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ORIGINAL PAPER

Paleolimnology of a freshwater estuary to inform Area of Concern nutrient delisting efforts

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Abstract The St. Louis River Estuary (SLRE), a freshwater estuary bordering Duluth, Minnesota, Superior, Wisconsin, and the most western point of Lake Superior (46.74°, − 92.13°), has a long history of human development since Euro-American settlement ~ 200 years ago. Due to degradation from logging, hydrologic modification, industrial practices, and untreated sewage, the SLRE was designated an Area of Concern in 1987. Action has been taken to restore water quality including the installation of the Western Lake Superior Sanitary District in 1978 to help remove beneficial use impairments. A better understanding of historical impacts and remediation is necessary to help document progress and knowledge gaps related to water quality, so a paleolimnological study of the SLRE was initiated. Various paleolimnological indicators (pigments, diatom communities, and diatom-inferred phosphorus) were analyzed from six cores taken throughout the SLRE and another from western Lake Superior. Reductions in eutrophic diatom taxa such as *Cyclotella meneghiniana* and *Stephanodiscus* after 1970 in certain cores suggest an improvement in water quality over the last 40 years. However, in cores taken from estuarine bay

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environments, persistence of eutrophic taxa such as *Cyclostephanos dubius* and *Stephanodiscus binderanus* indicate ongoing nutrient problems. Sedimentary pigments also indicate cyanobacteria increases in bays over the last two decades. Diatom model-inferred phosphorus and contemporary monitoring data suggest some of the problems associated with excess nutrient loads have been remediated, but modern conditions (internal phosphorus loading, changing climate) may be contributing to ongoing water quality impairments in some locations. The integrated record of biological, chemical, and physical indicators preserved in the sediments will aid state and federal agencies in determining where to target their resources.

Keywords Diatoms · Great lakes · Lake Superior · Beneficial use impairment · St. Louis River · Minnesota · Wisconsin

Introduction

The Laurentian Great Lakes' capacity for shipping, expansive timber stands, and iron-rich rock drew settlers to the region, leading to water quality impairments due to lack of infrastructure and regulation, especially in tributaries and estuaries where populations were condensed. Since European settlement the St. Louis River Estuary (SLRE) became one of the most impacted ecosystems in the Laurentian Great Lakes, beginning with the construction of the Duluth Shipping Canal in 1871, granting access to the eastern United States and beyond (MPCA and WDNR 1992). Approximately 1600 ha of open water and shoreline were filled with dredged material since 1861; dredging is still routine to maintain the port for commercial shipping (Devore 1978).

In the late 1800s to early 1900s, the St. Louis River watershed was almost entirely clear-cut by loggers, and land cover transitioned from forested to shrubland and agricultural land, leading to increased runoff of both water and soil. In order to control the transportation of timber downstream, 50–100 dams were installed on the river. Dams contribute to large changes in hydrologic regime and aquatic ecosystems (Baxter 1977; Bunn and Arthington 2002). Additionally, the SLRE was home to many sawmills, pulp mills, and paper mills. These were a major source of pollution to the estuary, discharging large quantities of sawdust and slab wood (MPCA and WDNR 1992).

To accommodate these growing industries the population of Duluth and Superior grew from an estimated 600 in 1865, to 100,000 by 1930 (MPCA and WDNR 1992). However, the region lacked proper stormwater and wastewater infrastructure, so untreated wastewater (e.g. human waste and high-phosphorus detergents) introduced nutrients and organic matter into the estuary, leading to episodic hypoxia (Hargis 1983; Carlson and Thomas 1984).

In 1966, the Federal Water Pollution Control Administration Great Lakes Regional Office made recommendations on strategies to reduce pollution, including installing wastewater and stormwater treatment facilities to reduce nutrient loading (FWPCA 1966). In response, the Western Lake Superior Sanitary District opened in 1978 to treat wastewater from a 1375 km^2 region including Duluth and surrounding communities (MPCA and WDNR 1992). A study comparing concentrations of various metals, nutrients, and physical parameters before and after 1978 showed water quality improvement in the SLRE including a decrease in total phosphorus, turbidity, total coliform, lead, and copper and an increase in dissolved oxygen (McCollor 1990).

To further address the polluted state of the estuary, in 1987 the St. Louis River Estuary was designated an Area of Concern, a program designed by the International Joint Commission, a governing body regulating waters shared by Canada and the United States, as a part of the Great Lakes Water Quality Agreement (IJC 1987). Each Area of Concern is defined by various beneficial use impairments that define the extent of degradation; of these the SLRE received 9 including one for excessive loading of sediment and nutrients (impairment 6) (MPCA and WDNR 1992). In 1992, a remedial action plan was released outlining the degradation of the SLRE and included a path for improvement (MPCA and WDNR 1992).

Agencies hope to remove all impairments and delist the Area of Concern by 2025. To achieve this, there has been a large effort to remediate the estuary and agencies have developed removal targets for impairment 6. Best management practices within the watershed and the installation of wastewater treatment facilities helped to reduce the flux of nutrients to the SLRE (MPCA and WDNR 2013), but the extent of nutrient reduction is poorly understood. A phosphorus dataset from an upstream and downstream location (beginning in 1958 and 1973 respectively) exists for the SLRE and consists of monthly measurements of surface water total phosphorus. These data show a reduction in phosphorus concentrations in the main estuary channel (Bellinger et al. 2016). Still, measurements of nutrient concentrations and sediment loading, and biological responses to these changes, are absent for most of the SLRE's past, especially pre-European settlement conditions.

A paleolimnological study of the SLRE was initiated to help to provide insight on long-term environmental impacts and remediation while considering the known human history of the watershed. We hypothesized that paleolimnology would provide valuable retrospective data in support of the Area of Concern delisting process. To date, paleoecological studies of such hydrologically complex, moving water systems have been uncommon, so we applied some additional considerations outside more traditional, lake-based paleolimnological approaches. Subfossil diatoms (Bacillariophyceae) and algal pigments were the primary indicators used. To examine the historical environmental conditions of the SLRE, relative abundances of diatom taxa before, during, and after European settlement were characterized. Changes in diatom assemblages and inferred environmental information were correlated with anthropogenic activities and validated with additional data, including fossil pigments (to provide quantitative information about nutrient effects and less desirable taxa such as cyanobacteria) and sediment organic content. The extent of degradation and recent Area of Concern remediation was clarified, and management recommendations relevant to Area of Concern beneficial use impairment removal are provided herein.

Study area

The St. Louis River (Fig. 1) flows 288 km through northeastern Minnesota draining an area of 9412 km^2. On average it delivers 73.3 m^3 s^{-1} of water to western Lake Superior, making it the largest tributary to Lake Superior in the United States. The drainage basin land cover consists of forests (61%), wetlands (24%), and grasslands (7%); the remaining 8% is developed (MPCA 2013). The farthest downstream portion (after Minnesota Highway 23) of the river before it joins Lake Superior is the St. Louis River Estuary (SLRE). In contrast to a mostly rural upstream, the dominant land use surrounding the SLRE is urban. The estuary is bordered by two major cities—Duluth, Minnesota and Superior, Wisconsin—which have a combined population of 113,000 people (United States Census Bureau 2010).

Methods

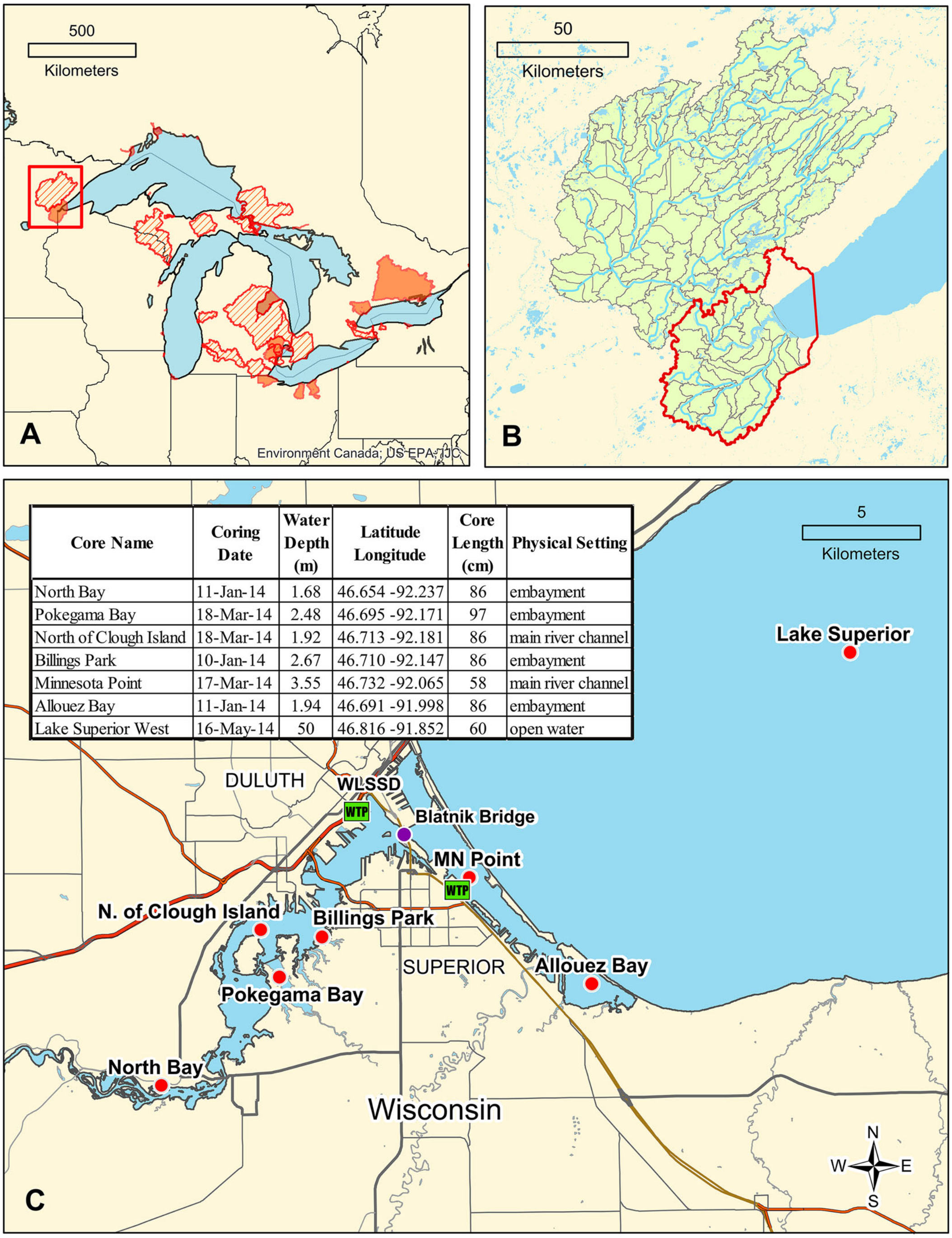
Site selection and coring

Sediment cores were taken from areas predicted to have undisturbed sediments and continuous depositional environments. Maps and hydrological data were used along with consultation with the US Army Corps of Engineers in order to avoid areas previously impacted by dredging or shipping activities. Sites were chosen to represent a variety of environments including different hydrologic regimes (bays, harbor, Lake Superior) and varying anthropogenic impacts (formerly polluted versus purportedly less impacted). A total of seven cores were collected; six cores from discrete locations in the lower SLRE and one core from western Lake Superior (Fig. 1).

