Diatom floristic change and lake paleoproduction as evidence of recent eutrophication in shallow lakes of the midwestern USA

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Abstract Intensive agricultural practices can dramatically change the landscape, thereby increasing the concentrations and rates at which nutrients are delivered to aquatic ecosystems. In the United States, concerns about accelerating rates of lake eutrophication related to increases in nutrient loading require a method of quantifying ecological changes that have occurred since European settlement. Because the application of traditional quantitative total phosphorus transfer functions in paleolimnology has proven difficult in shallow, hypereutrophic lakes, we used several approaches in this study to assess ecosystem changes associated with eutrophication of 32 natural lakes in the state of Iowa, USA. In addition to traditional transfer function methods, we estimated changes in primary productivity from the flux of biogenic silica (BSi) and organic carbon accumulation rates (OC AR). Additionally, we compared pre-disturbance diatom communities to modern diatom communities, i.e. floristic change, using non-metric multi-dimensional scaling and square chord distance. OC AR and BSi fluxes increased over time and were positively correlated with the time period of agricultural intensification in the region (post-1940). Ninety-one percent of the lakes in this study showed evidence for eutrophication based on geochemical proxies, and 88 % of lakes showed major floristic change in the diatom community. Whereas geochemical indicators showed consistent increases in productivity across most lakes, floristic changes reflected more complex interactions between other environmental drivers. The magnitude of floristic change did not directly correlate

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to nutrient-driven increases in primary production, but was driven by ecological diatom assembly related to lake depth. Transfer functions consistently perform poorly, especially for shallow lakes, and other techniques that combine geochemistry and diatom ecology are recommended for reconstructions of eutrophication.

Introduction

Intensive agricultural practices have had a dramatic effect on rates of eutrophication in aquatic ecosystems (Carpenter et al. 1998). This effect is largely a consequence of increased transport of nutrients, primarily nitrogen (N) and phosphorus (P), to freshwaters (Sharpley et al. 1994; Sims et al. 1998). In many freshwater lakes, phosphorus is the principal limiting nutrient for primary production (Schindler 1977), and even given a more recent understanding of co-limitation by both N and P (Elser et al. 2007), P enrichment has still been shown to be the most critical element regulating anthropogenic eutrophication (Schindler et al. 2008) and the undesirable phenomena that accompany it (i.e. Cyanobacteria blooms; Downing et al. 2001). Because of this, pollution by phosphorus is the primary cause of water quality degradation in most freshwater systems (Carpenter et al. 1998) and intensive agriculture is often a primary source of this pollution (Soranno et al. 1996).

Despite the well-established link between eutrophication and intensive agriculture, the effects are difficult to quantify because long-term water chemistry data are lacking for most aquatic ecosystems. This is especially true for shallow lakes (mean depth <3 m; Scheffer 1998) that, despite having a high susceptibility to anthropogenic eutrophication because of their relatively small volume, have rarely been the focus of long-term monitoring studies. It can be difficult to attribute eutrophication to agricultural impacts when the complex trajectory of non-point source P pollution is poorly understood (Withers and Haygarth 2007).

Anthropogenic eutrophication from phosphorus has negative impacts on fisheries (Jeppesen et al. 2000), recreation (Egan et al. 2009), and ecosystem function (Smith et al. 1999) and has an economic cost in the billions of dollars in the USA alone (Dodds et al. 2009). In regions of intensive agriculture, increased phosphorus loads are primarily from non-point sources, such as fertilizer run-off (Carpenter et al. 1998). This has caused shallow lakes that were historically described as clear and vegetated to become perennially turbid and barren of aquatic vegetation (Sand-Jensen et al. 2000). To understand the magnitude and rate of change associated with intensive agriculture, it is useful to establish the baseline, or reference condition, of these ecosystems prior to significant anthropogenic influence. This approach has been employed effectively to establish nutrient pollution criteria in heterogeneous landscapes where reference conditions may be highly variable and rigid standards may be unrealistic (Bennion and Battarbee 2007; Heiskary and Wilson 2008).

It is unlikely that the hypereutrophic state of many of the lakes in the agriculturally dominated midwestern USA (McDonald et al. 2014; Smith et al. 2014) existed prior to European disturbance (*ca*. AD 1850), despite recent work calling into question the extent of eutrophication in the United States (Bachmann et al. 2013). Given the lack of long-term monitoring data, however, paleolimnological methods are necessary to rigorously address this question. Indeed, paleolimnological data have provided some of the most convincing evidence for recent eutrophication and its impact on lake ecosystems (Davidson and Jeppesen 2013) and have been shown to reflect faithfully both the impact of, and recovery from anthropogenic eutrophication (Anderson et al. 1990). Sediments provide long-term records of lake history and preserve remains of organisms, such as diatom frustules, which serve as biological indicators of lake conditions, including total phosphorus (TP) concentrations (Hall and Smol 2010).

Diatoms were assumed to be the most reliable biological indicator of TP and have been widely used as a means of inferring past TP concentrations (Smol 2008). Initial assessments of the errors associated with TP training sets (Anderson and Rippey 1994) were addressed through training set amalgamation (e.g. Bennion et al. 1996). Subsequent studies, however, documented difficulty in using diatoms to infer TP enrichment quantitatively, particularly in shallow lakes, because of the dominance of benthic and epiphytic species that may be inconsistent in their response to TP (Fritz et al. 1993; Bennion et al. 2001;

Dong et al. 2008). Although the effectiveness of reconstructions in these systems is, in part, dependent on careful transfer function selection (Juggins et al. 2013), the validity of diatom-inferred TP (DI-TP) in shallow lakes is problematic and perhaps best avoided (Sayer 2001; Bennion et al. 2005; Sayer et al. 2010). Given the need to identify background conditions that predate monitoring data, however, alternative approaches are needed. Prior to the development of transfer functions, lake eutrophication was assessed using qualitative measures of diatom ecology, coupled with geochemical indicators (Brugam 1978; Battarbee 1986; Engstrom and Swain 1986). Given the problems associated with DI-TP (Juggins et al. 2013; Juggins 2013), a statistical assessment of diatom community change (Bennion and Simpson 2011), coupled with the use of a multiple proxies (Birks and Birks 2006) to corroborate the effects of lake eutrophication, is required.

The objective of this study was to assess the magnitude of eutrophication across a large number of shallow lakes in the state of Iowa. The study region is one of the most intensively farmed regions in North America, with at least 90 % of the land area in some form of agriculture (Arbuckle and Downing 2001). In this study we compared DI-TP transfer functions derived from shallow, eutrophic lakes to traditional methods of assessing lake eutrophication (BSi and OC accumulation rates) and statistical analysis of diatom floristics and community change (NMDS, permutational MANOVA), to assess regional responses to agricultural enrichment. We present an alternative approach for evaluating long-term eutrophication in shallow lakes where DI-TP was shown previously to be, at best, a qualitative indicator and, at worst, to provide spurious reconstructions (Sayer 2001; Juggins et al. 2013; Juggins 2013).

