Scaled-chrysophyte assemblage changes in the sediment records of lakes recovering from marked acidification and metal contamination near Wawa, Ontario, Canada

Christine M. GREENAWAY,1 Andrew M. PATERSON,2* Wendel (Bill) KELLER,3 John P. SMOL1

1Queen’s University, Paleoecological Environmental Assessment and Research Laboratory, Department of Biology, Kingston, Ontario, K7L 3N6, Canada; 2Ontario Ministry of the Environment, Dorset Environmental Science Centre, 1026 Bellwood Acres Road, P.O. Box 39, Dorset, Ontario, P0A 1E0, Canada; 3Laurentian University, Cooperative Freshwater Ecology Unit, Sudbury, Ontario, P3E 2C6, Canada

*Corresponding author: andrew.paterson@ontario.ca

ABSTRACT

A remarkable example of point-source lake acidification and metal pollution, and subsequent recovery in water quality, has occurred in lakes near the former iron sintering plant at Wawa (Ontario, Canada). Surface water pH levels in some of these lakes have increased from three to seven following local sulphur emission reductions and eventual closure of the sintering plant. Previous paleolimnological work documented striking successional changes in diatom species assemblages within dated sediment cores that could be related to past industrial activities. To gain additional insights into the chemical and biological recovery trajectories of the Wawa lakes, we used paleolimnological techniques to track euplanktonic scaled-chrysophyte (classes Chrysophyceae and Synurophyceae) species assemblage responses to historical water quality changes in five lakes. Coincident with the period of iron sintering from 1939 to 1998, striking successional changes were noted in the sedimentary profiles, with marked increases in the relative abundances of the acid- and metal-tolerant taxon Synura echinulata. The scaled chrysophyte changes pre-dated diatom responses, confirming the former’s status as reliable early warning indicators of lake acidification. Following closure of the sintering plant, species-specific chrysophyte responses to decreased emissions varied amongst the study lakes, perhaps reflecting differences in local bedrock geology and hydrological regime. Although some water chemistry variables may have recovered to near pre-industrial levels, similar to the diatom study, our data show that chrysophyte assemblages in the most recent sediments are now significantly different from pre-industrial assemblages.

Key words: Paleolimnology, chrysophytes, acidification, lakes, mining.

Received: January 2012. Accepted: May 2012.

INTRODUCTION

Sintering of low-grade siderite commenced in 1939 at a plant two kilometers northwest of Wawa (Ontario, Canada). Sulphur dioxide emissions increased steadily from 1939 to 1973, when they peaked at >250,000 tonnes per year (Rowe, 1999). By the 1950s, a teardrop-shaped fume-kill area had developed northeast of the sinter plant in the direction of predominant winds (Gordon and Gorham, 1963). Despite the presence of carbonate-bearing bedrock within some lake catchments, the acid neutralizing capacity of some lakes was exceeded. Acidified lakes reached extremely low pH values of less than four, while surrounding lakes remained near neutral (Gordon and Gorham, 1963; Rao and LeBlanc, 1967; Somers and Harvey, 1984).

Following a reduction of emissions since 1973, and final closure of the iron sintering plant in 1998, several lakes near Wawa showed signs of rapid chemical and biological recovery from acidification and metal-contamination (2003-2005, D.A. Jackson, University of Toronto, Ontario, unpublished data). Striking increases in pH and alkalinity, as well as decreases in SO4, Al, Fe and Mn concentrations, indicate that major changes in water chemistry have occurred since the late 1970s (Greenaway et al., 2012). These lakes provide a unique opportunity for studying biological recovery patterns in an area with a naturally-occurring high buffering capacity. They also provide an interesting comparison with the striking changes occurring in softwater lakes near Sudbury (Ontario), following marked declines in point-source deposition from the local copper and nickel smelting activities (Gunn, 1995).

Previous paleolimnological research showed that stratigraphically-preserved diatom microfossils in the sediment records of five lakes in the fume-kill area near Wawa have responded to both marked acidification and to chemical improvements in some lakes (Greenaway et al., 2012). However, the timing and rate of diatom species’ recovery was not synchronous among lakes, and was likely influenced by local bedrock geology and the hydrological regime of each lake (e.g. flushing rate). Furthermore, diatom commu-
nities did not appear to be progressing towards their pre-
disturbance assemblages, possibly due to high metal con-
centrations in surface sediments.

