Paleo-environmental evidence of ecosystem change in Lake St. Clair region of Laurentian Great Lakes basin: contrasting responses to land-use change and invasive mussels

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Abstract The Laurentian Great Lakes have been subject to substantial modification from diverse anthropogenic stressors, including nutrient enrichment, climate change, chemical and biological pollutants, and invasive species, yet little is known of the relative historical influence of these factors. Here we analyze diverse fossil metrics from vibracores at two sites, a bay area (Anchor Bay) and a tributary (Clinton River) in the Lake St. Clair ecosystem to determine the ecological responses from land-use practices and invasive mussel invasions. Sediment cores spanning over 100 years indicated that the expansion of non-native *Dreissena polymorpha* and *Dreissena rostriformis* (dreissenid mussels) into Anchor Bay site after the mid-1990s was associated with ∼ 60 to 95%

reduction in algal and cyanobacterial abundances and twofold increase in sedimentary organic matter (SOM) and bioavailable phosphorus. These increases in SOM and bioavailable phosphorus are relatively similar to increases inferred from the late nineteenth century when large portions of the watershed were cleared and drained for agriculture. In contrast, the Clinton River site experienced a continuous increase in the influx of nutrients, organic matter, and elevated sedimentary phototrophic pigments during the twentieth century and into the twenty-first century. Site comparisons suggest different mechanisms inducing changes in primary production varied, where Anchor Bay was mainly affected by the comparatively recent (since ca. mid-1990s) endogenous influence of invasive species, while the Clinton River site was primarily influenced by the input of exogenous anthropogenic nutrients over the past 100 years. These new findings illustrate that watershed management and policies within large

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lakes with multi-jurisdictional (national) Area of Concerns should consider site-specific regulatory mechanisms.

Introduction

Aquatic ecosystems have experienced intense changes caused by human influences. Growth of human populations resulted in changes of land cover from forested ecosystems to urban settings or intense agriculture (Sanderson et al. 2002) that now depends on heavy nitrogen and phosphorus fertilizer use (Bennett et al. 2001; Vitousek et al. 1997). Runoff from agricultural lands, as well as diverse forms of wastewater treatment plants, have intensified high nitrogen and phosphorus inputs to rivers, lakes and coastal oceans that degrade water quality (Arbuckle and Downing 2001; Turner and Rabalais 1994). Consequently, nonpoint allochthonous nutrient sources are a powerful agent that impact global freshwaters (Carpenter et al. 1998; McCrackin et al. 2017).

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Humans have also facilitated the worldwide spread of non-indigenous species that in turn alter the structure and function of aquatic ecosystems (Higgins and Vander Zanden 2010; Pimentel et al. 2005). Large lentic aquatic ecosystems (i.e., lakes, bays, and estuaries of surface areas > 500 km^2) may be particularly susceptible to the combined effects of land-use changes and invasive species. Bays and tributaries of large lakes have a long history of elevated nutrient loading (Beeton 1969; Savage et al. 2004; Schelske et al. 1983), and algal blooms (Harris and Vollenweider 1982; Levine et al. 2012) following profound changes in land use within their catchments. In addition, because of their prominence as a regional transportation hub, these large ecosystems are often subject to unusually intense colonization by diverse biological invaders (Hall and Mills 2000; Vanderploeg et al. 2002). In particular, non-native *Dreissenia* have colonized in many large lakes (Hall and Mills 2000; Higgins and Vander Zanden 2010) although their effects on water quality has not been uniform (Fahnenstiel et al. 1995; Higgins et al. 2011).

Lake St. Clair is a large (1114 km^2) and shallow (mean = 3 m) basin that connects the upper and lower Laurentian Great Lakes. The lake has been exposed to diverse exogenous and endogenous stressors in the past century (Baustian et al. 2014). Since 1988, Lake St. Clair is recognized as being the first site with established populations of non-indigenous *Dreissena polymorpha* (zebra mussels) in North America, approximately 3 years after their initial invasion (Griffiths et al. 1991; Vanderploeg et al. 2002). Subsequently, these bivalves (including *Dreissena rostriformis,* quagga mussels) have significantly altered the benthic and pelagic ecology of Lake St. Clair and adjacent freshwater ecosystems (Griffiths 1993; Nalepa et al. 1996; Vanderploeg et al. 2002). Additionally, expansion of the cities of Detroit (MI, USA) and Windsor (ONT, Canada) have resulted in concomitant agricultural development and suburbanization (Baustian et al. 2014).

Despite substantial environmental change, little ecological data is available until the 1970s to assess the relative impact of land use and invasive species on Lake St. Clair (Baustian et al. 2014; Leach 1972). To address this shortcoming, we quantified historical changes of multiple sedimentary proxies including fossil phototrophic pigments and sediment geochemistry at two sites to evaluate how increases in nutrients

and invasive species have differentially influenced a tributary site and an open-water location. We built upon previous analyses of historical trends of fecal indicator bacteria by Brooks et al. (2016) to quantify historical ecological changes in the indicators of nutrient enrichment. We hypothesized that this aquatic ecosystem experienced site-specific responses to long-term land-use change and more recently, rapid colonization by non-native bivalves.

Study site

Lake St. Clair is located between oligotrophic Lake Huron to the north and meso-eutrophic Lake Erie to the southeast (Fig. 1) (Leach 1991). Overall, the lake exhibits relatively high-water quality (low nutrient and chlorophyll *a* concentrations) because most of the water (98%) comes from Lake Huron via the St. Clair River (Leach 1991; Vanderploeg et al. 2002; Baustian