At each coring location, we attempted to collect at least 200 years of sediment in order to evaluate the SLRE's anthropogenic record related to European settlement. SLRE cores were collected in winter of 2014. A piston corer designed for sampling recent lake sediments was used (Glew et al. 2001). The core taken from western Lake Superior was collected in May 2014 from the US Environmental Protection Agency's research vessel *Lake Guardian* by use of a multicorer (methods described by Shaw Chraïbi et al. 2014). For each core, approximately one meter of sediment was collected and sectioned into 1-cm intervals (0.25-cm intervals for the first 10 cm and then 0.5-cm intervals for Lake Superior). Samples were extruded in intervals using a close-sectioning extruder and kept refrigerated for later analyses.

Sediment chronology and content

To determine age and sediment accumulation rates for the past 150 to 200 years, sediment cores were analyzed for ^{210}Pb activity. Lead-210 activity was



Core Name	Coring Date	Water Depth (m)	Latitude Longitude	Core Length (cm)	Physical Setting
North Bay	11-Jan-14	1.68	46.654 -92.237	86	embayment
Pokegama Bay	18-Mar-14	2.48	46.695 -92.171	97	embayment
North of Clough Island	18-Mar-14	1.92	46.713 -92.181	86	main river channel
Billings Park	10-Jan-14	2.67	46.710 -92.147	86	embayment
Minnesota Point	17-Mar-14	3.55	46.732 -92.065	58	main river channel
Allouez Bay	11-Jan-14	1.94	46.691 -91.998	86	embayment
Lake Superior West	16-May-14	50	46.816 -91.852	60	open water

Fig. 1 **a** Map indicating the location of the St. Louis River estuary (SLRE) Area of Concern relative to all Great Lakes Areas of Concerns (orange) and their associated watersheds (red hash) (Environment Canada, EPA, IJC 2013), **b** Map of the St. Louis River drainage basin and the boundary (red) of the Area of Concern, **c** Map and table of coring locations in the SLRE (red circles) and the surface water monitoring station (purple circle). WTP = locations of wastewater treatment plants

measured from its daughter product, ^{210}Po, which is considered to be in secular equilibrium with the parent isotope. Aliquots (0.5–3.0 g) of freeze-dried sediment were spiked with a known quantity of ^{209}Po ($\sim$ 4 pCi g^{-1}) as an internal yield tracer and the isotopes distilled at 550 °C after treatment with concentrated

HCl. Polonium isotopes were then directly plated onto Au planchets from a 0.5 N HCl solution. Activity was measured for 1–3 × 10^5 s using an Ortec alpha spectrometry system. Supported ^{210}Pb was estimated by mean activity in the lowest core samples and subtracted from upcore activity to calculate unsupported ^{210}Pb. Core dates and sedimentation rates were calculated using the constant rate of supply model (Appleby and Oldfield 1978; Appleby 2001). Dating and sedimentation errors represented first-order propagation of counting uncertainty (Binford 1990).

For one core with a problematic decay profile (North of Clough Island), gamma spectrometry was used to measure supported ^{210}Pb and identify the distribution of ^{137}Cs in the core (Ritchie and McHenry 1973). Activity was measured using an Ortec-EGG (Oak Ridge, TN) High-Purity, Germanium Crystal Well, Photon Detector (Well Detector) coupled to a Digital Gamma-Ray Spectrometer (Dspec).

Loss on ignition analysis to determine inorganic and organic content followed Dean (1974). Accumulation rates of inorganic and organic content were based on sediment chronology. Analysis of water content and carbonate content and accumulation are presented in Alexson (2016).

Pigments

On a subset of four cores, pigments (carotenoids and chlorins) were analyzed to examine historical algal communities according to methods in Alexson (2016) and based on Reuss (2005) and Ruess and Conley (2005). The pigments analyzed represented total algae (chlorophyll *a*, pheophytin *a*, and β-carotene), diatoms (diatoxanthin and fucoxanthin), and dinoflagellates (fucoxanthin), cryptophytes (alloxanthin), and cyanobacteria (aphanizophyll and myxoxanthophyll). Pigments were extracted from the freeze-dried sample using an acetone/water mixture (90/10 by volume) for 24 h at − 20° C in darkness. After extraction, the material was quantitatively analyzed using a Shimadzu High Performance Liquid Chromatographer equipped with a photodiode array detector (SPD-M10Avp). Aphanizophyll and myxoxanthophyll were analyzed at 508 nm (4 nm bandwidth) in the first chromatogram. In the second chromatogram fucoxanthin, alloxanthin, diatoxanthin, and β-carotene were analyzed at 449 nm (4 nm bandwidth) and chlorophyll *a*, pheophytin *a* were analyzed at 666 nm (4 nm bandwidth). Concentrations are reported as microgram of pigment per gram of organic matter.

Diatoms

For each core interval analyzed for diatoms, approximately 1 g of wet sediment was subsampled and digested with nitric acid and then hydrogen peroxide to remove all organic material and isolate siliceous microfossils. Samples were then rinsed with distilled water to neutralize acid and applied to coverslips quantitatively using the Battarbee (1986) method. Briefly, Battarbee's method involves drying diatom slurry on coverslips in a settling tray of known area, thereby allowing for quantitative assessment of diatom densities during microscopic assessment. Coverslips were mounted to microscope slides with Naphrax for identification and enumeration.

Diatoms were identified and enumerated by use of oil immersion on a light microscope (1250× magnification). Diatoms on each slide were identified along random transects until at least 400 diatom valves were enumerated. Each diatom was identified to species level according to Reavie and Kireta (2015), Krammer and Lange-Bertalot (1986–1991), Patrick and Reimer (1966–1975), and several other taxonomic works. For all core intervals, percent relative abundance and diatom accumulation (valves cm^{-2} year^{-1}) based on the quantitative Battarbee (1986) method were calculated.

Phytoliths, sponge spicules, chrysophyte scales and stomatocysts, and testate amoebae plates were also counted when observed, though only chrysophyte cysts were abundant enough for analysis. These siliceous remains can be used to infer environmental conditions and may provide additional insight on the ecological condition of the SLRE (Smol et al. 2001).

A cluster analysis was completed to characterize the stratigraphic zonation which may reflect historical events leading to reorganization of the diatom community. For common taxa (at least five occurrences with at least 5% abundance in one or more samples), a depth-constrained cluster analysis was done using the "chclust" function in R with the "rioja" package (Juggins 2014) to identify temporally constrained diatom assemblage zones. The CONISS algorithm (Grimm 1987) was used to perform clustering constrained to vertical stratigraphy based on dissimilarity in squared Euclidian distances among samples. The embedded function "bstick" was used to perform a broken-stick analysis and determine the minimum number of significant zones (Bennett 1996). In addition to zones determined by the broken stick analysis, zones were delineated based on apparent changes in abundance of species which are characteristic of certain environments; for instance, nutrient-tolerant *Stephanodiscus parvus* Stoermer & Håkansson is often associated with eutrophic environments (Stoermer and Håkansson 1984).

Ordination

In order to better assess the similarities among cores and track temporal trajectories, non-metric multidimensional scaling (NMDS) analyses were performed. NMDS is an ordination technique allowing for visualization of highly dimensional data in lower dimensional space. Multidimensional scaling examines distances between observations (e.g. samples or species); shorter distances indicate similarity. The statistical software R with the vegan package (R Core Team 2014; Oksanen et al. 2015) was used to create an NMDS plot from diatom relative abundance data. Species with a maximum relative abundance less than 5% were omitted to reduce analytical artifacts from rare species.

Diatom-inferred modeling

Diatom-inferred (DI) modeling translates fossil diatom data into a reconstruction of an environmental variable (Hall and Smol 1992; Ponader et al. 2007; Saunders 2011). To develop the DI models, diatom species in a training set of samples were related to total phosphorus (TP) measurements and species coefficients (phosphorus optima) were calculated. These species-specific coefficients were applied to the diatom assemblages in cores, and TP was inferred based on the relative abundances of fossil diatom taxa. Models were developed from two Great Lakes training sets: (1) open water (Reavie et al. 2014; used for the Lake Superior core) and (2) coastal embayments, wetlands, and high-energy areas (Reavie et al. 2006; used for the six estuary cores).

A set of analyses verified the efficacy of both models' ability to reconstruct phosphorus. An analog analysis determined similarities between diatom assemblages in the models and fossil assemblages. Using the R package analogue (Simpson and Oksanen 2015) assemblages from the model were matched to fossil assemblages following Flower et al. (1997) and Simpson et al. (2005). Analogs were determined using Bray–Curtis dissimilarity (Bray and Curtis 1957). Dissimilarities between fossil and modern samples were examined to determine how well fossil assemblages were represented in model assemblages. A constrained canonical correspondence analysis (CCA) was done to examine the relationship between modern phosphorus and diatom assemblages, and then fossil samples were ordinated passively to determine goodness of fit. Using the R packages vegan and analogue (Oksanen et al. 2015; Simpson and Oksanen 2015) a CCA defined residual distances of fossil assemblages (i.e. sample scores) and TP gradient (i.e. constrained CCA axis 1). Fossil residual distances within the 95% confidence interval of the modern sample distances were considered to have good fit to TP.

