

## Palaeolimnological assessment of lake acidification and environmental change in the Athabasca Oil Sands Region, Alberta

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### ABSTRACT

Exploitation of the Athabasca Oil Sands has expanded hugely over the last 40 years. Regional emissions of oxidised sulphur and nitrogen compounds increased rapidly over this period and similar emissions have been linked to lake acidification in other parts of North America and Europe. To determine whether lakes in the region have undergone acidification, 12 lakes within the Regional Municipality of Wood Buffalo and the Caribou Mountains were selected to cover chemical and spatial gradients and sediment cores were obtained for palaeolimnological analyses including radiometric dating, diatom analysis, isotopic analysis of bulk sediment <sup>13</sup>C and <sup>15</sup>N, and spheroidal carbonaceous particles (SCPs). All lake sediment cores show evidence of industrial contamination based on SCPs, but there is no clear industrial signal in stable isotopes. Most lakes showed changes in diatom assemblages and sediment C:N ratios consistent with nutrient enrichment over various timescales, with potential drivers including climatic change, forest fires and anthropogenic nitrogen deposition. Only one of the 12 lakes investigated showed strong evidence of acidification with a decline in diatom-inferred pH from 6.3 to 5.6 since 1970 linked to increasing relative abundances of the acidophilous diatom species *Actinella punctata*, *Asterionella ralfsii* and *Fragilariforma polygonata*. Analysis of mercury (Hg) in the acidified lake showed increasing sediment fluxes over the last 20 years, a possible indication of industrial contamination. The acidified lake is the smallest of those studied with the shortest residence time, suggesting a limited capacity for neutralisation of acid inputs in catchment soils or by in-lake processes.

Key words: diatoms, acid deposition, mercury, climate change, nitrogen deposition, <sup>13</sup>C, Canada

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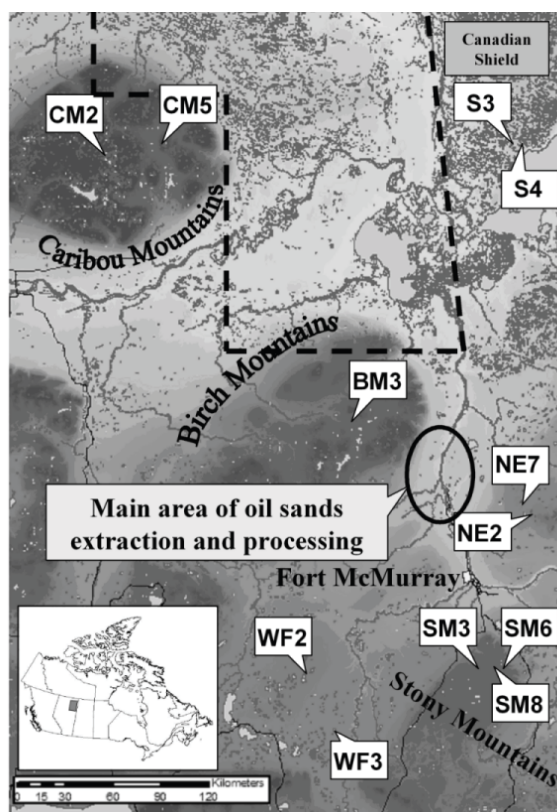
### 1. INTRODUCTION

Total reserves of oil within the Athabasca Oil Sands Region of northern Alberta are reported to be second in size only to those in Saudi Arabia. Low level extraction activities commenced in the region in the 1960s, but major global increases in the price of oil have led to a massive expansion of extraction activities in recent years. Production levels are predicted to increase by as much as three times from 2006 levels by 2015 (Pelley 2006). The subarctic boreal forest in this region contains large numbers of lakes which may be vulnerable to the combined effects of climate change and acid deposition produced by the emission of sulphur and nitrogen compounds from fossil fuel combustion (Schindler 1998).

Recent research programmes funded by multi-stakeholder groups in the region (e.g., the Cumulative Environmental Management Association, CEMA and the Wood Buffalo Environmental Association, WBEA) have investigated both the present and potential impacts of industrial activities associated with oil extraction on natural ecosystems and human health. Of particular concern are the impacts of industrial activities on traditional aboriginal uses of the land, including hunting and fishing. Lake acidification is a well-known impact of acid deposition in regions of slow weathering bedrock

and has occurred in eastern Canada and the USA (e.g., Schindler 1988; Charles 1991; Jeffries 1997; Stoddard *et al.* 1999; Jeffries *et al.* 2003; Whitfield *et al.* 2007) and many parts of Europe (e.g., Kamari *et al.* 1991; Henriksen *et al.* 1992; 1998; Curtis *et al.* 2000, 2005). Surveys of lake water chemistry in northern Alberta carried out by another multi-stakeholder group, the Regional Aquatics Monitoring Programme (RAMP) have identified acid sensitive lakes in many parts of the region (e.g., RAMP 2008). Hence the potential for acidification of surface waters by sulphur and nitrogen emissions from industrial activities in the Alberta Oil Sands Region requires urgent assessment.

The study of subfossil diatom remains in lake sediment cores is a well established technique for reconstructing changes in lakewater acidity through time and demonstrating acidification caused by acid deposition (e.g., Flower & Battarbee 1983; Battarbee *et al.* 1985; 1990; Smol *et al.* 1986). A previous palaeolimnological study of eight lakes in the Oil Sands Region found no evidence of acidification, but was focussed on larger lakes of relatively low acid-sensitivity (Hazewinkel *et al.* 2008). This study therefore concluded that the lack of evidence for acidification in these lakes did not indicate there was no risk of lake acidification in the region and that further, more focussed studies were needed.



**Fig. 1.** Distribution of study sites for lake sediment core analysis. Dotted line marks approximate location of Wood Buffalo National Park.

The aim of the present study was to expand the palaeolimnological approach to a further 12 lakes, to include smaller and more acid-sensitive sites across spatial and chemical gradients. In addition to diatom analysis and radiometric dating of sediment cores, several additional analyses for indicators of industrial contamination were included: spheroidal carbonaceous particles (SCPs) are unambiguous indicators of deposition arising from fossil fuel combustion; stable isotopes of  $^{13}\text{C}$  and  $^{15}\text{N}$  may provide evidence of disturbance to lake biogeochemistry *via*, amongst others, anthropogenic N deposition and, with associated C:N ratios, provide information on changes to sources of organic matter in lake sediments; and mercury analysis can provide evidence of possible industrial contamination.

