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# Paleolimnological evidence of mining and demographic impacts on Lac Dauriat, Schefferville (subarctic Québec, Canada)

Laurence Laperrière · Marie-Andrée Fallu · Sonja Hausmann · Reinhard Pienitz · Derek Muir

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Abstract Qualitative and quantitative analysis of fossil diatoms and geochemical signals preserved in the sediments of Lac Dauriat (subarctic Quebec) were performed to evaluate the impacts of nearby mining activity and the expansion of the town of Schefferville on the water quality of the lake, and to reconstruct the changes of its trophic status. The presence of taxa typical of nutrient-enriched

L. Laperrière · R. Pienitz (⊠) Centre d'études nordiques, Laboratoire de Paléolimnologie—Paléoécologie, Département de Géographie, Université Laval, Québec, QC, Canada G1K 7P4 e-mail: reinhard.pienitz@cen.ulaval.ca

L. Laperrière e-mail: laurence.laperriere.1@ulaval.ca

#### M.-A. Fallu

Département de chimie-biologie, Université du Québec à Trois-Rivières, C.P. 500, Trois-Rivières, QC, Canada G9A 5H7 e-mail: marie-andree\_fallu@uqtr.ca

#### S. Hausmann

Department of Geosciences, University of Arkansas, 102 A Ozark Hall, Fayetteville, AR 72701, USA e-mail: shausman@uark.edu

#### D. Muir

Aquatic Ecosystem Protection Research Division, Water Science and Technology Directorate, Environment Canada, Burlington, ON, Canada L7R 4A6 e-mail: derek.muir@ec.gc.ca environments (e.g., Cyclostephanos invisitatus, Nitzschia gracilis, Nitzschia perminuta) and the low percentages of chrysophytes were indicative of the advanced state of eutrophication of the lake during the peak of mining activity, and were evidence of the negative impacts of municipal waste on the water quality of Lac Dauriat. Sedimentary analysis of metals, notably lead, mercury, cadmium, bismuth, cobalt, copper and zinc, showed maximum concentrations between 1940 and 1960 with mining era to predevelopment enrichment factors ranging from 4.5 to 7.9. The changes seen in recent sediments reflected 3 distinct stages in the recent history of this ecosystem: (a) the non-perturbed, pre-mining (1882–1939), (b) the perturbed, mining period (1939-1977) with accelerated eutrophication, and (c) the post-mining period (1977-1999) with indications of natural recovery of the system after the installation of a water treatment plant in 1975, the closing of the mine in 1983, and the subsequent exodus of the town's population. Despite the trajectory towards a return to the lake's natural conditions, water resource managers and (paleo-) limnologists should be alarmed that the impacts of past human disturbance are still in evidence more than 20 years after the closure of the mines, and that Lac Dauriat has yet to reach its natural state of the period preceding extreme anthropogenic impact.

Keywords Paleolimnology · Diatoms ·

Geochemistry · Mining · Pollution · Eutrophication · Inferred phosphorus · Subarctic · Schefferville

# Introduction

The construction of the town of Schefferville began at the start of the 1950s with the goal of developing one of the most important iron mines in northern Québec, Canada (Dufour 1981; Dimroth 1981). Before this, the region had only Reserves of the Matimekosh and Naskapi First Nations. The railway linking Sept-Îles to Schefferville was completed in 1954, and mining began soon thereafter (Dionne 2005). During the same period as the construction of the railroad and opening of the mines, the town of Schefferville underwent a demographic explosion, growing from a few hundred inhabitants in 1954 to a population of 4,129 in 1979 (Archer 1983, cited in Choulik and Moore 1992). Prior to 1975, no system was in place for sewage treatment, and wastewater was directed untreated into Lac Dauriat, in the center of the town. In 1975, a sewage treatment plant was installed to treat the town's wastewater. By 1981, due to weakening of demand for iron, the population of Schefferville had declined to less than 2,700 inhabitants, and by 1989, 600 people (Choulik and Moore 1992). In 1983, the mines were permanently closed.

The present paleolimnological study of Lac Dauriat traces the history of pollution and the accelerated evolution of the processes of eutrophication in this subarctic lake. Little is known of the effects of sewage on subarctic lake ecosystems, however some work (including paleolimnological studies) has been completed on High Arctic lakes (Douglas and Smol 2000). Diatoms (Bacillariophyceae) are unicellular algae composed of a siliceous cell wall that are typically well preserved in sediments. Diatom community composition varies with changes in the physical and chemical conditions of lakes, making them excellent water quality indicators. Diatom assemblages have been used to reconstruct the evolution of water quality in freshwater ecosystems (e.g., Karst and Smol 1998; Guilizzoni et al. 2001; Saulnier-Talbot et al. 2003), and more specifically to determine lake trophic status (e.g., Anderson et al. 1990; Hall et al. 1997; Hausmann et al. 2002; Pienitz et al. 2006). Chrysophytes (Chrysophyceae) are also siliceous algae that preserve well in sediments. The ratio of chrysophytes to diatoms in sediments may also provide an indication of the degree of eutrophication of a temperate lake (Smol 1985).

Many studies have also evaluated the impacts of mining activity on aquatic ecosystems (e.g., Kerfoot et al. 1994, 1999; Kauppila 2006; Salonen et al. 2006). In the Schefferville region, Dubreuil (1981) attempted to reconstruct the changes in a waterway affected by mining activity. She concluded that "the physicochemical characteristics of the waters of the Kata River (situated approximately 13 km to the west of Schefferville) have apparently returned to premining conditions, as far as specific conductivity and suspended solids were concerned. However, it appears that the fauna and flora respond much more slowly to the improvement in water quality". Hausmann et al. (2002) showed that it took more than 88 years for Lake Seebergsee, in the Swiss Alps, to return to an oligotrophic state after a period of hypereutrophy caused by excessive fertilizer use and pasturage in the lake's catchment.