To determine if TP was related to changes in fossil species assemblages, we applied statistical analyses according to Reavie et al. (2014). Using the R package vegan (R Core Team 2014; Oksanen et al. 2015), each set of fossil data in a given core was summarized using principal components analysis (PCA) to derive axis scores representing the primary gradient of variation in the diatom assemblage data (Juggins and Birks 2012). A correlation coefficient (r) was calculated for historical diatom inferred total phosphorus (DI-TP) versus the axis 1 PCA scores. If |r| was significant (*t* test, $p < 0.05$), it was likely changes in fossil diatom assemblages in cores were at least in part determined by TP, and so use of the DI-TP model was considered appropriate.

To further analyze DI-TP, results were compared to the historical measured TP dataset presented in Bellinger et al. (2016). A lowess smoothing was applied to the measurements from the lower estuary (Blatnik Bridge) due to its closer proximity to coring locations, and plotted alongside DI-TP results.

Results

Sediment chronology

Exponential decay of ^{210}Pb with sediment depth was used to determine the validity of chronological profiles. With the exception of North of Clough

Island, cores showed a consistent record of sediment accumulation and were dateable (Fig. 2; Alexson 2016). ^{210}Pb data from North of Clough Island suggested recent disturbance, likely due to increased sedimentation from a 500-year flood that affected the SLRE in 2012 (Czuba et al. 2012). Unsupported (excess) ^{210}Pb data were relatively monotonous with depth, aside from an uppermost section above ~ 35 cm depth with higher concentrations. Supplementary dating using ^{137}Cs characterized high concentrations of that isotope around 1963 due to nuclear weapons testing (Krishnaswami and Lal 1978). Based on a peak in ^{137}Cs at 60 cm depth, we assigned a rough, recent chronology based on knowing the 1963 interval, acknowledging dates since 1963 are highly uncertain due to flood disturbance.

With the exception of North of Clough Island, cores showed increased sedimentation rates in the early 1900s or just prior (Fig. 3, left-most panels). Several cores demonstrated a rise in sedimentation rates: Allouez Bay and Billings Park had peaks around 1920–1930 and subsequently fell to sedimentation rates of 0.35–0.15 and 2.0–0.2 g cm^{-2} year^{-1} respectively. In both cores, sedimentation rates remain higher than pre-European settlement conditions (0.02 g cm^{-2} year^{-1} in Allouez Bay and 0.15 g cm^{-2} year^{-1} in Billings Park). In western Lake Superior, sedimentation rates peaked around 1970 at 0.12 g cm^{-2} year^{-1} with a secondary peak at 0.11 g cm^{-2} year^{-1} in 1900; rates recovered to near pre-European settlement conditions around 2000. This trend is similar to North Bay where there was a secondary peak in 1930 (0.3 g cm^{-2} year^{-1}) and a peak in 1970 (0.4 g cm^{-2} year^{-1}). Rates declined to 0.2 g cm^{-2} year^{-1} by 2000, but rates remained higher than pre-European settlement. In contrast, sedimentation rates continued to increase in cores from Minnesota Point and Pokegama Bay. At Minnesota Point, accumulation rates rose from less than 0.02–0.14 g cm^{-2} year^{-1}, with the greatest rate of change occurring in the last 40 years. Sedimentation rates at Pokegama Bay increased from 0.05 to

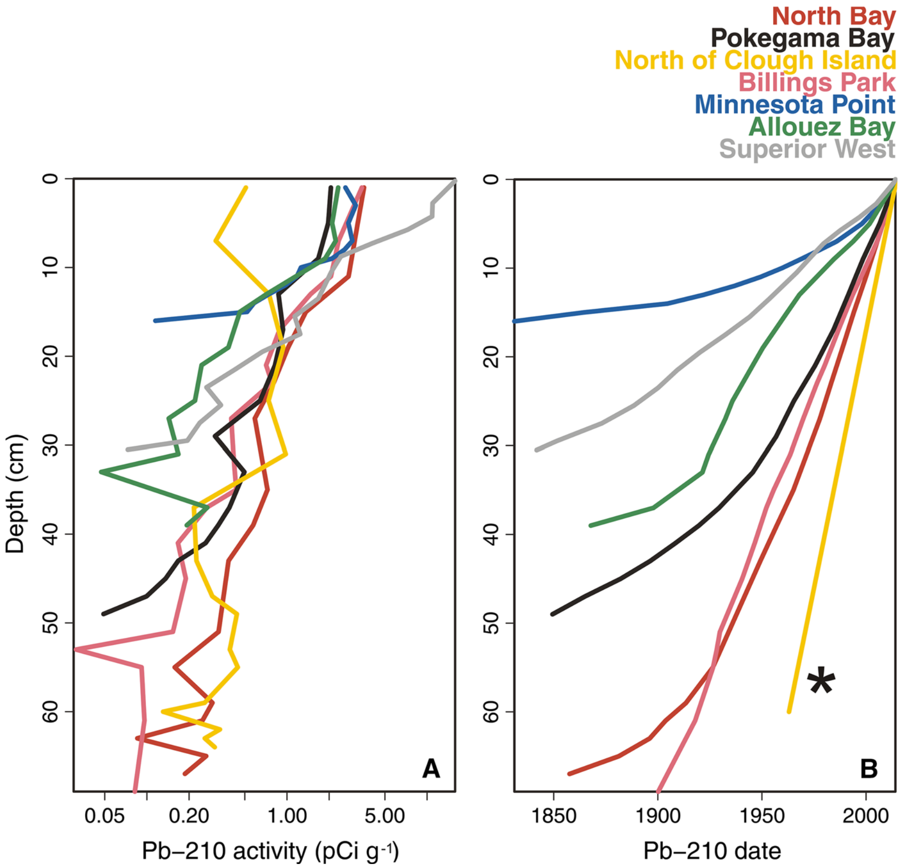


Fig. 2 **a** The magnitude of supported lead-210 (^{210}Pb) activity versus depth in the core. **b** ^{210}Pb inferred dates of the cores versus sediment depth. *The North of Clough core demonstrated a poor ^{210}Pb record, so we provide a very rough estimate of dates and accumulation rates based on ^{137}Cs data that indicated the ~ 1963 interval

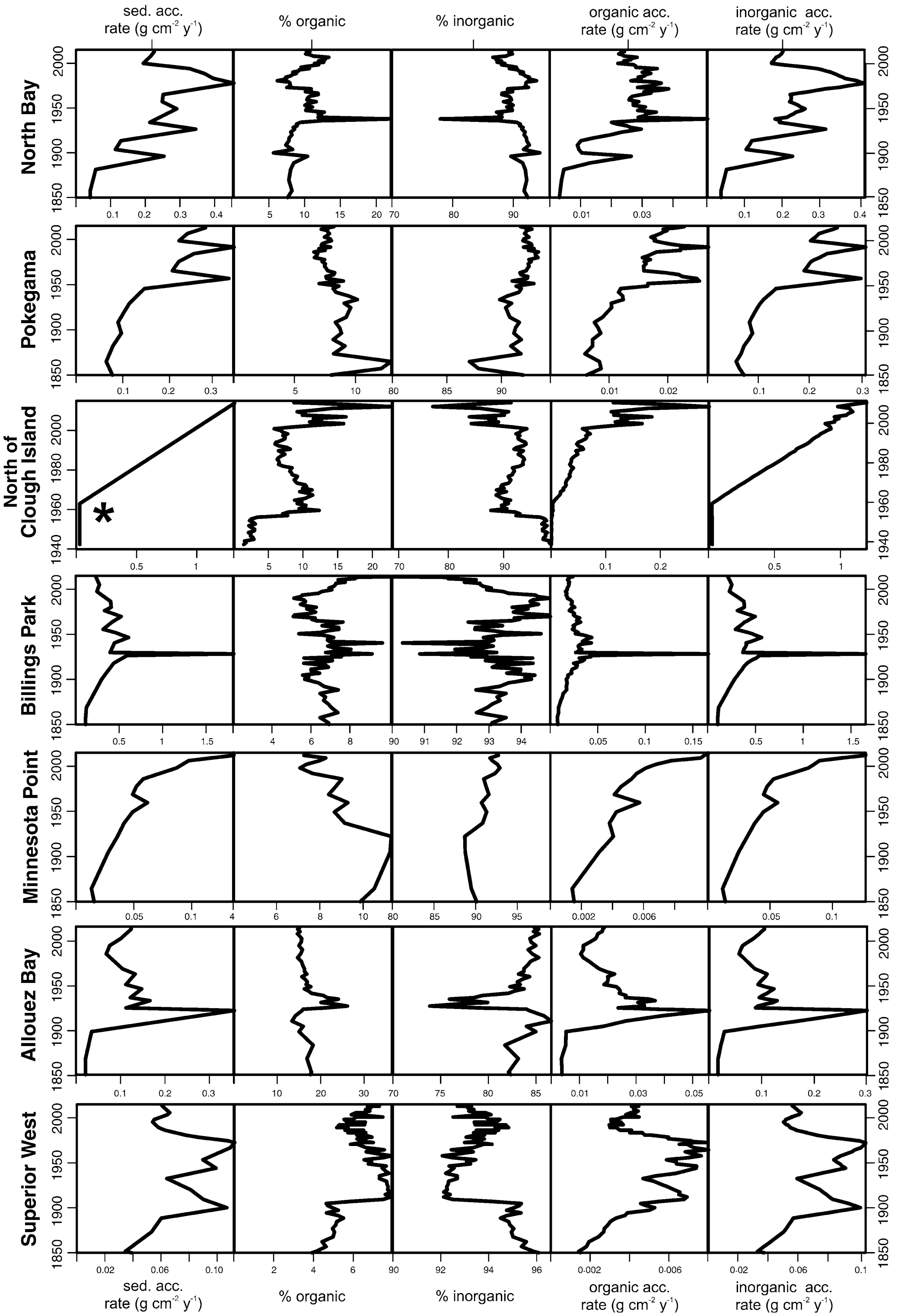


Fig. 3 Results of inorganic and organic content analyses of seven sediment cores from the SLRE and Lake Superior. *The North of Clough core demonstrated a poor ^{210}Pb record, so we provide a very rough estimate of dates and accumulation rates based on ^{137}Cs data that indicated the ~ 1963 interval. Note the x-axis (analyte) scales are different for each core

0.25 g cm^{-2} $year^{-1}$ with two peaks occurring at 1960 and 1990 (both around 0.35 g cm^{-2} $year^{-1}$). The accumulation profile for North of Clough Island was based on a single ^{137}Cs date, so we have great uncertainty about recent accumulation rates. Overall, differences in average sediment accumulation rates among cores reflected their physical settings, such as the lower rates in the more lacustrine areas (Minnesota Point and Lake Superior).

