

Regional climate changes drive increased scaled-chrysophyte abundance in lakes downwind of Athabasca Oil Sands nitrogen emissions

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Received: 21 July 2016 / Accepted: 29 June 2017 / Published online: 6 July 2017
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Abstract Several limnological and paleolimnological investigations have linked enhanced atmospheric nitrogen (N) deposition to nutrient enrichment and increased primary production. The Athabasca Oil Sands Region (AOSR) in northeast Alberta, Canada is a significant source of N emissions, particularly since development intensified during the 1990s, and recent paleolimnological investigations provide evidence of increased lake production in adjacent areas subject to enhanced N deposition. The AOSR, however, has also experienced atmospheric warming since ca. AD 1900, and therefore the relative effects of nutrient deposition and climate changes on lake production remain unclear.

We undertook a factorial-design paleolimnological assessment of 16 lakes in northwest Saskatchewan to quantify changes in abundance and species composition of scaled chrysophytes over the past 100 years. Study sites included both N-limited and P-limited lakes within control regions, as well as lakes that receive enhanced N deposition from the AOSR. We hypothesized that a change in algal communities within N-limited AOSR-impacted lakes, without concurrent changes in the other lake groups, would suggest AOSR-derived N as a driver of enhanced primary production. Instead, marked increases in concentrations of scaled chrysophytes, mainly *Mallomonas crassisquama*, occurred in the recent sediments in cores from all four lake groups (N-limited vs. P-limited, impacted vs. control), suggesting that regional climate change rather than N deposition was the paramount process

Electronic supplementary material The online version of this article (doi:10.1007/s10933-017-9987-6) contains supplementary material, which is available to authorized users.

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enhancing chrysophyte production. Because chrysophyte abundances tended to be higher in deep, lower-pH lakes, and chrysophyte time series were fit best by lake-specific generalized additive models, we infer that climate effects may have been mediated by additional catchment and/or lake-specific processes.

Keywords Athabasca Oil Sands · Nitrogen deposition · Climate change · Regional warming · Scaled chrysophytes

Introduction

The Athabasca Oil Sands Region (AOSR) in northeast Alberta, Canada, contains the third largest oil reserve on Earth, after Saudi Arabia and Venezuela. Development in the AOSR began in 1967, but accelerated during the 1990s because of increased demand for oil and reduced costs associated with production (Schindler 2010). The Canadian Association of Petroleum Producers (CAPP) expects production to reach ~5 million barrels per day (bpd) by the end of 2030, in comparison to 2.2 million bpd in 2014 (CAPP 2015). Development in the AOSR includes operation of bitumen upgraders, open pit and in situ mines, and diesel- and gas-powered machinery. These activities are sources of atmospheric pollutants including metals (Kelly et al. 2010; Laird et al. 2013), polycyclic aromatic hydrocarbons (Kurek et al. 2013), and nitrogen and sulfur oxides (NPRI 2015), while disturbance of the terrestrial environment also increases loading of dust and base cations into the atmosphere (Watmough et al. 2014). Concerns over the impacts of atmospheric deposition of these pollutants on nearby aquatic ecosystems has led to creation of a number of monitoring associations including the Wood Buffalo Environmental Association (WBEA), the Cumulative Environmental Management Association (CEMA), and the Regional Aquatics Monitoring Program (RAMP). Monitoring programs, however, were introduced ~30 years after oil production in the AOSR began, and operate mainly in close proximity to Fort McMurray, Alberta, a city that is considered to be the centre of industrial activity in the oil sands. Paleolimnological investigations, however, have been used to provide longer-term records of change associated with industrial activity in the oil sands, particularly with

respect to concerns about acidic deposition (Hazewinkel et al. 2008; Curtis et al. 2010; Laird et al. 2013).

Many lakes in the AOSR and regions downwind have been identified as sensitive to the impacts of acidic deposition because of the low acid neutralizing capacity (ANC) of the lake water. The Saskatchewan Ministry of the Environment (SKMOE) surveyed the water chemistry of 259 headwater lakes in northwest Saskatchewan between 2007 and 2008; 60% of the lakes were categorized as acid sensitive (50–200 $\mu\text{eq L}^{-1}$ ANC) and 8% as very sensitive (<50 $\mu\text{eq L}^{-1}$ ANC) (Scott et al. 2010). Subsequent analysis of diatom assemblages in sediment cores from ten of these lakes showed that widespread lake acidification had not occurred as a result of AOSR development (Laird et al. 2013), a finding similar to that at sites in closer proximity to Fort McMurray (Hazewinkel et al. 2008; Curtis et al. 2010). Findings from these studies, however, suggest a number of lakes have experienced increases in primary production, possibly as a consequence of nutrient enrichment and/or recent climate change.

Analysis of patterns in lake-water chemistry in Europe suggest that deposition of reactive nitrogen (Nr, in the forms NO_x , NH_x , N_2O) into lakes that are N-limited may cause changes in species composition and production of planktonic communities because of N enrichment (Bergström et al. 2005; Bergström and Jansson 2006). Similarly, paleolimnological investigations of lakes in alpine regions of the western U.S., where many oligotrophic lakes are N-limited, have also documented post-1950 increases in mesotrophic diatom taxa that have been associated with enhanced N deposition (Baron et al. 2000; Wolfe et al. 2001; Saros et al. 2011). Although the boreal landscape where the AOSR is located is different from that of western alpine regions, the AOSR is a significant point source of nitrogen emissions, releasing approximately 312 tonnes day^{-1} of NO_x (Deer Creek Energy Ltd. 2006). Although there have been relatively few studies investigating nitrogen deposition rates in northwest Saskatchewan, Fenn et al. (2015) indicated that N deposition rates in our study region are likely between ~1.1 and 1.2 kg DIN ha^{-1} year^{-1} . Within this impacted region, ~25% of the lakes are potentially N-limited (DIN:TP < 1.5) or co-limited by N and P (3.4 > DIN:TP > 1.5) (Scott et al. 2010), a pattern that suggests many lakes may be sensitive to ecological changes arising from enhanced N deposition (Bergström 2010). To date, little is known of the

ecological consequences of this AOSR-derived N, including its role as a possible driver for regional increases in primary production.

Enhanced lake production has also been linked to recent changes in climate, reviewed in Adrian et al. (2009). For example, paleolimnological investigations in boreal and subarctic regions have documented shifts in lake biota, including scaled chrysophytes and diatoms, which have been attributed to recent climate change (Wolfe and Perren 2001; Rühland et al. 2003; Rühland and Smol 2005). Such changes may arise from alterations in the duration of the growing season (Rühland and Smol 2005), thermal structure of lakes (Ginn et al. 2010), variation in lake hydrology (McGowan et al. 2011), changes in DOC dynamics (Paterson et al. 2004; Hyatt et al. 2010), and elevated $p\text{CO}_2$ in lakes, caused by either warming-induced processes or rising atmospheric CO_2 (Wolfe and Siver 2013). Similarly, paleolimnological investigations in the AOSR (Hazewinkel et al. 2008; Curtis et al. 2010) and in northern Saskatchewan (Laird et al. 2013) have also suggested that climate change may affect lake primary production, although the precise mechanism(s) has yet to be established. Taken together, these studies suggest that lakes downwind of the AOSR may be subject to effects of both nitrogen deposition and climate change.