et al. 2014). Anchor Bay receives about 34% of the St. Clair River flow via the North Channel (Bolsenga and Herdendorf 1993) and the habitat consists of dense benthic macrophyte coverage that has been heavily colonized by *D. polymorpha* with lake mean mussel densities ranging between about 1800 and 3200 individuals m^{-2} in years between 1994 and 2001 (Hunter and Simons 2004; Nalepa et al. 1996). Conversely, the Clinton River is one of four tributaries of Lake St. Clair, and is located on the western coast (Fig. 1). There, the waters are turbid and eutrophic with extensive shoreline hardening structures (Mavrommati et al. 2013). This area has experienced a low degree of *D. polymorpha* colonization based on qualitative density estimates (Schloesser et al. 1996; Selegean et al. 2001). The Clinton River and its drainage basin (~ 1978 km^2) have been heavily altered by suburban development around metropolitan Detroit (Baustian et al. 2014; Mavrommati et al.
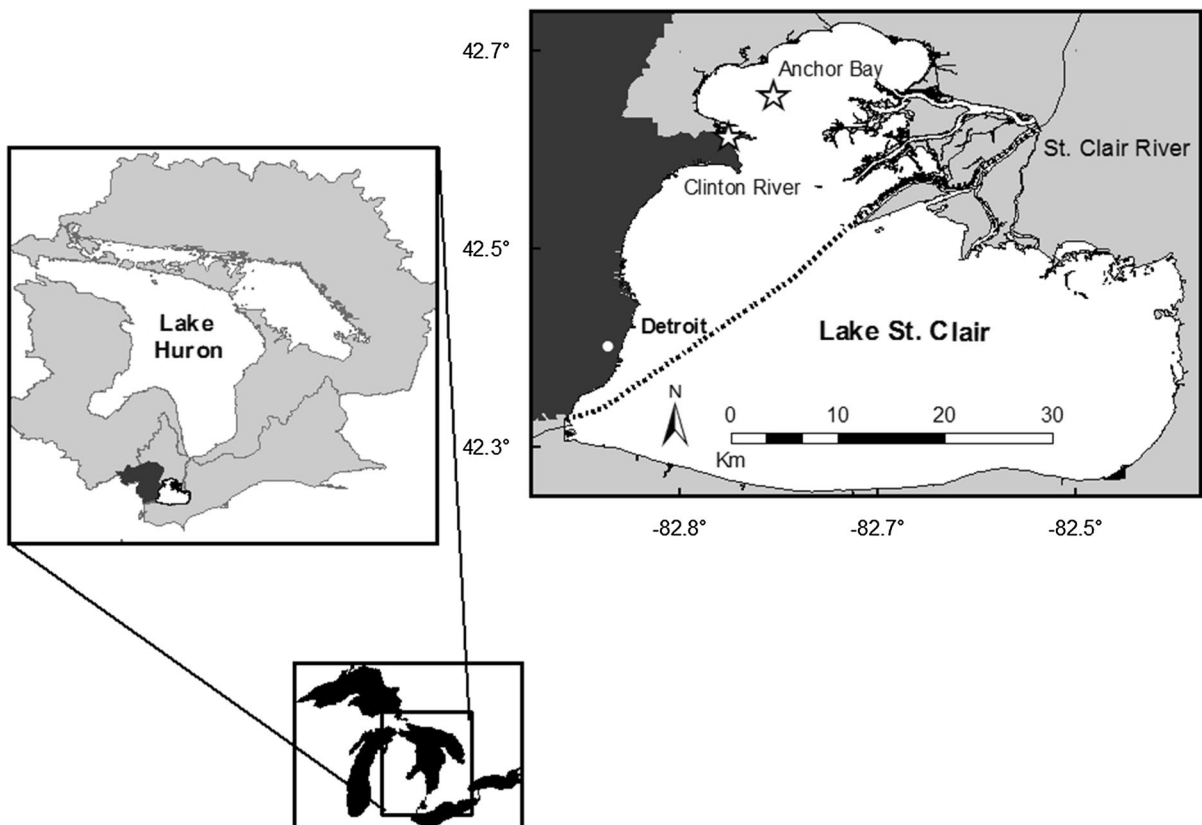

Fig. 1 Map of sediment core collection sites (stars) in Anchor Bay and of Clinton River (upper right map) in the western area of Lake St. Clair, Michigan, USA, part of the Laurentian Great Lakes system (lower left maps). Dashed line represents the

shipping channel that is part of Great Lakes-St. Lawrence Seaway. Dark grey represents Clinton River basin and light grey is the Lake Huron basin and other areas of the Lake St. Clair basin

2013). The watershed and river have been classified as an Area of Concern (AOC) since 1987 under the Great Lakes Water Quality Agreement (International Joint Commission 2006), reflecting local beneficial use impairments such as eutrophication or undesirable algae, beach closings due to fecal pollution, and degradation of fish and wildlife populations. Consequently, this area has been subject to considerable restoration plans and efforts among federal, state, and local institutions.

Materials and methods

Sediment core collection

Sediment vibracores were collected on 21 August 2012 at two sites; in Anchor Bay, in the western area of Lake St. Clair (42.62941° N and − 82.75462° W, 3.4 m depth) and near the mouth of the Clinton River (42.59482° N and − 82.79232° W, 3.3 m depth) located south of Anchor Bay (Fig. 1). Five sediment cores were collected at each site using clear cellulose acetate butyrate tubes ($\sim$ 2 m) with an inner diameter of 9.5 cm. Each core was capped, labeled and kept in the shade and cold with dry ice during the field operations until they were stored vertically at − 80 °C.

Laboratory analyses

Sediment core preparation

One frozen core from each site (AB4 = 86 cm long, CR4 = 58 cm long) was sliced in 2-cm increments with a horizontal band saw (Brooks et al. 2016). Peripheral sediment was removed from each sample to reduce bacterial contamination associated with core collection, and remaining frozen material was stored in Whirlpak[TM] bags. Cutting and cleaning implements were disinfected with 70% ethanol after each sediment section isolation. Sediment samples were thawed in a dark cold room (4–8 °C) and individually homogenized prior to subsampling for fossil pigments. An aliquot was also dried (24 h at 80 °C) for determination of water content before being ground with a mortar and pestle for subsequent analyses.

Radionuclide dating

About 25% of the mass of each sediment section was used for radiochemical analysis following Jweda and Baskaran (2011). [210]Pb activities were measured using its progeny [210]Po, assuming [210]Po and ^{210}Pb were in secular equilibrium. Briefly, aliquots of 1.5 g dried and pulverized samples were taken up in Teflon digestion vessels with 10 mL each of concentrated HF, HNO_3 and HCl and 0.75 mL of [209]Po spike (5.32 ± 0.06 dpm mL^{-1}). The digested solutions were dried on an open hot plate and then taken up in 5 mL of 6 M HCl. At this stage, most of the samples were completely dissolved and they were centrifuged if any residue was found. To the solution, 30 mL of distilled water was added and the sample containing Po was plated by spontaneous deposition onto a high-purity Ag disk. The disks were analyzed by alpha spectrometer with surface barrier detectors coupled to an Octete-PC (ORTEC Co.).

Gamma-emitting radionuclides (^{137}Cs and [226]Ra) were measured by placing $\sim$ 10 g of the dried and homogenized sediments into 10 mL counting vials and determining isotopic activities of ^{137}Cs and [226]Ra (for parent-supported ^{210}Pb level) using a high purity germanium well detector coupled to a Canberra InSpector multi-channel analyzer. No background peaks were observed for any of the assayed radionuclides. The gamma ray detector was calibrated with sediment standards: IAEA-300 for [137]Cs (661.6 keV) and RGU-1 for [226]Ra (via [214]Pb and [214]Bi at 352 keV and 609 keV, respectively) obtained from the International Atomic Energy Agency. Typical resolution (full width at half maximum) of the detector was $\sim$ 1.3 keV at 46 keV and $\sim$ 2.2 keV at 1.33 MeV (Jweda and Baskaran 2011).

In a freshwater system where there are large-scale watershed changes, ^{137}Cs often provides a more reliable chronology (Baskaran et al. 2014 and the references cited therein) than excess ^{210}Pb-based ([210]Pb$_{xs}$) chronology. Although the parent-supported ^{210}Pb activity of [226]Ra remained constant (1.2 ± 0.1 dpm g^{-1} dry mass) between 8 and 36 cm depth in AB4, [226]Ra activities increased below 36 cm burial depth to values between 1.8 and 3.9 dpm g^{-1}. Such increased activity could reflect recent submarine groundwater discharge enriched in [226]Ra or changes in granulometric parameters. In addition, hydrological discharge of [222]Rn results in [210]Pb$_{xs}$ activity can

influence chronology and is another reason why ^{137}Cs inferred mass accumulation rate was used to approximate sediment dates. Both the linear and mass sedimentation rates were comparable using the methodologies of ^{137}Cs and ^{210}Pb$_{xs}$ (Table 1) for each site. The timing of peak ^{137}Cs activity agreed with that provided by application of a constant flux:constant sedimentation (CFCS) model using the ^{210}Pb$_{xs}$ activities, and this suggests that the timing of events in the last 70 years is likely accurately captured. The timing in the early twentieth century and prior is subject to possible errors associated with variable sediment flux and sedimentation associated with land clearance and approximate dates are provided in the text at 25-year intervals from 1860 to 1950 and at 5-year intervals after 1960 to take this into consideration.