Using a multidisciplinary approach (biostratigraphy and geochemistry), the present study shows the impact and the lasting consequences of mining and of the demographic explosion of the town of Schefferville on the water quality and trophic state of boreal subarctic Lac Dauriat.

#### Study area

Lac Dauriat (54°48' N; 66°49' W) is situated at 550 m a.s.l. in the center of the town of Schefferville, in northern Quebec (Fig. 1). The lake has an area of 0.56 km<sup>2</sup> and a maximum measured depth of 4.5 m. Because the region has high snow accumulation in winter (average 330 cm), a large volume of runoff is produced during spring snowmelt (Drake and Freund 1980). The lake's renewal time is 60 days in winter, and only two days during spring snowmelt (Drake and Freund 1980). According to the study of Choulik and Moore (1992), Lac Dauriat was mesotrophic in 1992 by Wetzel's (2001) classification system. Concentrations of measured total phosphorus and chlorophyll a (Chl a) had their lowest values after 1975 (Fig. 2; Choulik and Moore 1992).

Lac Dauriat is a part of a chain of lakes that includes, going downstream, Lac Knob, Lac Dauriat, Lac Juin and Lac LaCosa, with drainage running from south to north (Fig. 1). The catchments of this region drain towards Ungava Bay via the Caniapiscau **Fig. 1** Topographic map of the Schefferville region and of Lac Dauriat. Aerial photographs of Schefferville (1973 and 2000) at 1:50,000 scale (approximately). *Source*: Québec Ministry of Natural Resources



River. Due to its geographic location, Lac Dauriat received the sewage effluent of the town of Schefferville throughout the mining period. Lac Knob, situated upstream, was used both for the town's drinking water and for recreational activities. The iron ore mining was conducted to the south and west of the town site and not directly upstream of Lac Dauriat (Fig. 1).

Geologically, Schefferville is situated in the Labrador Trough, on the Canadian Shield. The Labrador Trough is located to the west of the Churchill geological province, at the edge of the Superior province. Local bedrock is composed of lightly metamorphosed calcareous and dolomitic sedimentary rock with iron-rich layers (Landry and Mercier 1992). The geology of the Schefferville region is



**Fig. 2** Variations in concentrations of total phosphorus and Chl *a* measured from Lac Dauriat (modified from Choulik and Moore 1992)

characterized mainly by the presence of calcareous rocks and the abundance of iron oxides and hydroxides, including hematite, limonite and goethite. Glacial tills in the Labrador Trough are enriched in Fe, Zn and Mn and depleted in Cr (Klassen 1999).

The subarctic climate of the Schefferville region is marked by cold winters and short summers (Atlas of Canada, 2002). Schefferville's mean annual temperature is  $-5^{\circ}$ C, with a mean annual precipitation of 793.6 mm of which 415 cm falls as snow (Environment Canada 1993). The region has an average of 190 days with maximum temperature below 0°C (Environment Canada 1993).

Lac Dauriat's catchment is characterized by lichen woodland typical of the subarctic region. The majority are *Picea mariana* (black spruce), but also *Pinus banksiana* (Jack pine), *Abies balsamea* (balsam fir) and some deciduous trees such as *Betula pendula* (silver birch) and *Populus tremuloides* (quaking aspen) (Environment Canada 2003).

# Materials and methods

#### Coring

The two cores were retrieved with a Kajak–Brinkhurst type corer with a diameter of 6.5 cm. The first core (core Dauriat A) was 41 cm long and was subsampled at 1 cm intervals. These samples were used for elemental analysis at the National Laboratory for Environmental Testing (NLET) of Environment Canada in Burlington, Ontario. The second core (core Dauriat B) was 40 cm long, was subsampled at 0.5 cm intervals, and was analyzed at the Laboratoire de paléolimnologie et paléoécologie at Université Laval (Québec).

# <sup>210</sup>Pb dating

Eighteen samples from core B were dried at 70°C for 18 h, and 6 of these samples were sent to the GEOTOP laboratory of the University of Montreal to measure the remnant radioactivity of the sediments. The samples selected for dating represented intervals where changes were observed in diatom assemblages. Binford's (1990) constant rate of supply model (CRS) was used to calculate sedimentation rates.

# Loss-on-ignition

To determine the organic matter (OM) content in the sediments of Lac Dauriat, samples from core B were processed according the method of Dean (1974). The entire core was analyzed at 0.5 cm intervals, for a total of eighty samples. Samples were first heated to 100°C for 19 h, weighed, subsequently burned at 550°C for 6 h, and weighed again.

# Siliceous microfossils

Each sample was treated with a 1:1 mixture of sulfuric and nitric acid for 24 h. Samples were heated in a hot water bath ( $\sim 80^{\circ}$ C) for two hours, and were rinsed with distilled water each day for one week to return them to neutral pH. Microscope slides were mounted with Naphrax<sup>®</sup>. Forty slides were prepared at 1 cm intervals according to standard methods (Pienitz et al. 1995). Enumeration of diatoms was done at 1000× magnification under oil immersion, with a minimum of 500 diatom valves counted per sample. Species identifications were made primarily

following the floras of Krammer and Lange-Bertalot (1986, 1988, 1991a, b) and Fallu et al. (2000).