Scaled-chrysophytes (classes Chrysophyceae and Synurophyceae) comprise an alternate biological indicator group that is also commonly used in paleolimnological studies (Smol, 1995). Because they are exclusively planktonic, scaled-chrysophytes may provide novel insights into changes occurring in the pelagic zone of the Wawa fume-kill lakes. The siliceous nature of chrysophyte scales enables them to be well-preserved in lake sediment (Smol, 1995). These structures are often ornamented and easy to identify to species (Smol, 1988). Scaled-chrysophytes are highly abundant and ubiquitous across many ecosystems (Smol, 1980). Because they have narrow niche breadths, short life cycles, and fast migration rates, living communities are sensitive and respond rapidly to changing environmental conditions.

Sensitivities to changing lake water pH have been doc-
umented for many scaled-chrysophyte species, which make them an excellent indicator group for use in acidification and recovery studies (Paterson et al., 2001; Smol, 1995). Predictive techniques and an improved understand-
ing of ecological preferences allow for quantitative and qualitative inferences of historical pH based on scaled-
chrysophytes in the sediment record (e.g., Cumming et al., 1992a; S.S. Dixit et al., 1999, 2002; Paterson et al., 2002). These have been used to demonstrate regional acidification due to industrial SO2 emissions (Charles, 1990; Cum-
ming et al., 1992b; A.S. Dixit et al., 1992a,b; S.S. Dixit et al., 1992), as well as recovery trajectories following emission reductions (A.S. Dixit et al., 1992a,b; S.S. Dixit et al., 1989a; Smol et al., 1998). Many species have also been identified as metal-tolerant or metal-sensitive (S.S. Dixit et al., 1989b), making them useful indicators of general trends in metal contamination and recovery.

There are several advantages to combining diatoms and scaled-chrysophytes in paleoecological studies of acidification and recovery. Most importantly, there may be differences in the timing of diatom and scaled-chrysophyte species compositional change in the sediment record. For example, chrysophyte-inferred pH changes commonly pre-
date diatom-inferred changes in acidification studies (Hart-
mann and Steinberg, 1986; A.S. Dixit et al., 1992a,b; Smol
and Dixit, 1990). Furthermore, several studies have shown that the magnitude of acidification is much greater when inferred from chrysophytes than from diatoms, likely be-
because of their planktonic nature, and because many chrys-
ophyte taxa dominate the phytoplankton assemblage during
the critical spring melt period (Cumming et al., 1992b; S.S. Dixit et al., 2002; Gibson et al., 1987). The combined use
of diatoms and chrysophytes provides a more complete un-
derstanding of pH history than would be generated from using either group alone (e.g., Paterson et al., 2001).

In this paper, we use paleolimnological techniques to track scaled-chrysophyte assemblage responses to historical chemical changes in five lakes near Wawa that have been previously studied for diatom assemblage changes (Greenaway et al., 2012). We show marked increases in acid- and metal-tolerant chrysophyte species in the 1950s and 1960s, pre-dating diatom responses to acidification. Following closure of the iron sintering plant in 1973, we present evidence of biological recovery from acidification, although the recovery trajectory varies among the study lakes, both in terms of timing and in the chrysophyte species present.

Study sites

Wawa is located in the northern Algoma district, north-
east of Lake Superior, in the province of Ontario (Fig. 1). The study area straddles part of the Michipicoten green-
stone belt, a complex Archean metavolcanic-metasedimen-
tary assemblage recognized for its numerous banded iron formations containing massive siderite beds (Sage, 1994). The carbonate beds are composed dominantly of siderite and contain varying amounts of sulphides in the form of pyrite (Sage, 1993). Lakes northeast of Wawa that are as-
associated with these carbonate beds exhibit higher natural pH levels than are typical of lakes along the eastern shore of Lake Superior (Coker and Shilts, 1979).

Gordon and Gorham (1963) described five zones of terrestrial damage ranging from Very severe to Not obvi-
ous. The limits of the Severe zone (which included the Very severe zone, and most of which experienced extensive soil erosion resulting in a barren rock landscape) and the Moderate zone (beyond which terrestrial effects were not obvious) are outlined in Fig. 1. Many lakes within the Severe zone reached pH levels below four and obtained high metal concentrations at some point in the 1950s to 1970s (Somers and Harvey, 1984).

Sulphur dioxide emissions decreased from 1973 to 1998 when the sinter plant ceased production (Rowe, 1999). Recolonization by grasses, herbs and young white birch was already underway by 1998 (Ontario Ministry of the Environment, 1999). In 2006, the landscape was covered with sparsely populated white birch, reaching heights of 20 feet. No formal lake restoration efforts were put in place; however, remarkable natural chemical and biological recovery has recently been documented (Greenaway et al., 2012; D.A. Jackson, University of Toronto, Ontario, 2003-2005, unpublished data).