The goal of this study was to quantify the importance of nutrient enrichment via atmospheric N deposition and climate change on production of scaled chrysophytes in lakes downwind of the AOSR. Unlike previous studies, we determined algal response in N- and P-limited lakes within both “reference” and “impacted” regions to isolate the importance of climatic and N-based mechanisms. Specifically, we hypothesized that if deposition of AOSR-derived N is impacting lake primary production, chrysophyte response should be limited to N-limited lakes within the impact region. Additionally, we expected that if regional changes in climate or hydrology are influencing chrysophyte assemblages, then these effects should be ubiquitous among study lakes.

Materials and methods

Study design and lake selection

Between 2007 and 2011, the SKMOE sampled 259 lakes across the northwest region of Saskatchewan for

water chemistry (Scott et al. 2010). Results from this water chemistry survey were used in the lake selection process for this study. All water sampling was conducted at the central or deepest location in each lake in autumn (September–October) to reduce spatial and temporal variability in chemistry within and among lakes. Full details regarding water chemistry analytical methods can be found in Scott et al. (2010). Water chemistry data were used to categorize lakes as potentially N-limited or P-limited based on the molar dissolved inorganic nitrogen to total phosphorus ratio (DIN:TP). According to Bergström (2010), nitrogen-limited lakes are defined by DIN:TP ratios <1.5 , P-limited lakes by DIN:TP > 3.4 , and in between as either N or P, or co-limited. This approach has been considered advantageous over the more traditional TN:TP because TN often consists of refractory dissolved organic nitrogen (DON) compounds that are largely unavailable to phytoplankton (Bogard et al. 2012 and references therein), whereas DIN consists mainly of ammonium and nitrate, which are forms of N preferred by algae (Wetzel 2001). In contrast, bioavailable pools of phosphorus have been assumed to correspond with TP (Lewis and Wurtsbaugh 2008).

Study lakes were a priori chosen to be: (1) N-limited or co-limited with P (DIN:TP < 3.4), or (2) strongly P-limited (DIN:TP $> \sim 7$). Lakes with multiple years of water chemistry data (208 of the 259 lakes had two or more measurements) were favored in the lake selection process, especially when there was minimal variability in DIN:TP ratios among years. In addition to DIN:TP ratios, lakes were selected to have a minimum depth of four meters. Although widespread lake acidification in the study region is unlikely (Scott et al. 2010; Laird et al. 2013), lakes with lower alkalinity values ($<5 \text{ mg L}^{-1}$) were avoided to minimize the potential confounding influence of acidic deposition.

To disentangle the potential impacts of changes in regional climate and N deposition, lakes with DIN:TP < 3.4 (N-limited or N-P co-limited, referred to as N-limited hereafter) and DIN:TP > 7 (P-limited) were separated into reference and impact regions (Fig. 1). The impact region is a zone of enhanced atmospheric deposition identified by Environment Canada using a regional air pollution forecast model (Environment Canada 2011) that integrates meteorological and emissions data to forecast transport and deposition of atmospheric pollutants. The modeled deposition zone extends northeast from Fort

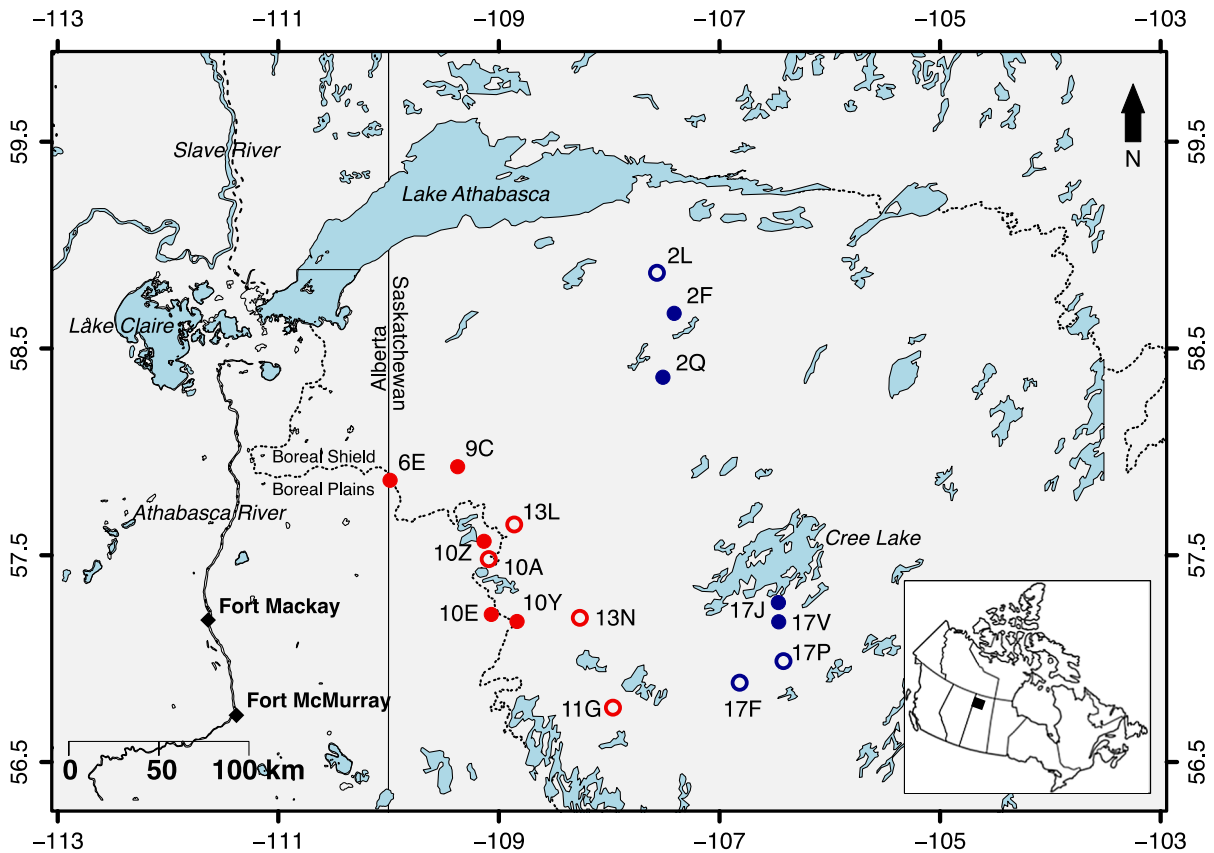


Fig. 1 Location of the sixteen study lakes in northwest Saskatchewan. The *dashed line* shows the boundary between the Boreal Shield and Boreal Plains ecozone. *Closed circle* N-limited, *open circle* P-limited, *red* impact lake, *blue* reference lake. (Color figure online)

McMurray and into northern Saskatchewan. Lakes in the reference region are outside the modeled enhanced deposition zone, either to the southeast or northeast, and both reference regions included lakes selected to have similar chemical and physical characteristics. This factorial design resulted in four categories of lakes: N-limited impact (NI) lakes, P-limited impact (PI) lakes, N-limited reference (NR) lakes, and P-limited reference (PR) lakes (Table 1). Based on the study design, disproportionate changes in scaled chrysophytes within NI lakes would suggest that N deposition is impacting primary production in these lakes, whereas a similar change in all lakes, irrespective of group, would suggest a response to a regional forcing factor such as warming.

