide possible management action to address any emerging issues.

The stable carbon isotope composition of sedimentary organic carbon ($\delta^{13}C_{org}$), a proxy for lacustrine productivity (Meyers, 1994), is often used to track the response of lakes to historic anthropogenic activities (i.e., nutrient loading) and subsequent regulation. This approach is based on the premise that the δ^{13}C of organic carbon produced photosynthetically responds to the rate of primary productivity in the water column (Schelske and Hodell, 1991; Meyers, 2003). In general, increases in lacustrine productivity should lead to increases in the deposition of total organic carbon (TOC) and total nitrogen (TN) concentrations along with changes in their stable isotope compositions ($\delta^{13}C_{org}$ and δ^{15}N, respectively). $\delta^{13}C_{org}$ and δ^{15}N are typically ^{13}C- and ^{15}N-enriched (depleted) with increasing (decreasing) in-lake primary production (Mckenzie, 1985; Meyers, 1997, 2003). Thus, the bulk isotope compositions as well as accumulation rates of C_{org} and TN can be used as a proxy for lacustrine productivity.

One caveat to this general approach is that sedimentary C and N are derived from both terrigenous and aquatic sources, thus increases or decreases cannot be unequivocally allocated to one source or the other. Similarly, the isotopic composition of sedimentary TOC is influenced by both terrigenous and aquatic sources, making it useful to look at molecular biomarkers (e.g., *n*-alkanes) to separate contributions from these sources. The two principal sources of hydrocarbons to lake sediments are those of photosynthetic algae and bacteria, dominated by the odd-numbered short chain *n*-alkanes(n-C_{17} + n-C_{19} + n-C_{21}) (Cranwell et al., 1987; Giger et al., 1980) and those contributed from vascular land plants, which contain large proportions of the odd-numbered long chain *n*-alkanes(n-C_{27} + n-C_{29} + n-C_{31}) that are produced in their epicuticular waxy coatings (Cranwell, 1981; Eglinton and Hamilton, 1963, 1967; Rieley et al., 1991). In order to circumvent the issue of source, the stable carbon isotope composition of *n*-alkanes ($\delta^{13}C_{n\text{-alkane}}$), when compared to the bulk $\delta^{13}C_{org}$ record, can provide an indication of the relative contributions of terrigenous and aquatic

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sourced organic carbon to the bulk $\delta^{13}C_{org}$ record (Bourbonniere and Meyers, 1996; Meyers, 2003).

The Laurentian Great Lakes have experienced dramatic changes in response to anthropogenic loadings and management activities. Studies of organic geochemical proxies preserved within sediment cores from Lakes Erie and Ontario have shown periods of increased lacustrine productivity in correspondence with watershed/regional development. Schelske and Hodell (1995) and more recently, Lu et al. (2010), found that increases in lacustrine productivity (increases in the $\delta^{13}C_{org}$) of Lake Erie were related to historic changes in anthropogenic phosphorus loading during the development of the watershed and subsequent decreases were in response to the implementation of phosphorus abatement programs in the mid-1970s. A study by Hodell and Schelske (1998) in Lake Ontario shows similar correspondence between productivity and anthropogenic activity as inferred from the sedimentary geochemical record. One study from Lake Superior, measuring sedimentary biogenic silica (BSi), provides evidence of low-level eutrophication associated with the late 1800s European habitation and subsequent development of the watershed (Schelske et al., 2006). To date, these findings based on BSi in Lake Superior have not been corroborated by other proxies.

Here, we report temporal trends in productivity over the last 150 years, through the use of bulk organic and stable isotope compositions of carbon and nitrogen as well as *n*-alkane molecular biomarker abundances and their stable carbon isotope compositions, as contained in the sediments of the western arm of Lake Superior. We compare two cores from the same location taken 6 years apart which allow us to determine not only the reproducibility of the sedimentary record but also evaluate the effect of early sedimentary diagenesis on the preservation of biomarker signals through time.

Regional setting and background

Lying along boundary of the United States (US) and Canada, Lake Superior (Fig. 1), the largest of the Laurentian Great Lakes and the world's largest freshwater lake by surface area, is often regaled as the most "pristine" of the Great Lakes. This is due, in part, to the small amount of surface runoff Lake Superior receives in relation to its volume, as well as to the fact that most of the 127,700 km^2 watershed (considered small, in comparison to its surface area with a terrigenous catchment area to lake area ratio of ~1.5:1) is sparsely populated and heavily forested with little agriculture. As a result, Lake Superior has not suffered from the high nutrient loadings or industrial pollution to the same extent as other Great Lakes (e.g., Lake Erie; Bourbonniere and Meyers, 1996; Schelske et al., 2006).