Elemental and isotopic analysis

The sediment organic matter (SOM) content of samples was estimated by loss-on-ignition method, which included initial drying at 80 °C (dry mass mean = 1.65 g, std. error = 0.02 g, n = 72) for at least 24 h to remove water prior to combustion for 2 h in a muffle furnace at 550 °C. Dried sediment was treated with 10% HCl overnight at 50 °C to remove carbonates prior to isotopic analysis.

Carbon and nitrogen stable isotope values and their abundances were measured in bulk sediments following Fry (2007) using an automated Eurovector elemental analyzer (with one gas chromatography column) coupled to an Isoprime isotope ratio mass spectrometer. Isotopic results were reported using the standard delta (δ) notation with respect to an international standard (Vienna Peedee Belemnite and atmospheric N$_2$ for carbon and nitrogen, respectively) and were used to infer historical changes in the sources (aquatic vs. terrestrial) of organic matter. Based on replicate isotopic standards, analytical precision was

calculated at ± 0.3‰. Analysis of an alanine standard was used to calculate the %C, %N, mass values, and C:N ratios.

Total phosphorus (TP) was determined by drying duplicate sediment samples overnight (~ 80 °C) followed by ashing at 550 °C for 2 h (Andersen 1976). Samples were acidified (15 mL, 1 N HCl, 15 min) to extract P and solutions were diluted to 100 mL. The resulting solution was analyzed by the ascorbic acid method (American Public Health Association 1998) using a Genesys 10S UV–Vis spectrophotometer (Thermo Fisher Scientific Inc, Walthman, MA). Bioavailable phosphorus (Bio-P) was extracted using Truog's solution (Truog 1930) on duplicate bulk dry sediments (~ 80 °C overnight) and P in solution was quantified by the ascorbic acid method as above.

Fossil pigments

Sediments from each core slice were kept frozen until analysis at the University of Regina's Institute of Environmental Change and Society. Sediments were freeze dried and chlorophyll a (chl a), carotenoid, and derivative pigments from algae were extracted overnight at − 4 °C in a solution of acetone, methanol and water (80:15:5) following Leavitt and Hodgson (2001). Extracts were filtered through a 0.22 μm pore PTFE filter, dried under N$_2$ gas and re-dissolved in a standard injection solvent mixture (Leavitt and Hodgson 2001). Pigments were separated and quantified using an Agilent 1100 high performance liquid chromatographic (HPLC) system fitted with an ODS Hypersil column (5 μm particle size) and photodiode array detector. Pigments were identified on the basis of spectral characteristics and chromatographic position relative to authentic standards commercially available from DHI Denmark. Pigment analysis was restricted to taxonomically-diagnostic carotenoids characteristic

Table 1 Linear sedimentation and mass accumulation rates obtained using ^{210}Pb$_{xs}$ and ^{137}Cs techniques from samples collected in Anchor Bay and Clinton River, Lake St. Clair, Michigan

Core	^{210}Pb$_{xs}$-based Linear sed. rate (cm year^{-1})	^{137}Cs-peak Linear sed. rate (cm year^{-1})	^{210}Pb$_{xs}$-based Mass accum. rate (g cm^{-2} year^{-1})	^{137}Cs-peak Mass accum. rate (g cm^{-2} year^{-1})
Anchor Bay-4	0.38	0.39	0.40	0.35
Clinton River-4	0.58	0.67	0.35	0.42

of the following algal/cyanbacterial groups: diatoms, chrysophytes and some dinoflagellates (fucoxanthin), mainly diatoms (diatoxanthin), cryptophytes (alloxanthin), chlorophytes (pheophytin *b*), chlorophytes and cyanobacteria (lutein-zeaxanthin), filamentous or colonial cyanobacteria (myxoxanthophyll), Nostocales cyanobacteria (canthaxanthin), all cyanobacteria (echinenone), purple sulfur bacteria (okenone), and the major *a*, *b*, and *c*-phorbins (chlorophyll related compounds) and their derivatives, although not all compounds were detected in every sample. The ultraviolet radiation (UVR) index is an index of the depth of UV penetration (lake transparency) and was estimated by dividing the UVR absorbing compound by the sum of four carotenoids (alloxanthin, diatoxanthin and leutin-zeaxanthin) and then multiplying by 100 (Leavitt et al. 1997). Pigment concentrations were expressed as nmol pigment g^{-1} organic matter, as recommended by Leavitt and Hodgson (2001).

Diatoms and fossil inferred phosphorus

Thawed sediment samples ($\sim$ 10 g) were digested with concentrated nitric acid on a hot plate, rinsed to constant pH with deionized water, and an aliquot was mounted on slides with Naphrax® high resolution mounting medium (Acker et al. 2002a, b). Diatom valves were identified to the species level and enumerated with a Leica DMLB microscope at 1000 × magnification until 500 valves were reached. Older samples from Anchor Bay (n = 22, before ca. 1900) had low density of diatom remains and could not be accurately enumerated.

The diatom inferred total P (DI-TP) concentration in Anchor Bay and the Clinton River were calculated using relative abundances of diatom taxa in core sections and a weighted-average model based on species distributions identified by the USEPA's National Lakes Assessment, NLA (Stevenson et al. 2013). Herein the weighted average model was based on the ln-transformed TP optimum of diatom taxa with $\geq$ 5 observations in a set of lakes in the National Lakes Assessment using methods of ter Braak and van Dam (1989). Lakes used in the model were limited to sites with similar maximum depth, morphology, elevation, maximum annual air temperature in watershed, annual maximum of monthly precipitation, Ca concentration, conductivity, latitude, and longitude to those of Lake St. Clair (Stevenson et al. 2013). The

resulting model had a coefficient of determination (r^2) of 0.63 between measured and model inferred ln-TP concentrations. The weighted average TP model was tested by cross validation using a randomly selected two-thirds of the lakes to develop the model and the other one-third of the lakes to test the model, resulting in an r^2 of 0.53 between measured and model inferred ln-TP concentrations.

Statistical analyses

Statistical analyses and data manipulations were performed in SAS 9.4 using an α = 0.05. Simple linear regression (SLR) was used to determine rates of change for SOM and DI-TP. Piecewise regression analysis was utilized to determine potential change points (i.e., change in slope) by using PROC NLIN on $\log_{10}$-transformed data. Piecewise regression analysis was conducted on two data sets (ca. prior to 1920 and ca. 1950–2010) for Anchor Bay because of the numerous slopes and on the entire time series data (ca. mid 1850s to present) for Clinton River. The slopes (betas) were examined prior to (beta1) and after (beta2) the change points (CP).