Study lakes and regional site description

The 16 study lakes from the four a priori groups (NI, PI, NR, PR) are mostly small (<100 ha) with the

exception of 2F, 9C, 10Y and 13N, which are closer to ~150 ha. Maximum depth (z_{max}) ranged from 3.8 to 28.7 m (Table 1). Lakes are circumneutral (mean pH 7.1; median pH 7.1; range 6.8–7.3), relatively low in nutrients (mean total phosphorus = $10.1 \mu\text{g L}^{-1}$; median = $10.9 \mu\text{g L}^{-1}$; range 3.3–18.0 $\mu\text{g L}^{-1}$), have low to moderate concentrations of DOC (mean DOC = 4.1 mg L^{-1} ; median = 3.8 mg L^{-1} ; range 1.6–7.1 mg L^{-1}), moderate to high alkalinity (mean = 10.5 mg L^{-1} ; median = 8.1 mg L^{-1} ; range 4.2–18.1 mg L^{-1}), and low specific conductivity (mean = $23.4 \mu\text{S cm}^{-1}$; median = $20.0 \mu\text{S cm}^{-1}$; range 13.8–35.5 $\mu\text{S cm}^{-1}$) (Table 1). Interannual variation in nutrient chemistry is presented in Electronic Supplementary Material (ESM) Table S1.

Impact sites are clustered along a northwest-southeast transect that spans ~170 km, with lakes located ~150–200 km east of Fort McMurray (Fig. 1). Reference lakes are clustered ~320 km northeast and ~300 km due east of Fort McMurray.

Table 1 Physical and chemical variables of the sixteen study lakes in northwest Saskatchewan

Lake	Collection date	Surface area (ha)	Coring depth (m)	pH	Alk (mg L ⁻¹)	Specific conductance (μS cm ⁻¹)	DOC (mg L ⁻¹)	Chl- <i>a</i> (μg L ⁻¹)	TN (μg L ⁻¹)	TP (μg L ⁻¹)	DIN:TP	Mean DIN:TP	pCO ₂
<i>N-limited</i> (DIN:TP < 3.4), <i>impact</i>													
9C	2007	155	10.5	7.10	15.0	33.0	1.8	7.3	266	18.0	1.4	–	974
10Z	2007	43	10.9	7.18	16.6	34.4	3.4	5.4	380	10.0	2.7	–	969
10E	2007	23	6.3	7.26	18.1	35.5	3.5	3.9	329	12.0	2.8	–	881
10Y	2007	170	6.5	7.15	17.2	33.7	4.7	6.8	532	12.0	3.3	–	1053
6E	2007–2011	18	6	7.27	16.5	33.4	3.4	6.1	315	16.5	3.3	2.7	942
<i>P-limited</i> (DIN:TP > 7), <i>impact</i>													
10A	2007–2011	38	9.5	7.11	10.0	23.6	4.6	2.6	246	5.5	8.2	–	739
13L	2008–2011	88	20.3	6.97	6.6	17.2	1.6	1.5	112	3.3	11.1	–	707
13N	2008–2011	150	12.2	7.13	11.6	27.2	7.1	3.1	253	5.0	13.4	–	730
11G	2007–2011	41	18.1	6.98	7.7	21.4	6.5	1.3	225	5.7	18.7	12.9	606
<i>N-limited</i> (DIN:TP < 3.4), <i>ref</i>													
17V	2008–2011	62	5.4	7.08	7.5	16.9	3.4	5.4	290	14.0	2.8	–	590
2F	2007–2011	129	7.5	6.94	7.3	17.7	4.0	4.7	279	11.8	3.0	–	695
2Q	2008–2011	60	9.8	6.96	6.2	13.8	4.2	4.4	361	12.0	3.3	–	693
17I	2007–2011	9	7.4	6.93	7.0	17.0	2.7	6.2	210	14.3	3.6	3.2	772
<i>P-limited</i> (DIN:TP > 7), <i>ref</i>													
17P	2008–2011	63	7.4	6.77	4.2	14.1	7.1	2.0	253	7.7	7.8	–	474
17F	2007–2011	21	7.9	7.04	7.8	17.6	4.4	3.2	299	6.5	7.8	–	624
2L	2008–2011	68	5.1	7.15	8.1	17.6	3.7	2.1	244	7.3	12.5	9.4	544

Lakes are organized by a priori groups identified by the factorial study design (*ref* reference lake). *Alk* alkalinity, *DOC* dissolved organic carbon, *Chl-*a** chlorophyll *a*, *TN* total nitrogen, *TP* total phosphorus, *DIN:TP* dissolved inorganic nitrogen to total phosphorus. No water chemistry data were collected from any of the lakes in 2010. Water chemistry was not surveyed in Lake 11G in 2008

Most study lakes are located in the Boreal Shield ecozone, with the exception of 10Z, 10E, 6E and 10A, which are located in the Boreal Plains ecozone. The portion of Boreal Shield in our study region is characterized by areas of exposed Precambrian crystalline bedrock with thin layers of overlying glacial till, glaciofluvial and glaciolacustrine deposits, and areas with a layer of younger sandstones, less basement rock exposure and thicker glacial deposits in the northern reaches near Lake Athabasca (Scott et al. 2010). Brunosolic soils are common in the study region, and luvisolic soils are found on silty and clayey glaciolacustrine deposits. Vegetation in the study region consists of jack pine (*Pinus banksiana*)/lichen forest with balsam fir (*Abies balsamea*) and trembling aspen (*Populus tremuloides*) in well drained mineral soils, and black spruce (*Picea mariana*) in poorly drained regions. Regional climate is characterized as ‘subarctic.’ Mean annual air temperature and precipitation recorded in nearby Fort McMurray is 1.2 °C and 487 mm (average 1980–2014), respectively. Mean winter and summer temperatures are –15.0 and 15.9 °C, respectively (average 1980–2014). In addition, mean annual air temperature in Fort McMurray has increased by ~2.3 °C since the early 1900s (ESM Fig. S1).

Sediment coring

Sediment cores were collected in February and April of 2014 from near the centre of most lakes using a Glew gravity corer (Glew et al. 2001) with an internal diameter of ~7.6 cm. Cores from all sites were sectioned into 0.5-cm intervals and placed into individual Whirlpak® bags. Sediments were shipped to Queen’s University where they were stored in a dark cold room (set to 4 °C) until processed for sediment analyses.

Core chronologies

²¹⁰Pb dating was carried out on sediment cores from all study lakes via gamma spectroscopy at the Paleoeological Environmental Assessment Research Laboratory (PEARL), Queen’s University, using procedures similar to Schelske et al. (1994). Samples for ²¹⁰Pb analysis were spaced at 1-cm intervals for the top 10 cm of each core and at 2-cm intervals thereafter. Sediment samples were freeze-dried,

packed into plastic tubes to ~2 cm height, sealed with 2-Ton epoxy and allowed to equilibrate (²¹⁴Bi to ²²⁶Ra) for at least two weeks. Radioactive decay was measured for 80,000 s using an Ortec germanium (Gr) crystal, well detector. Activities of total ²¹⁰Pb, ¹³⁷Cs and supported ²¹⁰Pb (via ²¹⁴Bi) were determined for each sample based on calibration to internal standards IAEA 312 and 385, and adjusted for sample heights in tubes, which varied from 1 to 4 cm. Chronologies were estimated based on unsupported ²¹⁰Pb activities, using the constant rate of supply (CRS) model in the ScienTissiME program (Mike Scheer, unpublished). Age-depth models were calculated in R version 3.1.2 (R Development Core Team 2010) using a cubic spline with a monotonicity constraint. The monotonic cubic spline does not force any specific polynomial form to the age model, and the monotonicity prevents reversals in depth-age relationships among adjacent samples.