Although Lake Superior is considered the least altered of the Laurentian Great Lakes, has been classified as ultra-oligotrophic and mostly retains its pristine water quality conditions (Munawar and Munawar, 1978; Weiler, 1978), changes in its physical, biological and chemical processes have been documented. Observations of rising nitrate concentrations since the 1900s (Sterner et al., 2007; Weiler, 1978), as well as increasing water temperatures over the past two centuries (Austin and Colman, 2007, 2008) and changes in primary productivity (Urban et al., 2005; Urban, 2007; Vollenweider et al., 1974) indicate that anthropogenic activities can impact Lake Superior.

The highest population density within the Lake Superior watershed is located in the St. Louis River drainage basin, which is also the second largest inflow to Lake Superior. The St. Louis River basin has been heavily impacted by anthropogenic changes and has been designated as one of 43 areas of concern (having impaired beneficial uses due to pollution) within the Laurentian Great Lakes by the International Joint Commission (IJC). The area of concern was later extended to include the Duluth-Superior Harbor region (Fig. 1).

The objective of this study is to define changes in the primary productivity of the western end of Lake Superior (Fig. 1) over the past 150 years in order to ascertain what the important drivers of change may have been and to assess the efficacy of regulatory action to address those changes. If anthropogenically induced changes in the trophic state of western Lake Superior have occurred, we should be able to track

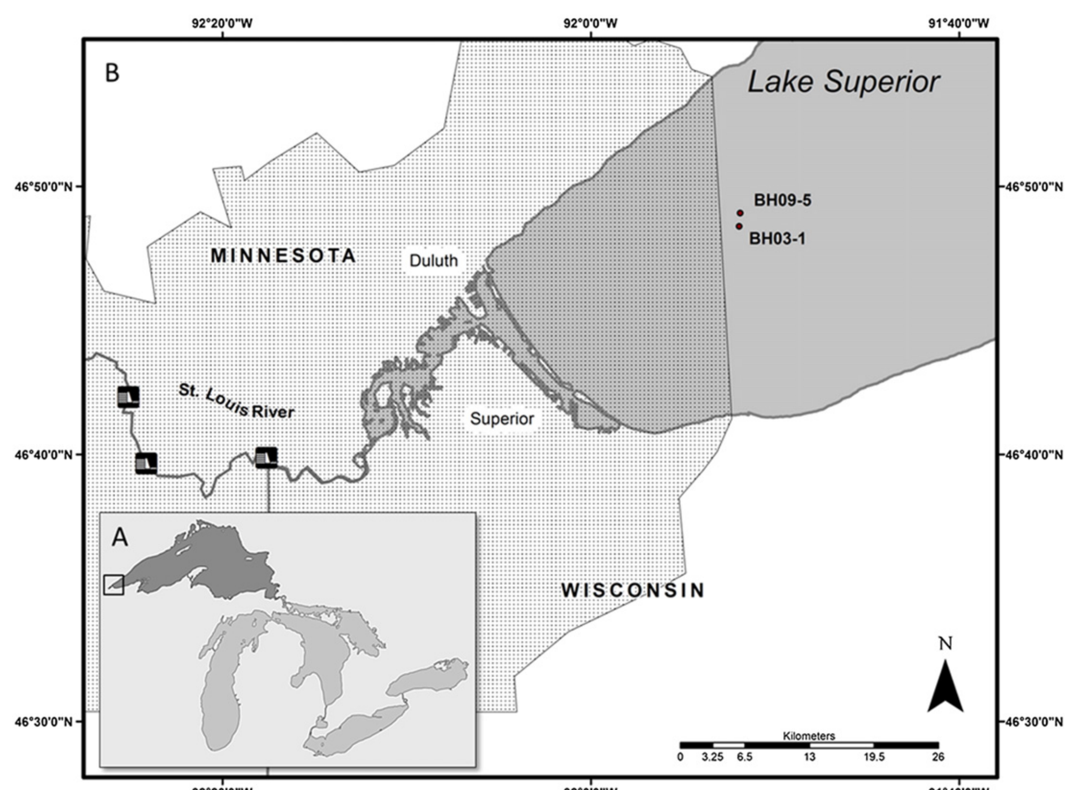

Fig. 1. (A) Map of Laurentian Great Lakes, (B) map of western Lake Superior with core locations, IJC designated Area of Concern (shaded area) and the St. Louis river with dam locations (left to right, Scanlon Dam, Thomson Dam, and Fond du Lac Dam).