# Total phosphorus reconstruction

In order to quantify variations in past limnological conditions, we used a total phosphorus (TP) inference model. The geology of Lac Dauriat's catchment was dominantly calcareous, therefore a transfer function was applied from Swiss lakes with similar bedrock geology, rather than from northern Quebec lakes with dominantly granitic bedrock. The degree of similarity between Lac Dauriat's fossil diatom assemblages and those from modern Swiss lakes (Hausmann and Kienast 2006), Labrador lakes (Fallu et al. 2002) and northern Québec lakes (Fallu and Pienitz 1999) was examined using detrended correspondence analysis (DCA), an indirect ordination method. This analysis indicated that the fossil diatom assemblages of Lac Dauriat were most closely associated with those from lakes of similar geological provenance (i.e., calcareous; Fig. 3). Therefore, we used the TP inference model from Switzerland (Hausmann and Kienast 2006). This model was composed of 50 lakes distributed on a TP gradient from 4 to 522  $\mu$ g l<sup>-1</sup> (mean:  $128 \ \mu g \ l^{-1}$ ; median:  $44 \ \mu g \ l^{-1}$ ; standard deviation 160  $\mu$ g l<sup>-1</sup>). TP concentrations were asymmetrical, thus they were log(x + 1) transformed in order to normalize their distribution. All ordinations were carried out using the software CANOCO (version 4.0; ter Braak and Šmilauer 1998).



Fig. 3 Comparison of diatom assemblages in sediments from northern Québec lakes (*diamonds*), from Québec-Labrador (*filled squares*) and from Switzerland (*open squares*) with diatom assemblages from Lac Dauriat (*triangles*), using detrended correspondence analysis (DCA)

#### Elemental geochemistry

Core A was analyzed for 33 elements present in the sediments of Lac Dauriat. In brief, 0.5 g freeze dried sediment (total of 21 slices corresponding to 1 sample per 2 cm depth) was weighed into a Teflon<sup>®</sup> vessel and a mixture of nitric acid, hydrochloric acid and hydrogen peroxide (ratio 9:2:1) was added. The vessel was assembled, sealed and fitted onto a microwave rotor in a high-pressure microwave oven. The sample was digested and the temperature maintained at 200°C for 15 min (Environment Canada 1994). Hg concentrations were determined by cold vapour atomic absorption spectrophotometry (CVAAS), while As, Be, Bi, Cd, Co, Ga, La, Li, Mo, Ni, Pb, Rb, Sb, Tl, U, Cu, Pt, Pd, and Rh analyses were done using inductively coupled plasma mass spectrometry (ICP-MS) (PQ-2, VG Elemental). Concentrations of Al, Ba, Cr, Fe, Mn, P, Sr, V, Zn, Ca, Mg, Na and K were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). The accuracy of analyses was verified by laboratory tests of blanks and certified reference materials (CRMs) of the National Research Council of Canada and the National Institute of Standards and Technology (NIST) (CNRC Mess-2, INST RM 8704, CRNC PACS-1). Results for the three CRMs had values averaging 83% of certified values (median: 87%) for 17 elements.

#### Results

#### Lithostratigraphy

Sediments were reddish-brown between 40 cm and 33 cm depth (core A), and became increasingly pale towards the top of the core. From 32.5 to 6 cm, the core was rich in black organic matter (gyttja) and contained traces of oil (visible during sampling). From the 6 cm horizon to the surface, the sediments were reddish-brown, with a gentle transition to darker brown beginning at 5 cm depth.

#### Loss-on-ignition

From 40 to 33 cm (the pre-mining period from 1882 to 1939; Fig. 4), the OM content stayed almost constant at approximately 7%. The pre-mining interval was



Fig. 4 Relative abundance profiles of common diatom taxa  $(\geq 2\%$  in at least one level) and of organic matter content in the sediments (by loss on ignition) in core Dauriat B. The division

distinguished by the lowest OM content among the three periods. The sediments between 32 and 18 cm corresponded with the mining period (1939–1977; Fig. 4); these sediments had the highest measured OM content in the core. At the 31 cm level the OM content had risen to 9%. Above this horizon OM increased rapidly, reaching a maximum of approximately 32% at the 20.5 cm level. The post-mining period (1977–1999, 18–0 cm; Fig. 4) was characterized by a decrease in OM content. Organic matter dropped rapidly between 18 and 15 cm, followed by a gradual but sustained decrease with alternating peaks and valleys, varying between 23 and 15%.

# <sup>210</sup>Pb dating

The decline in <sup>210</sup>Pb activity in sediments with depth is shown in Fig. 5. The basal age of the core was estimated at 1882 AD. Agreement between dates estimated using the CRS model and known activity in the lake catchment was very good. The pre-mining

of zones was determined using the software Zone (see text for explanation)

period (1882-1939) was characterized by a constant sedimentation rate of  $0.10 \text{ g cm}^{-2} \text{ year}^{-1}$  and low unsupported <sup>210</sup>Pb concentrations between 3 and 6 dpm  $g^{-1}$  (Fig. 5). Between 1939 and 1977, corresponding to the mining period, the sedimentation rate more than doubled, increasing from 0.13 to 0.28 g  $cm^{-2} year^{-1}$ . This increase was gradual and continuous. The radioactivity was centered around 7 dpm  $g^{-1}$ . The sedimentation rate then diminished continuously after 1977, corresponding with the postmining period (1977-1999). The sedimentation rate decreased from a maximum of 0.28 g cm<sup>-2</sup> year<sup>-1</sup> in 1981 to 0.18 g  $\rm cm^{-2}\, year^{-1}$  in 1999, and the rate of decrease accelerated between 1988 and 1999. Unsupported <sup>210</sup>Pb activity was between 8 and 22 dpm  $g^{-1}$ between 1981 and 1999.