Scaled-chrysophyte analysis

For each sample, ~0.2–0.3 g of wet sediment was subsampled into a 20-mL glass vial. A 50:50 molar mixture of concentrated sulfuric and nitric acid was added and heated in a hot water bath at ~75 °C for 7–8 h to remove organic matter. After settling for 24 h, the samples were aspirated to ~5 mL and then rinsed with double deionized water. This procedure was repeated until the sample reached the same pH as the double deionized water (7–8 rinses). The samples were then drawn down to ~5 mL. A known volume of microspheres (concentration = 2.0×10^7 spheres mL⁻¹) was added to each sample to allow calculation of scaled-chrysophyte concentrations. Four successive dilutions for each sample were pipetted onto coverslips and were allowed to air-dry overnight. The coverslips were then heated on a warming plate to remove any remaining moisture, and permanently mounted onto glass microscope slides using Naphrax®.

Chrysophyte scales and diatoms were enumerated on the same slides with a Leica DMRB microscope and a 100× oil immersion objective (numerical aperture = 1.3) using differential interference contrast optics at 1000× magnification. Because of the low concentration and diversity of chrysophyte scales in most samples, for calculations of relative abundance, at least 100 scales were counted. Counts of

species composition were discontinued when <15 scales were counted on a single transect. Taxonomic identification of scales was based on standardized taxonomic literature including Nicholls and Gerrath (1985) and Siver (1991), and an unpublished reference collection at the PEARL lab. Chrysophyte concentrations were calculated relative to the artificial microspheres, following Battarbee et al. (2001). The scale-to-diatom index (S-to-D index) was calculated according to: $[\text{number of scales}/(\text{number of scales} + \text{number of diatom valves})] \times 100$, based on counts of at least 400 diatom valves.

Organic carbon content

Sediments were analyzed for percent organic carbon (%C) to assess major changes in sedimentation regimes or sediment in-wash events. Samples of 40–60 mg mass were first acidified to remove carbonate minerals by repeated exposure to 0.3 M HCl. After acidification, sediments were washed with nanopure H₂O until the pH was the same as that of the rinse water. Carbon content of acidified sediments was quantified by combustion, following methods of Savage et al. (2004). All elemental analyses were conducted at the Institute of Environmental Change and Society (IECS), University of Regina.

Statistical methods

Non-metric multidimensional scaling (nMDS) was used to reduce the complexity of the lake physical and chemical environmental data (Clark and Warwick 2001), and assess the overall relative similarity of the sixteen study lakes in two-dimensional (2D) ordination space. nMDS was based on a distance matrix using Euclidean distances, which is appropriate because the dataset did not include null values. The nMDS was performed using the R programming language (version 3.1.2; R Development Core Team 2010) with the *vegan* package (Oksanen et al. 2016), using square root-transformed physical and chemical environmental variables.

The ratio of chrysophyte scales to diatoms (S-to-D index) was used to quantify the historical changes in the abundance of scaled chrysophytes. Additionally, because chrysophytes are planktonic, the S-to-D index can indicate a general change in the planktonic community. The S-to-D index is also advantageous

because it is independent of sedimentation rates (Smol 1985). However, because both the numerator and denominator can affect the ratio, Pearson correlation coefficients were calculated for each core to assess how changes in sedimentary concentrations of chrysophyte scales affected the S-to-D index. Significant and positive correlations between the two metrics were interpreted to indicate that fluctuations in chrysophyte abundance are regulating variation in the S-to-D index.

Generalized additive models (GAMs) were used to test whether changes in gross composition of siliceous algae (S-to-D index) exhibited common trends through time within each of the four lake groups (NI, PI, NR, and PR). Two classes of GAMs were evaluated; a *lake* model that evaluated whether changes in the S-to-D index were lake-specific, and a *factorial* model that assumed four lake-response groups according to the factorial study design (N- and P-limited; impact and reference). The *lake* model consisted of a global thin plate spline (TPS) to capture the common trend across all sites, plus separate lake-specific splines that capture the deviations from the common trend by placing the smoothness penalty on the first derivative of these splines. The *factorial* model replaces the lake-specific splines with separate TPSs for each lake response group, but still assumes that lakes within each response group all follow the same common trend. The relative fit of *lake* and *factorial* models was evaluated based on degrees of freedom (DF) and the Bayesian Information Criterion (BIC). Overall, the model with the lowest BIC value is considered to perform best. Models were fitted using the R programming language (version 3.1.2; R Development Core Team 2010) with the *mgcv* package (Wood 2011, 2016).

Lastly, an additional exploratory analysis was undertaken to explore the relationship between scaled-chrysophyte abundance and the physical and chemical characteristics of the lakes. To do this, the maximum scale concentration in the top of each sediment core was classified as high, medium, or low. Sites that exceeded concentrations of 300 scales g⁻¹ dry wt⁻¹ were classified as high (9C, 17P, 17F), sites that had concentrations between 30 and 300 scales g⁻¹ dry wt⁻¹ were classified as medium (2Q, 13L, 13N and 6E), and sites that did not exceed 30 scales g⁻¹ dry wt⁻¹ were classified as low (17J, 2F, 11G, 17V, 10A, 2L, 10E, 10Y and

10Z). A canonical variate analysis (CVA) was then performed to identify environmental variables that could separate the three a priori defined groups of chrysophyte scale abundance. CVA was run in CANOCO v.5 using forward selection (ter Braak and Šmilauer 2012). Environmental variables were log transformed if appropriate.

Results

Lake selection

The selection of the majority of the study lakes was based on two or more water chemistry samples, with only four of our study lakes based on a single sample (9C, 10Z, 10E and 10Y). Non-metric multidimensional scaling (nMDS) ordination of the physical and chemical variables of the study lakes confirmed that the DIN:TP ratio was a central variable separating the lakes in ordination space, regardless of the designation as an impact or reference site. The impact and reference N-limited lakes plot to the left side of the ordination, whereas the P-limited sites plot to the right side (Fig. 2). Within the nMDS, the physical and chemical characteristics of the reference and impact sites overlap (Fig. 2).

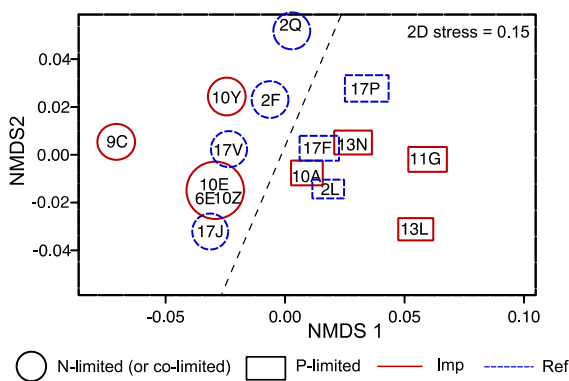


Fig. 2 Non-metric multidimensional scaling (nMDS) of physical and chemical variables for the sixteen study lakes in northwest Saskatchewan. Nutrient limitation status and impact/reference designation according to the factorial study design are also indicated. The *dashed line* in the centre of the ordination shows the separation between N-limited and P-limited lakes. *Imp* impact lakes, *Ref* reference lakes