Study site

Lakes in this study are located in the midwestern United States where tall-grass prairie was converted for agricultural land use in the mid-1800s (Van Zant et al. 1979). Water bodies in the calibration set include both natural lakes and impoundments, but reconstructions were limited to natural lakes, all of which were formed by the retreat of glaciers in the early Holocene (*ca*. 10,000 years ago) (Jones and Bachmann 1978). Most of the lakes in this region are shallow, though

Table 1 Summary of lake characteristics for 56 Iowa lakes and impoundments included in this study

Lake characteristic	Mean	Median	Standard deviation	Range	
Max depth (m)	4.96	3.57	5.43	0.98	38.73
Secchi depth (m)	0.99	0.62	1.09	0.11	5.18
Total phosphorus (μg/L)	143	100	118	9	506
Total nitrogen (mg/L)	2.46	1.86	1.93	0.33	10.19
pH	8.6	8.5	0.3	8.2	9.6
Alkalinity (mg/L)	155	157	36	47	212

some have mean depths up to 10 m. Since European settlement, this region has been subject to some of the most intensive agricultural practices in the world, with >90 % of the land cover converted to agriculture by 1920, >80 % of wetlands drained by 1940, and a five-fold increase in maize yield per unit area in the last 50 years (Heathcote and Downing 2012). This study focused on 32 natural lakes in a region that currently has 92 % of its area under agricultural cultivation (Arbuckle and Downing 2001). Summary statistics for characteristics of the study lakes are presented in Table 1.

Materials and methods

Sediment coring and sample preparation

Sediment cores were collected from the 32 natural lakes in this study using a piston corer (Wright 1991) attached to a 7-cm-diameter, 270-cm-long polycarbonate tube. Coring sites were located in a flat area in the deepest basin of the lake (Wright 1980), identified from digitized bathymetric maps. After core retrieval, the uppermost soft sediment was extruded and sectioned at 1-cm increments in the field to prevent distortion and mixing of the flocculent layers during transport and storage. The remaining portion of the core was capped in the polycarbonate tube and sectioned at 1-cm intervals in the laboratory. We used a gravity corer to collect surface sediment samples from 56 lakes between 23 July and 9 August 2007, which were employed to construct a transfer function and estimate historic nutrient concentrations. The upper 1 cm was extruded and assumed to represent the

Table 2 Date of extraction and sampling location for long cores collected in this study

Lake	Date collected	N UTM zone 15	E UTM zone 15	Water depth (m)	Core length (cm)
Black Hawk Lake	8/5/2009	4685309	334050	1.73	46
Burt Lake	2/21/2010	4817635	388256	0.9	51
Center Lake	6/22/2008	4808658	326988	4.67	156
Clear Lake	7/13/2010	4774952	467148	4.6	104
Crystal Lake	7/3/2009	4786732	434818	1.22	77
Diamond Lake (Dickinson Co.)	7/14/2010	4816622	322749	1.5	61
East Lake Okoboji	6/23/2008	4805389	328946	6.53	192
Five Island Lake	5/20/2010	4779873	366244	1.42	59
High Lake	5/19/2010	4795593	361639	2.2	95
Ingham Lake	5/19/2010	4797335	362179	2.65	89
Iowa Lake (Emmett County)	8/12/2009	4817559	381898	2.61	104
Lake Cornelia	8/7/2009	4737459	443679	2.6	42
Lake Minnewashta	9/22/2007	4802982	327895	4.87	184
Little Spirit Lake	6/23/2008	4819957	328113	2.84	65
Little Wall Lake	6/22/2009	4679752	447003	1.62	56
Lost Island Lake	9/11/2009	4781524	345236	3.8	86
Lower Gar	9/22/2007	4802028	328183	1.62	83
Morse Lake	8/7/2009	4743063	443514	2.02	54
North Twin Lake	6/26/2009	4705866	366698	2.95	109
Pickerel Lake	7/14/2010	4752202	343144	1.48	88
Rice Lake	7/1/2009	4804677	458470	1.55	89
Silver Lake (Dickinson Co.)	6/22/2008	4812521	311146	2.63	121
Silver Lake (Palo Alto Co.)	5/20/2010	4766215	346045	2	53
Silver Lake (Worth County)	7/1/2009	4814316	466061	1.7	185
Storm Lake	9/11/2009	4721800	319598	2.4	34
Trumbull Lake	9/11/2009	4784188	341696	0.9	47
Tuttle Lake	8/12/2009	4817098	370566	1.32	105
Upper Gar	9/22/2007	4803986	328211	2.11	73
Virgin Lake	2/21/2010	4774045	346028	1.69	84
West Lake Okoboji	6/21/2008	4802764	324204	9.62	206
West Swan Lake	5/19/2010	4801454	363840	1.75	51
West Twin Lake	8/7/2009	4753855	440335	1.7	84

Water depth was measured at the time of collection and core length was measured in the field

last 1–3 years of sedimentation (Fritz 1990). All cores were stored at 4 °C. Descriptions of core locations and recovery are in Table 2.

^{210}Pb dating

Fifteen to 20 samples from each core were freeze-dried and ^{210}Pb activity was measured by alpha spectrometry. Native ^{210}Po and a ^{209}Po yield-spike were distilled from 0.5 to 1.5 g dry sediment at 550 °C, plated onto silver planchets from a 0.5 mol L^{-1} HCl solution, and measured for 1–6 days with an Ortec alpha spectroscopy system (Eakins and Morrison 1978). Excess (unsupported) ^{210}Pb was calculated by subtracting supported activity from the total activity measured at each level, with supported ^{210}Pb estimated from the asymptotic activity at depth. Dates and sedimentation rates were determined with the constant rate of supply model and confidence intervals were calculated by first-order error analysis of counting uncertainty (Appleby 2001).

Biogenic silica and organic carbon analysis

Biogenic silica (BSi) fluxes were calculated for a subset of eight lakes in this study (Center Lake [CNT], East Lake Okoboji [ELO], Lake Minnewashta [MIN], Lower Gar Lake [LGR], Upper Gar Lake [UGR], West Lake Okoboji [WLO], and West Swan Lake [WSL]), selected to represent a broad range of size and trophic state. Biogenic silica represents Si fixed by algae such as diatoms, and is positively correlated with primary production (Schelske et al. 1983; Triplett et al. 2012). Sediment BSi concentrations were measured using a time-step digestion method in a weak base (1 % Na_2CO_3), with subsequent determination of dissolved silicate by the molybdate-blue spectrophotometric method (Conley and Schelske 2001) at the Department of Geology, Lund University, Sweden. A correction for the contribution from mineral Si was applied based on the residual dissolution rate following complete dissolution of all BSi. BSi fluxes were calculated by multiplying the concentration of BSi in dry mass of each section by the mass accumulation rate of total sediment determined from ^{210}Pb dating.

Organic carbon accumulation rate (OC AR) reflects total in-lake primary production combined with erosion of organic-rich topsoil from the watershed (Heathcote et al. 2013). Percent organic matter in each dated sediment section was determined by loss-on-ignition at 550 °C for 3 h and converted to percent organic carbon by multiplying by 0.5 (Dean 1974). OC AR was estimated for each section by multiplying the organic carbon content by the mass accumulation rate determined from ^{210}Pb dating, as for BSi. OC AR was plotted versus time to show temporal trends and the significance of changes in historic (pre-1900) versus modern (1990-present) OC AR was assessed using a one-way paired t test for change greater than 0, i.e. increasing OC AR.