#### Siliceous microfossils

A total of 168 diatom taxa were identified in the sediments of the core. Three distinct zones (Fig. 4) were





Fig. 5 Decay curves of <sup>210</sup>Pb activity based on core Dauriat B

identified in the diatom assemblages with optimal partitioning using sums of squares criterion with the software Zone version 1.2 (S. Juggins 2002, non-published program, http://www.campus.ncl.ac.uk/staff/ Stephen.Juggins/software/softhome.htm). Chrysophyte cysts and scales were counted with the goal of calculating the ratio of chrysophytes to diatoms (Smol 1985). Zone 1: Pre-mining period (1882–1939; 40–32 cm)

The majority of enumerated diatoms in this zone were from the species Fragilaria pinnata Ehrenberg (5-30%), Gyrosigma acuminatum (2–25%), Achnanthes nodosa (Kützing) Rabenhorst (2-10%), Navicula aboensis (2-5%), F. construens (Ehrenberg) Grunow (2-20%), F. brevistriata (7-25%), Cyclostephanos invisitatus (7-20%) and Achnanthes minutissima Kützing (7–10%). At the base of the core (ca. 1882), F. pinnata comprised up to 30% of diatom assemblages while F. construens represented up to 20%. The presence of G. acuminatum was restricted to this zone; towards 1890 this taxon reached 20% relative abundance. F. construens and F. brevistriata were more abundant at the end of the pre-mining zone. The percentage of chrysophyte cysts and scales varied respectively between 0.8 and 4.5% and 0 and 0.6%.

# Zone 2: Mining period (1939–1977; 32–18 cm)

The transition from zone one to zone two was pronounced. There was a rapid and dramatic increase in the abundance of Cyclostephanos invisitatus, and many taxa from zone 1 disappeared completely. This zone was characterized by the overwhelming dominance of C. invisitatus, which represented up to 80% of the diatom assemblage between 1950 and 1965, at approximately 28 cm depth. Furthermore, this zone contained lower relative abundances of other taxa such as Nitzschia acicularis (Kützing) W. Smith, N. perminuta, Diatoma tenuis, Cyclotella pseudostelligera and Asterionella formosa (all below 20%). The percentage of chrysophyte cysts relative to diatom valves was even lower in this zone than in zone 1, never exceeding 2.7%. Chrysophyte scales (relative to diatom valves) were more abundant than in the previous zone, but never exceeded 3.4%.

#### Zone 3: Post-mining period (1977–1999; 18–0 cm)

Beginning in 1980, the abundance of *Cyclostephanos invisitatus* dropped abruptly to approximately 20% and remained at that level until the surface of the core. *Asterionella formosa* increased in zone 3 to abundances around 10%, with a maximum of 30% near 1990. An increase in the relative abundance of

Aulacoseira granulata began in the mid-1980s, reaching 30% in 1997. With limited exceptions (e.g., *Fragilaria construens* and *F. brevistriata*, present below 10%) the taxa formerly dominant in zone 1 were almost completely absent and were replaced by *F. delicatissima* (W.S.) Lange-Bertalot (10–20%), *Asterionella formosa* (5–25%), *Tabellaria flocculosa* (around 10%), *Nitzschia gracilis* (10–20%) as well as *Aulacoseira granulata* (10–30%). The percentage of chrysophyte cysts and scales was generally higher relative to the previous zones, varying between 0 and 10.5% and 0 and 29.3%, respectively.

# Total phosphorus reconstruction

The relationship between diatom species and TP was modeled using weighted averaging partial least squares (WA-PLS version 1.0) (Juggins and ter Braak, unpublished program). This showed a strong relationship between diatom assemblage composition and TP, with a jackknifed  $r^2$  of 0.62 and a root mean squared error of prediction of 0.30 log (PT + 1) [µg 1<sup>-1</sup>]. Quantitative reconstruction of TP was done using the software C<sup>2</sup> (version 1.3, S. Juggins, 2003, non-published program, http://www.campus.ncl.ac.uk/staff/Stephen.Juggins/ software/softhome.htm).

From 1880 to 1940, diatom-inferred (DI) TP indicated concentrations around 30 µg l<sup>-1</sup> (Fig. 6). These inferred concentrations increased to 140 µg l<sup>-1</sup> by 1950, subsequently dropped to approximately 60 µg l<sup>-1</sup> near 1970, and increased again to 170 µg l<sup>-1</sup> in 1975. After 1975, DI-TP concentrations decreased to approximately 30 µg l<sup>-1</sup>, similar to those observed at the base of the core. The inferred TP concentrations are strongly driven by the abundance of *Cyclostephanos invisitatus* ( $r^2 = 0.91$ ). DI-TP also showed values near those of lakewater TP measured between 1977 and 1990 (Fig. 6). The mean residual between inferred and measured TP was 14 µg l<sup>-1</sup> (n = 15; standard deviation = 10 µg l<sup>-1</sup>).

Elemental geochemistry

Average concentrations and fluxes of the 33 elements in pre-mining, mining era and post-mining horizons of sediment core A are presented in Table 1.



Fig. 6 (a) Reconstruction of total phosphorus inferred from diatom assemblages and measured total phosphorus (Choulik and Moore 1992) between 1975 and 1990. (b) Values of log(x + 1) inferred DI-total phosphorus with their prediction errors. All analyses based on core Dauriat B

Elements Sr, Ba, Cr, Ga, K, Li, Mg, Rb, Pd, Pt, Rh, Sr, Tl, and V, varied little throughout the core (mining-pre-mining enrichment factor based on fluxes (EF) <2), were present in very low concentrations, or both. Na had concentrations <500 mg kg<sup>-1</sup> throughout the core, while each of the other elements listed above were present in lower concentrations (i.e., <100 mg kg<sup>-1</sup>). Elements U, Al, Mo, La, Sb, Rh, Fe, As had relatively low EFs (>2  $\leq$  3) during the mining era while Pb, Hg, Cd, Bi, Co, Zn, Cu, Ni, Mn, P, Ca, Be all had EFs >3 indicating significant enrichment associated with town development and mining activity in the area.

Figure 7 presents the concentration profiles from geochemical analyses of core A for major elements.