Exploratory analysis of how the combined fossil proxies

$$(\log_{10}(x + 1)) \tag{1}$$

of fossil pigments, organic matter, nutrients, and fecal indicator bacteria may co-vary over time at the two sites was conducted with a correlation matrix based on principal component analysis (PCA) with the PROC PRINCOMP statement. Complete data sets were used in a time series for Anchor Bay (ca. 1900 to present) and Clinton River (ca. 1920 to present). Measurements of genetic markers representing two fecal indicator organisms, *Escherichia coli* and *Enterococci*, were from Brooks et al. (2016). Both piecewise regression and PCA helped to assess the co-variation of sedimentary proxies.

Results

Sediment chronology and accumulation rates

The ^{137}Cs profiles exhibited a pattern consistent with historical records of atmospheric atomic bomb testing (Fig. 2). Based on the 1963 global fallout peak of

^{137}Cs, the corresponding linear sedimentation rate for Anchor Bay was 0.39 cm y^{-1} and for Clinton River was 0.67 cm y^{-1} (Table 1). Using a constant flux:constant sedimentation (CFCS) model, the ^{210}Pb$_{xs}$-based chronology appears to agree reasonably well with the ^{137}Cs-peak based chronology (Table 1, ESM1). This is similar to an earlier study from the same watershed in which there was good agreement of ages based on ^{210}Pb$_{xs}$-based CFCS-model and ^{137}Cs-peak based model on four sediment cores but with less reliability using the constant rate of supply (CRS) and constant initial concentration (CIC) age models (Jweda and Baskaran 2011). However, the presence of ^{137}Cs in samples deposited before 1952 (after the

Fig. 2 Vertical profiles of **a** mass depth, **b** linear depth of ^{137}Cs concentration for Anchor Bay (AB) and Clinton River (CR). **a** Adapted from Brooks et al. (2016)

first test in 1945, 18 tests were conducted in 1951) suggest some post-depositional mobility of ^{137}Cs by diffusion and/or physical and biological mixing, similar to patterns seen elsewhere in Lake St. Clair (Jweda and Baskaran 2011; Wang et al. 2017) and other freshwater systems (Davis et al. 1984). In both cores, the ^{210}Pb$_{xs}$ activities in the upper 5–10 cm were not constant, which commonly result from bioturbation (ESM1 and ESM2), therefore the spread of the ^{137}Cs peak likely arose from resuspension of the uppermost sediment layers at the time of initial deposition (Fig. 2).

Measured inventories of ^{210}Pb$_{xs}$ varied by a factor of two between the sites, with 73.8 dpm cm^{-2} at Anchor Bay site and 143 dpm cm^{-2} at Clinton River site. Both values are higher than what is expected from overhead atmospheric fallout for this watershed (Jweda and Baskaran 2011) and likely due to contribution from watershed erosional input. This difference may reflect variation in sediment focusing and/or differences in the amount of excessive influx of allochthonous material at the two sites. Peak ^{137}Cs activities were used at Anchor Bay to calculate a linear sedimentation rate of 0.39 cm y^{-1} and mass accumulation rate of 0.35 g cm^{-2} y^{-1} (Table 1). Earlier study from the same watershed showed that the comparison of ^{137}Cs-peak based chronology and sediment ages derived from the ^{210}Pb$_{xs}$-CFCS model were also better than those from CRS and CIC models (Jweda and Baskaran 2011). It has been shown that ^{210}Pb based chronology can be impacted by large-scale changes in the watershed of a freshwater system, whereas ^{137}Cs-peak can yield reliable chronology (Baskaran et al. 2014). Note that the penetration depth of ^{137}Cs corresponding to 1952 is less reliable due to post-depositional diffusion of ^{137}Cs and > 75% of the deposited ^{137}Cs in 1952 has decayed away (Wang et al. 2017).

Based on the ^{137}Cs-peak and the sediment mass accumulation rate, the year of deposition of each sedimentary layer was calculated. The core at Anchor Bay spanned a wider range of ages (ca. mid-1700s to present) compared to Clinton River (ca. 1890–present), although a constant time interval of mid-1800s to present was used for the ecological interpretation herein. As noted above, high correspondence between ^{210}Pb and ^{137}Cs chronologies after the mid-twentieth century inferred that modern events are likely accurately captured, whereas the comparative effects of
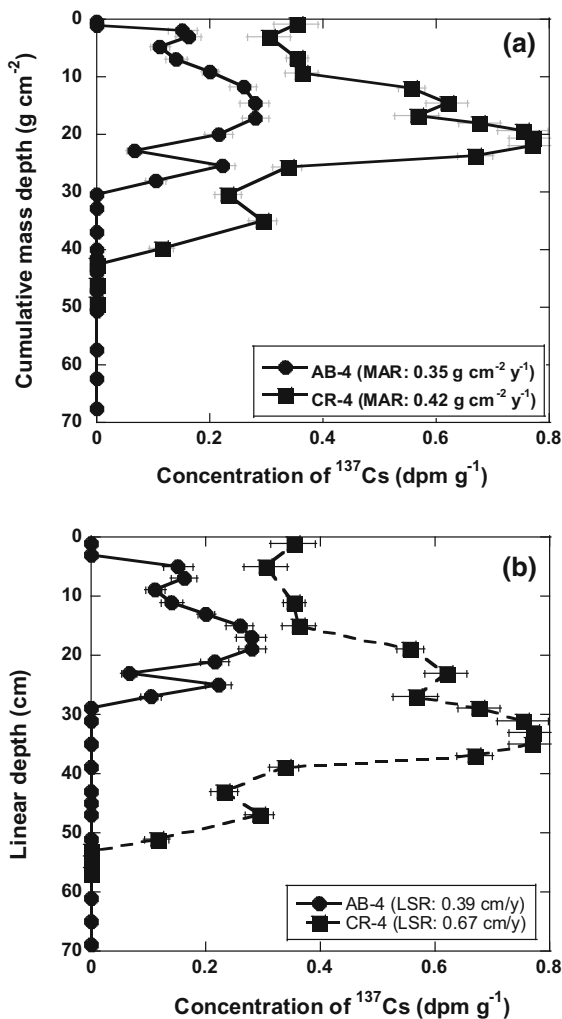
earlier events (e.g., land clearance) are less accurately constrained (early twentieth century).

Elemental and isotopic stratigraphy

At Anchor Bay site, the SOM content increased rapidly from ∼ 7% to a maximum of ∼ 23% at the end of the nineteenth century, before declining to a plateau of ∼ 2% for almost 100 years (Fig. 3a). Since the late-1990s, SOM content in the Anchor Bay core increased by 0.75% per year (based from SLR, $r^2 = 0.99$, $p = 0.0003$, n = 5) to values near 10% in the uppermost deposits (Fig. 3a, Table 2). The sedimentary carbon (% C) and nitrogen (% N) increased rapidly to a peak at the end of the nineteenth century (Fig. 3b, c), followed by a decline to stable levels until ca. 2000, after which % C and % N content increased to a secondary maximum (near 7 and 0.3%, respectively). The % C and % N of Anchor Bay site exhibited similar historical patterns to that of the SOM (Fig. 3a–c). Overall, C:N ratios at Anchor Bay increased from 14 in basal sediments to ∼ 20 at the start of the twentieth century and then fluctuated thereafter (Fig. 3d).