Five lakes that had previously been documented as being acidic and metal-contaminated (Somers, 1980) were chosen for scaled-chrysophyte analyses. These are: Little Soulier, Otter, Talbot, Lagarde and Blueberry lakes. Physical and chemical characteristics of the study lakes can be found in Tables 1 and 2.
METHODS

Field work took place between June 6 and 9, 2006. Sediment cores were taken near the deepest point of each lake basin, using a depth sounder and the available bathymetric maps (from Somers, 1980) as a guide. In some lakes, a secondary basin was chosen for coring because of its enhanced accessibility (Otter lake), or to avoid an area with visible shoreline erosion along a steep bank (Talbot lake).

Sediment cores were extracted using a Glew (1989) gravity corer with 7.6 cm diameter Lexan® tubes that were 50 cm in length. A minimum core length of 22 cm was obtained from all lakes except Talbot lake, for which the longest obtainable core was 18 cm. On shore, a Glew (1988) vertical extruder was used to section each core into 0.25 cm intervals for the top 10 cm and 0.5 cm thereafter. Sediment intervals were stored in individual Whirlpak® sample bags and transported in coolers for processing at the Paleoecological Environmental Assessment and Research Laboratory, Queen’s University, Kingston, Ontario.

Radiometric dates were calculated to establish continuous age/depth relationships in sediment cores from all five lakes. Selected sediment intervals were dried using a Virtus® freeze-dryer and prepared for analysis following procedures outlined in Schelske et al. (1994). Gamma emissions from each sample were measured by spectrometry using an EG&G Ortec® germanium detector. Gross counts from regions of interest within the energy spectrum were used to calculate the activities of 137Cs, total 210Pb and 214Bi (measured as an estimate of 226Ra-supported 210Pb), as outlined in Schelske et al. (1994). 210Pb dates and sediment accumulation rates were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield, 1978) and CRS computer program developed by Binford (1990). Dates were extrapolated for the last three cm of each core assuming a constant accumulation rate prior to human disturbance.

Preparation of slides for scaled-chrysophyte and diatom analyses (Greenaway et al., 2012) followed standard laboratory procedures as outlined in Battarbee et al. (2001). Sediment sub-samples were first treated with hydrochloric acid to remove carbonates and iron precipitates and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.

Chrysophyte scales were enumerated at 1000× magnification using a LEICA DMR2 light microscope with differential interference contrast and an oil immersion objective (numerical aperture =1.3). Scales were identified and then with a strong nitric-sulphuric acid mixture to remove the remaining organic material. Both treatments were followed by rinsing with de-ionized water until a neutral pH was achieved. The residual siliceous slurry was mounted on glass slides with Naphrax®.
to the lowest possible taxonomic level using standard chrysophyte flora descriptions (Asmund and Kristiansen, 1986; Siver, 1991; Takahashi, 1978; Kling and Kristiansen, 1983; Nicholls, 1982; Nicholls and Gerrath, 1985). A number of small or medium-sized, unidentifiable Mallomonas species were combined into the groups Mallomonas small or Mallomonas medium (sensu Paterson et al., 2001). We appreciate that these groupings may combine several diverse taxa, but in all cases the population sizes of these categories were small and so did not affect our overall interpretations. The ratio of the percent abundance of chrysophyte scales to diatom frustules was also calculated. In the sediment core from Little Soulier lake, intervals were selected to match the high-resolution sampling pattern used for diatom analysis (Greenaway et al., 2012). In the four other study lakes, intervals were selected at a much coarser resolution, with the purpose of providing a preliminary assessment of general changes through time.

Prior to the species data analyses, raw scaled-chrysophyte species counts were standardized to relative abundance within each interval. As marked in the figures, some sediment intervals were counted to a low sample size (i.e. <50 scales) because chrysophyte scales occurred at very low density relative to diatom frustules. The relative abundance of species in samples with counts of 50 scales or fewer should be interpreted with caution because it is not possible to verify that the relative abundance of each species was stable between incremental counts. Within each core, only those species that were present in at least four intervals and present at relative abundances of more than 1% in at least two of the intervals were included in the numerical analyses. One interval was removed altogether from the analysis (10 cm interval in Blueberry lake), because the scales showed significant clumping on the microscope slide, preventing a proper assessment of species’ abundances.