## 2. METHODS

### 2.1. Site selection and lake coring

The study region incorporates the Regional Municipality of Wood Buffalo (RMWB; area 68,454 km<sup>2</sup>, 2006 population *ca* 90,000) and the Caribou Mountains west of Wood Buffalo National Park (approximately 11,000 km<sup>2</sup>; Fig. 1). Selection of lakes for coring was based partly on a previous study of surface sediments from 45 lakes in the region and core bottom samples from a subset of these lakes (Pla *et al.* 2006). Diatom analysis of the 45 surface sediment samples obtained during 2003 and 2004 was used in conjunction with contemporary

water chemistry from the RAMP Acid Sensitive Lakes programme (RAMP 2007) to derive the previous diatom-pH transfer function using bootstrapped weighted averaging partial-least-squares regression (WA-PLS: ter Braak *et al.* 1993; RMSEP<sub>boot</sub> = 0.38, maximum bias = 0.65; see Hazewinkel *et al.* 2008 for full description of sites and methods). Sediment core bottom samples, undated but assumed to be pre-industrial, were analysed for diatoms for comparison with surface sediment samples and both the magnitude of change in diatom assemblages (measured as chord distance; Overpeck *et al.* 1985; Gavin *et al.* 2003) and diatom-inferred pH from the transfer function were calculated. The sediment core top data from this previous study were used in combination with the new cores collected for the present study to derive a new diatom-pH inference model.

Final site selection for new coring was to provide regional coverage and a gradient of acid sensitivity from low (pH >6.5) to sensitive (pH 6.0–6.5) and acidic (pH <6.0) lakes (Fig. 1, Tab. 1). Based on the previous work comparing core surface and bottom samples (Pla *et al.* 2006), all selected lakes with existing data showed major changes in diatom assemblages measured as chord distance, but a variety of changes in diatom-inferred pH (DI-pH) from no change to a large decline in DI-pH from core bottoms to surface samples. Some of the lakes selected for coring were not included in the previous study so no measure of diatom change or DI-pH were available. Lakes SM8 and NE7 were priori-

**Tab. 1.** Twelve lakes selected for palaeolimnological study. \* Data from Bennett *et al.* (2008).

CEMA Code	Coring location		Lake area*	Max depth*	Lake vol.*	Catchment area*	C:L ratio	Residence time*	Core ID	Coring date	Coring depth	Core length	Acid sensitivity	Sediment Hg concentration
	Latitude	Longitude												
	(decimal degrees)													
<i>Birch Mountains</i>														
BM3	57.65232	112.61289	96.6	4.6	1.33	28.6	29.6	0.46	ALB02	21-Aug-06	3.10	0–25.5	low	129.7
<i>Caribou Mountains</i>														
CM2	59.11909	115.12837	955	6.0	27.32	37.9	4.0	2.06	ALB15	25-Aug-06	5.40	0–35.0	low	111.1
CM5	59.23804	114.52351	55.2	1.5	0.87	2.6	4.7	1.49	ALB16	25-Aug-06	1.30	0–18.0	sensitive	107.1
<i>North-east of Fort McMurray</i>														
NE2	57.09281	110.75042	33.7	1.8	0.43	17.0	50.5	0.33	ALB09	23-Aug-06	1.65	0–24.5	sensitive	121.6
NE7	57.14667	110.86483	11.2	2.0	0.11	4.1	36.4	0.19	ALB21	30-Aug-06	1.50	0–25.0	acidic	137.8
<i>Shield lakes north of Lake Athabasca</i>														
S3	59.19059	110.67251	144.8	10.6	4.84	29.7	20.5	1.31	ALB18	26-Aug-06	10.50	0–33.5	low	66.8
S4	59.16801	110.56855	141.6	9.5	5.64	123.1	86.9	2.41	ALB17	26-Aug-06	9.50	0–32.0	low	123.7
<i>Stony Mountains</i>														
SM3	56.20155	111.36388	186.1	3.1	2.69	7.7	4.1	1.55	ALB05	22-Aug-06	3.10	0–26.0	sensitive	91.7
SM6	56.22227	111.17004	69.9	1.6	0.62	3.4	4.9	0.81	ALB04	22-Aug-06	1.60	0–19.0	acidic	93.5
SM8	56.21567	111.20536	191.3	2.5	1.69	9.7	5.1	0.85	ALB03	22-Aug-06	1.40	0–18.5	acidic	93.6
<i>West of Fort McMurray</i>														
WF2	56.24551	113.14144	75.5	1.8	0.71	23.4	30.9	1.45	ALB12	24-Aug-06	1.60	0–38.0	low	89.7
WF3	55.90871	112.86468	216.4	2.0	2.09	38.1	17.6	1.02	ALB11	24-Aug-06	1.20	0–25.0	acidic	102.7

tised since these sites were to be intensively monitored for use in application of the dynamic acidification model MAGIC (Whitfield *et al.* 2010, this issue). Details of the 12 finally selected lakes are given in table 1 and their locations in figure 1.

Sediment coring was carried out by UCL staff joining the RAMP regional lakes survey during August 2006. Duplicate cores were obtained using a HTH gravity corer (Renberg & Hansson 2008) from the deepest part of each lake where possible, directly from a float plane or (for very small lakes) float helicopter. The primary core, judged by visual assessment as the least disturbed and/or longest core, was used for palaeolimnological analysis while the second core was extruded and retained to provide archived back-up material. Intact cores were transported back to the field station where they were extruded at 0.5 cm intervals and samples kept refrigerated at 4 °C prior to analysis. Water chemistry samples collected at the same time for the RAMP survey provided the latest data points for the RAMP 2007 Annual Report, summarised for cored lakes in table 2. See RAMP (2007) for water chemistry analytical methods.

## 2.2. Palaeolimnological analyses

### 2.2.1. Sediment sub-sampling

The suite of analyses performed on each core included the following: (1) lithostratigraphy (dry weight and loss-on-ignition (LOI)), (2) radiometric dating ( $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ ), (3) diatom analysis, (4) spheroidal carbonate particle (SCP) analysis and (5) sediment isotopic analysis ( $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ ). In addition, mercury analysis was undertaken on the core from NE7.

Since several of these analyses are destructive, the following sequential strategy was employed to ensure sufficient sediment material for all analyses, based on the 0.5 cm extrusion intervals: (1) wet density was sampled every 3 cm (used in  $^{210}\text{Pb}$  method) starting at the surface sample (0–0.5 cm, 3.0–3.5 cm, etc.) and all intervals were subsequently dried, (2) dry weight and LOI were determined on subsamples from the surface sample and then every second interval starting at 0.5–1.0 cm, (3) intervals for  $^{210}\text{Pb}$  dating were tailored to each core, based on an initial skeleton analysis and then in-filled to cover the record in more detail, (4) diatom analysis; depending on core length, 18–20 levels were analysed sequentially, usually at 1 cm intervals, (5) levels for SCP analysis were selected to cover the last 150 years based on the chronology determined by the  $^{210}\text{Pb}$  results and (6) sediment isotopic analysis of subsample ( $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ ) on the 0.25 and 0.75 cm samples and thence every 1 cm. Hg analyses were performed on all surface sediment samples and the site with the greatest concentration was selected for down-core Hg analysis.