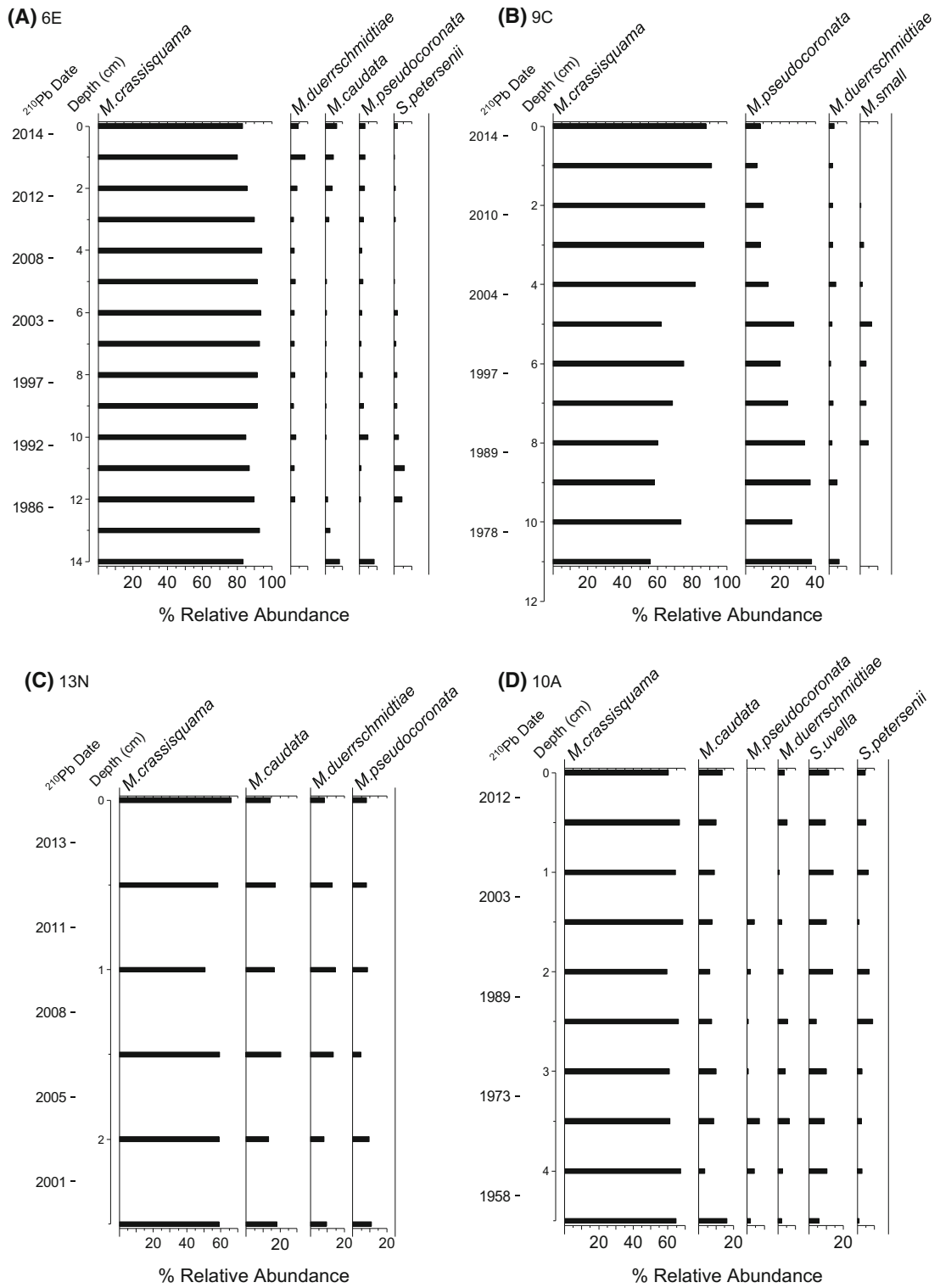
Fig. 3 Stratigraphies of scaled-chrysophyte relative abundances in eight of the sixteen study lakes in northwest Saskatchewan. Lakes are ordered by the four a priori lake groups identified by the factorial study design. **a, b** N-limited or N and P co-limited reference lakes (*NI* lakes). **c, e** P-limited reference lakes (*PI* lakes). **f** N-limited or N and P co-limited reference lake (*NR* lake). **g, h** P-limited reference lakes (*PR* lakes)

Core chronologies

The majority of cores showed good ($0.8 < r^2 < 0.9$) to very good ($r^2 > 0.9$) first order exponential decay of total ^{210}Pb activity (ESM Fig. S2). Lakes 10E, 10Y and 2L are exceptions as their r^2 values are lower, at 0.69, 0.74 and 0.69 respectively. In addition, the relationship between log unsupported ^{210}Pb and cumulative dry mass was strong for most lakes ($r^2 = 0.77\text{--}0.96$) suggesting strong chronologies could be developed. Two lakes (2L and 10E) had weaker relationships with $r^2 = 0.53$ and 0.56 respectively, suggesting chronologies for these lakes need to be interpreted with more caution. Background (supported) levels of ^{210}Pb were reached at a range of depths in the sixteen sediment cores: 25–35 cm (2F, 2Q, 6E, 10E), 15–25 cm (2L, 9C, 17J, 17V) and 5–15 cm (10A, 11G, 13L, 13N, 17F, 17P). Lake 10Y did not reach background levels of ^{210}Pb until 40 cm. The majority of lakes had sufficient sedimentation rates to achieve the desired decadal to sub-decadal temporal resolution since ~ 1900 for scaled-chrysophyte analysis, with analysis undertaken at either 0.5-cm or 1-cm intervals. Two exceptions were Lakes 17P and 17F, which had lower sedimentation rates and a temporal resolution closer to only $\sim 12\text{--}15$ years was possible. Some cores showed evidence of increased sedimentation and/or mixing in the uppermost samples (e.g. Lakes 6E, 10E, 10Y and 2F), however there are at least two cores in each of the four a priori lake groups with little evidence of potential mixing, suggesting that the timing of changes should be accurately represented across all groups (ESM Fig. S2).

Scaled-chrysophyte species assemblages

Sediment cores from eight of the sixteen lakes had sufficient concentrations for enumeration and identification of scaled chrysophytes to the species level: 6E and 9C (NI lakes), 10A, 13N and 13L (PI lakes), 2Q