To explore scaled-chrysophyte assemblage shifts through time, the species assemblage from each sediment interval was compared to the average pre-industrial species assemblage using the Bray-Curtis dissimilarity coefficient (Clarke and Warwick, 1994). The average pre-industrial assemblage was calculated from all intervals that were 210Pb-dated as earlier than ~1939, the year when sintering commenced at the sinter plant near Wawa.

RESULTS AND DISCUSSION

Species compositions of scaled-chrysophytes recorded in the sediment of the study lakes changed markedly in the second half of the 20th century (Figs. 2 to 6). Although responses were variable between lakes, most changes corresponded with the documented period of acidification in the Very severe zone (Gordon and Gorham, 1963; Somers and Harvey, 1984). Interestingly, the ratio of chrysophyte scales to diatom frustules also changed markedly throughout the lake sediment records, with the lowest ratios observed during the period of intense acidification.

Nine chrysophyte species were observed at high enough relative abundances (i.e. greater than one percent in at least two intervals) to warrant further discussion. As this is the first such study from the Wawa region, discussion of ecological optima of the various taxa will be based on calibration studies from other regions, with an emphasis on comparable studies from Sudbury, Ontario, due to its proximity to Wawa and similar industrial history (i.e. metals mining).

Pre-disturbance species assemblages

In all lake sediment cores, the pre-industrial scaled-chrysophyte species assemblages were dominated by Mallomonas duerschmidtiae and/or Mallomonas pseu-

---

Tab. 2. Lake water chemistry data measured in 1978-79 and in 2006 in the fume-kill lakes selected for this study.

<table>
<thead>
<tr>
<th></th>
<th>Little Soulier lake</th>
<th>Otter lake</th>
<th>Talbot lake</th>
<th>Lagarde lake</th>
<th>Blueberry lake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity (CaCO3, mg L⁻¹)</td>
<td>0.00</td>
<td>19.40</td>
<td>0.00</td>
<td>14.90</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.40</td>
<td>0.00</td>
<td>14.90</td>
<td>0.00</td>
</tr>
<tr>
<td>pH</td>
<td>3.16</td>
<td>6.97</td>
<td>3.09</td>
<td>7.14</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.97</td>
<td>3.09</td>
<td>7.14</td>
<td>3.30</td>
</tr>
<tr>
<td>Specific conductivity (µS cm⁻¹)</td>
<td>819.3</td>
<td>98.4</td>
<td>904.0</td>
<td>88.4</td>
<td>95.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>98.4</td>
<td>904.0</td>
<td>88.4</td>
<td>95.2</td>
</tr>
<tr>
<td>Secchi depth (m)</td>
<td>6.5</td>
<td>6.3</td>
<td>7.3</td>
<td>5.3</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.3</td>
<td>7.3</td>
<td>5.3</td>
<td>8.2</td>
</tr>
<tr>
<td>Sulphate (mg L⁻¹)</td>
<td>242.00</td>
<td>23.60</td>
<td>55.00</td>
<td>22.00</td>
<td>187.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.60</td>
<td>55.00</td>
<td>22.00</td>
<td>187.00</td>
</tr>
<tr>
<td>Calcium (mg L⁻¹)</td>
<td>33.00</td>
<td>15.00</td>
<td>43.60</td>
<td>13.20</td>
<td>32.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.00</td>
<td>43.60</td>
<td>13.20</td>
<td>32.40</td>
</tr>
<tr>
<td>Magnesium (mg L⁻¹)</td>
<td>21.20</td>
<td>3.12</td>
<td>30.30</td>
<td>2.82</td>
<td>18.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.12</td>
<td>30.30</td>
<td>2.82</td>
<td>18.40</td>
</tr>
<tr>
<td>Chloride (mg L⁻¹)</td>
<td>1.40</td>
<td>0.20</td>
<td>1.50</td>
<td>0.20</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.20</td>
<td>1.50</td>
<td>0.20</td>
<td>1.05</td>
</tr>
<tr>
<td>Potassium (mg L⁻¹)</td>
<td>1.00</td>
<td>0.23</td>
<td>1.20</td>
<td>0.18</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.23</td>
<td>1.20</td>
<td>0.18</td>
<td>0.78</td>
</tr>
<tr>
<td>Aluminium (µg L⁻¹)</td>
<td>3090</td>
<td>4.86</td>
<td>5430</td>
<td>6.26</td>
<td>3680</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.86</td>
<td>5430</td>
<td>6.26</td>
<td>3680</td>
</tr>
<tr>
<td>Copper (µg L⁻¹)</td>
<td>26</td>
<td>0.40</td>
<td>33</td>
<td>0.38</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>33</td>
<td>0.38</td>
<td>18</td>
</tr>
<tr>
<td>Iron (µg L⁻¹)</td>
<td>4</td>
<td>78.40</td>
<td>9040</td>
<td>134.00</td>
<td>4420</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78.40</td>
<td>9040</td>
<td>134.00</td>
<td>4420</td>
</tr>
<tr>
<td>Manganese (µg L⁻¹)</td>
<td>4332</td>
<td>19.50</td>
<td>6381</td>
<td>18.90</td>
<td>3710</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.50</td>
<td>6381</td>
<td>18.90</td>
<td>3710</td>
</tr>
</tbody>
</table>