### 2.2.2. Dry weight and loss-on-ignition (LOI) analysis

Sediment dry weight and LOI determinations were made gravimetrically following heating of sediment sub-samples to 105 °C and 550 °C respectively. These analyses are routinely carried out during stratigraphic studies to provide a check for major changes in organic matter content of sediment cores which might indicate changes in sedimentation regimes or sediment in-wash events. Wet density measurements were undertaken on every sixth sample by evenly filling wet sediment into a 2 cm<sup>3</sup> measurement vial and weighing on an electronic analytical balance to four decimal places.

**Tab. 2.** Selected water chemistry for the 12 cored lakes (source: RAMP 2007).

CEMA Code		Cond ( $\mu\text{S cm}^{-1}$ )	pH	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	NH <sub>4</sub>	NO <sub>3</sub>	Alk	ANC	TDN ( $\mu\text{g L}^{-1}$ )	TDP ( $\mu\text{g L}^{-1}$ )	DOC ( $\text{mg L}^{-1}$ )
				(μeq L <sup>-1</sup> )												
BM3	Min	46.2	6.87	280.4	155.5	82.7	DL	2.1	107.9	1.1	DL	253.8	409.7	693.3	31.1	17.3
BM3	Mean	55.5	7.05	324.6	168.5	110.5	12.3	3.5	154.4	2.4	1.3	309.0	459.2	903.1	46.6	20.9
BM3	Max	60.9	7.30	377.2	185.1	122.7	16.9	5.2	200.7	4.0	0.6	372.0	499.3	1590.5	59.9	23.3
CM2	Min	20.1	6.80	195.1	86.8	18.2	DL	3.2	30.9	0.8	DL	194.2	266.8	417.1	6.9	12.0
CM2	Mean	28.5	6.87	212.3	90.6	23.0	6.6	4.2	40.3	3.4	1.1	211.3	290.3	612.5	9.9	13.5
CM2	Max	32.4	6.99	253.5	101.2	29.1	10.7	5.3	52.8	2.0	0.7	242.0	337.8	1050.1	14.2	15.9
CM5	Min	15.8	6.04	150.7	55.1	14.4	DL	2.7	18.2	1.0	DL	83.6	200.1	565.8	14.3	17.8
CM5	Mean	20.2	6.27	165.7	61.1	31.6	3.9	4.0	27.5	1.7	0.8	112.0	231.6	978.1	19.0	21.6
CM5	Max	22.7	6.48	188.6	70.0	63.8	6.1	6.2	30.6	5.1	0.4	130.0	296.4	2425.3	23.5	28.2
NE2	Min	23.6	6.05	183.6	89.7	20.9	DL	1.4	8.3	0.8	DL	131.9	285.3	455.1	6.4	25.7
NE2	Mean	26.8	6.26	225.8	106.4	28.3	4.1	2.8	12.2	1.2	0.8	157.0	350.1	753.1	9.7	30.4
NE2	Max	30.6	6.70	287.9	120.9	33.9	6.9	3.7	15.6	0.6	0.6	201.8	430.4	1660.0	12.1	33.7
NE7	Min	19.3	4.90	114.8	65.0	16.3	DL	2.1	6.2	0.9	DL	52.6	188.7	527.8	6.9	27.0
NE7	Mean	22.4	5.13	167.8	80.0	21.9	1.6	4.8	9.2	2.3	1.5	62.5	258.1	636.9	7.7	31.6
NE7	Max	24.0	5.37	203.6	93.0	26.5	3.8	9.5	15.9	6.0	0.6	78.4	306.9	724.0	8.3	34.2
S3	Min	39.3	7.03	226.0	128.3	62.5	9.2	30.0	7.4	1.2	DL	301.2	389.9	398.9	2.9	14.2
S3	Mean	42.1	7.08	243.2	136.0	67.4	13.3	33.9	14.3	1.5	0.5	306.9	412.7	525.0	3.4	19.8
S3	Max	49.8	7.14	302.9	153.0	71.3	18.7	37.1	25.1	0.6	0.5	311.6	483.9	636.1	4.1	33.4
S4	Min	50.8	7.20	286.4	178.5	60.4	15.1	29.6	20.4	0.8	DL	410.6	491.2	388.3	1.2	12.1
S4	Mean	53.6	7.23	315.9	193.6	66.1	17.7	31.7	31.8	0.7	0.2	435.9	530.3	448.1	3.8	15.2
S4	Max	55.1	7.29	407.2	218.8	73.9	27.9	39.7	49.2	0.5	0.2	451.8	639.3	533.0	5.0	24.2
SM3	Min	11.7	6.37	86.8	41.1	22.9	2.6	3.6	7.9	0.8	DL	90.0	142.7	440.0	5.1	11.9
SM3	Mean	15.5	6.42	94.6	47.8	26.5	8.6	6.1	19.1	0.5	0.1	98.3	152.8	467.0	5.5	12.4
SM3	Max	17.2	6.47	109.3	53.5	29.2	10.5	9.5	27.0	0.5	0.2	103.2	166.2	515.0	6.2	13.0
SM6	Min	11.6	5.09	54.9	29.0	15.1	DL	3.3	19.7	1.1	0.7	32.6	76.5	611.0	16.7	12.0
SM6	Mean	13.6	5.30	64.5	33.8	22.9	10.0	4.2	24.8	3.0	2.8	41.1	102.2	722.5	25.6	15.4
SM6	Max	15.6	5.45	74.4	41.1	33.5	13.3	5.3	34.7	5.4	4.5	49.6	123.1	828.0	44.8	16.7
SM8	Min	12.1	4.82	47.4	22.3	14.9	DL	3.2	25.9	1.5	DL	21.2	56.9	593.0	20.2	14.3
SM8	Mean	13.1	5.01	56.6	25.7	25.1	8.8	5.6	30.4	2.0	0.2	30.2	82.0	772.1	28.3	17.0
SM8	Max	14.1	5.18	65.9	28.8	39.1	13.8	7.3	39.8	0.7	0.5	37.2	100.6	1120.0	33.2	20.1
WF2	Min	27.4	6.53	210.6	74.9	29.6	7.2	7.3	19.1	1.0	9.6	158.0	287.1	953.5	24.0	19.0
WF2	Mean	33.5	6.67	248.7	81.5	35.7	17.7	10.4	35.3	2.6	22.5	192.2	318.0	1301.3	37.8	20.4
WF2	Max	38.2	6.79	317.9	93.8	54.7	23.3	13.1	42.9	4.7	6.0	216.2	432.3	1924.1	70.3	21.5
WF3	Min	20.2	4.76	92.8	57.4	35.7	1.8	3.4	18.5	0.9	0.1	22.6	166.5	647.7	13.5	30.0
WF3	Mean	24.3	5.11	146.4	63.0	46.7	11.0	12.3	33.9	5.6	1.0	60.3	225.5	944.3	25.8	33.3
WF3	Max	28.8	5.67	166.2	69.9	63.9	16.9	41.9	56.7	0.5	0.4	95.8	218.4	1464.6	50.2	35.6