Sedimentary organic matter content of Clinton River site varied little over time relative to Anchor Bay site (Fig. 3a, e). Overall, SOM at Clinton River ranged between ∼ 2 and 9% in surficial sediments, with a notable increase ca. 1950 (Fig. 3e) and relatively constant values thereafter near 7–9%. Sedimentary carbon and nitrogen at Clinton River site increased from < 0.5% in basal sediments to maxima in the surface sediments, with a sharper increase occurring since ca. 1950 (Fig. 3f, g). C:N ratios were variable in Clinton River (Fig. 3h) with a sustained increase above 20 after ca. 1980.

The $\delta^{13}C$ and $\delta^{15}N$ values of the SOM tended to co-vary through time at both sites (Fig. 4). At Anchor Bay site, both C and N isotope values increased throughout the twentieth century, before declining after ca. 1985 (Fig. 4a, b). Values of $\delta^{13}C$ values at Clinton River site increased from − 28.5 to − 26‰ by the 1980s, then declined to near baseline levels during the past 30 years (Fig. 4c), whereas $\delta^{15}N$ values at Clinton River site exhibited high variability during the early twentieth century before rising smoothly from a ∼ 2‰ minimum ca. 1930 to ∼ 4‰ at present (Fig. 4d).
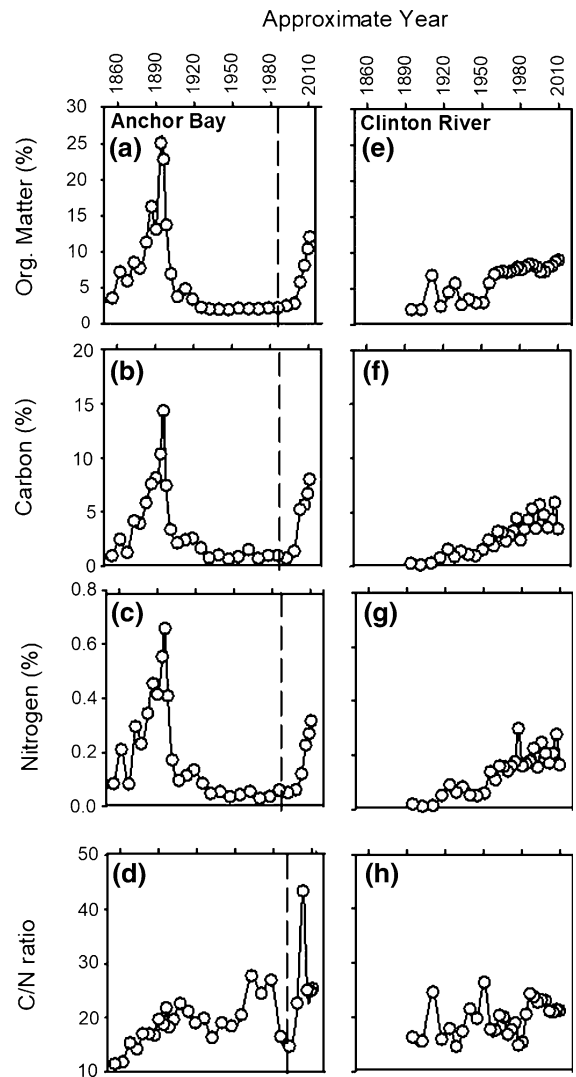

Fig. 3 Sedimentary percent organic matter (SOM; **a**, **e**), percent carbon (**b**, **f**), percent nitrogen (**c**, **g**), and C:N ratios (**d**, **h**) from approximate years of 1850 to 2011 at two sites, Anchor Bay (left side, **a–d**), Lake St. Clair and of the Clinton River (right side, **e–h**), Michigan, USA. Dashed line at ca. 1985 on Anchor Bay plots indicate the earliest time of arrival of the invasive *Dreissena polymorpha* and *Dreissena rostriformis*. **b**, **c**, **f**, **g** Adapted from Brooks et al. (2016). Approximate chronology derived from ^{137}Cs activities that are located in the Methods, Results, and ESM1

Mean sedimentary bioavailable phosphorus (Bio-P) and mean TP exhibited similar patterns over time at each site (Fig. 5). Bio-P decreased within older sediments to ca. 1900 in Anchor Bay, remained low and stable for ∼ 100 years, then increased after ca. 1995 (Fig. 5a, Table 2), whereas TP concentrations

Table 2 Piecewise regression results of temporal patterns of select sedimentary environmental indicators (Env. Ind.) from vibracores collected in Anchor Bay (ca. pre-1920 and ca. 1950–2010), Lake St. Clair and of Clinton River (ca. mid-1800s to present), Michigan, USA

Site	Env. Ind	Par.	Est.	SE	t value	p value
Anchor Bay	Org. Matter	CP	**1900**	2.338	809.96	< 0.0001
Pre-ca. 1920		Beta1	0.017	0.004	4.12	0.0021
		Beta2	− 0.047	0.007	− 7.07	< 0.0001
	Bio-P	NA				
	TP	CP	**1900**	4.349	431.0	< 0.0001
		Beta1	0.013	0.005	2.63	0.0253
		Beta2	− 0.016	0.005	− 3.02	0.0129
	DI TP	NA				
	B-caro	CP	**1900**	3.852	490.5	< 0.0001
		Beta1	0.004	0.003	1.2	0.255
		Beta2	0.021	0.005	4.7	0.0007
	Chl a	CP	**1900**	4.68	404.3	< 0.0001
		Beta1	0.004	0.003	1.47	0.17
		Beta2	0.019	0.005	3.65	0.0038
	Pheo	NA				
Anchor Bay	Org. Matter	CP	**2000**	0.8724	2289.03	< 0.0001
post-ca. 1950		Beta1	0.001	0.001	1.17	0.2788
		beta2	0.043	0.003	13.75	< 0.0001
	Bio-P	CP	**1995**	3.6055	553.17	< 0.0001
		Beta1	− 0.003	0.002	− 1.42	0.1991
		Beta2	0.029	0.008	3.72	0.0075
	TP	NA				
	DI TP	NA				
	B-caro	CP	**1995**	2.3802	838.12	< 0.0001
		Beta1	0.008	0.003	3.09	0.0176
		Beta2	− 0.049	0.009	− 5.53	0.0009
	Chl a	CP	**1995**	2.0032	995.76	< 0.0001
		Beta1	0.024	0.004	6.73	0.0003
		Beta2	− 0.081	0.012	− 6.62	0.0003
	Pheo	CP	**2000**	2.6652	748.94	< 0.0001
		Beta1	0.006	0.003	1.97	0.0897
		Beta2	− 0.050	0.011	− 4.68	0.0023
Clinton River	Org. Matter	CP	**1980**	18	109	< 0.0001
		Beta1	0.005	0.001	5.450	< 0.0001
		Beta2	− 0.004	0.003	− 1.180	0.2502
	Bio-P	CP	**1950**	46	42	< 0.0001
		Beta1	0.007	0.004	1.780	0.0865
		Beta2	− 0.003	0.005	− 0.720	0.4776
	TP	CP	**1980**	104	19	< 0.0001
		Beta1	0.010	0.002	5.430	< 0.0001
		Beta2	− 0.001	0.005	− 0.240	0.8152
	DI TP	CP	**1950**	12	167	< 0.0001
		Beta1	0.000	0.000	0.050	0.964