Sediment content

Cores from Allouez Bay and North Bay had the most distinct changes in organic content with a peak in the 1930s and a concomitant increase in % inorganic material (Fig. 3). An increase in organic content was also seen at North of Clough Island since 2000, and due to uncertainty in dating may reflect a depositional layer from the 2012 flood (Czuba et al. 2012).

Accumulation rates of organic and inorganic components largely followed total sedimentation rates, although there were some anomalies. In North of Clough Island, there was lower accumulation of organic material from 1970 to 2000 and increased accumulation from 2000 until present.

Pigments

Pigments in four estuary cores (North Bay, Billings Park, North of Clough Island, and Minnesota Point; Fig. 4) tracked historical shifts in algal groups. Pigments representative of total algae (chlorophyll *a*, pheophytin *a*, and *β*-carotene) showed increased algal production in recent sediments since ~ 1990 in North Bay and Billings Park. Fucoxanthin and diatoxanthin were higher in North Bay and Billings Park. Fucoxanthin (diatoms and dinoflagellates) increased rapidly in more recent intervals, since 1990 in North Bay and 2005 in Billings Park, whereas diatoxanthin (diatoms) showed a gradual increase since 1980. Pigments from cyanobacteria (aphanizophyll and myxoxanthophyll) have increased in both North Bay and Billings Park in the last 20 years. Although there was a strong peak in alloxanthin (representing cryptophytes) around 1970, since ~ 1980 pigment concentrations in Minnesota Point and North of Clough Island cores remained relatively low and steady. Because some pigments degrade with time (e.g. chlorophyll *a* tends to have low stability; Leavitt and Hodgson 2001), we note recent increases occur in pigments with known reliability in long-term preservation in sedimentary records (pheophytin *a*, fucoxanthin, diatoxanthin, aphanizophyll, and myxoxanthophyll, and especially *β*-carotene).

Diatoms

A total of 654 diatom taxa were observed from 88 genera. In SLRE cores, both benthic and planktonic diatoms were common whereas the species composition in Lake Superior was mostly planktonic. Diatom accumulation rates in North Bay, Pokegama Bay, Billings Park, and Allouez Bay peaked in the mid-twentieth century (Fig. 5) whereas accumulation rates were highest around 2000 in Minnesota Point and North of Clough Island. North Bay and Allouez Bay shifted to centric-dominated (i.e. planktonic) assemblages (~ 1900 and ~ 1940 respectively) and had mostly consistent proportions of pennates to centrics. Chrysophyte stomatocyst to diatom ratio was higher in earlier intervals of the North Bay, Pokegama Bay, Billings Park, Minnesota Point, and Allouez Bay cores. Chrysophytes are more competitive in oligotrophic environments; therefore, higher ratios of chrysophyte cysts to diatoms are associated with lower nutrients (Smol 1985). Long-term trends showed a decrease in chrysophyte stomatocyst to diatom ratio indicating increased nutrient loading. In North Bay, Allouez Bay, and Billings Park this ratio continued to decline, while it stabilized in Minnesota Point and Pokegama Bay (around 1970 and 1950 respectively). Accumulation rates of stomatocysts generally had similar stratigraphies to those of diatoms.

Several estuary cores (North Bay, Pokegama Bay, Minnesota Point, and Allouez Bay) transitioned (~ 1850–1900) from benthic diatoms (*Staurosira* Ehrenberg and *Staurosirella* Williams and Round) to assemblages dominated by planktonic *Aulacoseira* Thwaites (Fig. 6).

North Bay

North Bay had two significant zones determined by the broken stick analysis, pre and post-1900. However, based on apparent shifts in diatom assemblages, we delineated three zones in the core: (A) pre-1900, (B) 1900–1945, and (C) post-1945 (Fig. 6a). The core was made up of mostly planktonic diatoms (*Aulacoseira*, *Fragilaria* Lyngbye, and *Stephanodiscus*

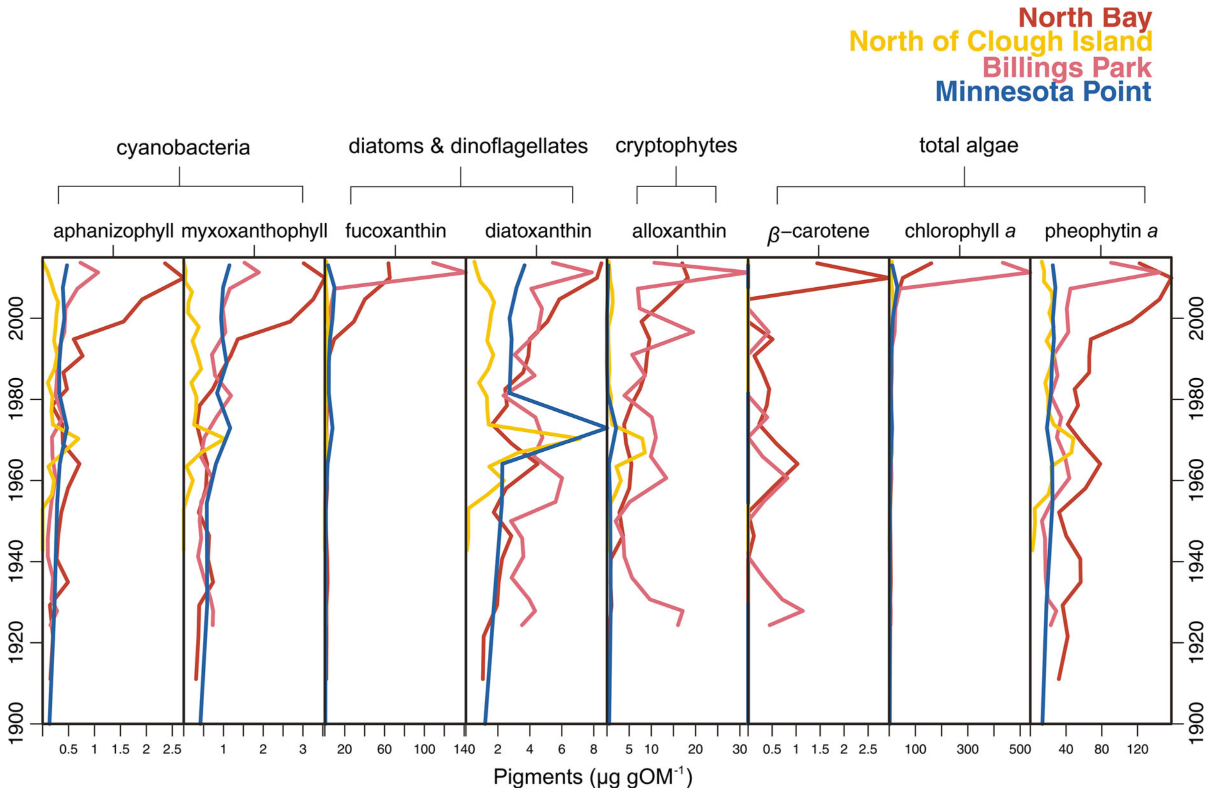


Fig. 4 Recent concentrations of various algal pigments determined by HPLC in four SLRE cores

Ehrenberg), but was also accompanied by some benthic genera (*Staurosira*, *Achnanthidium* Kützing, *Cocconeis* Ehrenberg, and *Navicula* Bory de Saint-Vincent). *Staurosira construens* var. *venter* (Ehrenberg) Hamilton and *Staurosirella pinnata* (Ehrenberg) Williams & Round dominated Zone A (combined ~ 20%). These epipsammic and epidemic diatoms indicate a low-nutrient, benthic-dominated community (Estepp and Reavie 2015; Morales 2010a). In the early 1900s (Zone B), species comprising the modern assemblage increased in abundance while *S. construens* var. *venter* and *S. pinnata* declined. Higher-nutrient indicators *Aulacoseira ambigua* (Grunow) Simonsen, *Stephanodiscus parvus*, *Cyclotella meneghiniana* Kützing, and *Stephanodiscus hantzschii* Grunow (Stoermer et al. 1985; Stoermer and Yang 1970; Stoermer and Håkansson 1984) appeared in greater abundance in Zone C. Since their initial increase, some species (*C. meneghiniana* and *S. hantzschii*) declined in the last decade, although a few high nutrient-tolerant taxa (*Aulacoseira granulata* (Ehrenberg) Simonsen and *S. parvus*) became more abundant. Also in Zone C, benthic and epiphytic taxa like *Cocconeis placentula* Ehrenberg (Round et al. 1990), and *Navicula gregaria* Donkin (Round et al. 1990) increased in abundance, reflecting a probable, local increase in macrophyte habitat. Benthic *Fragilaria vaucheriae* Petersen (Morales 2010b) and *Fragilaria mesolepta* Rabenhorst (Potapova and Spaulding 2013) were also higher in Zone C.

Pokegama Bay

Centric diatoms dominated the core from Pokegama Bay (Fig. 6b). While only four zones were determined to be significant by broken stick analysis, we interpreted five zones based on changes in characteristic species. The historical community in Zone A (pre-1830) consisted of *S. pinnata* (benthic; Estepp and Reavie 2015), *Achnanthidium minutissimum* (Kützing) Czarnecki (epiphytic; Potapova 2009), and *Aulacoseira pusilla* (Meister) Tuji & Houk (planktonic; Potapova 2010). In Zone B (1830–1910), *A. pusilla*, joined by *A. granulata* and *A. ambigua* increased in