Diatom identification and analysis

Surficial diatom samples, hereafter referred to as "modern," were cleaned of organic material using acid digestion and quadruple rinsed with de-ionized water to remove oxidative by-products (Stoermer et al. 1995). Diatom frustules were settled onto cover slips and mounted on slides in Naphrax (Refractive Index: 1.74) (Battarbee et al. 2001). Additionally, diatom samples were prepared from each of the 32 piston

cores at a depth corresponding to the maximum ^{210}Pb age (pre-1900, if possible) and mounted on slides, as above. This age was chosen because it pre-dates most European settlement in the region and is hereafter referred to as "historic."

Slides were viewed at 1,000× magnification using a Leica DM2000 light microscope with differential interference contrast (DIC) microscopy. For each slide, a minimum of 300 diatom frustules were counted along randomly selected transects (Battarbee et al. 2001). Diatoms were identified to species level using appropriate keys (Krammer and Lange-Bertalot 1991; Patrick and Reimer 1966). Relative abundances of individual species were calculated by dividing the number of valves from each species by the total number of valves counted on each slide.

Water chemistry

Water chemistry data were obtained from 56 regional lakes, including the 32 lakes cored for this study. Lakes were sampled three times annually between May and September of 2006 and 2007. Upper mixed-zone samples (2 m) were collected from each lake and transported in opaque, 1-L plastic bottles. In addition to TP, measurements of alkalinity (ALK), pH, total nitrogen (TN), and chlorophyll a were made to help characterize the amount of unique variation explained by TP, after accounting for other environmental factors that affect diatom community structure. ALK and TP were measured following standard methods (American Public Health Association 1998) and pH was measured using a Thermo Scientific Orion 950 analytical titrator. Chlorophyll a was extracted in acetone using a probe sonicator and measured using a fluorometer (Jeffrey et al. 1997). TN was measured using the second derivative ultraviolet spectroscopy method (Crumpton et al. 1992).

Calibration set development

We incorporated surficial diatom samples from 56 lakes into a previously published 89-lake diatom training set from the same region, which was developed by the Science Museum of Minnesota's St. Croix Watershed Research Station (Ramstack et al. 2004; Edlund and Ramstack 2006). Merging data from Minnesota, where agriculture is less prevalent, produced a broader TP gradient by incorporating more

lakes with lower TP concentrations. The TP gradient ranged from 9 to 506 µg/L, and of the 145 lakes in this training set, 4 % had average TP concentrations below 10 µg/L (oligotrophic) and 31 % had TP concentrations between 10 and 30 µg/L (mesotrophic). This nutrient gradient likely provides a distribution similar to historic conditions in our study region.

Correlations between the environmental variables and diatom species assemblages were evaluated by redundancy analysis (RDA) (Šmilauer and Lepš 2003) using the software R (R Core Team 2013) in the "vegan" community ecology package (Oksanen et al. 2013). Extremely rare species, with a maximum abundance <1 % and occurring in less than two samples, were excluded from the analysis to reduce bias (Ramstack et al. 2004), and relative abundance data were transformed to Hellinger distance (Legendre and Gallagher 2001). Environmental variables other than pH were normalized by log transformation. Significant variables (Monte Carlo permutation test: $p < 0.05$ for a minimum of 999 permutations) were determined by performing partial RDAs on each variable (TP, ALK, pH, maximum depth, chlorophyll a) and testing the unique amount of variance explained once the combined effect of the other variables was taken into account (Borcard et al. 1992).

Individual species responses along TP gradients were characterized using a Huisman-Olff-Fresco (HOF) model (Huisman et al. 1993) to fit a series of increasingly complex responses to species abundances as a function of all significant environmental variables (determined from the above RDA). HOF models effectively model relative abundance data by using increasingly complex non-linear regression and incorporating the structure inherent in percentage data by setting a known upper-bound (here 100 %) to mimic a wide variety of ecological responses along a partial or complete environmental gradient. Because these models have up to five parameters, only species with at least 10 occurrences were used. The six hierarchical trends fit by the HOF model were flat, monotone, plateau, symmetric, skewed and bimodal. Flat models indicate no response, monotone indicates a decreasing or increasing response, plateau indicates an increase towards an upper limit (asymptote), symmetric indicates a symmetrical unimodal response, skewed indicates a skewed unimodal response, and bimodal indicates multiple possible optima. The output of these models provides both the likelihood of occurrence of a species over an environmental gradient as well as the species optima (maximum probability of occurrence) for a given environmental variable. HOF modeling was done using the "eHOF" package (Jansen and Oksanen 2013) in R.

The best candidate HOF model was selected based on the lowest Akaike Information Criterion (AIC) value (Akaike 1974), which weighs the goodness of fit of a model against a penalty for adding additional parameters and is only relevant in relation to other candidate models for the same predicted variable. The model with the lowest AIC value is considered the best fit, relative to the other models tested, for the variable that is being predicted. Models were considered to have strong support if ΔAIC of the next best model was >10 and models with ΔAIC < 2 were considered to be competitive with the "best" model. In the case of competing models, the simplest model (least parameters) was chosen (Burnham and Anderson 2004).

Weighted Averaging (WA) and Weighted Averaging—Partial Least Squares (WA-PLS) regression were used to develop a diatom inferred–total phosphorus (DI-TP) transfer function to apply to the subfossil diatom assemblages and reconstruct historic TP concentrations (Hall and Smol 1992; ter Braak and Juggins 1993). The error of the transfer function was evaluated from the root mean squared error of prediction (RMSEP) of the predicted DI-TP concentrations for the lakes in the training set, with bootstrapping used for cross-validation (Efron and Gong 1983). The variance explained by the transfer function after cross-validation is defined as R^2_{boot}. The transfer functions were developed using C2 statistical software (Juggins 2005).

Quantifying floristic change

General changes in diatom community structure across all 32 ^{210}Pb-dated lakes were summarized by paired box-plots of diatom species relative abundances in historic versus modern sediment samples. Fossil samples were passively plotted onto the training set RDA using the "predict.cca" function in the "vegan" package (Oksanen et al. 2013) to check for directional change along the constrained environmental vectors (Juggins et al. 2013). Floristic change between top and bottom samples was quantified by square chord distance (SCD; Overpeck et al. 1985) using the "analogue" package (Simpson and Oksanen

2013) in R (R Core Team 2013). Using this measure, samples with an SCD of 2 are completely dissimilar and samples with an SCD of 0 are perfectly similar. Major floristic change was characterized following Bennion and Simpson (2011), whereas we assumed an SCD of 0.39 as the 2.5th percentile of change and that samples with an SCD > 0.39 had undergone "biologically important change."

Differences between historic and modern diatom communities were summarized through non-metric multi-dimensional scaling (NMDS) using the Bray-Curtis dissimilarity index (McCune et al. 2002). This method calculates how dissimilar each section is to every other section based on the presence and relative abundance of all species present, on a scale of 0–1. For this metric, "1" indicates no common species and "0" indicates identical species composition. The matrix was than approximated onto an ordination using NMDS, where a point's proximity to others reflected the dissimilarity matrix (points closer to each other are more similar in community structure). The goodness of fit of the ordination to the dissimilarity matrix is given by Kruskal's stress for which a value of <20 is considered ecologically interpretable (McCune et al. 2002). Standard error ellipses for each time period are shown using the "ordiellipse" function in the "vegan" package in R (Oksanen et al. 2013). Significant difference between historic and modern diatom samples was assessed by permutational MANOVA (permanova; Anderson 2001) on the Bray-Curtis distance matrix grouped by time period (historic and modern) using the "adonis" function in the "vegan" package for R (Oksanen et al. 2013).