### 2.2.3. Radiometric dating

Sediment samples were analysed for <sup>210</sup>Pb, <sup>226</sup>Ra, <sup>137</sup>Cs and <sup>241</sup>Am by direct gamma assay in the Bloomsbury Environmental Isotope Facility (BEIF) at University College London, using an ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector. <sup>210</sup>Pb was determined *via* its gamma emissions at 46.5 keV, and <sup>226</sup>Ra by the 295 keV and 352 keV gamma rays emitted by its daughter isotope <sup>214</sup>Pb following three weeks storage in sealed containers to allow radioactive equilibration. Caesium-137 and <sup>241</sup>Am were measured by their emissions at 662 keV and 59.5 keV. The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy gamma rays within the sample. Core chronologies were calculated using the constant rate of supply (CRS) model (Appleby 2001).

### 2.2.4. Diatom analysis

Diatom slides were prepared according to Battarbee *et al.* (2001) and identifications followed the published

literature (Hohn & Hellerman 1963; Patrick & Reimer 1966–1977; Krammer & Lange-Bertalot 1986, 1988, 1991; Lange-Bertalot & Krammer 1989; Camburn & Charles 2000; Flower 2005; Siver *et al.* 2005). Diatom analysis was undertaken using a Leitz Labrolux light microscope equipped with a phase contrast oil immersion 1.3 NA × 100 objective. Approximately 300 valves were counted in each level (except for those sediment sections where diatom preservation was poor).

A revised Weighted Averaging – Partial Least Squares regression (WA-PLS) (ter Braak *et al.* 1993) diatom-pH transfer function model based on the previous 45 sediment core top samples (Pla & Curtis 2006; Hazewinkel *et al.* 2008) plus the current study sites was used to reconstruct pH histories for lake sediment cores, following taxonomic harmonization of diatom counts and combination of the two core top datasets. All diatom taxa and all surface sediments were used to build the new model and all counts from the sediment record were used for pH reconstruction. No taxa were omitted to avoid poor correlation between sediment core taxa and training set taxa, in order to produce the most correct reconstruction despite the potential loss of predictive power from the model. Model performance was

**Tab. 3.** Diatom-pH transfer function (WA-PLS) models using 1–5 components (C1–C5).

Name	RMSE	R <sup>2</sup>	Av. Bias	Max. Bias	Boot. R <sup>2</sup>	Boot. Av. Bias	Boot. Max. Bias	RMSE s1	RMSE s2	RMSEP
C1	0.3055	0.8528	0.0000	0.7323	0.6876	-0.0315	0.8704	0.1298	0.4588	0.4768
C2	0.1672	0.9559	0.0000	0.2617	0.6902	-0.0588	0.8433	0.1522	0.4490	0.4741
C3	0.1073	0.9818	0.0000	0.1736	0.6921	-0.0568	0.8360	0.1729	0.4471	0.4794
C4	0.0718	0.9919	0.0000	0.1121	0.6867	-0.0589	0.8749	0.1822	0.4511	0.4865
C5	0.0480	0.9964	0.0000	0.0399	0.6815	-0.0608	0.9092	0.1925	0.4547	0.4938

assessed using bootstrap cross-validation (Birks *et al.* 1990).

WA-PLS models with between 1 and 5 components were produced and evaluated in terms of RMSEP<sub>boot</sub> (Tab. 3). The simplest one component model (C1: RMSEP<sub>boot</sub> = 0.4768, R<sup>2</sup> = 0.6876) performed almost as well as the two component model (C2: RMSEP<sub>boot</sub> = 0.4741, R<sup>2</sup> = 0.6902) with a deterioration in RMSEP<sub>boot</sub> thereafter as further components were added (Tab. 3). Hence the one-component model (WA-PLS C1) was used here to determine diatom-inferred pH for reconstruction.

### 2.2.5. Spheroidal carbonaceous particles

Spheroidal carbonaceous particle (SCP) analyses were undertaken following the method described in Rose (1994). SCPs were counted using a light microscope at ×400 magnification and the sediment concentration calculated in units of 'number of particles per gram dry mass of sediment' (g DM<sup>-1</sup>). The criteria for SCP identification under the light microscope followed Rose (2008). Analytical blanks and SCP reference material (Rose 2008) were included in each batch of sample digestions. Reference concentrations agreed with the expected values while no SCPs were observed in the blanks. The detection limit for the technique is *ca* 100 gDM<sup>-1</sup> and concentrations have an accuracy of *ca* ± 45 gDM<sup>-1</sup>.

### 2.2.6. Stable isotope analysis

Bulk organic matter sub-samples from sediment cores from each lake were air dried at 40 °C or below. These sub-samples were then milled to a fine powder using a Retsch mixer mill. Approximately 0.001 g of milled sediment was transferred to pre-weighed tin capsules, which were then sealed. The amount of dried sediment in each capsule was recorded.

The samples were analysed for total N and C, <sup>14</sup>N/<sup>15</sup>N and <sup>12</sup>C/<sup>13</sup>C at the UC Davis Stable Isotope Facility, California, USA on Hydra 20-20 or Anca-GSL isotope ratio mass spectrometers. The concentration of N and C in the samples is expressed as grams N or C per gram dry weight of sediment. The isotopic ratio of <sup>14</sup>N/<sup>15</sup>N and <sup>12</sup>C/<sup>13</sup>C is expressed using the delta (δ) notation in parts per thousand (or *per mille*, ‰), where δ<sup>15</sup>N (‰) and δ<sup>13</sup>C (‰) = [(R<sub>sample</sub> / R<sub>standard</sub>) - 1] × 1000, where R is the <sup>14</sup>N/<sup>15</sup>N or <sup>12</sup>C/<sup>13</sup>C ratio in the measured sample or the appropriate standard. The stan-

dard for nitrogen is the δ<sup>15</sup>N of atmospheric nitrogen (commonly referred to as AIR), and for δ<sup>13</sup>C the standard is Vienna Pee Dee Belemnite (VPDB). The C/N ratio was calculated from the mass of N and C and converted to atomic ratios by multiplying the mass ratios by 1.167 (the ratio of the atomic weights of N and C).

### 2.2.7. Mercury analysis

Mercury analyses were performed on surface sediment subsamples from the cored lakes and then down the core profile for the lake with the greatest surface sediment concentration using freeze dried, milled samples on a Milestone DMA-80 Direct Mercury analyser. Concentration data were converted to fluxes using sediment accumulation rates calculated from the <sup>210</sup>Pb chronology.