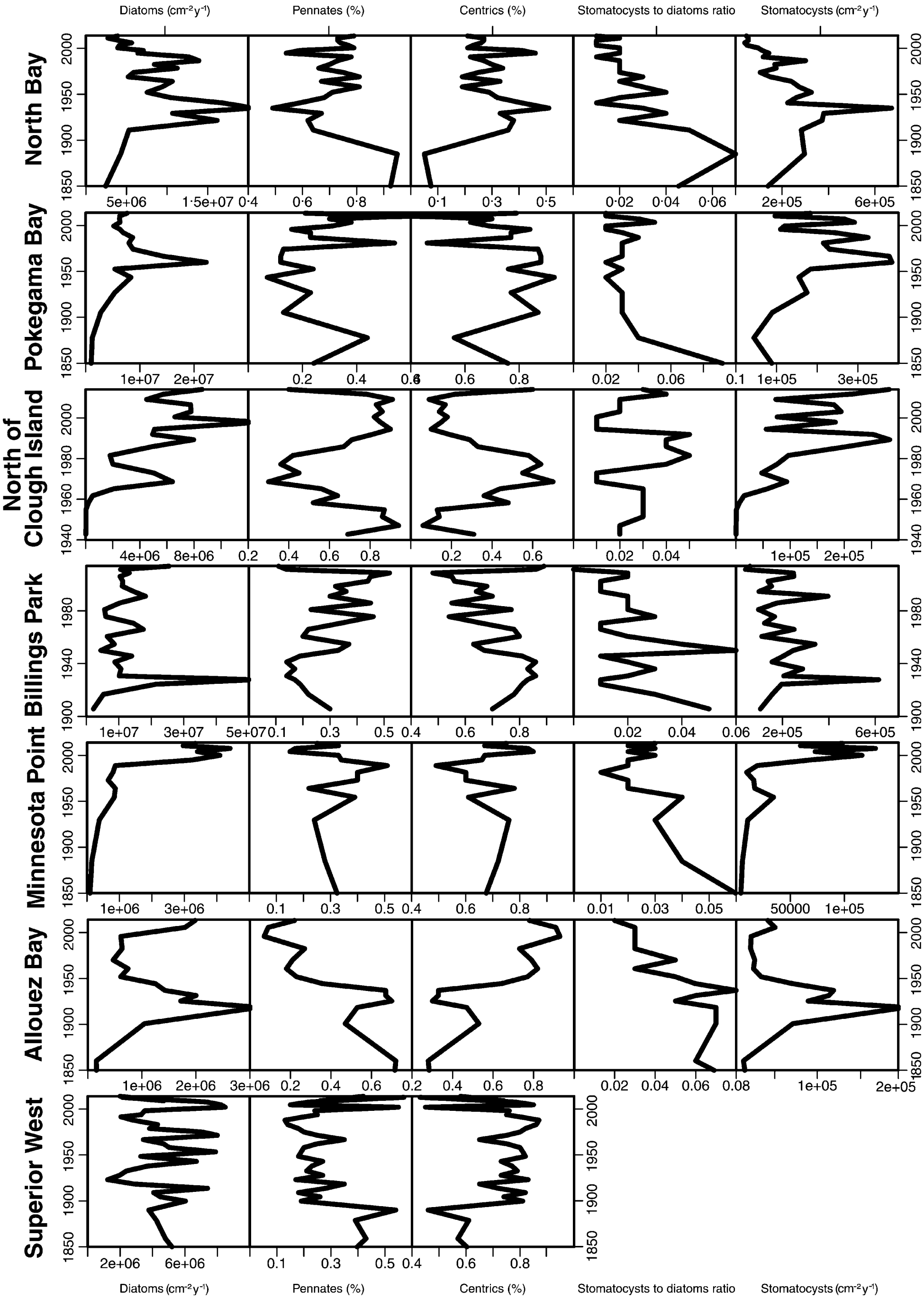


Fig. 5 Diatom accumulation rates, % pennates, % centrics, ratio of chrysophyte stomatocysts to diatoms, and chrysophyte stomatocyst accumulation rates of seven cores in the SLRE and Lake Superior. Chrysophyte stomatocysts were not in great enough abundance in Lake Superior to be plotted. Note that x-axis scales vary among cores to better illustrate temporal trends

abundance to dominate the assemblage. *A. ambigua* and *A. granulata* continued to increase in Zone C (1910–1970) until their peak (35% in 1940, 45% in 1960) after which they declined. Eutrophic *S. parvus* also increased in this period until it declined in Zone D (1970–1980), though its abundance was still higher

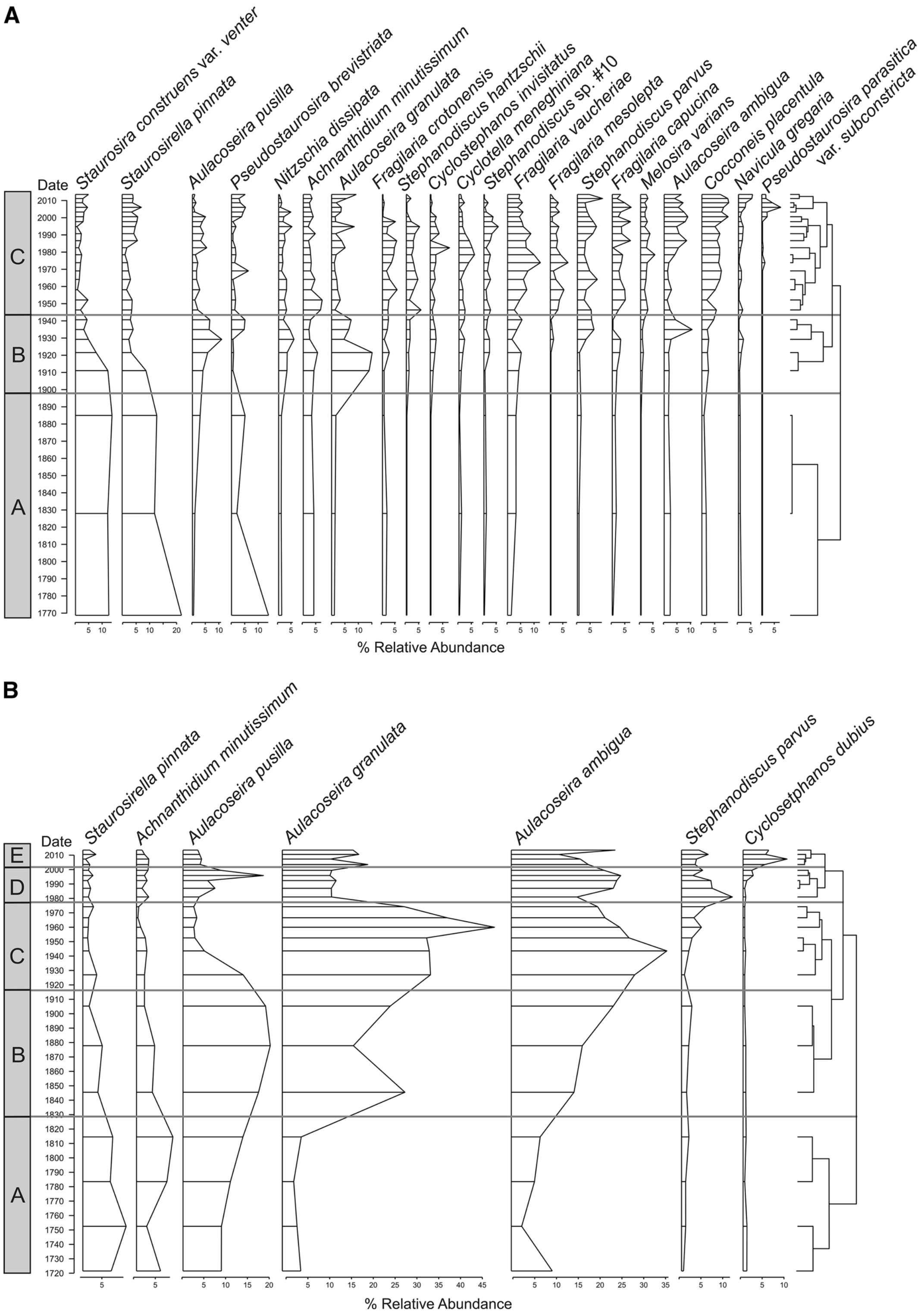


Fig. 6 Relative abundances of the most common taxa in the core taken from **a** North Bay, **b** Pokegama Bay, **c** North of Clough Island, **d** Billings Park, **e** Minnesota Point, **f** Allouez Bay, and **g** Western Lake Superior. The labeled zones represent changes in assemblages determined by cluster analysis