Table 2 continued

Site	Env. Ind	Par.	Est.	SE	*t* value	*p* value
		Beta2	0.001	0.000	2.830	0.0091
	B-caro	CP	**2010**	2	954	< 0.0001
		Beta1	0.009	0.001	8.490	< 0.0001
		Beta2	0.117	0.101	1.160	0.2585
	Chl *a*	CP	**2000**	2	1019	< 0.0001
		Beta1	0.010	0.001	13.150	< 0.0001
		Beta2	0.063	0.020	3.190	0.0038
	Pheo	CP	**2000**	8	238	< 0.0001
		Beta1	0.014	0.002	8.720	< 0.0001
		Beta2	0.036	0.068	0.530	0.6036

Statistical parameters (Par.) include the CP = change point approximate date, Beta1 = slope of the line prior to the change point, and Beta2 = slope of the line after the change point. Org. Matter = organic matter, Bio-P = bioavailable phosphorus, TP = total phosphorus, DI-TP = diatom-inferred total phosphorus B-Caro = beta carotene, chl *a* = chlorophyll *a*, and Pheo = pheophytin a. NA = piecewise regression model was not applicable to that time-series data set. All data were log (x + 1) transformed

Estimated year (Est.) in bold indicates significant change point

increased slowly through the fossil record, with only two exceptional peaks (ca. 1900, near 2010; Fig. 5b, Table 2). At the Clinton River site, the mean Bio-P and

Fig. 4 Sedimentary $\delta^{13}C$ (**a**, **c**) and $\delta^{15}N$ nitrogen (**b**, **d**) from samples representing approximate years of 1850 to 2011 at two sites, and Anchor Bay (left side, **a**, **b**), Lake St. Clair, and Clinton River (right side, **c**, **d**) Michigan, USA. Dashed line at ca. 1985 on Anchor Bay plots indicate the earliest time of arrival of the invasive *Dreissena polymorpha* and *Dreissena rostriformis*. Chronology as Fig. 3

TP concentrations were low in the early 1900s and steadily increased over time to the present (Fig. 5d, e).

Diatom-inferred total phosphorus

Historical changes in diatom-inferred total phosphorus (DI-TP) concentrations indicated different nutrient histories at the two sites (Fig. 5c, f). In Anchor Bay site, DI-TP concentrations were stable during the twentieth century and into twenty-first century (SLR, $r^2 = 0.009$, $p = 0.68$, n = 20) (Fig. 5c, Table 2). At Clinton River site, the DI-TP concentrations were similar from the late-1800s to the mid-twentieth century, then increased significantly ($p = 0.0091$) until ca. 2010 (Table 2, Fig. 5f).

Fossil pigments

Analysis of fossil carotenoids, chlorophylls and derivatives indicate that the abundance of most algae and cyanobacteria increased during the twentieth century at the Anchor Bay and Clinton River sites, but that production declined after the mid-1990s at the Anchor Bay site alone (Fig. 6a, Table 2). For example, phototrophic abundance at Anchor Bay increased from low levels in the late nineteenth century to a maximum ca. 1990s before declining over fivefold thereafter (Fig. 6a). Concentrations of pigments representing
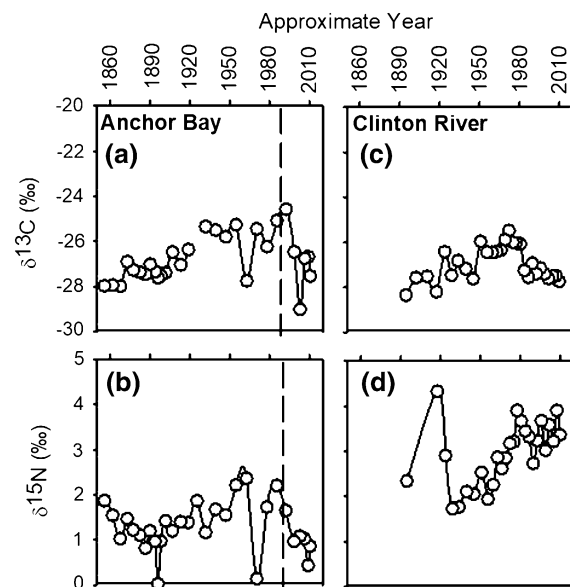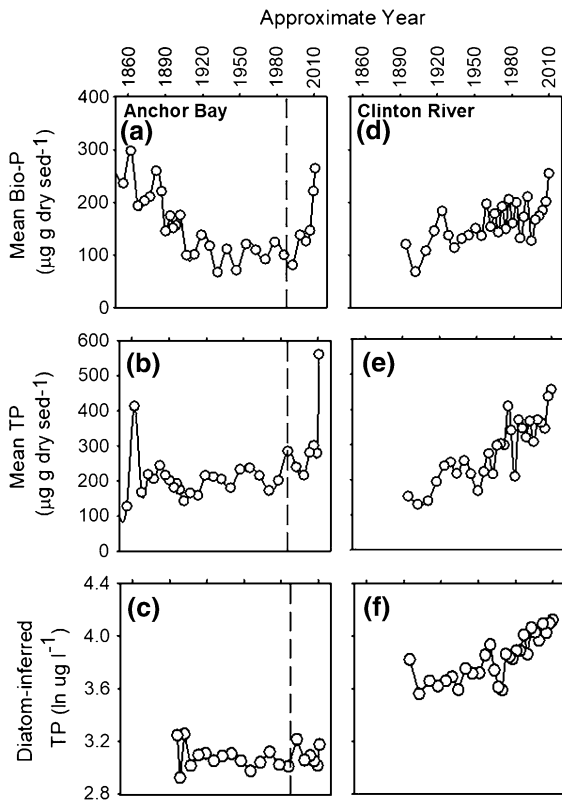
diatoms (fucoxanthin) and cryptophytes (alloxanthin) increased sharply (40–100 and 13–25 nmol g^{-1} org matter, respectively) after ca. 1980. Concentrations of all biomarker pigments declined since the 1990s and reached low values in the surficial sediments (Fig. 6a, Table 2). Pigments from chlorophytes (b-phorbins) and cyanobacteria (echinenone, canthaxanthin) were most common at Anchor Bay during the twentieth century, whereas the siliceous algae contributed the highest pigment levels after 1990. The chl *a*:pheophyin *a* ratio started to increase during the 1970s, peaked in the 1990s, then decreased since that time. Similarly, water clarity as indicated by UVR index was high at Anchor Bay during the late-1800s, decreased to low levels until the 1940s, and increased to a transient peak during the 1970s (Fig. 6a).