## 3. RESULTS

### 3.1. Lithostratigraphic analysis

The cores show a wide range in organic matter content as illustrated by LOI values ranging from <20% in S3 to >80% in WF2. The presence of dramatic short-term fluctuations in dry weight or LOI can indicate that stratigraphic integrity has been compromised e.g., through discontinuities in the record. While there are few such indications in the present core records, there are small shifts in LOI in the bottom of core ALB04 (lake SM6) and at 5 cm depth in both ALB02 (lake BM3) and ALB05 (lake SM3) (data not shown, see Curtis *et al.* 2009).

### 3.2. Sediment core chronologies

Dating of sediment cores using <sup>210</sup>Pb and <sup>137</sup>Cs reveals a large range of sediment accumulation rates, but all 12 cores encompass at least 100 years of accumulated sediment. Most cores showed straightforward dating profiles, although three showed possible evidence of missing surface sediments (lakes SM8, WF3 and S3) introducing uncertainty into the interpretation of very recent changes. Age-depth profiles and sedimentation rates for individual cores are presented in Curtis *et al.* (2009).

### 3.3. Diatom analysis

The sedimentary diatom assemblages examined in the 12 cores displayed a wide diversity of species, both planktonic and benthic, that are closely linked to

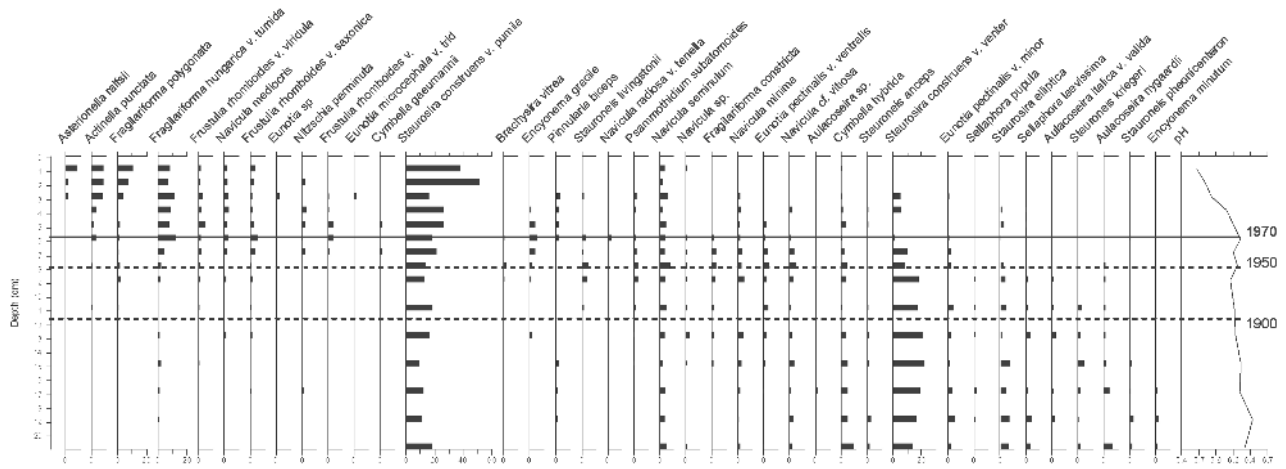


Fig. 2. Diatom inferred pH change in lake NE7 (core ALB21).

Tab. 4. Summary of the principal overall changes indicated by trends in diatom frequency abundances in 12 lake sediment cores.

Lake / Core	Acidified	Nutrient enriched	High diatom plankton	Species diversity
BM3 / ALB02	No – slight pH increase	yes	yes	high
CM2 / ALB15	No – pH increasing since pre-1900	yes	yes	moderate
CM5 / ALB16	No – pH increasing since 1980s	yes	no	poor
NE2 / ALB09	No – no pH change	no	no	moderate
NE7 / ALB21	Yes – pH decline	no	no	moderate
S3 / ALB18	No – no pH change	yes	no	moderate
S4 / ALB17	No – no pH change	yes	yes	high
SM3 / ALB05	No – slight pH decline	no	no	low
SM6 / ALB04	No – no pH change	yes	no	moderate
SM8 / ALB03	No – pH increasing since pre-1900	slightly	no	low
WF2 / ALB12	No – pH increasing since c. 1990	yes	no	moderate
WF3 / ALB11	No – pH increasing since pre-1900	yes	yes	moderate

regional water quality variations as well as to specific local site factors. Many of the species are cosmopolitan but North American species (e.g., *Stephanodiscus niagarae* Ehr., *Cyclotella michiganiana* Skv.) often contribute significantly to the diatom phytoplankton component. Endemic benthic taxa are less significant but occurrences of rare taxa such as *Carpantogramma crucicula* (Grun. ex Cl.) Ross, *Pinnularia cuneicephala* Smith, *P. latevittata* v. *domingensis* Cleve and *Staurosira stodderi* Lewis are noteworthy. Some small naviculoids in several cores, present in relatively low abundances, were taxonomically problematic.

Diatom analysis of the 12 cores indicates that the lakes can be placed broadly into three categories that indicate lake acidification, nutrient enrichment or an absence of significant change. The diatom stratigraphies of three cores are presented to indicate these categories. Only one of the sites (lake NE7, core ALB21) indicates marked recent acidification (Fig. 2). Diatom assemblages in this core were moderately diverse (123 taxa being identified) and showed marked species changes. Although circum-neutral species such as tycho planktonic *Staurosira construens* v. *pumila* dominated the diatom assemblages, acid water indicator diatoms and especially *Actinella punctata* appear towards the core

top (Fig. 2). *Actinella punctata* indicates strongly acid water and has pH optima of 5.1 in North American (Dixit *et al.* 1993) and 5.2 in European (Birks *et al.* 1990) data sets. It appears in the core at between 6 and 7 cm depth (ca 1970) and increases in abundance particularly in the upper 3 cm or from ca 1990. Other acid indicating species such as the planktonic *Asterionella ralfsii* and tycho planktonic *Fragilariforma polygonata* also showed sharp increases in the upper 3 cm of sediment. *Frustulia rhomboides* v. *saxonica* and several circum-neutral *Cymbella* and *Navicula* taxa showed small abundance peaks around 5.5–7.5 cm depth (ca 1950–70). Other circum-neutral and tycho planktonic taxa such as *Staurosira elliptica* and several *Aulacoseira* spp. showed abundance declines towards the core top. No species typical of nutrient enrichment were observed. Overall, this core provides strong evidence that the lake has been recently acidified with a marked DI-pH decline from about pH 6.3 to pH 5.6 since 1970 (Fig. 2). Although two other cores (ALB04 from lake SM6 and ALB09 from lake NE2, Tab. 4) indicated slight acidification, only NE7 displayed a convincing declining pH trend.