Element	Pre-mining 1860–1933 Conc mg $kg^{-1}$ dw	Mining era 1938–1978 Conc mg $kg^{-1}$ dw	Post-mining 1984–1999 Conc mg $kg^{-1}$ dw	Enrichment-mining vs. pre-mining	$\begin{array}{c} \text{Pre-mining} \\ 1860-1933 \\ \text{Flux } \mu\text{g} \\ \text{cm}^{-2} \text{ year}^{-1} \end{array}$	Mining era 1938–1978 Flux µg cm <sup>-2</sup> year <sup>-1</sup>	Post-mining (1984–1999) Flux $\mu$ g cm <sup>-2</sup> year <sup>-1</sup>	Enrichment-mining vs. pre-mining
Mining a	und urban de	velopment re	lated elements					
Pb	21.9	117.7	94.9	5.37	0.68	5.34	4.57	7.86
Hg	0.44	1.97	1.12	4.52	0.01	0.09	0.05	6.81
Cd	0.87	3.54	2.68	4.08	0.03	0.16	0.13	5.92
Bi	0.27	0.95	0.93	3.55	0.01	0.04	0.04	5.58
Co	21.4	73.1	65.9	3.41	0.61	3.39	3.17	5.52
Zn	229	779	479	3.41	7.18	37.06	23.14	5.16
Cu	64.5	214	142	3.32	2.11	9.97	6.81	4.73
Ni	38.1	103.1	70.9	2.71	1.07	4.91	3.41	4.60
Mn	801	2,222	2,558	2.77	22.2	99.4	123.3	4.48
Р	1,579	4,639	2,700	2.94	51.1	218	130	4.26
Ca	1,367	2,938	2,835	2.15	37.0	134	138	3.61
Be	2.10	4.51	3.67	2.15	0.06	0.21	0.18	3.50
As	12.7	23.9	22.8	1.89	0.36	1.08	1.10	2.97
Fe	108,500	186,182	185,250	1.72	2,917	8,410	8,969	2.88
Rh	0.002	0.004	0.007	1.93	0.0001	0.0002	0.0004	2.83
Sb	0.42	0.77	0.68	1.85	0.01	0.04	0.03	2.79
La	38.5	52.0	45.8	1.35	1.04	2.37	2.21	2.27
Mo	2.70	3.78	2.78	1.40	0.08	0.17	0.13	2.17
Al	36,550	44,627	32,600	1.22	1,004	2,059	1,570	2.05
U	4.73	5.74	5.02	1.21	0.13	0.26	0.24	2.04
Elements	s showing lin	nited or no e	nrichment					
Sr	16.5	16.9	15.8	1.02	0.44	0.78	0.77	1.77
Ba	149	133	87.0	0.89	4.08	6.15	4.22	1.51
Pt	0.008	0.006	0.006	0.85	0.0002	0.0003	0.0003	1.49
Cr	58.7	48.7	42.8	0.83	1.57	2.19	2.06	1.39
Tl	0.28	0.23	0.23	0.82	0.01	0.01	0.01	1.37
V	79.5	60.5	60.8	0.76	2.16	2.72	2.93	1.26
Li	28.0	18.0	20.1	0.64	0.74	0.81	0.97	1.09
Mg	5,713	3,430	3,598	0.60	151	154	174	1.02
Ga	9.61	5.24	4.85	0.55	0.26	0.24	0.23	0.91
Κ	9,048	4,985	4,373	0.55	243	222	211	0.91
Pd	3.84	2.01	1.58	0.52	0.10	0.09	0.08	0.89
Rb	49.6	25.8	22.6	0.52	1.33	1.15	1.09	0.86
Na	<500	<500	<500					
Sed rate	0.03	0.05	0.05	1.72				

Table 1 Concentrations, fluxes and enrichment factors of 33 elements in Lac Dauriat sediment core A in horizons from the premining, mining and post-mining eras<sup>a</sup>

<sup>a</sup> Flux = Concentrations (ng/g)  $\times$  sedimentation rate (g cm<sup>-2</sup> year<sup>-1</sup>) for each horizon

Enrichment = concentration or flux during mining era divided by value during pre-mining era

At the base of the core, between 1860 and 1890, Al, Fe, K, Mg and Mn were very abundant (Fig. 7). Their mean concentrations were  $>30,000 \text{ mg kg}^{-1}$  for Al,

>10,000 mg kg<sup>-1</sup> for Fe, between 7,000 mg kg<sup>-1</sup> and 10,000 mg kg<sup>-1</sup> for K, and between 5,000 mg kg<sup>-1</sup> and 6,000 mg kg<sup>-1</sup> for Mg. In 1950, the



Fig. 7 Profiles of elemental concentrations from the sediments of Lac Dauriat based on core Dauriat A. Note that the scales (all in  $mg kg^{-1}$ ) vary between elements. The division of zones was determined using the software Zone (see text for explanations)

concentrations of Al, Ca, and Fe reached 63,200 mg kg<sup>-1</sup>, 3,690 mg kg<sup>-1</sup>, and 143,000 mg kg<sup>-1</sup>, respectively, corresponding to EFs of 2.05, 3.61 and 2.88, respectively. Between 1930 and 1960, there were large increases (EF > 3) in Be, Ca, P, Mn, Ni, Cu,

Zn, Co, Bi, Cd, Hg, and Pb. Between 1933 and 1960, total Hg increased to 6.38 mg kg<sup>-1</sup> in the horizon dated to 1943, then declined sharply to below 2 mg kg<sup>-1</sup> in the rest of the core, while Pb also increased to a maximum of 131 mg kg<sup>-1</sup> in 1943 but

showed only a small decline thereafter. P reached maximum concentrations (7,380 mg kg<sup>-1</sup>) in horizons dated to 1938 (Fig. 7). Al, Ca, Fe, K, Mg, Mn and Sr were present in high abundances near the surface of the core (1984–1999). Their concentrations between 1984 and 1999 were >30,000 mg kg<sup>-1</sup> for Al, >2,500 mg kg<sup>-1</sup> for Ca, >170,000 mg kg<sup>-1</sup> for Fe, >4,000 mg kg<sup>-1</sup> for K, >3,000 mg kg<sup>-1</sup> for Mg, >2,000 mg kg<sup>-1</sup> for Mn, and > 20 mg kg<sup>-1</sup> for Sr (Fig. 7).