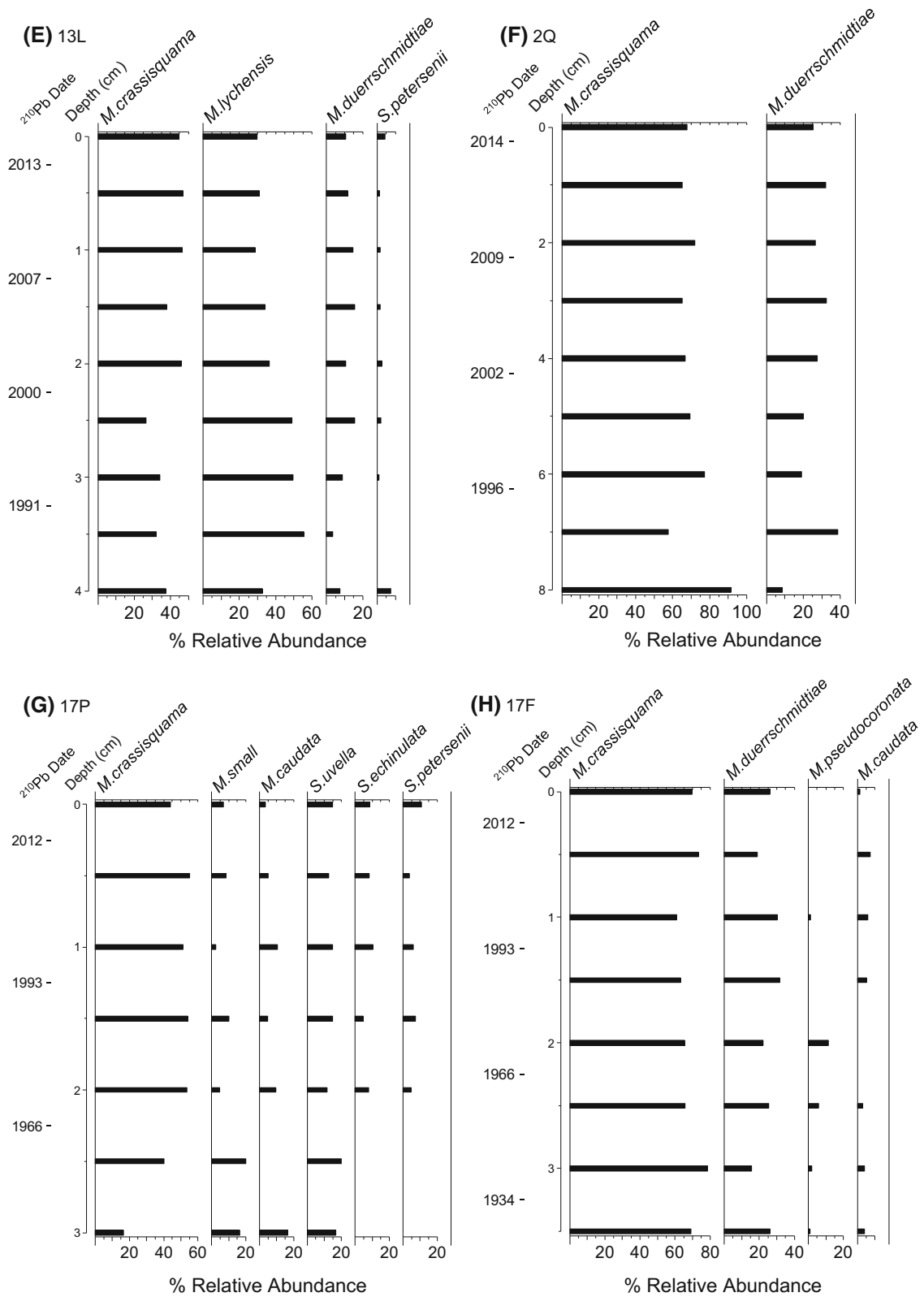


Fig. 3 continued

Table 2 Model summary for the factorial generalized additive models (GAMs) for the S-to-D time-series data, and results from the model selection process

Covariate	EDF	Ref.df	F	<i>p</i> value
<i>Factorial model</i>				
NI	3.26	3.81	7.13	<0.05
NR	1.50	1.65	8.96	<0.05
PI	1.49	1.65	5.29	<0.05
PR	1.32	1.45	3.08	<0.1
Lake	51.94	140.00	6.61	<0.05
Model	DF	BIC	LL	Deviance explained
<i>Model selection</i>				
Factorial	67.99	1328.05	−465.87	86
Lake	62.00	1304.31	−471.46	85.5

For each smoothing term, *EDF* effective degrees of freedom, *Ref.df* reference degrees of freedom, *F* F-statistic, and *p* value are shown. The Lake term is treated as a random effect. Model selection shows *DF* degrees of freedom, *BIC* Bayesian Information Criteria, *LL* log-likelihood, and deviance explained by each model

(NR lake), and 17P and 17F (PR lakes). A total of 15 scaled-chrysophyte taxa were identified throughout these sediment cores, and were predominantly taxa of the unicellular genus *Mallomonas*. *M. crassisquama* (Asmund) Fott was the predominant taxon in all cores, exhibiting relative abundances ranging from 40 to 90% (Fig. 3). In Lake 13L, which is one of the deepest lakes in this study ($z_{\max} = 26.2$ m), *Mallomonas lychensis* Conrad was the main scaled-chrysophyte taxon, accounting for ~40% of the assemblage. Other common *Mallomonas* included *M. duerrschmidtiae* Siver, Hamer and Kling, *M. pseudocoronata* Prescott and *M. caudata* Ivanov. Taxa of the colonial genus *Synura* were only seen in some cores (6E, 10A, 13L, 17P) at low relative abundances (<15%), with the exception of 17P which included *S. uvella* Ehrenberg as ~20% of the assemblage in some intervals (Fig. 3).

Chrysophyte species composition changed little since ca. AD 1900 in most lakes (Fig. 3). One exception, Lake 9C, exhibited a decline in *M. pseudocoronata* from ~40% relative abundance ca. AD 1980 to ~5% after ca. AD 2001. Lake 13L also showed a decline in *M. lychensis* post ca. AD 2000 (Fig. 3). In contrast, total concentrations of fossil scales increased in most cores (ESM Fig. S3), although the absolute magnitude and timing of the increases varied among sites. Scale concentrations were highest in the top of 9C and 17P, near 500×10^7 scales g^{-1} dry weight, whereas the maximum scale

concentration in 10A was 25×10^7 scales g^{-1} dry weight. Maximum scale concentrations in the other five cores ranged from 140 to 300×10^7 scales g^{-1} dry weight (ESM Fig. S3). Overall, scale concentrations were significantly ($p < 0.001$) and positively correlated ($0.78 < r^2 < 0.98$) to changes in the S-to-D index in all lakes.

Percent organic carbon

Organic C content ranged between 10 and 45% among lakes (ESM Fig. S3). There were no consistent temporal changes in %C in any lake group during the twentieth century, with the exception of three of the PI lakes (10A, 13N and 11G), which showed a trend towards lower %C in the recent sediments. In addition, some sites exhibited highly variable carbon content (6E, 10E, 17V), whereas others showed little fluctuation through time (e.g. 2Q, 17P, 17F).

Generalized additive models (GAMs)

The *factorial* model indicated that historical changes in the S-to-D index were significant across all lake groups ($\alpha < 0.05$), with the exception of the PR group ($0.05 < \alpha < 0.1$) (Table 2). The GAM smoothers extracted from each lake group (i.e. the common trends) also indicated that the S-to-D index increased significantly in each of the four lake groups (ESM Fig