Several sites showed increases in diatom-inferred pH (alkalinisation) and many of the sites appear to have

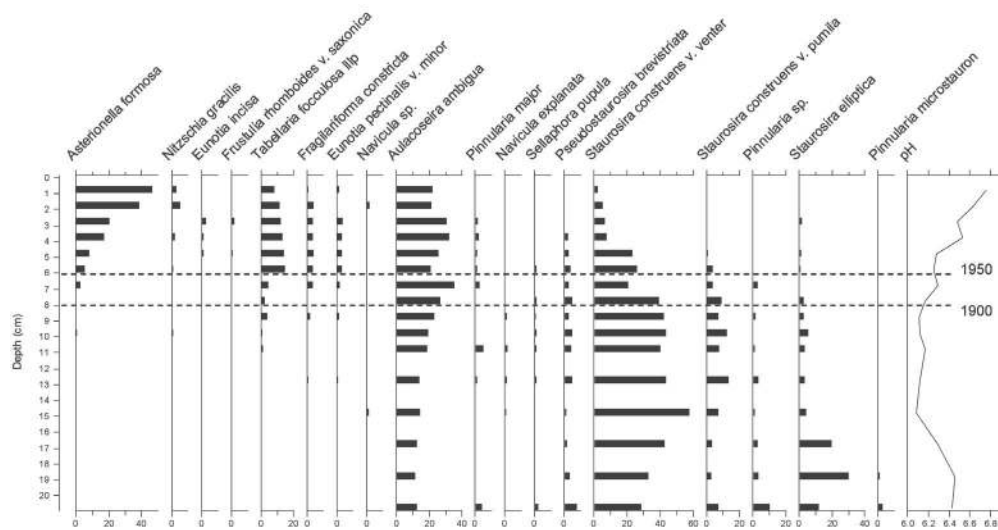


Fig. 3. Increasing abundance of the planktonic diatom *Asterionella formosa* and diatom-inferred pH in lake WF3 (core ALB11).

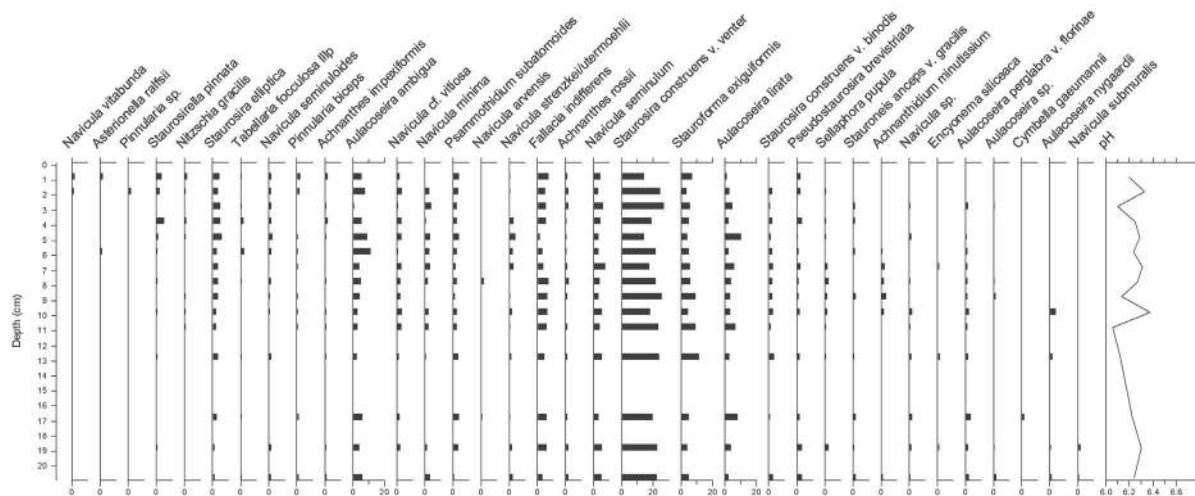


Fig. 4. Stable diatom communities in lake NE2 (core ALB09).

experienced nutrient enrichment in the recent past (Tab. 4). This is typically demonstrated by the increasing abundance of planktonic diatoms commonly associated with more nutrient rich conditions, for example the major increase of *Asterionella formosa* in lake WF3 (core ALB11; Fig. 3). This taxon was unrecorded below 12 cm depth and showed a major abundance increase from above 7 cm depth (ca 1936) to reach almost 50% of the total diatom assemblage in surface sediment. Another planktonic diatom, *Aulacoseira ambigua*, also indicative of nutrient enrichment, also showed increasing frequency abundances, from the core base to the most recent sediment. Less common but also indicating increased nutrients, *Nitzschia gracilis* increased in the recent sediment. Commensurate with the increasing abundances of these taxa indicating higher nutrient status, several fragilarioids declined in the core. These taxa are primarily benthic but are easily resuspended into the water column and *Stauroneis elliptica* and *St.*

*construens v. venter* both show strong declines and only *Fragilariforma constricta* shows a small increase. Similarly, some of the more uncommon but larger benthic *Pinnularia* species have also declined in abundance. Possibly, these changes could reflect diminished underwater light availability as a result of the development of the planktonic diatoms and doubtless other phytoplankton; alternatively, nutrient or light optima of the benthic species may have changed. Overall, the diatom stratigraphy of this core shows a large increase in planktonic diatom species that indicates strong nutrient enrichment of the lake. There is a corresponding increase in diatom-inferred pH from pre-1900 to the present day, although higher pH values were also indicated at the core base.

Diatom analysis in two cores (ALB09 from lake NE2 and ALB04 from lake SM6) showed no marked trend changes in diatom abundances indicating an absence of significant eutrophication or acidification. The diatom frequency diagram for lake NE2 (Fig. 4)