*From Somers (1980) and Somers and Harvey (1984); † from Greenaway (2009) and Greenaway et al. (2012); § in a 1979 resample of Little Soulier lake, Fe was measured to be 2080 µg L⁻¹ (Somers, 1980); na, not available.
**Scaled-chrysophyte responses to recovery from acidification**

**docoronata**, and were characterized by minimal species compositional change (Figs. 2 to 6). The taxon *M. duerrschmidtiae* was originally described from acidic lakes low in specific conductivity and total phosphorus in the United States (Siver et al., 1990). The pH optimum (5.8) calculated from 105 lakes in Sudbury (S.S. Dixit et al., 2002) is comparable to that calculated from 146 lakes in the northeastern USA (pH optimum 6.2; S.S. Dixit et al., 1999), where it was described as being most abundant in moderate to low pH waters. It has also dominated pre-disturbance species assemblages in many Sudbury lakes (Uutala et al., 1994; A.S. Dixit et al., 1996; S.S. Dixit et al., 2002) and has been referred to as a generalist in other studies (Uutala et al., 1994). Meanwhile, *M. pseudocoronata* is commonly found in circumneutral to alkaline waters (Cumming et al., 1992a; S.S. Dixit et al., 1999, 2002) and in Sudbury has a pH optimum of 6.7 (S.S. Dixit et al., 2002). The co-dominance of *M. pseudocoronata* implies that these lakes were probably circumneutral prior to the onset of sintering. This is substantiated by the low, but stable, down-core abundance of *M. caudata* in most cores, which is commonly restricted to circumneutral lakes (pH optimum 6.5 in Sudbury; S.S. Dixit et al., 2002).

**Responses to acidification and metal contamination**

The nature of species compositional changes following the onset of sintering (1939) varied among lakes. In all lake sediment cores, the appearance or increase in the relative abundance of new species was contemporaneous with a decrease in the relative abundances of *M. duerrschmidtiae* and *M. pseudocoronata*. The most consistent response was an increase in the relative abundance of *Synura echinulata* in each lake’s sediment core (Figs. 2 to 6). The peak relative abundance of this species ranged from 15 to 50%, and it did not always become the most abundant species in the assemblage; however, the similarity of its response to that in Sudbury lakes (pH optimum 5.8; S.S. Dixit et al., 2002) is worth noting. *S. echinulata* has frequently been observed to be abundant in acidic and metal-contaminated lakes in Sudbury (S.S. Dixit et al., 1989a,b, 2002; A.S. Dixit et al., 1992b), despite being described as bimodal along the pH gradient from lakes in the Adirondack Mountains and in south-central Ontario (Cumming et al., 1992a; Paterson et al., 2001), and considered to be tolerant of a wide pH range in the northeastern USA (S.S. Dixit et al., 1999).

Increases in the relative abundances of *Mallomonas crassissquama* and *M. hamata* in some of the Wawa lakes during the period of acidification were inconsistent with trends observed for these species in other regions. *M. crassissquama*, with a pH optimum of 6.6 in Sudbury lakes (S.S. Dixit et al., 1999; Siver et al., 1990), is commonly found in circumneutral lakes, and rarely identified in sediments from very acidic lakes. This taxon has also been reported as aluminum-sensitive in the Adirondack Mountains (Cumming et al., 1992a), and potentially cop-

---

**Fig. 2.** Little Soulier lake sediment core scaled to $^{210}$Pb-inferred dates, showing: i) the relative abundance of common scaled-chrysophyte taxa; ii) the Bray-Curtis dissimilarity between each scaled-chrysophyte species assemblage and the average pre-industrial (pre-1939) assemblage; and iii) the percent of chrysophyte scales relative to diatom frustules.
Fig. 3. Otter lake sediment core scaled to $^{210}$Pb-inferred dates, showing: i) the relative abundance of common scaled-chrysophyte taxa; ii) the Bray-Curtis dissimilarity between each scaled-chrysophyte species assemblage and the average pre-industrial (pre-1939) assemblage; and iii) the percent of chrysophyte scales relative to diatom frustules. Dashed bars indicate intervals for which sample sizes were ≤50, due to the low concentration of scales.