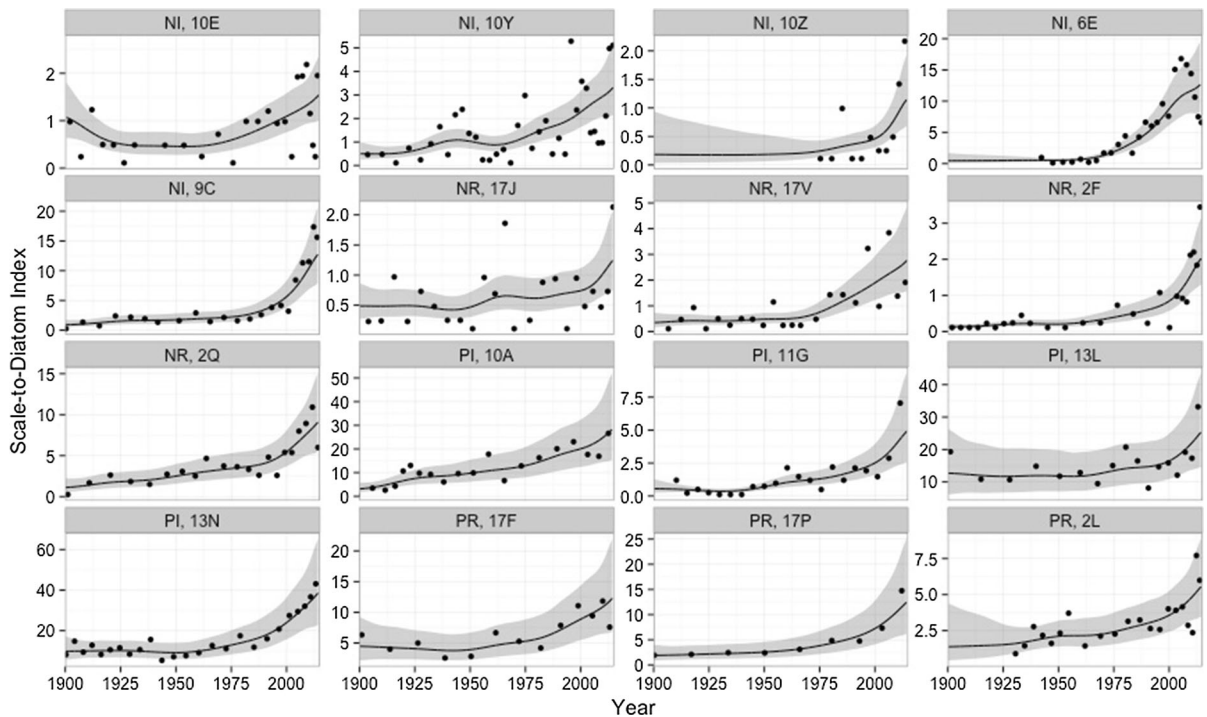


Fig. 4 Predicted change through time in the S-to-D index under the *Lake* model. Individual points in each plot show the observed S-to-D index value. Lakes are ordered by lake category: *NI* N-limited impact lakes *NR* N-limited reference

lakes *PI* P-limited impact lakes *PR* P-limited reference lakes. The shaded region in each plot represents the 95% confidence intervals. Note that the y-scale varies among plots

S4). Model evaluation indicated that the *lake* model explained a similar amount of variation as the *factorial* model (85.5 and 86%, respectively), while using fewer degrees of freedom (62.0 and 68.0, respectively). The *lake* model also had a lower BIC than the *factorial* model (1304 and 1328, respectively) (Table 2). The change through time in the S-to-D index predicted by GAM smoothers in the *lake* model indicated coherent late twentieth century (ca. AD 1980) increases in chrysophyte abundance in the majority of the sixteen study lakes, though the magnitude of the increase varies among lakes (Fig. 4).

Exploratory CVA

CVA explained 71% of the variance in the concentration of chrysophyte scales in surface sediments on the first two axes ($\lambda_1 = 0.60$, $\lambda_2 = 0.11$). Maximum lake depth (z_{\max}) was the only significant physical/chemical variable that could distinguish among lakes on the basis of surface sediment scale concentrations (low, medium, high). CVA with depth explained 25.4% of

the variation in scale concentrations ($p = 0.01$). Although pH also explained 10.2% of scale density variation, the prediction was not statistically significant ($p = 0.14$), but it was retained in the CVA ordination as an active explanatory variable. Overall, medium ($30\text{--}300 \times 10^7$ scales g^{-1} dry wt) and high ($>300 \times 10^7$ scales g^{-1} dry wt.) chrysophyte abundances tended to occur in deeper (mean $z_{\max} = 14.1$ m) and circumneutral lakes (mean pH ~ 7). Lakes identified as those with low chrysophyte abundance (<30 scales g^{-1} dry wt) tended to be shallower (mean $z_{\max} = 7.9$ m) and slightly higher pH lakes (mean pH 7.1), though the pH gradient is short.

Discussion

Analysis of historical changes in the species composition and abundance of scaled chrysophytes revealed increases in production of this phytoplankton group during the twentieth century, irrespective of the reference or impact or N- or P-limited lake grouping.

In all lakes, *M. crassisquama* was the dominant taxon, a species that is common in many lakes because it occurs across a large range of important environmental variables, including nutrients, temperature, and pH (Siver 1991, 1995). In addition, there was very little change in the historical composition of scaled-chrysophyte assemblages (Fig. 3). Instead, marked increases in chrysophyte abundance occurred in the majority of study lakes and across all four a priori groups during the last half of the twentieth century (Fig. 4). Together, these patterns suggest that chrysophyte communities were not responding to the deposition of N from the AOSR. Rather, the spatially coherent increases in the abundance of scaled chrysophytes in the recent sediments in a number of the study lakes (Fig. 4, ESM Fig. S4) are more consistent with the operation of a regional control, such as atmospheric warming or changes in hydrology.

N deposition and chrysophyte ecology

Chrysophytes are often considered to be more competitive in nutrient-poor water because of their small size and large surface area to volume ratio (Sandgren 1988; Siver 1995). For example, in a survey of 15 unproductive lakes in Wyoming, United States, chrysophytes were shown to prefer low-N conditions, as they accounted for a higher proportion of the total algal assemblage in lakes with low N concentrations than in lakes with high N concentrations (Lafrancois et al. 2003). In addition, N additions to mesocosm experiments in nitrate-poor lakes of the Colorado Front Range initiated a shift in phytoplankton species from chrysophytes towards chlorophytes, cyanophytes and diatoms (Baron et al. 2005). A number of other lake surveys have also associated chrysophytes with low nutrient conditions (Schindler and Holmgren 1971; Eloranta 1986; Siver and Chock 1986). Given their preference for oligotrophic conditions, the historical increase in scaled chrysophytes in our study lakes is inconsistent with the effects of fertilization through N deposition (Fig. 4, ESM Fig. S3). This qualitative interpretation of the scaled-chrysophyte abundance data is also supported by the results from the GAM analysis, which indicated that gross changes in the abundance of chrysophytes (as S-to-D index) changed significantly in three of four lake impact groups, with the exception of the PR group ($0.05 < \alpha < 0.1$), in the late twentieth century

(Table 2, ESM Fig. S4). Nevertheless, because the GAM model selection process also indicated that lake-specific models best explained variation in the S-to-D index (lower BIC), we infer that climate effects may be moderated through differences in site-specific characteristics, such as lake morphology (Kraemer et al. 2015) or catchment filter characteristics (Blenckner 2005; Leavitt et al. 2009).

We also infer that deposition of N from the AOSR did not alter chrysophyte abundance via indirect biogeochemical mechanisms. For example, acidic deposition can increase the availability of Al and Fe minerals in soils, and consequently increase P adsorption, thereby reducing P export to lakes and streams (McDowell et al. 2002). A recent study by Arseneau (2014) suggested that the oligotrophication of lakes in the Adirondack (NY) region as a result of this process may have played a role in changing scaled-chrysophyte assemblages since ca. AD 1900. Although enhanced terrestrial P adsorption caused by soil acidification and subsequent declines in lake-water P may be favourable for scaled-chrysophyte production, this is an unlikely mechanism in northern Saskatchewan lakes, as multiple paleolimnological investigations in the AOSR and northern Saskatchewan provide little evidence of widespread acidification (Hazewinkel et al. 2008; Curtis et al. 2010; Laird et al. 2013). The reason for lack of acidic-deposition-related effects in the study lakes is uncertain, although it has been suggested that deposition of base cations from atmospheric sources may neutralize the effects of acid influx (Watmough et al. 2014).