# Discussion

Zone 1: Pre-mining period, from 1882 to 1939 (40–32 cm)

In zone 1 (1882–1939), diatom assemblages (Fig. 4) and elemental profiles (Fig. 7) show that the aquatic environment had been little affected by pollution or sewage inputs. During this period, the population of the region comprised the Indian Reserves of the Matimekosh and the Naskapi. Some small-scale mine prospecting took place before the 1950s (Louis Edmond Hamelin, personal communication). This work, which included deforestation of Lac Dauriat's catchment, would have led to increased runoff, combined with the construction of the railroad, probably triggering the process of eutrophication near the end of the 1930s. These factors likely favoured increases in lake Fe, as a sustained increase in Fe was observed after the start of the 1930s (Fig. 7). Increases in the sedimentary concentrations of As, Cu, Hg, La, Mn, P, Pb, and Zn were also observed, again likely caused by the construction in progress. These elements are often present in increased abundances as a result of anthropogenic activity, such as mining (Lenntech, 2006). The soil of the Schefferville region is naturally rich in iron, which favours phosphorus retention (Choulik and Moore 1992). Diatom assemblages indicative of oligo-mesotrophic conditions were observed after 1880, including Fragilaria pinnata, F. construens and F. brevistriata.

The presence of several taxa with a high tolerance for organic pollution, including *F. pinnata, F. brevistriata* and *Achnanthes minutissima*, suggests an elevated lake water pH (Academy of Natural Sciences, Philadelphia 2004). These three species also live in weakly saline (0.9‰) and well-oxygenated waters (Academy of Natural Sciences, Philadelphia 2004). *F. pinnata* and *A. minutissima* can tolerate elevated concentrations of organic nitrogen and are both beta-mesosaprobic (Lecointe et al. 1993), indicating tolerance for organic matter in water. *F. brevistriata* is considered to be oligosaprobic, and assemblages of *F. construens* and *F. brevistriata* are typically indicators of alkaline waters. The TP optimum of *F. brevistriata* was 75 µg  $1^{-1}$  and that of *F. pinnata* was 55 µg  $1^{-1}$  (Hausmann and Kienast 2006).

The low percentage of chrysophyte cysts and scales indicates that a mesotrophic environment existed during the period 1882–1939, as chrysophytes are planktonic organisms that are rare in polluted, nutrient and phosphorus-rich waters (Duff et al. 1995; Quinlan et al. 1998). In 1914, phosphorus concentrations were below 800 mg kg<sup>-1</sup>, but they multiplied to reach 5,970 mg kg<sup>-1</sup> by 1927 (Fig. 7). The weak abundance of chrysophyte cysts suggests that the onset of the processes of eutrophication may have occurred.

Diatom assemblages, the presence of chrysophyte cysts and scales, and the low concentrations of elements present in this zone show that Lac Dauriat was little affected by mining and associated activities. Given that advanced eutrophication of the lake had not yet occurred, it was expected that the organic matter content of the sediments was low relative to the two subsequent zones, as witnessed by LOI (Fig. 4). Nevertheless, the construction of the railroad and the town of Schefferville may have contributed to the onset of eutrophication.

Zone 2: Mining period, from 1939 to 1977 (32–18 cm)

From 1956 to 1976, the population of Schefferville increased from 1632 to 4025 (Archer 1983, cited in Choulik and Moore 1992). Until 1975, no system for wastewater treatment was in place. The discharge of municipal sewage into Lac Dauriat was likely the principal cause of the accelerated eutrophication of the lake. This effluent was rich in nutrients such as phosphorus and nitrogen and provided the essential elements for the growth of algae, including diatoms. These algal blooms created anoxic conditions and selected species capable of surviving in extreme conditions. According to Drake and Freund (1980), problems related to algal blooms were observed in the lake at the end of summer, after the period of high runoff. There was an increase in the concentration of sedimentary phosphorus after 1927 (Fig. 7) and in inferred TP after 1940 (Fig. 6). These concentrations remained high up to the end of the 1970s (Figs. 6 and 7). Accordingly, diatom assemblages indicative of strongly polluted environments (i.e., the predominance of Cyclostephanos invisitatus) were found in zone 2 (Fig. 4). This dominant species exceeded 80% relative abundance during the period from 1950 to 1965 (Fig. 4). As determined by the TP model (Hausmann and Kienast 2006), the TP optimum of Cyclostephanos invisitatus was  $150 \ \mu g \ l^{-1}$ , also indicative of hypereutrophic conditions.

According to Choulik and Moore (1992), the Chl a concentration of Lac Dauriat was >40  $\mu$ g l<sup>-1</sup> between 1967 and 1975 (Fig. 2). This elevated concentration indicates high contributions of organic matter to the lake. TP concentrations peaked in 1975 (Fig. 2; Choulik and Moore 1992). Because of high levels of organic pollution in the lake, bacterial decomposition was probably also accelerated, which may have contributed to high nutrient concentrations that permitted proliferation of algae and an increase in biomass. In fact, 32.5% of the sediment was composed of organic matter at the 20.5 cm horizon. This coincides with the darkest coloured sediments between 20 and 30 cm, corresponding to 1950-1977, where organic matter content reached its highest levels (Fig. 4).