Fig. 4. Talbot lake sediment core scaled to $^{210}$Pb-inferred dates, showing: i) the relative abundance of common scaled-chrysophyte taxa; ii) the Bray-Curtis dissimilarity between each scaled-chrysophyte species assemblage and the average pre-industrial (pre-1939) assemblage; and iii) the percent of chrysophyte scales relative to diatom frustules. Dashed bars indicate intervals for which sample sizes were ≤50, due to the low concentration of scales.
Fig. 5. Lagarde lake sediment core scaled to $^{210}$Pb-inferred dates, showing: i) the relative abundance of common scaled-chrysophyte taxa; ii) the Bray-Curtis dissimilarity between each scaled-chrysophyte species assemblage and the average pre-industrial (pre-1939) assemblage; and iii) the percent of chrysophyte scales relative to diatom frustules. Dashed bars indicate intervals for which sample sizes were ≤50, due to the low concentration of scales.

Fig. 6. Blueberry lake sediment core scaled to $^{210}$Pb-inferred dates, showing: i) the relative abundance of common scaled-chrysophyte taxa; ii) the Bray-Curtis dissimilarity between each scaled-chrysophyte species assemblage and the average pre-industrial (pre-1939) assemblage; and iii) the percent of chrysophyte scales relative to diatom frustules. Dashed bars indicate intervals for which sample sizes were ≤50, due to the low concentration of scales.
per- and nickel-sensitive in Sudbury (S.S. Dixit et al., 1989b). *M. hamata* was observed to be a common taxon of acidic lakes in the Adirondacks (Cumming et al., 1992a), but was less common in Sudbury lakes (pH optimum in Sudbury 5.9; S.S. Dixit et al., 2002), again due to copper- and nickel-sensitivity (S.S. Dixit et al., 1989b, 1992, 2002). However, these taxa were present and increased to sub-dominance in some of the Wawa lake sediment cores following the onset of sintering. In the late 1970s, copper and nickel concentrations were higher in the four *fume-kill* lakes closest to the sinter plant (Cu 12-26 µg L⁻¹; Ni 5-33 µg L⁻¹; Somers, 1980), relative to background concentrations from surrounding lakes (Cu 0-2 µg L⁻¹; Ni 0 µg L⁻¹; Somers, 1980), although not comparable to the extremely high concentrations of some Sudbury lakes (S.S. Dixit et al., 1989b). Aluminum concentrations were much more elevated in the *fume-kill* lakes (2260 µg L⁻¹ - 5430 µg L⁻¹; Somers, 1980; Somers and Harvey, 1984). Clearly, the factors affecting acid- and metal-sensitivity are complex and likely elementspecific, which may explain why variation in species responses is prevalent across regions.

One additional species, *S. petersenii*, also became more abundant in each lake sediment core after sintering commenced. This increase was relatively small in Little Soulier, Otter and Talbot lakes (Figs. 2 to 4), but greater (5-10%) in Lagarde and Blueberry lakes (Figs. 5 and 6). *S. petersenii* has been described as pH-indifferent in Sudbury (S.S. Dixit et al., 2002) and was most abundant around pH 7.0 across the northeastern USA (S.S. Dixit et al., 1999). Its abundance has recently increased in many Ontario lakes (S.S. Dixit et al., 2002; Paterson et al., 2001, 2004), although not directly with changes in lake pH. Meanwhile, *S. sphagnicola* (Sudbury pH optimum 6.2; S.S. Dixit et al., 2002) increased to high abundance only in Blueberry lake. Increases in the abundance of *Synura* scales in sediment cores in lakes across Ontario may reflect the influence of acidification, climate change, or both (Hyatt et al., 2010; Paterson et al., 2004, 2008; Schindler et al., 1996). For example, although the specific mechanisms for their rise have not yet been determined, colonial chrysophytes may realize a competitive advantage under conditions of increased light penetration and associated altered thermal regimes (Paterson et al., 2004; Hyatt et al., 2010). A recent work in New Hampshire lakes (Davis et al., 2006) has also reported increases in colonial chrysophytes that are coeval with increases in coal combustion products and major and trace metals in lake sediments. Iron, in particular, has been shown to be a limiting nutrient for some freshwater algae, and the higher abundances of some chrysophyte taxa in highly coloured lakes has been related to readily available, chelated forms of iron and other trace metals in such lakes (Sandgren, 1988).