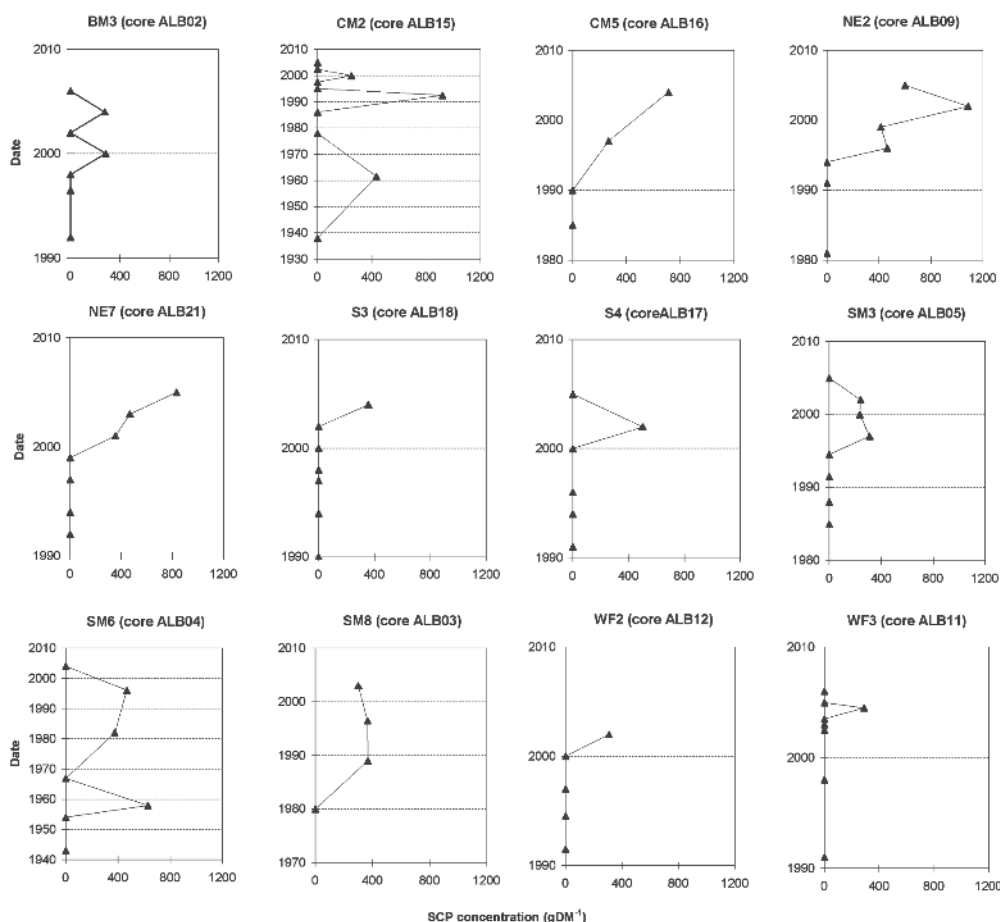


Fig. 5. SCP concentration profiles for the 12 cores plotted on radiometric date axes.

showed relatively small changes in species composition. The semi-benthic fragilarioid species *Staurosira construens* v. *venter* was common throughout the sediment core with abundances fluctuating around 20% without any clear trend change. Several diatoms showed a small trend towards higher abundances from the core base to around 7–5 cm sediment depth (*ca* 1960–1976) before declining. One of these species *Aulacoseira ambigua* is an indicator of higher nutrient conditions. Only two low abundance species increased above 6 cm depth (1969), *Asterionella ralfsii* and *Staurosira elliptica*. The former species is planktonic in habit and could indicate a small acidity change, but the minor increase in *A. ambigua* could indicate slight nutrient enrichment around 5 cm depth in the core (*ca* 1976) with a subsequent decline suggesting that this change was not sustained. Overall, the diatom stratigraphy of this core indicates fairly stable conditions with hints of acidity and nutrient changes which are not detectable in the diatom-inferred pH, which shows no convincing trend.

### 3.4. SCP analysis

Spheroidal carbonaceous particles (SCPs) provide an unambiguous indicator of contamination from high-temperature fossil fuel combustion (coal and fuel oil,

but not gas) because they are not produced from wood, biomass or charcoal combustion (e.g., forest fires) and hence have no natural sources (Rose 2001). SCPs were found at low but detectable concentrations in all cores. The highest recorded concentration exceeded 1000 gDM<sup>-1</sup> only in lake NE2 (core ALB09; see Fig. 5). No SCPs were detected below 5 cm in any core suggesting any contamination is recent. This is confirmed by the radiometric dating which shows that the earliest presence of SCP contamination was found in lake SM6 (core ALB04) in the late 1950s and in lake CM2 (core ALB15) in the 1960s (Fig. 5). Temporal profiles are highly irregular and, given the low concentrations, the SCP temporal records are likely to be linked to detection limits of the analytical technique. As a consequence, the first presence of SCPs in the cores is not synchronous across the region and the profiles show no consistent temporal trends.

Full SCP inventories were calculated for each core. These provide a measure of the full record of contamination at each lake. These have also been normalised to the <sup>210</sup>Pb inventories for each core in order to allow for both sediment focussing effects in each lake and enhanced catchment inputs from, for example, bare rock areas. Both SCP inventories and SCP/<sup>210</sup>Pb inventory



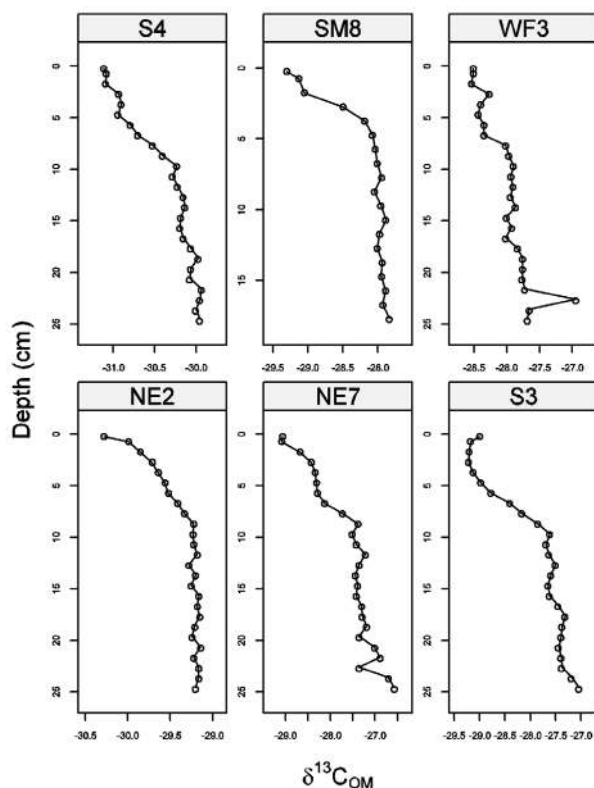


Fig. 6.  $\delta^{13}\text{C}$  in bulk sediment organic matter of selected lakes.

ratios confirm the low contamination status of all the lakes. Analysis of the full dataset shows no relationship of any SCP parameter (surface and peak concentrations; surface fluxes; inventories and inventory ratios) with distance from the centre of the Oil Sands processing activities. This indicates that these activities are not a major source of these particulate contaminants. The SCP data also show no agreement with the Hg surface sediment concentrations (see below).

### 3.5. Stable isotope analysis

The  $\delta^{13}\text{C}$  and C/N ratio profiles demonstrate the clearest signs of alterations in lake biogeochemistry, including sources of organic matter and changes in productivity. Figure 6 shows the measured  $\delta^{13}\text{C}$  profiles for selected lakes.