Results

Core lithology and dating

Retrieved sediment cores were between 34 and 206 cm long, and with the possible exception of Storm Lake, all extended back into pre-settlement times. Sediments were largely fine-grained, with organic content (core averages) ranging from 4 to 42 % (mean = 21 %) (ESM Fig. 1). The average sediment dry density was low (<0.2–0.4 g dry/cm^3 wet volume) in all but three cores (Black Hawk, Storm, Trumbull) (ESM Fig. 1). These three contained intervals with density values >0.8 g cm^{-3},

suggesting periods of prolonged drying sufficient to desiccate the sediments. More than half of the cores exhibited marked declines in organic content (%OM) in more recent sediments, which likely represent increased erosion associated the onset of Euro-American settlement (ESM Fig. 1). This settlement marker helped confirm the results of ^{210}Pb dating.

Stratigraphic profiles of total ^{210}Pb were largely non-exponential and showed changes in slope, typically an up-core flattening, which represents accelerated sediment accumulation (ESM Fig. 2). Supported (background) ^{210}Pb was fairly similar among cores (0.60 ± 0.21 pCi g^{-1}, Table 3) and was well defined in all cases by multiple intervals at depth with near-constant activity. Excess (unsupported) ^{210}Pb was generally low, even for the most recent (surface) sediments, in which values ranged from 1.8 to 9.4 pCi g^{-1} (Table 3; ESM Fig. 1).

A combination of low ^{210}Pb and irregular activity profile can contribute to uncertainty in ^{210}Pb dating. Most cores, however, could be reliably dated, as indicated by the close correspondence between ^{210}Pb dates and the settlement horizon identified in %OM profiles. Of the 22 cores with identifiable settlement markers, 21 dated to between 1837 and 1880 (mean = 1856, Table 3, Fig. 1), which is a reasonable approximation for the timing of Euro-American settlement in this region according to US Census data (Van Zant et al. 1979). Uncertainty (±1 SD) associated with settlement dates for the individual cores ranged from 6 to 36 years (mean = 18 years, Fig. 1), whereas uncertainty for dates ca. 1900 was less than ±10 years for all chronologies that extend back to the mid-1800s. The oldest dates on four cores (Clear, Storm Trumbull, and High) were substantially younger than ca. 1860, though the cores themselves, except possibly Storm, were probably long enough to contain pre-settlement strata. Although most of the core chronologies appear reasonable, four are possibly problematic. Storm and Trumbull likely dried out in recent times, based on their high dry density, and Clear and Silver (Worth Co.) had measurable excess ^{210}Pb limited to the uppermost 5 cm (ESM Fig. 2), suggesting a possible hiatus in sediment accumulation.

Dry-mass accumulation rates increased significantly in all the study lakes since settlement (ESM Fig. 3). Present-day rates (i.e. since 2000) averaged 1.44 ± 0.78 kg m^{-2} year^{-1} (±1 SD), whereas pre-1900 rates averaged 0.31 ± 0.18 kg m^{-2} year^{-1}

Table 3 Lead-210 dating parameters and sediment accumulation rates for cores from the study lakes

| Lake	Excess ^{210}Pb at surface (pCi g^{-1})	Supported ^{210}Pb (pCi g^{-1})	Mean ^{210}Pb flux (pCi cm^{-2} year^{-1})	Mass sed. rate since 2000 (kg m^{-2} year^{-1})	Mass sed. rate before 1900 (kg m^{-2} year^{-1})	Linear sed. rate 1900-present (mm year^{-1})	LOI decline depth (cm)	LOI decline date
Black Hawk	1.94	0.45	0.24	1.21	0.40	1.9	24	1856
Burt	2.37	0.42	0.85	3.29	0.36	3.9	44	1850
Center	7.13	0.69	0.97	1.43	0.56	3.8	54	1857
Clear	4.74	0.56	0.03	0.05	–	0.6	–	–
Cornelia	4.16	0.62	0.45	0.91	0.05	1.9	24	<1800
Crystal	3.64	0.55	0.98	2.93	0.52	5.3	62	1877
Diamond	3.82	0.58	0.81	2.23	0.25	3.3	36	1849
East Okoboji	6.52	0.56	0.97	1.46	0.37	4.8	62	1851
Five Island	2.50	0.52	0.61	2.32	0.61	2.7	–	–
High	2.72	1.51	0.53	1.78	0.42	4.7	–	–
Ingham	4.67	0.73	0.48	1.12	0.09	4.4	45	1859
Iowa	3.45	0.50	0.82	1.94	0.48	5.0	63	1866
Little Spirit	3.58	0.82	0.73	1.96	0.31	3.0	35	1849
Little Wall	3.90	0.57	0.27	0.57	0.12	2.4	31	1856
Lost Island	4.35	0.65	0.41	0.81	0.06	2.1	28	1837
Lower Gar	2.30	0.37	0.43	1.55	0.25	2.1	27	1842
Minnewashta	6.46	0.42	1.75	2.90	0.56	8.2	90	1858
Morse	4.46	0.73	0.81	1.69	0.19	2.5	32	1854
North Twin	4.46	0.66	0.55	1.08	0.40	3.7	–	–
Pickerel	3.30	0.52	0.56	1.61	0.43	3.1	43	1850
Rice	9.44	0.34	0.38	0.35	0.12	2.3	–	–
Silver (Dickinson)	2.80	0.56	0.32	1.04	0.17	1.7	21	1848
Silver (Palo Alto)	3.07	0.44	0.67	2.08	0.21	2.6	31	1864
Silver (Worth)	3.76	0.50	0.02	0.05	0.04	0.7	–	–
Storm	1.88	0.94	0.33	1.33	–	1.6	–	–
Trumbull	1.83	0.52	0.30	1.23	–	3.7	–	–
Tuttle	2.20	0.66	0.43	1.59	0.24	2.2	–	–
Upper Gar	4.02	0.39	0.30	0.71	0.38	2.2	28	1860
Virgin	4.38	0.49	0.63	1.25	0.25	2.9	34	1880
West Okoboji	8.04	0.56	0.84	0.98	0.26	3.3	42	1851
West Swan	3.84	0.59	0.39	0.95	0.15	2.0	–	–
West Twin	4.37	0.67	0.97	1.64	0.70	4.6	61	1863
Mean	4.07	0.60	0.59	1.44	0.31	3.1	42	1856
SD	1.78	0.21	0.34	0.78	0.18	1.5	17	11

(Table 3). The ratio of increase (post-2000/pre-1900) for individual lakes ranged from 1.2 to 16.9, with a mean of 5.9. Linear rates of sediment accumulation ranged from 0.6 to 8.2 mm year^{-1} since 1900. Roughly half the cores exhibited some degree of sediment focusing, as indicated by core-specific fluxes of ^{210}Pb (Table 3) in excess of that attributable to

direct atmospheric deposition, $\sim$0.5 pCi cm^{-2} year^{-1} (Lamborg et al. 2013). The two cores with very short activity profiles, (Clear and Silver, Worth Co.) also had very low ^{210}Pb fluxes (0.02–0.03 pCi cm^{-2} year^{-1}), further evidence that the locations from which the cores were collected had only recently become depositional zones for fine-grained sediments.