**Differential response of scaled-chrysophytes and diatoms**

In all five lakes, clear indications of species compositional change occurred in sediment dated from approximately the late 1950s and throughout the 1960s. This coincides with the time period when Gordon and Gorham (1963) measured very low pH in small lakes and ponds in the *Very severe* zone. In Little Soulier, Otter and Talbot lakes, early signs of change in benthic diatom species compositions were recorded around the same period; however, the major diatom species compositional changes in all five lakes occurred at varying times throughout the next few decades (Greenaway et al., 2012). Thus, scaled-chrysophyte species appear to have responded earlier than diatoms to lake acidification in the Wawa *fume-kill* area. This was particularly notable in Lagarde lake, in which diatom species’ responses (as recorded in the sediment) were delayed until ~1990, but chrysophyte species responses in the sediment commenced in the late 1950s.

A lag in response of diatoms relative to scaled-chrysophytes has been observed in other lakes (Hartmann and Steinberg, 1986; A.S. Dixit et al., 1992a,b; Cumming et al., 1994), and may be related to differences in habitat. Lake sediments are an important source of alkalinity in many lakes (Carignan, 1985; Schiff and Anderson, 1986; Schindler et al., 1986), and the majority of the acid- and metal-indicator diatom species in these lakes were benthic forms (Greenaway et al., 2012). The pre-disturbance benthic diatom communities in the Wawa *fume-kill* area lakes likely experienced a microhabitat that was well-buffered relative to the overlying water column, thus allowing them to persist for some time after the onset of surface water acidification.

The period of rapid transition in species composition, and the period of intense acidification (~1950-1970), were also characterized by very low abundances of chrysophyte scales relative to diatom frustules (Figs. 2 to 6). In some cases (e.g. Talbot lake), the decrease in the ratio of chrysophyte scales to diatom frustules appeared to precede the onset of chrysophyte species compositional change, suggesting that this measure may be useful as an early warning indicator of lake acidification. Furthermore, scaled-chrysophytes appear to be show an enhanced sensitivity to chemical changes occurring within the water column, compared to diatom assemblages, because of their planktonic nature.

**Responses to chemical improvements in water column**

The study lakes have exhibited striking chemical improvements since the late 1970s, including an increase in pH and alkalinity and a decrease in metal concentrations in the water column (Greenaway et al., 2012; D.A. Jackson, University of Toronto, Ontario, 2003-2005, unpub-
lished data). Similar to diatom community responses (Greenaway et al., 2012), the responses of scaled-chrysophyte communities varied among lakes (Fig. 7). Broadly, the lakes can be divided into three general groups, with some overlap, based on the chrysophyte response to chemical improvements.

The first group, including Little Soulier, Otter and Blueberry lakes, show qualitative evidence for biological recovery. In these lake sediment cores, the relative abundance of *S. echinulata* began to decrease in intervals dated from approximately the 1990s (Figs. 2, 3 and 6). A decrease in this acid- and metal-tolerant taxon (A.S. Dixit et al., 1992a,b; S.S. Dixit et al., 1989b, 2002) is most likely a reflection of the improving water quality conditions in these lakes, and was most obvious in the high-resolution sediment core analysis from the Little Soulier lake (Fig. 2). Interestingly, the decrease in *S. echinulata* at the top of the Blueberry lake core contrasts sharply with the diatom analysis, in which virtually no response to water quality improvements was observed (Greenaway et al., 2012). At least for Blueberry lake, this again suggests a lagged response of the diatom community to chemical changes in water quality, although this time in response to chemical recovery. The more rapid response of scaled-chrysophytes to improvements in chemical water quality may be due to their planktonic nature and rapid species turnover rates. Scaled-chrysophytes appear to be reliable early-warning indicators of both acidification and chemical recovery in some lakes.

In contrast, the scaled-chrysophyte record in the Talbot lake sediment core appears to have stabilized in the 1970s, showing virtually no evidence for reversal in the acidification trend (Fig. 4), although a very small decrease in *S. echinulata* in the top sediment interval may be an early indication of recovery. In the Talbot lake diatom record (Greenaway et al., 2012), evidence for recovery was also limited to the top interval of the core. However, diatom evidence constituted a decrease in several taxa and therefore was considered to be more substantial than the decrease seen here. Despite measured water chemistry improvements following closure of the sinter plant in 1998, it can be inferred from the lack of strong evidence for recovery in either the chrysophyte or diatom sediment record that chemical improvements were likely to have