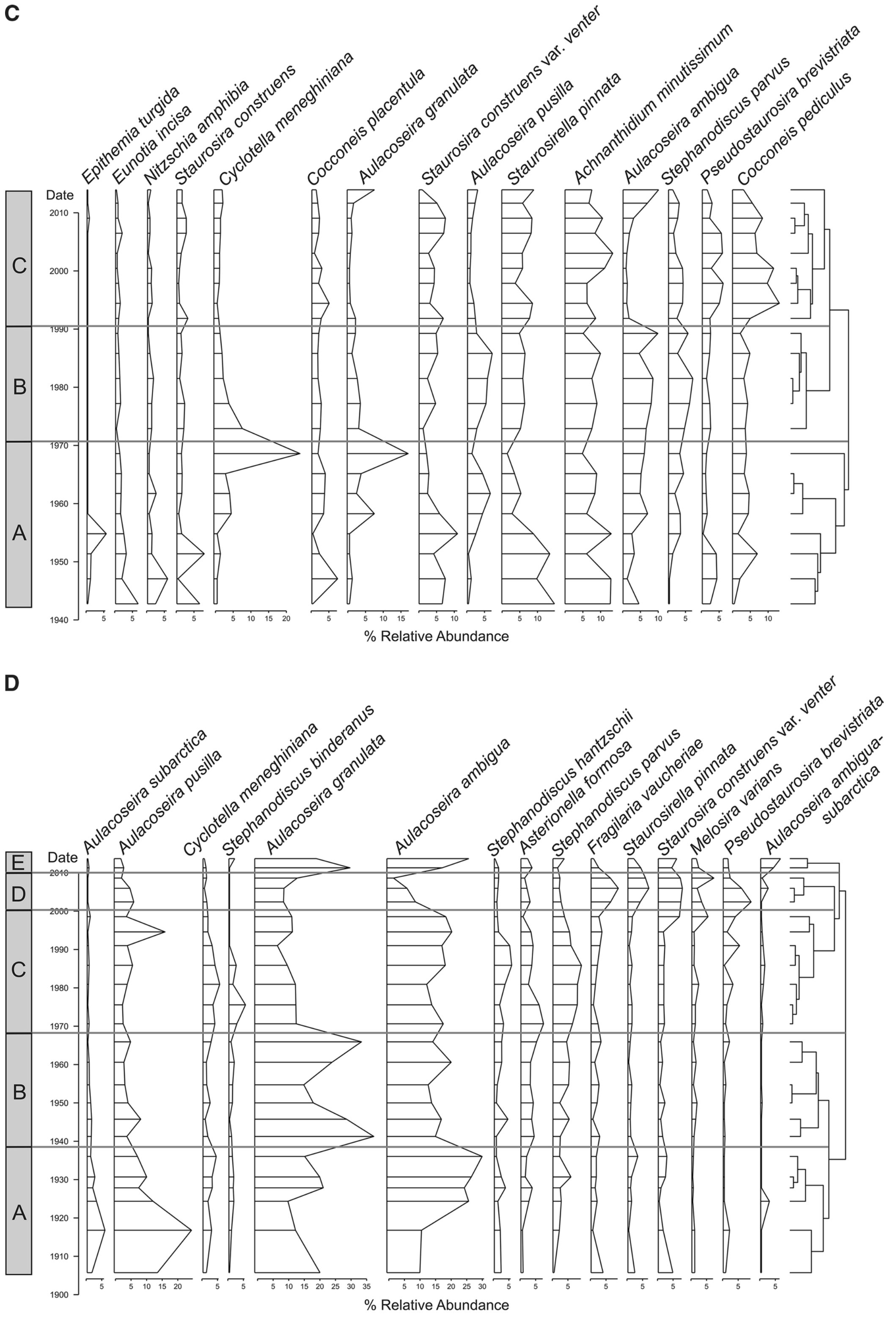
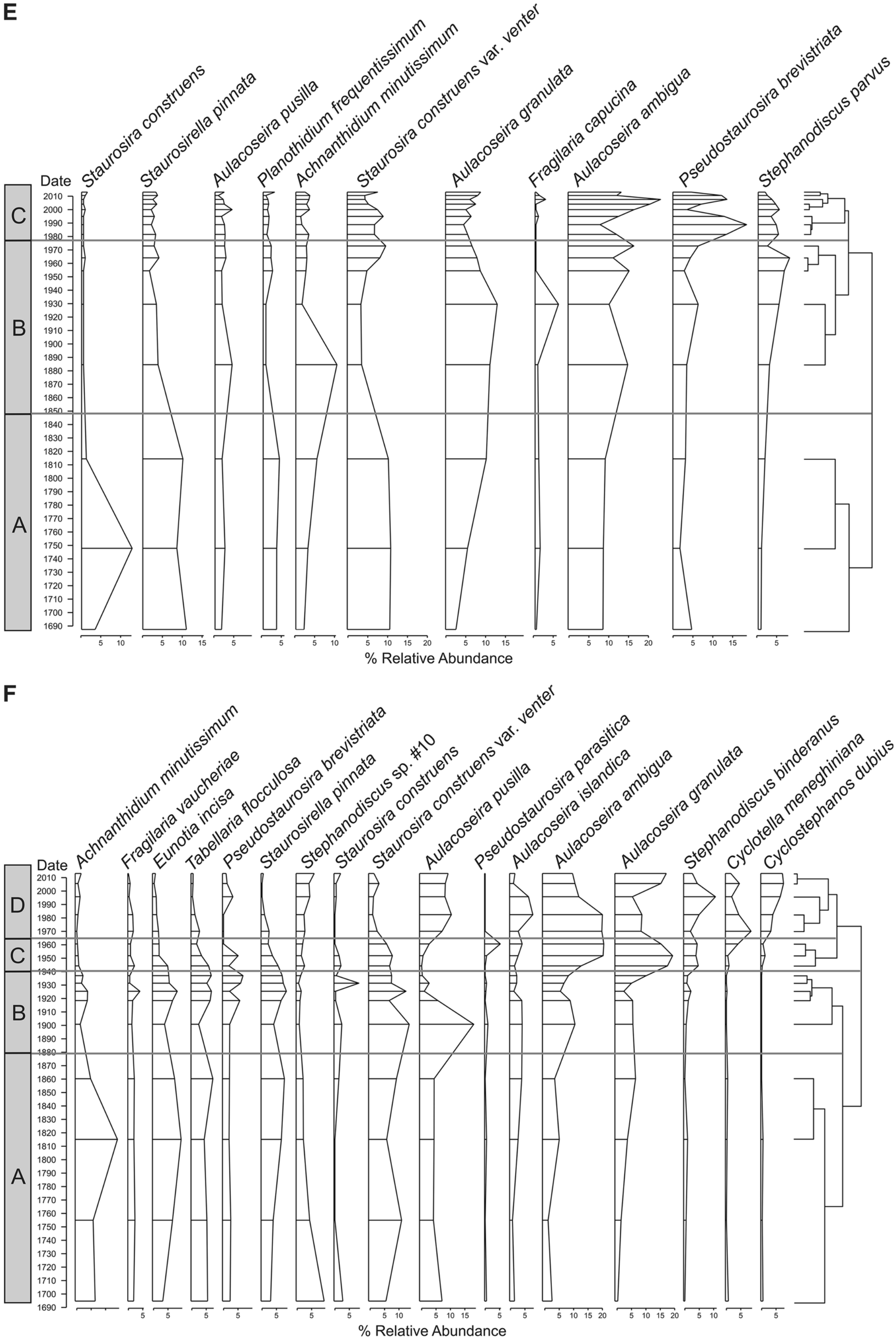


Fig. 6 continued



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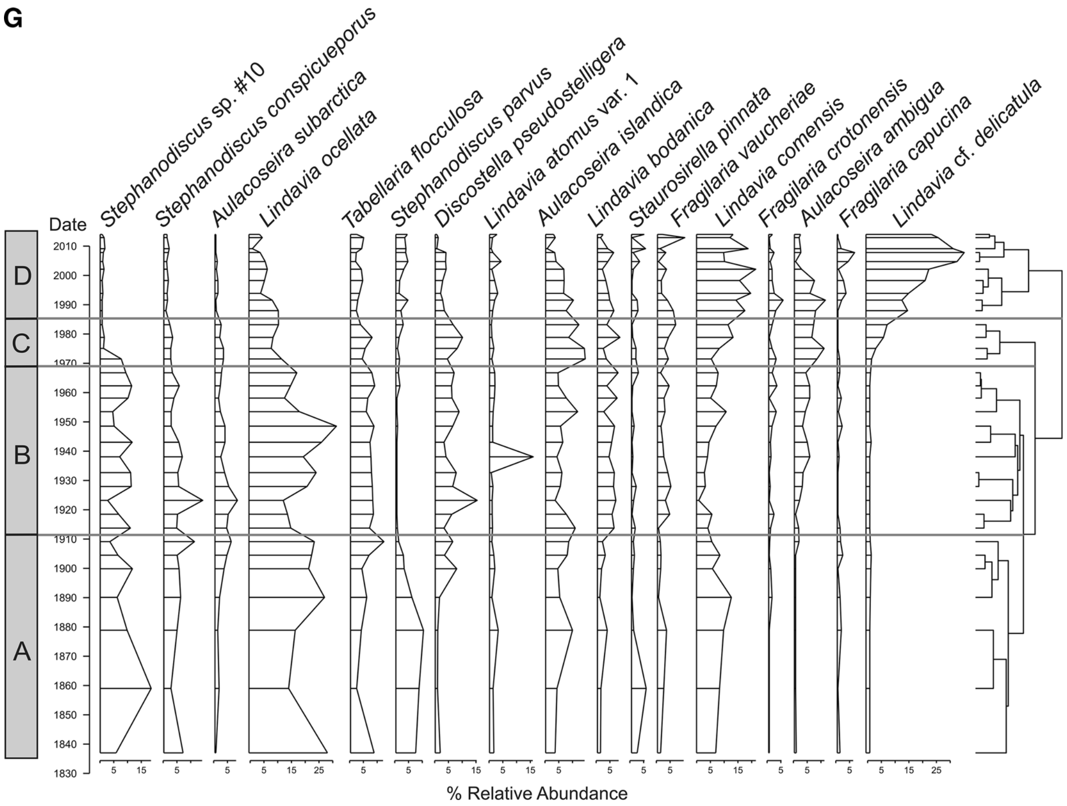

Fig. 6 continued

than pre-European settlement. In Zone E (post-2000), *Aulacoseira* still dominated (~ 40%) but was partly replaced by another eutrophic diatom, *Cyclostephanos dubius* (Fricke) Round (Hickel and Håkansson 1987), whose abundance grew to around 10% of the diatom assemblage.

North of Clough Island

The diatom record from North of Clough Island only extended back to 1940, so pre-impact conditions cannot be determined (Fig. 6c). The broken stick analysis determined at least three temporal zones were significant. In Zone A (pre-1970), eutrophic indicators *C. meneghiniana* and *A. granulata* peaked in the late 1960s (20% abundance) and then rapidly returned to earlier conditions (1–4%) in Zone B (1970–1990). In Zone B, *S. parvus* also increased, but abundance decreased around 1990 (the start of Zone C). Common genera were *Cyclotella* (Kützing) Brébisson, *Cocconeis*, *Aulacoseira*, *Achnanthidium*, *Staurosira*, and *Staurosirella*. We again note great uncertainty in the timing of changes in this core due to the recent flood, which may have deposited allochthonous material in an undetermined layer near the core surface. We have confidence the uppermost ~ 2 intervals represent post-flood deposition, and the assemblage (*S. pinnata*, *A. minutissimum*, and *A. ambigua*) indicates lower nutrients than pre-1970 taxa.

Billings Park

The core from Billings Park was dominated by planktonic diatoms, especially species from the genus *Aulacoseira* (Fig. 6d). The core had three significant zones; however, we determined five zones showed important changes in assemblages. The assemblage was made up of largely *A. pusilla*, A. *granulata*, and *A. ambigua* in Zone A (~ 1900–1940), but shifted to *A. granulata* and *A. ambigua* dominance in Zone B (1940–1970). Nutrient-tolerant diatoms *S. parvus*, *S. hantzschii*, *Stephanodiscus binderanus* (Kützing)

Krieger, and *C. meneghiniana* increased in abundance in Zone C (1970–2000), followed by a partial decline as they were replaced by small, benthic species (e.g. *S. construens* var. *venter*, *S. pinnata*, and *Pseudostaurosira brevistriata* (Grunow) Williams & Round) in Zone D (2000–2010). Zone E (post-2010) shifted back to an *Aulacoseira*-dominated assemblage similar to before ∼ 1970.

Minnesota Point

The core from Minnesota Point was comprised of centric and araphid planktonic diatoms with a smaller proportion of benthic species (Fig. 6e). Three zones (two were determined significant by broken stick analysis) were identified: (A) pre-1850, (B) 1850–1980, and (C) post-1980. *Staurosira construens* Ehrenberg, *S. pinnata*, *S. construens* var. *venter*, *A. granulata*, and *A. ambigua* dominated Zone A, which existed as far back as ∼ 1700. In Zone B, *Staurosira* and *Staurosirella* decreased and there was some growth in the already dominant *Aulacoseira* population. Eutrophic *S. parvus* increased and reached a maximum abundance (< 10%) in ∼ 1965 and returned to near pre-European settlement abundances (< 5%) in Zone C. Also in Zone C, *A. granulata*, *A. ambigua*, and *P. brevistriata* increased.