Anderson (1990) indicates that species from the genus *Cyclostephanos* respond positively to increases in phosphorus. Indeed, the rapidly increasing phosphorus concentrations in the 1930s (Fig. 7) are paralleled by an increase in *Cyclostephanos invisitatus*. This species is cosmopolitan, planktonic, and has a high tolerance to pollution (Krammer and Lange-Bertalot 1991a). It is widespread, and is found in running and stagnant waters. It frequently co-exists with *Stephanodiscus hantzschii* Grunow (absent in our core, but also difficult to differentiate from *C. invisitatus*), and is often associated with saprobic waters rich in organic matter (Krammer and Lange-Bertalot 1991a). Håkansson (2002) also found that *C. invisitatus* tolerates high nutrient concentrations,

such as those found in zone 2. Asterionella formosa, Nitzschia perminuta and Diatoma tenuis, also present in this zone, are indicative of alkaline environments and can tolerate sustained eutrophication (Krammer and Lange-Bertalot 1988, 1991 a). Between 1948 and 1966, Ca concentrations were at their highest levels, always exceeding 3,000 mg kg<sup>-1</sup>. The TP optimum for Asterionella formosa was 130  $\mu$ g l<sup>-1</sup> (Hausmann and Kienast 2006). Diatoma tenuis is an alphamesosaprobic taxon, indicating that it is tolerant of high levels of organic matter (Omnidia database; Lecointe et al. 1993). Gyrosigma acuminatum typically decreases in abundance with pollution (Krammer and Lange-Bertalot 1986), a trend that is also apparent in this zone (Fig. 4). Other taxa that were present in zone 1 that had low tolerance for organic matter content are poorly represented in zone 2. Thus, after zone 1 (1882–1939), eutrophication was strongly accelerated due to intense and continued inflows of sewage.

The percentage of chrysophyte cysts and scales stayed low, likely resulting from the accelerated nutrient enrichment and marked eutrophication in Lac Dauriat. Because the lake essentially functioned as a sewer during this period, inflows of municipal waste probably eliminated almost completely the presence of chrysophytes.

Concentrations of sedimentary As, Ca, Co, Cu, Fe, Hg, Mn, Pb, Sr and Zn increased markedly after the 1950s (Fig. 7), a decade that also marked the beginning of mining excavations and town development (Hilton 1968). Ni, Sr and Al reached maxima later in the mining era in horizons dated to the 1970s. The increase in Hg during the 1940s was unusual in that the concentration increased and then declined rapidly yielding a sharp peak, which suggests a spill or release of Hg during town site construction rather than from mining activity. Most other elements with high EFs in the mining era remained elevated in the post-mining era (Fig. 7). However, EFs for all elements were < 8 which is more typical of urban enrichments. For example, Van Metre and Callender (1997) found an EF of 6 for Pb in White Rock Lake (Dallas TX) following a shift from agriculture to urban use in the 1950s.

Other subarctic and arctic lakes with direct impacts of mining wastes generally have much higher EFs. In Lac Dufault, a lake in the Abitibi region of western Québec with several base metal mines operating in its watershed since the 1920s, maximum sediment concentrations of Cd, Cu, Pb and Zn were about  $10-20 \times$  higher than maxima in Lac Dauriat (Cattaneo et al. 2004; Couillard et al. 2004). Lake Orijärvi in Finland, which was impacted directly by mining waste (Salonen et al. 2006) had  $50-100 \times$  higher concentrations of Cd, Cu, Pb and Zn in sediments compared to Lac Dauriat. Lake Kuetsjärvi in the Kola Peninsula (Northwestern Russia) was impacted by a copper–nickel smelter within its watershed. EFs for Ni (26), Cu (14) and Hg (11) in Kuetsjärvi sediments were higher than Lac Dauriat while EFs for Co, Zn, Cd, Pb, Fe and Mn were similar, ranging from 1.2–5.5.

Concentrations and fluxes of heavy metals in Lac Dauriat were generally higher than in Lac Oksana, a reference lake located about 40 km southeast of Schefferville (54.48 °N, 66.47 °W) with low (fluxbased) EFs for Fe, Hg, Mn, and Pb of 0.65, 1.12, 2.0 and 1.08 (Muir, unpublished data 2006). This isolated lake would receive only air-borne anthropogenic inputs of metals, thereby illustrating the limited impact from regional atmospheric transport of metals from iron ore mining in the Schefferville area. While not receiving direct runoff from mining activity, Lac Dauriat nevertheless shows enrichment of Fe, Zn and Mn, which is typical of Labrador Trough glacial tills (Klassen 1999).

After 1976, organic matter content gradually diminished (Fig. 4). Moreover, the abundance of the pollution indicator *Cyclostephanos* invisitatus decreased and was replaced by other species such as Achnanthes minutissima, Cyclotella stelligera and Asterionella formosa (Fig. 4). Although A. minutissima can withstand elevated levels of organic nitrogen, the return or appearance of these other species shows that the environment had begun to recover (Lecointe et al. 1993). These sudden changes in diatom assemblage composition coincided directly with the installation of a wastewater treatment plant in 1975, also demonstrating the importance of these decontamination measures for preserving water quality in lacustrine ecosystems. Because diatoms are sensitive to changes in their environmental conditions, floristic variations as dramatic as those seen in this zone of the Lac Dauriat core are not surprising. Accordingly, the time interval that these limnological changes produced an explosion of Cyclostephanos invisitatus was relatively short-around thirty years.