---

**Fig. 7.** A comparison of the Bray-Curtis dissimilarity trends through time in Little Soulier (LS), Otter (OT), Talbot (TA), Lagarde (LA), and Blueberry (BL) lakes. The Bray-Curtis dissimilarity was calculated between each scaled-chrysophyte species assemblage and the average pre-industrial (pre-1939) assemblage from that lake. Historical sulphur dioxide emissions from the sinter plant are also shown (data from Rowe, 1999).
been recent. Talbot lake is a small, but relatively deep lake with an estimated flushing time of ~1.7 years (Greenaway, 2009). It is the first major lake within the Talbot Creek watershed. In contrast, Little Soulier and Otter lakes are small, shallow, secondary and tertiary lakes of the Talbot Creek watershed, with much shorter flushing times, as well as higher ratios of catchment and sediment to lake volume. These varied hydrological regimes may explain why Talbot lake appears to have lagged behind Little Soulier and Otter lakes in timing of chemical recovery, and in evidence for diatom and chrysophyte recovery from the sediment record (Fig. 7).

A final group of lakes was characterized by a shift to *Synura*-dominated assemblages within the most recent intervals of the lake sediment cores. In Lagarde and Blueberry lakes, the recovery trajectories are unlikely to include a return to pre-disturbance chrysophyte assemblages in light of the shift to *Synura* species (Figs. 5 and 6). In Lagarde lake, the continued increase of *S. echinulata* towards the top of the core makes it appear that Lagarde lake is still acidifying. More likely, this reflects the shift to *Synura*-dominated assemblages that has been observed across much of Ontario (Paterson et al., 2001, 2004; S.S. Dixit et al., 2002). *S. petersenii*, an important contributor to these shifts in many lakes, also shows signs of a continued increase in relative abundance. In Blueberry lake, both *S. echinulata* and *S. sphagnicola* began decreasing in sediment dated from approximately the 1990s, but this was coincident with increases in the relative abundance of *S. petersenii*.

Similarly, in recent studies of phytoplankton data from intensively-studied lakes in southcentral Ontario (Paterson et al., 2008), and paleoecological data from the southern Canadian Shield (Paterson et al., 2001, 2004), increases in the abundance of colonial chrysophytes (including *Synura*) have also been reported. In other regions, the timing of these increases is coeval with water chemistry changes associated with industrial activity since the mid 1900s, and physical changes in lakes associated with recent warming. Moreover, in a meta-analysis of paleolimnological data from more than 250 lakes across northeastern North America, Hyatt et al. (2010) hypothesized that the increases in colonial chrysophytes may be related to long-term declines in total phosphorus concentrations associated with catchment acidification and recent warming (Eimers et al., 2009). Clearly, further work will be required to determine the site-specific causes of increases in *Synura* taxa in the Wawa *fume-kill* area lakes.

**CONCLUSIONS**

In summary, the scaled-chrysophytes species compositions in the five study lakes from a *fume-kill* area near Wawa were altered markedly in response to a period of iron sintering from 1939 to 1998. The most consistent response was an increase in acid- and metal-tolerant *Synura echinulata* in each lake’s core. Similar to many previous acidification studies, the response of scaled-chrysophytes in the *fume-kill* lake sediment records predated the response of diatoms, substantiating the value of using both proxies in paleolimnological pH reconstructions. Following water quality improvements, the response of scaled-chrysophytes was variable across the study lakes. In some lakes, recovery was interpreted from a decrease in the acid- and metal-tolerant species *S. echinulata* towards the top of the core. Two lakes appear to have shifted from a *Mallomonas*-dominated to a *Synura*-dominated species assemblage, implying that there may have been alterations to nutrient dynamics and/or thermal regimes of these lakes (Hyatt et al., 2010). Although pH and other water quality variables may have recovered in some systems, the chrysophyte assemblages present in the recent sediments are still markedly different from those thriving during predisturbance times.

**ACKNOWLEDGEMENTS**

The authors would like to thank Don A. Jackson and Keith M. Somers for their general observations and invaluable background information concerning the Wawa lakes. They are also grateful to Adam Jeziorski and Amy E. Tropea for their assistance in the field. This work was funded through a Natural Sciences and Engineering Research Council grant to John P. Smol.

**REFERENCES**


Scaled-chrysophyte responses to recovery from acidification


Greenaway CM, 2009. Diatoms community responses to water quality improvements in lakes recovering from acidification and metal-contamination near Wawa, Ontario, Canada: a paleolimnological perspective. M.Sc. thesis, Department of Biology, Queen’s University, Kingston, ON, Canada.