Table 4 The proportion of diatom species whose response to a given environmental variable was best characterized by each of the hierarchical HOF models

Model	TP	Max. depth	ALK	pH
Flat	0.48	0.47	0.50	0.51
Monotone	0.06	0.06	0.14	0.06
Plateau	0.00	0.01	0.00	0.01
Symmetric	0.27	0.34	0.15	0.22
Skewed	0.06	0.03	0.10	0.09
Bimodal	0.14	0.09	0.11	0.11
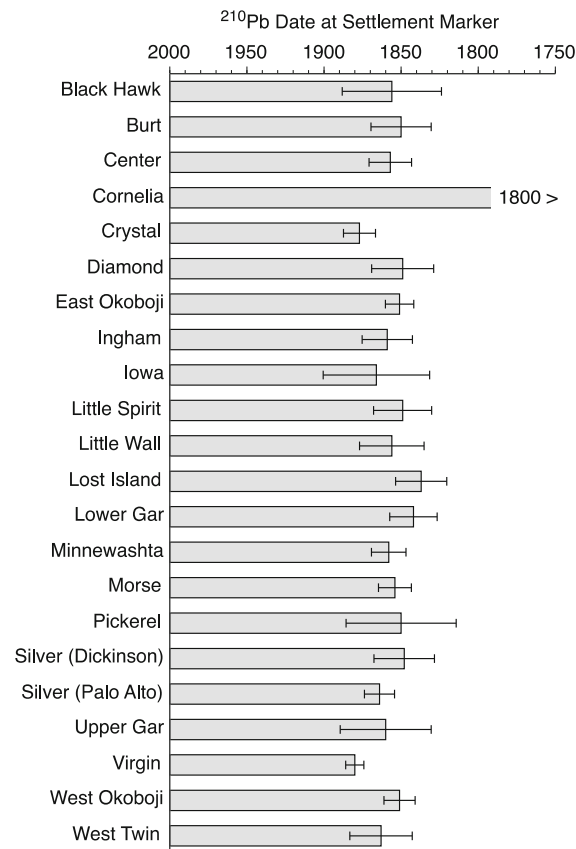
Fig. 1 ^{210}Pb dates corresponding to settlement horizon as identified from core profiles for % organic matter (ESM Fig. 1). *Error bars* represent dating uncertainty (±1 SD) propagated from counting statistics

Biogenic silica and organic carbon accumulation

Biogenic silica (BSi) fluxes increased in 7 of 8 lakes that were analyzed (Fig. 2). The average flux of BSi increased 3.5-fold from 21 g m^{-2} year^{-1} pre-settlement to 72 g m^{-2} year^{-1} in the most recent (modern)

sections (Table 5). Six of the eight lakes followed a similar trajectory of little change in BSi from 1800 to 1950, followed by synchronous increases to the present (Fig. 2). The remaining two lakes, MIN and UGR, showed increases in BSi following land clearance between 1850 and 1900. BSi fluxes in MIN continued to increase at a rate greater than the remaining seven lakes, whereas UGR showed a sharp decrease after 1950, followed by a steady rise more closely correlated with the remaining six lakes.

OC AR in the 32 lakes followed a trend similar to biogenic silica, increasing in all but three lakes, Clear, Trumbull, and Silver [Worth] (Fig. 2). OC AR increased from a pre-settlement average of 28 g C m^{-2} year^{-1} to a modern average of 121 g C m^{-2} year^{-1} across all lakes (+93 g C m^{-2} year^{-1}, $t_{29} = 7.8$, $p < 0.001$; Table 5). This is equivalent to an average 4.3-fold increase in deposition of organic matter in the last ~110 years.

Correlation between diatom community structure and environmental variables

The relationship between diatom community structure and TP, pH, alkalinity, and maximum depth is summarized in an RDA biplot (Fig. 3a). RDA axis 1 and 2 explained 14.9 and 5.3 % the variation in diatom community structure, respectively. All four variables explained a significant amount of variation ($p < 0.05$) in diatom community structure, although there was considerable overlap. TP explained 13.2 % of the variation, but only 2.7 % of the variance explained was unique. Maximum depth, alkalinity, and pH explained 12.2, 4.8, and 6.6 % of the variance (4.0, 0.9, and 1.2 % unique), respectively (Fig. 3b).

Individual species responses to TP, maximum depth, alkalinity, and pH gradients in the training set were characterized by fitting HOF models (Table 4). Models were based on 88 species that were present in at least 10 sites. 36 % of those species showed no response (flat) across all environmental variables. Approximately half (47–51 %) of the species in the training set had no response for any one variable. Unimodal responses (symmetric or skewed) were the most common (non-flat) response, ranging from 25 to 38 % of the species responses across the training set. Diatoms responded similarly to TP and maximum depth, alkalinity and pH in 30, 24, and 31 % of the diatom species based on best response model shape.
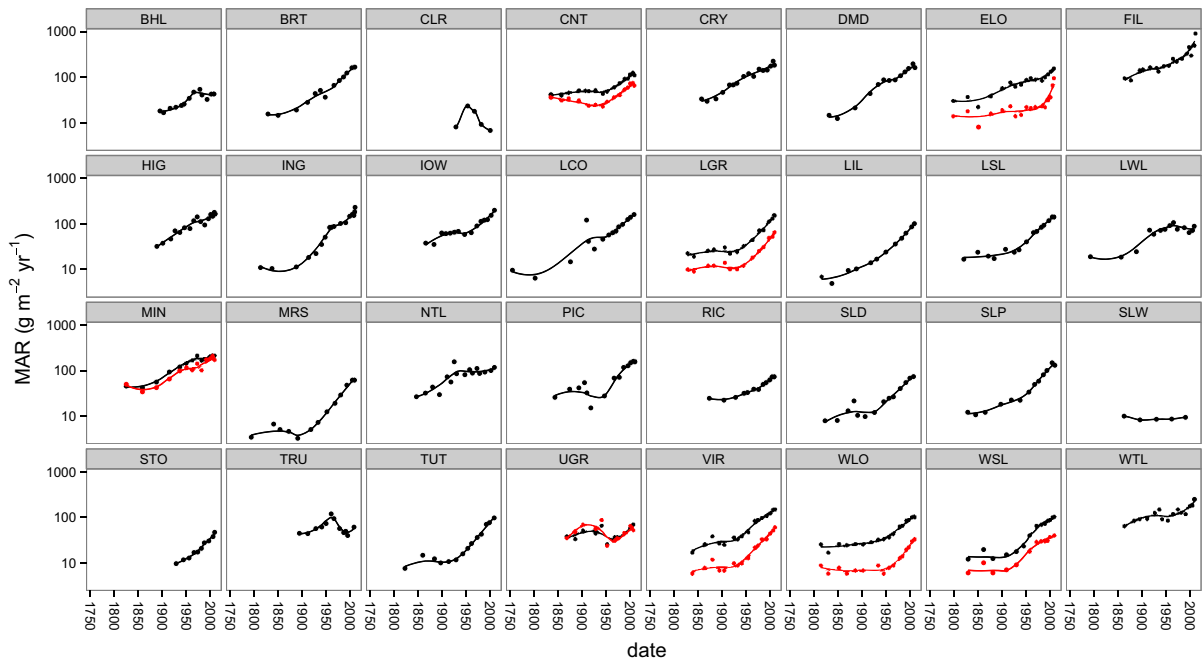
Fig. 2 Biogenic silica (*red*) and organic carbon (*black*) accumulation rates (g m^{-2} year^{-1}) over time across all 32 lakes in this study

Transfer functions derived from both WA and WA-PLS were considered for reconstructing DI-TP. Because the 2nd component of the WA-PLS was not significant, only the WA transfer function is discussed further. As has been observed elsewhere (Fritz et al. 1993; Ramstack et al. 2004), the transfer function error (RMSEP = 0.31 log$_{10}$ µg L^{-1}) was high relative to the reconstructed change in DI-TP (+0.11 log$_{10}$ µg L^{-1}) and had a systematic bias in residual error. The transfer function over-predicted at low TP concentrations and under-predicted at >100 µg TP l^{-1} (ESM) and its application to sediment diatom assemblages was considered inappropriate. See the electronic supplementary material for a more detailed description of the transfer function performance.