Zone 3: Post-mining period, from 1977 to 1999 (18–0 cm)

In 1979, the population reached its maximum of 4,129 inhabitants (Archer 1983, cited in Choulik and Moore 1992). There was a large drop in nutrient inputs to the lake after 1975, following the opening of the waste water treatment plant, but also following the depopulation of Schefferville after 1979 and the closing of the mine in 1983. After 1982, the measured concentration of Chl *a* dropped dramatically to 15.3  $\mu$ g l<sup>-1</sup>, and further still to 6.4  $\mu$ g l<sup>-1</sup> in 1990 (Fig. 2; Choulik and Moore 1992). All these changes reflect that nutrient inputs (from municipal sewage) were considerably lower in Lac Dauriat, and explain the decrease in pollution-tolerant diatom taxa and the increase in the percentage of chrysophyte cysts. Phosphorus concentrations were below 3,000 mg  $kg^{-1}$  after 1977 (Fig. 7). The presence of populations of Cyclotella stelligera, Asterionella formosa, Fragilaria delicatissima and F. capucina may be indicative of a progressive change from alkaline waters towards a neutral to weakly acidic pH. The change in nutrients, including the decrease in phosphorus, could also explain the return of certain taxa. Nevertheless, Aulacoseira granulata was present in high abundances near the surface, indicating a nutrient rich, eutrophic environment (Jenny et al. 2002). The abundance of Cyclostephanos invisitatus varied about the 20% level in zone 3 (Fig. 4), a percentage comparable with that of zone 1. However, the concentration of sediment organic matter in zone 3 was more than double the level at the start of the 1870s (Fig. 4). The persistence of new species such as Aulacoseira granulata shows that the lake has still not reached its natural, pre-disturbance equilibrium.

Although the renewal time of Lake Seebergsee, in the Swiss Alps, is not known, it is probable that Lac Dauriat's renewal time is shorter because it is part of a chain of lakes, and not a headwater lake like Lake Seebergsee. Lake Seebergsee took more than eight decades to return to its original oligotrophic state (Hausmann et al. 2002), while Lac Dauriat is still in a mesotrophic state after more than 20 years. The percentage of chrysophyte cysts and scales was considerably higher in zone 3 than in the other zones and is evidence of less eutrophic environments, as chrysophytes cannot tolerate high nutrient waters (Smol 1985; Duff et al. 1995).

Mercury fluxes increased post-1960 from 0.023 in 1960 to 0.054  $\mu$ g cm<sup>-2</sup>year<sup>-1</sup> at the surface horizon correspond to an anthropogenic EF of about 2. This recent increase may be due to atmospheric deposition of anthropogenic Hg which has increased more than 2-fold over pre-1850 background in eastern North America (Landers et al. 1998; Muir et al. 2003). Elements such as Al, Ca, Fe, K, Mg, Mn, P and Pb still had elevated concentrations in sediments after 1977 until 1999, however concentrations were relatively stable. It appears that the huge influx of these elements in the lake decreased subsequent to the installation of sewage treatment and the exodus of the population. In addition to inputs from treated and untreated municipal waste, these elements could have come from a combination of road runoff, erosion from disturbance of the bedrock and glacial tills during town construction, and airborne deposition to the impervious surfaces in the town and from mining sites 5 to 10 km to the west and north of the lake. Eutrophication therefore slowed, and the trophic status of Lac Dauriat appears to have stabilized.

# Conclusions

Diatom assemblages, as well as ratios of chrysophytes, organic matter, and sedimentary elemental concentration, permitted the distinction of three strikingly different periods of limnological conditions during the recent history of Lac Dauriat. These changes were easily correlated with historical events in its catchment: the pre-mining period (up to 1939), the mining period (1939–1977), and the post-mining recovery period (1977–1999).

Lac Dauriat currently shows signs of recovery, but it still has not reached its natural, pre-mining equilibrium. The percent organic matter in 1999 was higher than that of the pre-mining period, as was the rate of sedimentation, levels of toxic heavy metals such as As, Cd and Pb, while fossil diatom assemblages suggested a mesotrophic environment in 1999. TP concentration decreased markedly after the installation of a wastewater treatment plant in 1975, and further decreased following the mines' closure in 1983 with the associated depopulation of the town. The species *Cyclostephanos invisitatus*, *Aulacoseira granulata*, *Nitzschia gracilis* and *Asterionella formosa* were dominant, and were capable of adapting to environments rich in organic matter. The near complete disappearance of certain taxa (e.g., Gyrosigma acuminatum, Achnanthes nodosa, Navicula aboensis) during the mining period, and the simultaneous appearance of new species (e.g., Fragilaria capucina, Aulacoseira granulata) illustrate the rapid adaptation of diatoms in the face of physical and chemical limnological changes. Sediment concentrations post-1980 of As, Cd, Cr, Cu, Pb, Hg and Zn exceed interim sediment quality guidelines for protection of aquatic life (Environment Canada 2002). Although their effects on individual algal taxa are unknown, sediment concentrations of three elements (As, Hg and Zn) greatly exceeded probable effect level concentrations for effects on sediment dwelling organisms during the mining era. Following a period of strong pollution and fertilization, such as that seen in Lac Dauriat, many years are necessary for the lake to reach its original ecological state. The detrimental effects on the environment are still in evidence more than 20 years after the closure of the mines, and Lac Dauriat has yet to reach its natural state of the period preceding extreme anthropogenic impact.

Our multi-proxy approach shows in a striking way the close lake-catchment linkages and the profound changes that occurred in this freshwater ecosystem along with the "rise" and "fall" of the town of Schefferville and its mining activities. In this respect, our study should be representative of the fate of many northern lake ecosystems that are located at the centre of important mining activities. Rapidly growing northern communities with limited access to sewage disposal due to lack of infrastructure (septic tanks, sewers, and sewage treatment plants) and/or presence of permafrost may therefore face serious challenges related to nutrient enrichment in freshwater ecosystems as a result of increased human activities in their catchments.

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