Total pigment abundance (as β-carotene, phaeophytin *a*, chl *a*) at Clinton River site was low prior to ca. 1925, increased to a plateau at ca. 1950, then rose more sharply after the early 2000s (Fig. 6b, Table 2). Similar historical variation was also recorded for Clinton River pigments derived from cyanobacteria (echinenone, canthaxanthin), chlorophytes (chl *b*, pheophytin *b*), total bloom-forming taxa (lutein-zeaxanthin), diatoms (diatoxanthin) and cryptophytes (alloxanthin) (Fig. 6b). Overall, concentrations of pigments from chlorophytes and cyanobacteria were higher than those of other remaining taxonomic groups, with the exception of labile fucoxanthin (siliceous algae), which was most abundant in the uppermost sediments (Fig. 6b). Overall, the chl *a*:pheophytin *a* ratios were stable at Clinton River,
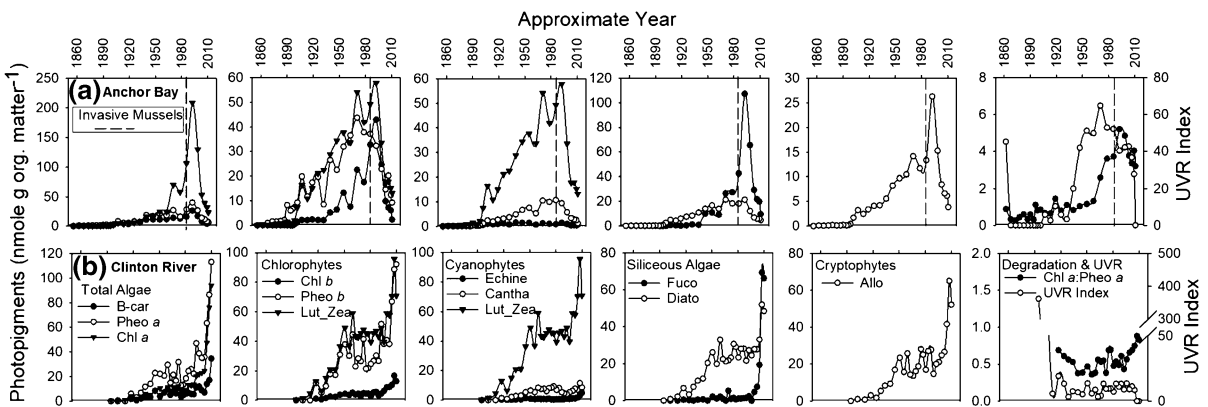

Fig. 5 Sedimentary mean bioavailable phosphorus (**a, d**), mean total phosphorus (**b, e**), and diatom-inferred TP (**c, f**) from approximate years of 1850 to 2011 at two sites, in Anchor Bay (left side, **a–c**), Lake St. Clair and of the Clinton River (right side, **d–f**), Michigan, USA. Dashed line at ca. 1985 on Anchor Bay plots indicate the earliest time of arrival of the invasive *Dreissena polymorpha* and *Dreissena rostriformis*. **b, e** Adapted from Brooks et al. (2016). Chronology as Fig. 3

Fig. 6 Photopigment concentrations from approximate years of 1850 to 2011 of sediment cores collected at **a** Anchor Bay (top row), Lake St. Clair, **b** of the Clinton River (bottom row), Michigan, USA. Dashed line at ca. 1985 on Anchor Bay plots indicates the earliest time of arrival of the invasive *Dreissena polymorpha* and *Dreissena rostriformis*. UVR index is a water clarity indicator (depth of UV penetration within lakes). Chronology as Fig. 3

suggesting limited changes in the preservation environment of the past 100 years, whereas the UVR index was briefly elevated in the early 1900s before declining to low levels since then (Fig. 6b).

Co-variation of sedimentary proxies

Principal component analysis showed that the first two components accounted for 71.0% and 74.2% of the historical environmental variability at Anchor Bay and Clinton River sites, respectively (Fig. 7a, b, Table 3). The historical trajectory at the Anchor Bay site included increasing fossil pigment concentrations along the first principal component (53.2%) after ca. 1900 and until ca. 1950 (Fig. 7a). Since that time, the Anchor Bay site first experienced elevated TP and Bio-P content along the second principal component axis (17.8%) (Fig. 7a, Table 3), before sharp declines

Table 3 Principal component scores (eigenvectors) for the historical environmental indicators (Env. Ind.) at two sites, in Anchor Bay, Lake St. Clair and of the Clinton River, Michigan, USA

Env. Ind	Anchor Bay		Clinton River	
	Prin1	Prin2	Prin1	Prin2
Fuco	0.23	0.30	0.22	− 0.17
Allo	0.30	0.11	0.26	0.22
Diato	0.30	− 0.03	0.25	0.27
Lut_Zea	0.30	− 0.02	0.25	0.28
Cantha	0.30	− 0.05	0.22	0.41
Chl b	0.28	0.13	0.27	0.05
Chl a	0.26	0.24	0.27	− 0.09
Echine	0.21	− 0.32	0.23	− 0.09
Phaeo b	0.28	− 0.04	0.26	0.14
Pheo a	0.30	0.07	0.26	0.04
B-car	0.30	− 0.01	0.25	0.08
Org. Matter	− 0.25	0.25	0.20	− 0.01
TP	0.05	0.32	0.21	− 0.21
Bio-P	− 0.16	0.29	0.17	− 0.17
$\delta^{15}N$	0.15	− 0.21	0.11	− 0.29
$\delta^{13}C$	0.07	− 0.29	− 0.06	0.54
C:N	− 0.01	0.37	0.13	− 0.03
Enterococcus spp.	0.10	0.16	0.24	− 0.20
E. coli	0.06	0.42	0.25	− 0.21
DI-TP	− 0.07	0.07	0.23	− 0.18

Full names of environmental indicators are listed in Table 2. All data were log (x + 1) transformed except $\delta^{13}C$ and $\delta^{15}N$

in pigment concentrations after ca. 1990s despite continued increases in nutrient availability (Table 2). At the Clinton River site, the first principal component axis (65.2% of variance) was defined by gradients of fossil pigment concentration, total phosphorus, DI-TP, and organic matter content (Fig. 7b, Table 3), whereas the second principal component axis (9.0%) was defined by a negative influence of total phosphorus loading. The temporal pattern indicates that the Bio-P and DI-TP increased from ca. 1950 to ca. 1980 and alterations in the concentrations of sedimentary organic matter, and TP after ca. 1980 (Fig. 7b, Table 2).

Fig. 7 Principal component analysis of historical environmental indicators representing approximate years of ca. 1890–2010 at two sites, **a** Anchor Bay, Lake St. Clair, **b** Clinton River, Michigan, USA

Discussion

Analysis of diverse sediment proxies at two contrasting sites provide the first clear fossil evidence of the significant impacts of non-native *Dreissena* in Anchor Bay, Lake St. Clair, a pivotal ecosystem linking the upper and lower Laurentian Great lakes, as well as eutrophication, particularly at the Clinton River. Both sites recorded sustained increases in abundance of most algal and cyanobacterial groups during the twentieth century. However, site histories diverge sharply after invasion of *Dreissena* into Anchor Bay ca. 1995, with phytoplankton abundance declining ~ 70%, while SOM and Bio-P increased ~ 200%, within 10 years of invasion. The delay in response may be due to the spatial and temporal heterogeneity of *D. polymorpha* both in density and biomass combined with the local environmental conditions of Anchor Bay (Higgins et al. 2011). These findings provide new information on the long-term ecological changes of this region, including that nutrient enrichment and invasive bivalves were significant agents of change and builds off previous work by Brooks et al. (2016) that utilized the same cores for assessing long-term associations of anthropogenic and climatic variables with fecal indicator bacteria.