The limited response of scaled chrysophytes to deposition of AOSR-derived N may arise because N influx to northwest Saskatchewan is less than that required to initiate a critical ecosystem change. Saros et al. (2011) determined that a critical load of 1.4 kg N ha⁻¹ year⁻¹ of wet N deposition was required to elicit changes in diatom production in response to nutrient enrichment in alpine lakes of the western United States. Additionally, Baron (2006) used a combination of fossil diatom analysis and hindcast models to estimate that the critical threshold for diatom community change was also ~ 1.5 kg N ha⁻¹ year⁻¹ in the Colorado Front Range. In contrast, recent work by Fenn et al. (2015) showed that deposition of DIN from the AOSR declined exponentially with distance from the industrial center near Fort McMurray (Fig. 1), and reached values of 1.1 and 1.2 kg ha⁻¹ year⁻¹ (canopy

and open sites, respectively) at a downwind distance similar to that of our study sites (110–130 km). These measurements are somewhat lower than the previous estimates of critical nitrogen deposition loads to elicit algal responses in the western United States (Baron 2006; Saros et al. 2011). In addition, the alpine regions of the western United States are characterized by little upstream vegetation and steep topography, which create low saturation and leaching thresholds. In contrast, northwest Saskatchewan is relatively heavily forested and has low relief, and may be efficient at storing additional N and preventing further leaching into water bodies. Finally, consistent with the hypothesis that chrysophytes are not responding to N deposition, we note that increases in algal abundance also appear to occur before the substantial increase of N emissions in the 1990s in a number of the lakes (Fig. 4, ESM Fig. S3).

Climate change

Increases in scaled chrysophyte microfossils (stomatocysts and scales) and major assemblage changes have been observed during the twentieth century in many regions, including the mid and high Arctic (Wolfe and Perren 2001; Wolfe and Siver 2013), eastern Canada (Ginn et al. 2010), subarctic and Boreal regions (Laird et al. 2013; Wolfe and Siver 2013), and south-central and northern Ontario (Pater-son et al. 2004; Flear 2011). Such regional changes are often associated with reorganization of climate systems, although the precise mechanism underlying the change is either unknown or may vary among regions.

Climate change, including regional warming, may favour increased abundance of scaled chrysophytes in northern Saskatchewan. Temperature records from Fort McMurray indicate that mean annual air temperatures have increased by ~ 2.3 °C since the early 1900s (ESM Fig. S1). Warming can change the timing of ice-out on lakes and create longer and stronger periods of thermal stratification, ultimately resulting in changes in algal production and composition (Adrian et al. 2009). These conditions may provide motile (flagellated) algae, such as chrysophytes, a competitive advantage over non-motile algae because they can seek out optimal temperature, nutrient and light conditions within the water column (Winder and Sommer 2012). Under more mixed conditions, this advantage is reduced as non-flagellated algae,

including diatoms, have the ability to remain suspended in the water column and compete for light and nutrients. Our CVA of surficial sediment scale concentrations (high, medium, low) also identified maximum water depth as the only significant variable separating these three groups. This pattern is consistent with effects of regional warming as a driver of chrysophyte population expansion because deeper lakes may be less prone to wind-induced mixing, and are expected to experience the largest changes in thermal stability in response to warming (Adrian et al. 2009; Kraemer et al. 2015).

In general, our findings are consistent with those of Laird et al. (2013) and Wolfe and Siver (2013) who also documented marked post ca. 1980 increases in *Mallomonas* scales from lakes in northern Alberta and northern Saskatchewan. The consistency in the timing of increased chrysophyte abundance across this region further suggests a regional stressor, such as climate, as a driver of these changes (Fig. 4). We note, however, that lake morphometry may have interactive effects with climatic mechanisms, as chrysophytes in deep, circumneutral lakes showed a larger response than chrysophytes in shallow, more alkaline systems. Additionally, as noted by Blenckner (2005), individual lake catchments may act as site-specific filters of climatic forcing, resulting in response differences of individual basins to a common forcing mechanism. It is difficult, however, to identify which catchment features might be acting as climate filters, and we recommend further analysis of a larger number of lakes.

Regional increases in the abundance of scaled chrysophytes may also reflect regulation by other climatic mechanisms. For example, Wolfe and Siver (2013) suggested that increased $p\text{CO}_2$, arising from elevated lake temperatures, DOM influx, or atmospheric CO_2 content may favour the production of chrysophytes, which do not possess the carbon-concentrating mechanism that is needed to compete with other algae in low- CO_2 environments (Raven et al. 2005). Although the number of study lakes in the current investigation is low, we currently do not favour this explanation for chrysophyte population expansion because scale concentrations in modern sediments are unrelated ($r = 0.39$, $p > 0.1$) to modern $p\text{CO}_2$ in our lakes, even when calculated using the same methods as Wolfe and Siver (2013). Similarly, although regional changes in seasonal precipitation may

influence lake ecosystems, we currently lack basin-specific data on runoff processes. To address this issue, future studies will use stable isotopes to evaluate historical changes in regional hydrology (McGowan et al. 2011).

Representation and interpretation of microfossils

In principle, the abrupt increases in chrysophyte concentrations in recent decades in many of the lakes could arise from diagenetic dissolution of siliceous remains. Poor preservation of siliceous microfossils is sometimes recorded in lakes with high pH or salinity (Barker et al. 1990). This mechanism, however, appears unlikely in these dilute lakes, as scales were well preserved throughout the sediment cores from all sites and showed few signs of pitting or disarticulation, even within the lightly silicified components of some scales (e.g. anterior wing on *M. pseudocoronata*). Similarly, there was little evidence of diagenetic dissolution in diatoms, and a well-preserved flora existed prior to the increase in scale abundance in our cores (Laird et al. 2017). If dissolution and poor preservation of the microfossils was a factor, the chrysophytes and the diatoms should both be affected.

Changes in sedimentation, such as a large influx of allochthonous material and changes in sediment accumulation rates can also influence the accumulation of microfossils in sediments (Battarbee et al. 2001). Estimates of organic carbon were used as an additional independent line of evidence of changes in sedimentation in our study lakes, and were plotted with chrysophyte scale concentrations to facilitate comparison (ESM Fig. S3). Although some profiles are highly variable through time (e.g. 17V and 10Y), there are no consistent directional trends in C content, suggesting that changes in organic sedimentation are likely not a controlling factor on chrysophyte scale concentration. Therefore, the recent increases in scaled-chrysophyte abundance is not considered to be an artifact of poor preservation and/or changes in sedimentation, but rather a reflection of other important limnological variables that are responding to environmental change.

Conclusions

This investigation was the first to study potential nutrient enrichment effects on chrysophyte production

from N deposition in lakes downwind of the AOSR in northwest Saskatchewan. Application of a factorial design and GAM analysis demonstrated that chrysophyte populations in northwest Saskatchewan lakes are presently not responding to enhanced N deposition. Instead, we find that increases in scaled chrysophytes observed in the majority of the lakes across the study region are more consistent with a regional forcing mechanism, such as changes in lake warming in response to atmospheric warming. The significant relationship between fossil scaled-chrysophyte abundances in recent sediments and lake depth identified in a canonical variate analysis (CVA) provides further evidence that regional (climatic) processes, in combination with a lake-specific response, may be regulating chrysophyte production. Together, these findings suggest that emissions from industrial activity in the AOSR are not currently having a detectable influence on siliceous primary producers in downwind lakes of northwest Saskatchewan. Monitoring should continue in this region to identify potential future industrial influences as well as climate-related impacts.

Acknowledgements We thank Steve Wilke for assistance in the field, and our helicopter pilot Shane O’Neil from Star Helicopters. Funding was provided by Canadian Network for Research and Innovation in Machining Technology, Natural Sciences and Engineering Research Council of Canada (Grant Nos. STPGP/447139-2013), Environment Canada, Saskatchewan Ministry of Environment, Saskatchewan Water Security Agency

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