Floristic change

Qualitative estimates of changes in trophic state condition in these lakes were made based on the shifts in diatom taxa with well-described ecologies. Common trends across the 32 lakes consisted of the partial or complete replacement of taxa with lower TP preferences, such as the planktonic diatom *Aulacoseira distans*, by more eutrophic (more frequently found at high TP concentrations) planktonic species

such as *Stephanodiscus minutulus*, *S. hantszschii*, *S. niagarae* and *Aulacoseira italica* (ESM Fig. 4).

Lakes in this study showed a range of floristic change based on SCD. Lakes ranged from no floristic change (SCD < 0.39) to almost complete floristic turnover (West Lake Okoboji: SCD = 1.98) (Fig. 4). Only four of the 32 lakes in this study showed low or no floristic change between historic and modern diatom communities (Silver [Palo Alto], Pickerel, West Swan, Morse) and all are currently hypereutrophic (modern TP range 158–298 µg L^{-1}). The remaining 28 lakes had major floristic change between the two periods with 23 % percent of the variance (R^2 = 0.23, p = 0.006) explained by a positive correlation between SCD and lake depth (Fig. 4a, b). Adding modern TP concentration to a multiple regression with lake depth improved the fit (R^2 = 0.30, p = 0.003), but did not explain a significant portion of additional variation compared to lake depth alone (p = 0.62). Floristic change had no relationship to ΔOC AR or ΔBSi (data not shown), indicating that the magnitude of change in primary production was not the only driver controlling the change in diatom communities in these lakes.

Plotting Bray-Curtis dissimilarities through an NMDS ordination showed the relative differences between

Table 5 Biogenic silica (BSi) and organic carbon (OC AR) fluxes for the most recent (modern) and oldest dated section (historic) for each lake

Lake	Max ^{210}Pb dated section ($\pm$SE)	Historic BSi (g m^{-2} year^{-1})	Modern BSi (g m^{-2} year^{-1})	Historic OC AR (g m^{-2} year^{-1})	Modern OC AR (g m^{-2} year^{-1})
Black Hawk Lake	1895 $\pm$ 20	–	–	18	39
Burt Lake	1829 $\pm$ 37	–	–	16	150
Center Lake	1835 $\pm$ 31	36	64	44	107
Clear Lake	1929 $\pm$ 38	–	–	–	7
Crystal Lake	1857 $\pm$ 22	–	–	32	181
Diamond Lake	1831 $\pm$ 34	–	–	16	170
East Lake Okoboji	1799 $\pm$ 28	14	94	32	131
Five Island Lake	1863 $\pm$ 36	–	–	105	479
High Lake	1889 $\pm$ 67	–	–	32	155
Ingham Lake	1813 $\pm$ 39	–	–	11	163
Iowa Lake	1866 $\pm$ 35	–	–	45	158
Lake Cornelia	1755 $\pm$ 96	–	–	10	141
Lake Minnewashta	1825 $\pm$ 21	50	173	48	199
Little Spirit Lake	1820 $\pm$ 45	–	–	19	133
Little Wall Lake	1792 $\pm$ 44	–	–	21	75
Lost Island Lake	1814 $\pm$ 33	–	–	8	83
Lower Gar Lake	1829 $\pm$ 23	10	63	23	128
Morse Lake	1794 $\pm$ 62	–	–	5	57
North Twin Lake	1849 $\pm$ 39	–	–	33	109
Pickerel Lake	1843 $\pm$ 41	–	–	35	148
Rice Lake	1873 $\pm$ 9	–	–	25	66
Silver Lake (Dickinson)	1823 $\pm$ 42	–	–	12	65
Silver Lake (Palo Alto)	1828 $\pm$ 29	–	–	13	126
Silver Lake (Worth)	1863 $\pm$ 32	–	–	9	9
Storm Lake	1929 $\pm$ 21	–	–	–	38
Trumbull Lake	1894 $\pm$ 41	–	–	44	50
Tuttle Lake	1822 $\pm$ 56	–	–	11	81
Upper Gar Lake	1869 $\pm$ 29	35	52	36	64
Virgin Lake	1838 $\pm$ 21	6	60	27	127
West Lake Okoboji	1813 $\pm$ 30	9	33	24	92
West Swan Lake	1829 $\pm$ 22	6	40	15	87
West Twin Lake	1863 $\pm$ 37	–	–	78	198
Mean (SD)	–	21 (17)	72 (45)	28 (21)	121 (83)

The mean and standard deviation (in parentheses) for each time period, across all 32 lakes, is included

historic and modern diatom community structure. The NMDS plot had a stress value of 19, indicating good agreement with the dissimilarity matrix. Figure 5 shows the NMDS plot, shaded by time period, as well as the ellipses based on the standard error for the NMDS scores of each group. Species scores for diatoms typical of eutrophic conditions (i.e. *Stephanodiscus* spp., *A. italica*)

plotted closest to the centroid associated with the modern sections. *A. distans*, which is not typical of eutrophic systems, was more closely associated with the historic sections. Time period explained a significant amount of variation in the permanova of the historic and modern samples (4 %, $p = 0.001$, permutations = 999).
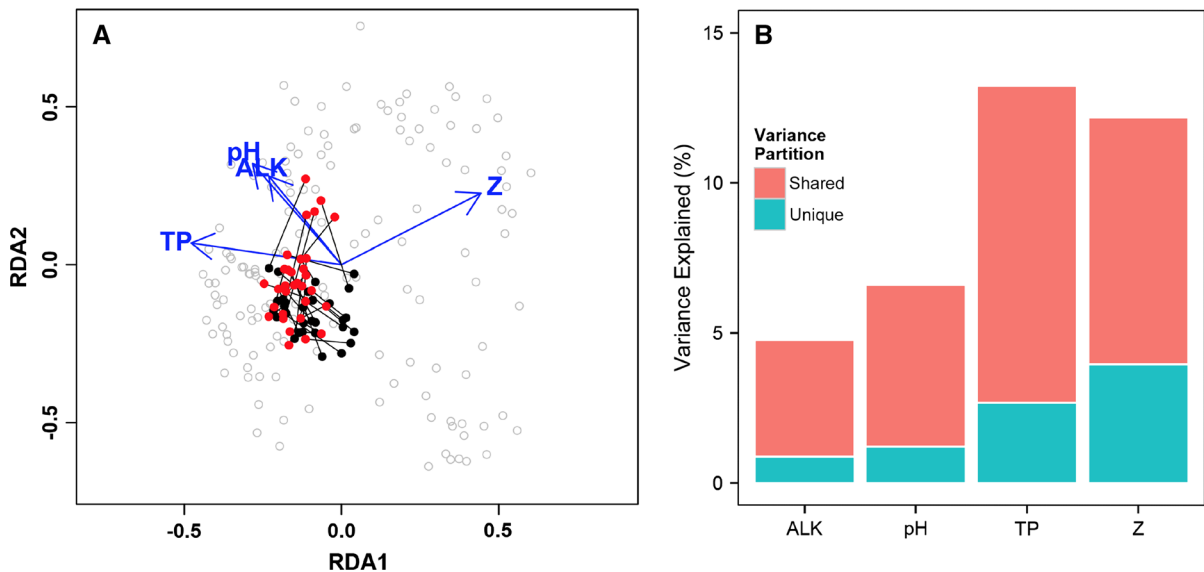
Fig. 3 Constrained ordination of diatom species vs environmental variables. **a** Redundancy analysis (RDA) of diatom community data versus environmental characteristics for the surficial diatom samples. Lakes are represented by *grey open circles* and the eigenvectors for each of the constrained environmental variables are shown as *blue arrows*. Historic (*black circles*) and modern (*red circles*) diatom samples were passively plotted onto the training set to indicate their trajectory along the given environmental gradients. **b** Variance partitioning from partial RDAs of the four significant environmental variables indicating the percentage of unique (*green*) and shared (*pink*) variance explained