Anchor Bay

Paleolimnological analyses revealed that the ecological condition of Anchor Bay has experienced dramatic changes since ca. 1990 compared to the ~ 100 years prior and that these changes reflect the sequential effects of nutrient influx and exotic *Dreissena* invasion. Concentrations of most sedimentary components associated with phytoplankton production (SOM, TP, Bio-P, pigments) increased modestly during the twentieth century, reflecting the combined effects of forest clearance, agricultural development and urbanization. However, *Dreissena* are thought to have first entered the Lake St. Clair ecosystem in 1985 and, once well established, were efficient (with their high biomass and density, David et al. 2009; Nalepa et al. 1996) at removing phytoplankton biomass from the water column. Consistent with this narrative, sedimentary concentrations of the indicators of total phototroph abundance (chl *a*, pheophytin *a*, β-carotene) at Anchor Bay site declined sharply after ca. 1995, with chl *a* declining from 200 to

25 nmol g^{-1} organic matter, despite the tendency for this labile compound to be over represented in surficial sediments (Leavitt and Hodgson 2001). Although the extent of pigment decline varied among biomarkers (− 60 to − 95%), uniform patterns of decline occurred during an interval when the pigment preservation environment was similar, as recorded by relatively stable Chl *a*:pheophytin *a* ratios (Leavitt and Hodgson 2001). In general, the magnitude of fossil pigment decline is similar to previous estimates of the reduction of pelagic primary production attributed to the suspension feeding of *Dreissenia* (Higgins and Vander Zanden 2010). Because fossil pigments integrate material from throughout the lake, we can infer that the decline in planktonic production was not offset by increased abundance of phytobenthos (benthic diatom data not shown), as seen in some shallow lakes undergoing critical transitions (McGowan et al. 2005). The decline in δ^{13}C and δ^{15}N values post-*Dreisenna* invasion also suggests a reduction in pelagic primary production coupled with an increase in urbanization of the watershed (Leavitt et al. 2006; Savage et al. 2004).

Concomitant changes in sedimentary pigments, P fractions, and SOM suggest that phytoplankton consumed by *Dreissena* may have been deposited in shallow-water sediments as feces and pseudofeces (Auer et al. 2010; David et al. 2009; Higgins et al. 2008; Nalepa and Gauvin 1988; Nalepa et al. 1996). For example, the concentrations of bioavailable P and sedimentary organic matter tripled since ca. 1995 concomitant with establishment of *D. polymorpha* and *D. rostriformis* that entered the system around 1985–1988 (Griffiths 1993; Griffiths et al. 1991). These changes in conditions (fossil pigments, P fractions and SOM) were similar to those observed after *Dreissena* invasion of Saginaw Bay, Lake Huron (Fahnenstiel et al. 1995), Lake Simcoe, Ontario (Hawryshyn et al. 2012), and Green Bay, Lake Michigan (Qualls et al. 2007), suggesting that areas throughout the Great Lakes Basin were responding similarly to establishment of the exotic bivalves.

Forest and land clearance in support of agriculture also appeared to influence sediment character at Anchor Bay in Lake St. Clair (Brooks et al. 2016), although we recognize our chronology is less reliable at the base of the cores. For example, high organic matter loading to sediments (as SOM, % C, % N, Bio-P) was also observed during the late-1800s when urban

expansion, forestry, and agricultural intensification led to deforestation and discharge from pulp mills (Meyers 2003; Schulte et al. 2007; Williams 1989). Similar patterns of organic matter conditions ca. 1900 were observed from sediment cores in the southern region of Lake Huron in the Province of Ontario (Meyers 2003). Consistent with this interpretation, C:N ratios of the sediments increased from algal-like values (∼ 12:1) to those characteristic of terrestrial vegetation (∼ 20:1) during the late nineteenth and early twentieth centuries (Meyers 2003). Perennial submerged aquatic vegetation expanded their distribution in the lake by responding to the increased light levels produced by algal drawdown by *D. polymorpha* and could also influence these sedimentary proxy results by increasing organic matter and phototrophic pigment concentrations (Hunter and Simons 2004). However, despite marked effects of land-use practices, effects of *Dreissena* were detected in the macrophyte-rich basin of Lake St. Clair. Lastly, we did not observe increased light levels as expected with less pelagic primary production and instead the UVR index suggests light levels decreased since the invasion.

Clinton River

Fossil analyses provided evidence of human impacts at the Clinton River site as far back as ca. 1900, as indicated by the high sedimentary TP (measured and diatom-inferred) and increased $\delta^{15}N$ values (3–7‰) indicative of urbanization or animal wastes (Leavitt et al. 2006; Savage et al. 2004) as well as correlation of % TN with *E. coli* concentrations (Brooks et al. 2016). In general, $\delta^{13}C$ and $\delta^{15}N$ values of SOM were within the ranges expected for a mixture of phytoplankton and terrestrial organic matter in the Great Lakes region (Lu et al. 2010; McCusker et al. 1999; Tenzer et al. 1999). However, the variable and high C:N ratios in Clinton River also suggest periodic influx of terrestrial material (woody or herbaceous) during much of the twentieth century (Meyers 2003).

Water quality indicated by sedimentary TP and Bio-P content at Clinton River site appeared to decline starting in the mid-twentieth century, likely reflecting the increased urbanization in metropolitan Detroit (Brooks et al. 2016). Elevated nutrient influxes from diffuse and point sources (Baustian et al. 2014) are suggested by increasing sedimentary content of both P fractions after ca. 1950s (Figs. 3, 4, 5). Historical phosphorus fluctuations have been recorded throughout the Laurentian Great Lakes and globally; nutrient levels have tended to be moderate until the early 1950s, and then increased greatly because human population growth and intensified agricultural practices increased nutrient delivery to the coastal zone (Cordell et al. 2009; Meyers 2003).

Limited monitoring data from the Clinton River also confirms interpretations that high turbidity, phosphorus content, and phytoplankton abundance were observed during the 1990s in response to influx of nutrients, particularly from storm water runoff (Esman 2007; Michigan Department of Environmental Quality 1998). Furthermore, changes in fossil pigments are consistent with management concerns that water quality measures such as high TP and chl *a* in the Clinton River and its spillway have continued to be degraded during the past 30 years (Brooks et al. 2016; Environmental Consulting and Technology 2007). In this study, application of diverse paleolimnological indicators provided essential management information on timing and magnitude of degradation in an Area of Concern that connects the Laurentian Great Lakes, which was not previously available.

Conclusions

Comparative paleolimnological analyses at two sites in a large lake ecosystem demonstrate that optimal management requires site-specific information on the causes and extent of environmental change. At Anchor Bay, water quality degradation arose initially from widespread land-use change, with algal and cyanobacterial abundance increasing over time, followed by rapid and profound declines in production within 10 years after the introduction of *Dreissena*. In contrast, water quality at the Clinton River tributary site has been influenced continuously by urban and agricultural development over 100 years, with more marked declines in water quality in the past 30 years. Together, these findings show that localized site-specific histories are needed to account for spatial variability in regulatory mechanisms and focus effectively management strategies in large lake ecosystems.

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