Allouez Bay

Allouez Bay consisted of mostly planktonic diatoms (Fig. 6f). Although the broken stick analysis only found two significant zones, we delineated four zones based on apparent changes in diatom assemblages. The historical assemblage (Zone A, pre-1880) was very diverse, including the phytoplankton *Aulacoseira subarctica* (O. Müller) Haworth, *A. pusilla*, *A. ambigua*, *A. granulata*, *Stephanodiscus* sp. #10, the epiphytic *A. minutissimum* and *Eunotia incisa* Smith ex Gregory, and the benthic *S. construens* var. *venter* (each ∼ 5%). In Zone B (1880–1940), *A. ambigua* and *A. granulata* grew to dominate the assemblage, indicating greater planktonic dominance and probable nutrient enrichment. They continued to rise and reached a maximum (together 40% of the assemblage) in Zone C (1940–1960). In Zone D (post-1960), eutrophic indicators *S. binderanus*, *C. meneghiniana*, and *C. dubius* (Stoermer et al. 1987; Hickel and Håkansson 1987) began to increase in abundance, each occupying 5–10% of the assemblage in the upper intervals.

Lake Superior

The species assemblage in Lake Superior was dominated by planktonic, centric diatom species (*Lindavia* (Schutt) De Toni & Forti, *Cyclotella*, *Stephanodiscus*, and *Aulacoseira*) (Fig. 6g). Zone A (pre-1910) was dominated by *S.* sp. #10, *Lindavia ocellata* (Pantocsek) T. Nakov et al., *Lindavia atomus* var. 1, and *Lindavia comensis* (Grunow in Van Heurck) T. Nakov et al., taxa generally reflecting low nutrients. *Stephanodiscus conspicueporus* Stoermer, Håkansson & Theriot, *A. subarctica*, *A. islandica*, and *A. ambigua*, mesotrophic diatoms indicating higher nutrients in oligotrophic Lake Superior (Stoermer 1993) increased in Zone B (1900–1970) but decreased in Zone C (1970–1985). Small centric diatoms, *L. comensis* and *Lindavia* cf. *delicatula* (Hustedt) T. Nakov et al. (Reavie and Kireta 2015), began increasing in Zone C and increased to a combined abundance of ∼ 40% in Zone D (post-1985). These low-nutrient taxa may be related to climate-driven physical changes in the lake (Shaw Chraïbi et al. 2014; Reavie et al. 2017a).

Ordination

Based on an initial ordination of diatom samples from all cores, Lake Superior was highly dissimilar to SLRE cores, indicating substantial differences in common taxa between the lake and SLRE (Fig. 7a). Therefore, the analysis was repeated to examine (1) all cores, (2) Lake Superior, and (3) SLRE cores to better visualize historical trajectories in NMDS ordinations.

NMDS of Lake Superior (Fig. 7b) reflected a constant reorganization of the diatom assemblage, from a pre-1900 assemblage dominated by *S.* sp. #10, *L. ocellata*, and *L. comensis*, followed by an increase in higher nutrient taxa (e.g. *A. subarctica* and *A. islandica*) in the upper right quadrant. Migration to the left reflected current conditions dominated by small centrics such as *L. comensis* and *L.* cf. *delicatula*.

With the exception of Billings Park, the oldest intervals of each SLRE core fell within the lower, right quadrant (Fig. 7c), indicating consistent assemblage baselines of *S. construens*, *S. construens* var. *venter*, and *S. pinnata*. Into the twentieth century assemblages migrated to the upper, left quadrant, representing assemblage shifts associated with higher nutrients (e.g. *C. meneghiniana* and *S. parvus*). The most recent sample scores in Billings Park, Pokegama Bay, and Allouez Bay were especially constrained to the left of the ordination in accordance with higher relative abundances of *C. dubius, S. binderanus*, and *Aulacoseira* spp. In general, fossil assemblages in the SLRE exhibited consistent reorganization, and there was little evidence that recent diatom communities have returned to pre-impact assemblages.

Diatom-inferred modeling

Based on model validation, there was a significant relationship between changes in TP and diatom assemblages in all cores (i.e. DI-TP strongly correlated with the primary gradient of variation in assemblages in each core). Further, analog analyses showed good fit between fossil assemblages and model training sets in all cases (ESM1; Alexson 2016).

DI-TP results (Fig. 8) indicated western Lake Superior had much lower concentrations of TP (3–6 μg L^{-1}) than the SLRE (15–80 μg L^{-1}). DI-TP increased during the mid-twentieth century in open water cores (Lake Superior, Minnesota Point, and North of Clough Island), followed by a decline in western Lake Superior and North of Clough Island cores and stabilization in the Minnesota Point core. Cores taken from SLRE bays (North Bay, Billings Park, Allouez Bay, and Pokegama Bay) generally showed increasing DI-TP since the mid-twentieth century.

DI-TP in western Lake Superior showed increasing TP concentrations in the early 1900s with a maximum concentration of 5.5 μg L^{-1} around 1930 and a secondary peak (5 μg L^{-1}) around 1970. After 1970, TP decreased and stabilized around pre-European settlement concentrations (~ 3 μg L^{-1}), similar to observations in other Lake Superior cores (Shaw Chraïbi et al. 2014).

In the SLRE, the open-water environments (Minnesota Point and North of Clough Island) showed stabilization or a decrease of TP. The DI-TP from North of Clough Island showed an increase from 25 to 65 μg L^{-1}, peaking around 1970. Because there was no diatom record from the North of Clough Island core before 1940, it was not possible to compare pre and post-European settlement conditions. The North of Clough Island reconstruction indicated an increase in the late 1900s from 25 to 35 μg L^{-1} TP. After a peak in 1980, DI-TP stabilized around 30 μg L^{-1}. Again, due to uncertainty in accumulation, we inferred higher nutrients in the 1960s and lower nutrients today, but timing of transitions are ambiguous.

Cores from bay environments showed modern conditions of increasing DI-TP. Cores from Allouez Bay and Pokegama Bay both remained at near-constant concentrations of DI-TP (30 and 45 μg L^{-1}, respectively) until ~ 1950, after which TP concentration increased to as high as ~ 80 μg L^{-1}. DI-TP began to increase around 1920 at North Bay and rose from ~ 50 to ~ 60 μg L^{-1} in modern intervals. In Billings Park DI-TP increased from ~ 1950 to ~ 2000 (from ~ 20 to 38 μg L^{-1}), followed by two modern intervals with lower DI-TP (~ 20 μg L^{-1}).

Compared to historical measured TP from a location in the lower estuary (at Blatnik Bridge; Bellinger et al. 2016), DI-TP concentrations were lower in all cores (Fig. 8); however, the general trend of declining monitored TP in recent decades was similar to DI-TP from North of Clough Island and Lake Superior cores. The monitoring dataset from Bellinger et al. (2016) at Blatnik Bridge spanning 1973–2014 showed a peak of TP in ~ 1980 (~ 180 μg L^{-1}) and afterward a steady decrease in TP concentration to approximately 40 μg L^{-1} (based on the lowess smoothing), closely matching modern DI-TP of ~ 30 μg L^{-1} from Minnesota Point and North of Clough Island cores.

Discussion

These paleolimnological data describe the history of anthropogenic influence on the SLRE and western Lake Superior and reveal where remediation may be occurring. As previously detailed by Reavie and Edlund (2010), paleolimnology in lotic environments can be challenging. We believe we have overcome these limitations through application of multiple fossil indicators and careful selection of core locations.

Evidence of early impacts from logging and subsequent modifications of the drainage basin and the St. Louis River were found in the paleorecord. When logging was at its peak (~ 1850–1900), a transition in SLRE diatom communities from benthic genera (*Staurosira* and *Staurosirella*) to centric,

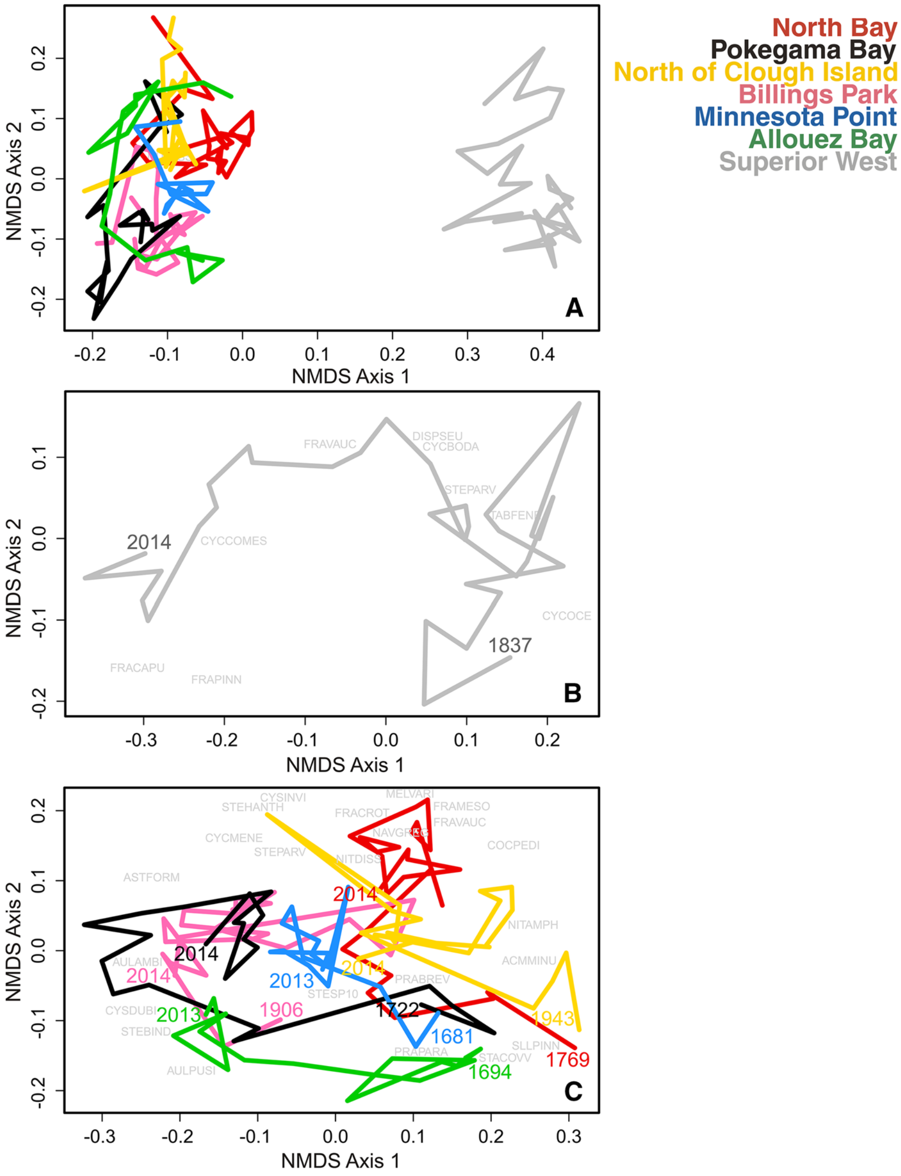

Fig. 7 NMDS analysis of diatom species assemblages (> 5% relative abundance) in **a** all seven cores from the SLRE and Lake Superior (stress of 0.1258), **b** Lake Superior (stress of 0.0889), and **c** the SLRE (stress of 0.1663)

planktonic diatoms (e.g. *Aulacoseira*) in North Bay, Pokegama Bay, Minnesota Point, and Allouez Bay suggested a physical transformation to a more lacustrine (but still fluvial) system because of hydrological manipulation by damming and dredging of the St. Louis River.