Discussion

Temporal trends in eutrophication

The majority of the study lakes showed unambiguous increases in both organic carbon (91 %, n = 32) and biogenic silica (88 %, n = 8) accumulation rates over the last 180 years, since European settlement in the region. Because monitoring data are non-existent for the period when Europeans arrived and began modifying the landscape, it is helpful to have multiple corroborating lines of evidence to determine changes since pre-settlement periods. OC AR, often referred to as organic carbon burial, has been shown to be closely correlated with both eutrophication and landscape change related to intensive agriculture (Heathcote et al. 2013; Anderson et al. 2014). It incorporates both in-lake productivity and contributions of eroded materials from the catchment, which may be accompanied by both dissolved and sediment-bound nutrients (Heathcote and Downing 2012).

Although OC AR consistently increased across most systems in this study, the timing of this change is divided between two major categories. In general, OC AR either increased directly following land clearance (90 % complete by 1900) or in response to the post-World War II rapid intensification of agriculture (*ca.* 1940–1950), with most lakes falling into the latter category (Fig. 2). This difference may reflect either watershed-scale discrepancies in the extent of agricultural influence following settlement, or limnological factors such as lake depth that may have buffered some systems more than others against eutrophication. Regardless of the exact timing, across all lakes in this study, organic carbon accumulation has increased more than fourfold since 1850. All the lakes in this study are currently eutrophic to hypereutrophic (Table 1), and it is clear that current levels of primary productivity are related to changes in trophic state that occurred over the last 70–100 years.

Increases in OC AR in these lakes are of similar magnitude to those reported in other recent studies of lakes that became culturally eutrophic over approximately the same time period. In a study that included lakes of similar glacial origin and European settlement history in the state of Minnesota (USA), Anderson et al. (2013) found that lakes which had undergone severe eutrophication had increased OC AR by fourfold between 1850 and 2000. Similarly, data from anthropogenically eutrophic lakes in northern and
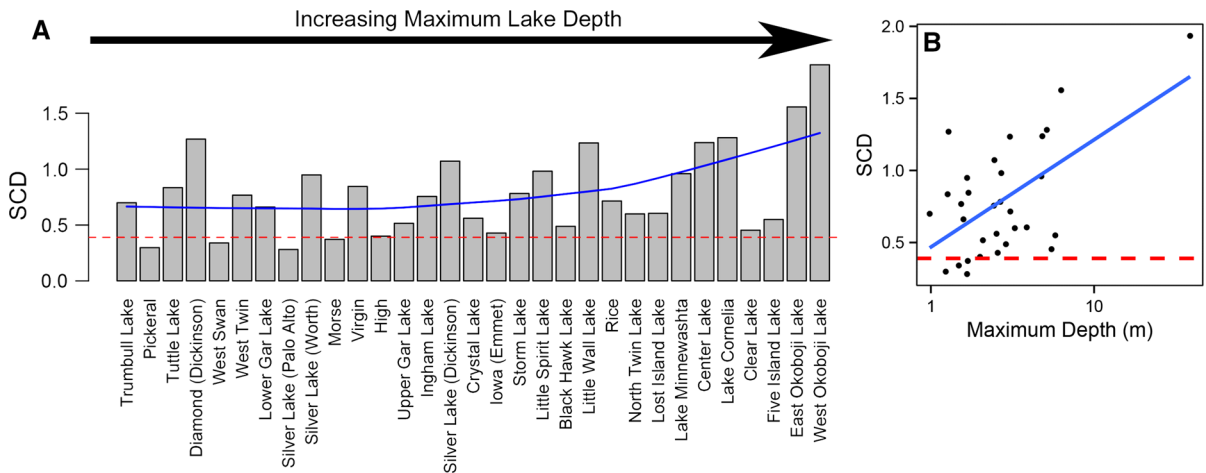
Fig. 4 Relationship between SCD and maximum depth for lakes (Burt Lake was excluded because there was no depth information) **a** Barplot of square chord distance (SCD) between historic and modern diatom communities for all lakes with maximum depth data. Lakes are organized along a gradient of increasing maximum depth (*left* to *right*). The 2.5th percentile (0.39) is indicated by a *red dashed line*. The *solid blue line* shows a LOWESS smooth of SCD along the gradient of maximum depth. **b** SCD plotted against maximum depth. The *red dashed line* indicates the 2.5th percentile for SCD and the *solid blue line* is the least squares regression *line* for the data
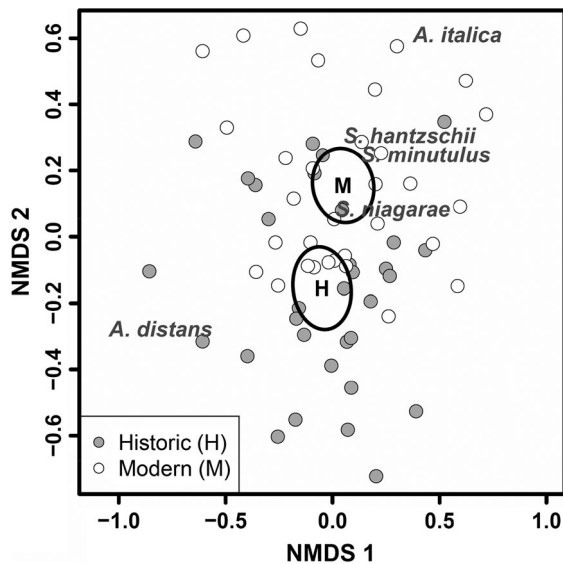
Fig. 5 Non-metric multi-dimensional scaling ordination of Bray-Curtis distances between modern (M; *white*) and historic (H; *grey*) diatom samples. Confidence ellipses represent the 95 % confidence interval around the centroid for each group. Diatom species mentioned in the text are also plotted to illustrate their association with each group

central Europe showed a ∼two-fold increase in OC AR since 1800 (Anderson et al. 2014). The average modern OC AR in lakes from this study (121 g C m^{-2}

year^{-1}) was higher than the mean recorded in either of the previous studies (range 70–100 g C m^{-2} year^{-1}), but well within the total range recorded, which perhaps is not surprising given the lakes in this study are among the most eutrophic in the world (Downing et al. 2008).

In general, BSi flux for the lakes in this study was similar to OC AR in direction and magnitude over the last 180 years (Fig. 2). The average BSi flux prior to settlement (21 g BSi m^{-2} year^{-1}) was slightly higher than the current worldwide average for lakes of 15 g BSi m^{-2} year^{-1} (Harrison et al. 2012). The relative changes in BSi flux in these systems, two- to 10-fold increases, are similar to what Triplett et al. (2012) found in riverine impoundments in the same region following eutrophication (four and 16-fold increases). The average relative change in BSi flux was slightly less than that seen in OC AR (3.5-fold vs 4.3-fold), however, it should be noted that BSi only incorporates silicified algae (diatoms and Chrysophytes), which become a decreasing proportion of the algal community as eutrophication increases and lakes become more dominated by Cyanobacteria (Downing et al. 2001). Thus, in lakes which have undergone extreme eutrophication, OC AR may be a better indicator of primary production than BSi or diatom valve accumulation, given the relatively small contribution of

silicified algae to total algal biomass in these systems (Downing, unpublished; http://limnology.eeob.iastate.edu/lakereport/).

Together, these two geochemical indicators provide strong evidence that lakes in this region have undergone significant eutrophication in the last 180 years, coincident with European settlement and the rise of intensive agriculture, as has long been recognized in other areas of the USA (Brugam 1978; Carney 1982). The results from this study are in stark contrast to recent work by Bachmann et al. (2013) who found no evidence for agriculturally driven eutrophication across the United States. Although we cannot comment on the extent of eutrophication in the entire USA based on these data, our lakes are representative of eutrophic lakes in the agriculturally intensive Midwest that were largely excluded from the above study. For this region at least, anthropogenic eutrophication has been intense (up to fourfold increases in sedimented primary production) and widespread (increases in 91 % of lakes).

Floristic response to eutrophication in shallow lakes

Changes in the sediment geochemistry outlined above indicate a clear history of eutrophication in our study lakes. The reflection of this change in the diatom community, however, provides a good example of the difficulties in reconstructing DI-TP in shallow lakes. Although TP explains the most total variation in the RDA of the training set diatoms (13.2 %), 90 % of this variation is confounded with other variables, most notably lake depth and pH (Fig. 3b). Based on HOF modeling we found that a majority (52 %) of the diatom species responded to TP, although in almost all cases this response was confounded with maximum depth, alkalinity and pH. Only 9 % of the diatom species in the training set were found to respond to a single environmental variable (with all other response models being flat), and only a single species responded to TP alone.

When the modern and historic fossil diatom assemblages are passively plotted onto the RDA (Fig. 3a), there is no consistent trajectory across all lakes. Although it is clear, and perhaps unsurprising, that the diatom community has changed as a result of eutrophication, that change does not solely reflect changes in water-column TP concentrations, but rather

a combination of factors that represent a trophic-state change, including nutrient enrichment, loss of macrophytes, light limitation, and increasing pH/alkalinity. The composite of these changes in diatom flora can be integrated by estimating unconstrained floristic change through distance metrics and NMDS ordination of the diatom species abundances. Modern samples were closely associated to the eutrophilic clade of *Stephanodiscus* species (Fig. 5) and were significantly different from historic samples based on permanova ($p = 0.001$). Similarly, the SCD between historic and modern samples indicated major floristic change in 88 % of the lakes, although this change was not correlated with changes in primary production or contemporary TP concentrations, as might be expected, but instead with maximum lake depth (Fig. 4). It should be noted that SCD quantifies floristic change in terms of taxonomic distance, which does not necessarily translate into functional ecological difference, but is nevertheless a useful proxy for community turnover among sites.

The lack of correlation between the change in OC AR (or BSi flux) and SCD ($R^2 = 0.03$, $p = 0.38$) is also clear evidence of the difficulties associated with reconstructing TP in shallow eutrophic lakes. Although there are robust geochemical indicators of eutrophication in the majority of these lakes (91 and 88 % of lakes showed increases in OC AR and BSi flux), the magnitude of floristic change and indicators of increasing primary production were not strongly correlated. In these shallow lakes, the magnitude of floristic change was instead most strongly correlated to the maximum lake depth (Fig. 5). Because SCD was positively correlated with depth, it is unlikely that this relationship represents a dilution effect of increasing lake volume, whereby deeper lakes were less susceptible to eutrophication, but rather represents a transition in diatom community ecology between shallow and deeper lakes that could easily confound nutrient reconstructions.

This potential confounding factor is likely related to the dominance of littoral diatoms in shallow lakes, what Bennion et al. (2001) dubbed the "*Staurosira, Pseudostaurosira*, and *Staurosirella* problem," referring to a suite of non-planktonic araphid diatoms that are abundant in shallow lakes across a large trophic state gradient. In this study, both *Staurosira* and *Pseudostaurosira* are highly abundant (>50 % relative abundance) in both historic and modern samples

(ESM Fig. 4). These species have broad ecological tolerances, are unlikely to be impacted directly by changing TP concentrations, and are more susceptible to light limitation or substrate availability (Sayer 2001). Although it is possible to remove these species from training-set and fossil assemblages, they are often the most abundant diatoms present (up to 75 % in this study), and the paucity of remaining taxa with modern analogues, after such removal, only serves to increase prediction error (Bennion et al. 2001). Thus, whether these species are included or not, their presence likely introduces additional uncertainty into nutrient transfer functions.

An alternative approach to reconstructing eutrophication in shallow lakes

Paleolimnological studies of eutrophication have a long history, back to Pennington's (1943) qualitative study of the diatom response to the enrichment of Lake Windermere. Traditional approaches were based on diatom community changes (*Cyclotella–Aulacoseira–Stephanodiscus*), coupled with diatom and organic matter accumulation rates (Brugam 1978; Battarbee 1986). In deeper lakes, this approach provides an unambiguous record of enrichment, community turnover and increased productivity. With the advent of transfer functions these coupled diatom ecology-mass flux relationships were largely replaced by DI-TP profiles (Hall and Smol 1992; Bennion et al. 1996). Mounting evidence for generic problems with transfer functions (Juggins et al. 2013; Juggins 2013), and specifically, with their application to shallow lakes (Fritz et al. 1993; Bennion et al. 2001; Sayer 2001), call for an alternative approach or at least a return to more "traditional" methods with multiple indicators of change.

Conclusions

Shallow lakes in regions with intensive agriculture have undergone dramatic eutrophication over the last 180 years that is clearly shown using geochemical indicators of primary production (OC AR and BSi). This change is also reflected by floristic shifts in diatom taxa between historic and modern time periods, though the magnitude of floristic change is moderated by a complex interaction between nutrients, substrate and lake depth. Although deeper, thermally stratified lakes

have shown unambiguous changes in diatom community composition in response to known nutrient enrichment (Anderson 1989), such changes tend to be much less marked in shallow systems. Shallow, agriculturally eutrophic lakes tend to be predominantly benthic- or littoral-dominated systems (Sayer et al. 2010) and thus transfer functions reduce ecological complexity to a single, often inappropriate variable (Juggins 2013). With the recognition of transfer-function problems in shallow lakes, alternative methods for reconstructing trophic state, including geochemical indicators of productivity and floristic changes related to diatom ecology, are more appropriate.

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