By the 1930s, with growing industries and a growing population to support them, the SLRE's ecology changed. Increased sedimentation rates, greater abundance of eutrophic diatom species, and higher DI-TP dominated the paleorecord. This was likely due to the combined effects of untreated wastewater and runoff from a landscape transformed by logging. With the construction of Fond du Lac Dam (upstream of all core locations) in 1924, decreased sedimentation rates were expected due to the retention effect of the new reservoir. However, it is clear other factors (algal production and watershed disruptions leading to increased erosion) contributed to increased sediment loads at some locations. Since 1970, sedimentation decreased in all cores with the exception of Minnesota Point and Pokegama Bay, and nutrient trajectories varied among locations. Cores from SLRE open-water environments suggested a remediation or

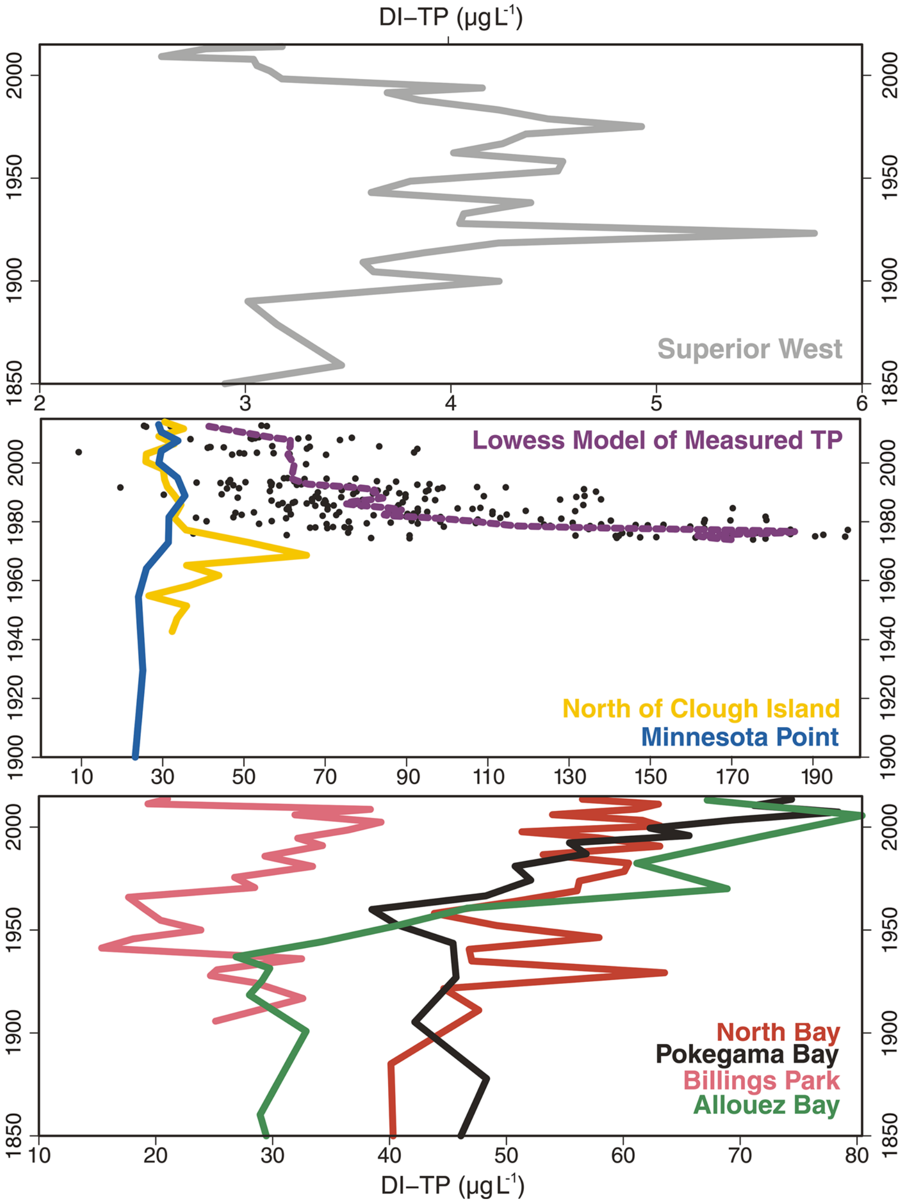

Fig. 8 Diatom-inferred total phosphorus from all cores. The purple line represents a lowess model of total phosphorus measurements (black dots) from the Blatnik Bridge from 1973 to 2012 as reported in Bellinger et al. (2016)

stabilization of phosphorus loading, while excess loading may be continuing in embayments. Fossil pigments corroborate this recent trend with increased concentrations of pigments from total algae and those from cyanobacteria in two bay locations.

Changes in legislation such as the Clean Water Act in 1972 accompanied by restoration efforts are associated with recovery we observed in some cores. The recovery is defined partly by a decrease in nutrient-tolerant diatoms—*Aulacoseira* spp. and *S. conspicueporus* in western Lake Superior, *Aulacoseira* spp. and *C. meneghiniana* in North of Clough Island, and *S. parvus* in Minnesota Point. This was affirmed by a decrease in DI-TP—a reduction in Lake Superior and North of Clough Island and apparent stabilization in Minnesota Point.

Results from these cores mostly agreed with monitoring data from Bellinger et al. (2016). Though the overall measured TP trend matched DI-TP, concentrations found by Bellinger et al. were much higher than those inferred by the model. This discrepancy may be due to the natural variability in the SLRE as the nearest coring location (Minnesota Point) is ~ 3.5 km away.

Fossil data from four cores taken from bay environments suggest continued high nutrients in these parts of the SLRE. Higher populations of all algae groups (notably cyanobacteria), a growth in abundance of nutrient-tolerant diatoms (*C. dubius*, *C. meneghiniana, S. parvus*, and *S. binderanus*), and increased DI-TP all support this conclusion. Recent persistence of high concentrations of nutrients in parts of the SLRE may be due to more localized nutrient sources, potentially from recent residential development and continued presence of industry, or enhanced internal loading of sedimentary nutrient pools. But, contemporary anthropogenic issues facing other water bodies such as those reported in Lake Erie—internal phosphorus loading and higher runoff from high-intensity rain events associated with climate change (Kane et al. 2009; Matisoff et al. 2016)—may also be responsible. Nearby in Lake of the Woods, a shallow, multinational lake bordering Canada and the United States, cyanobacterial blooms and high nutrient levels persist despite a reduction in allochthonous phosphorus. In that case, thermal stratification may be enhancing internal phosphorus loading and altering nutrient stoichiometry to favor nitrogen-fixing cyanobacteria (Reavie et al. 2017b). Similarly in Switzerland's Lake Zurich enhanced stratification due to warmer atmospheric temperatures has aggravated hypoxia and increased sediment phosphorus releases in lakes (North et al. 2014). Such possible drivers need additional study in the SLRE.

There is little doubt efforts to remediate the SLRE reduced the flux and concentration of nutrients in the SLRE (Bellinger et al. 2016). To meet beneficial use impairment removal targets, the portion of Lake Superior in the Area of Concern must have TP concentrations below 10 $\mu g\ L^{-1}$, the upper limit for oligotrophic designation, and the estuary must be below 30 $\mu g\ L^{-1}$, the upper limit for mesotrophic designation according to Minnesota standards (MPCA and WDNR 2013). According to DI-TP, western Lake Superior has always fallen within passing criteria, and is suitable for delisting. Minnesota Point, North of Clough Island, and Billings Park (at least according to the most recent interval) have TP concentrations around or below 30 $\mu g\ L^{-1}$, also meeting delisting criteria; whereas, North Bay, Pokegama Bay, and Allouez Bay exceed desired concentrations and may not be acceptable for delisting. Pre-impact concentrations of DI-TP at North Bay and Pokegama Bay (40–45 $\mu g\ L^{-1}$) surpass delisting criteria, so a criterion of 30 $\mu g\ L^{-1}$ may be unrealistic for these areas as they appear to be naturally higher in water column TP. Delisting goals may need reconsideration to accommodate the natural state of and variability within the estuary and address more modern stressors like climate change and internal phosphorus loading not well understood at the time of the Area of Concern listing. Managing agencies may choose to remove the nutrient beneficial use impairment with the intention of addressing these modern issues driving water quality in the estuary.

Presently, only four American and three Canadian Areas of Concern in the Great Lakes have been delisted, leaving 36 still listed. Although there have been paleolimnological studies in Areas of Concern in the past (Reavie et al. 1998; Yang et al. 1993), there have been few studies done intentionally to advise Area of Concern programs. In a similar study to ours, Dixit et al. (1998) examined sedimentary metals, accumulation rates, and diatom taxa to understand the anthropogenic influence in Spanish Harbor of Lake Ontario to inform a management plan. They found similar anthropogenic activities facing the SLRE (paper mills, iron smelting, and untreated wastewater) led to increased metal concentrations and nutrients. In a similar program, the European Union Water Framework Directive has used paleolimnology extensively to aid in management of impacted surface waters (Bennion and Battarbee 2007). As demonstrated here and elsewhere, paleolimnological investigations can be useful in not only developing management plans, but also gauging the success of remediation efforts to ensure progress in degraded surface waters.

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