The  $\delta^{13}\text{C}$  values are all indicative of contributions from lacustrine organic matter (algae) or C3 land plants, with values of  $-27\text{‰}$  to  $-31\text{‰}$  observed across the set of study lakes. The observed changes in  $\delta^{13}\text{C}$  values are all towards isotopically lighter organic matter in more recent sediments, but changes are small, on the order of  $<1\text{‰}$ – $2\text{‰}$ . The changes in lakes S3, S4, NE2, NE7 and SM8 document the most significant shifts in  $\delta^{13}\text{C}$  values following relatively stable periods of isotopically heavier material (Fig. 6). In lakes S3, S4 and NE7 the observed switch to isotopically lighter organic matter occurred around 1930, while the changes in NE2 and SM8 occur somewhat later.

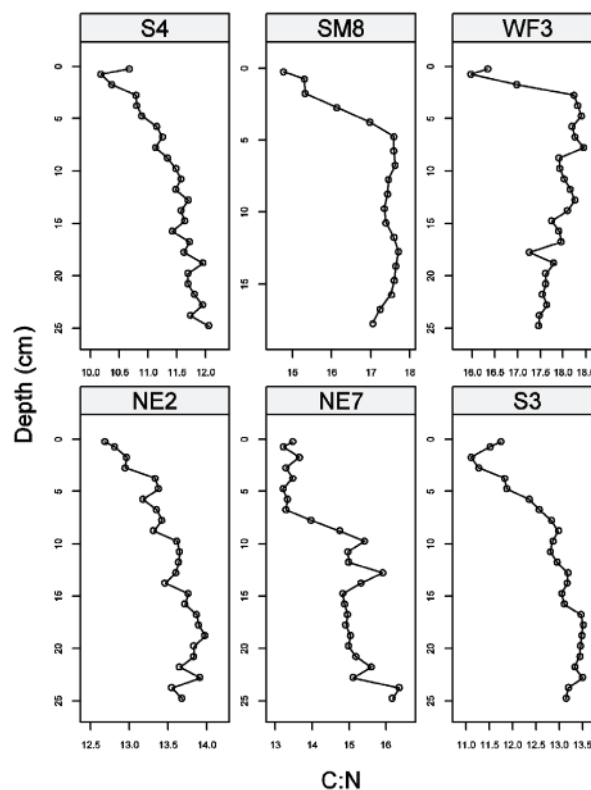


Fig. 7. C:N ratio in bulk sediment organic matter of selected lakes.

There are few strong, consistent shifts in the  $\delta^{15}\text{N}$  values, with most lakes having low ( $\sim 2\text{‰}$  to  $3\text{‰}$ ) but highly variable  $\delta^{15}\text{N}$  values. There are clear increases of  $\sim 1\text{‰}$  in  $\delta^{15}\text{N}$  values in lakes CM5 and NE7 and to a lesser extent in WF2 and SM8. In WF2, CM5 and NE7, the trends occur throughout the retrieved sediment cores and precede the industrialisation in Western countries and the later Oil Sands activities, whereas the increase of  $\sim 1\text{‰}$  in the upper 2–3 cm of SM8 occurs in the middle of the 20<sup>th</sup> Century. Small declining trends in  $\delta^{15}\text{N}$  values are observed in WF3, S3 and S4, with larger changes in BM3 and SM3. These trends commence in the 19<sup>th</sup> Century and therefore do not indicate any changes in N biogeochemistry concurrent with increased industrialisation in the region associated with Oil Sands activities.

Figure 7 shows the C/N ratios of the sediment material from selected lakes expressed as atomic ratios. The trends in C/N ratio largely exhibit the same patterns as those described for C isotopes above, except for lakes WF3 and CM2. C/N ratios are generally low, ranging from 7–18. These values are within the range expected for lacustrine algae (*ca* 5–8) and C3 land plants (*ca* 16+), but outside the range of values expected for C4 land plants (*ca* 35+). The observed values can therefore be interpreted as mixtures of lacustrine algae and C3 land plant sources, with lower C/N ratios reflecting a greater proportional input from aquatic algae. In the majority of sites there are decreases in the C/N ratio

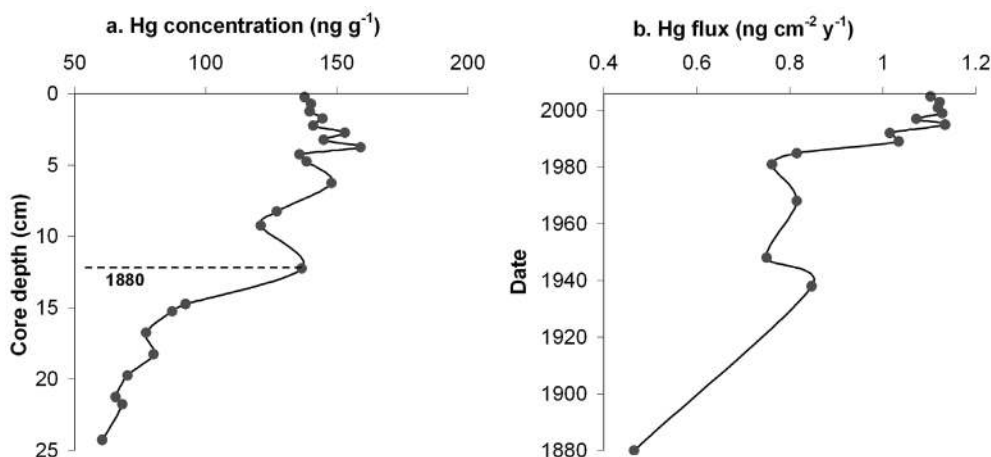


Fig. 8. Concentration and sediment deposition flux of mercury in lake NE7.

suggesting increased contributions from aquatic sources of organic matter.

### 3.6. Mercury analysis

Mercury concentrations in lake surface sediments varied between 67–138  $\text{ng g}^{-1}$  with no obvious spatial pattern (Tab. 1). The highest value occurs in the acidified lake NE7 (core ALB21) and down-core analysis of Hg concentrations at this site show a clear increasing trend from at least the 19<sup>th</sup> Century to the present (Fig. 8). Mercury flux to the lake sediment also shows a general increase from the 1880s upwards with a sharp increase in the last 20 years, suggesting that the input of Hg into this lake has increased during the historical past. While the long-term trend could be due to increasing global anthropogenic emissions, the recent increase suggests a local input in combination with the recent increase in sedimentation. The recent Hg fluxes reported here are comparable to those reported for Lochnagar in north-east Scotland (Tipping *et al.* 2007), a lake which is known to be impacted by anthropogenic pollution from industrial processes and fossil fuel combustion.

## 4. DISCUSSION

### 4.1. Acidification and industrial contamination of lakes in the Oil Sands Region

Only one of the 12 study sites, lake NE7, shows acidification according to diatom analysis. This is the smallest lake studied and one of the shallowest, with the shortest hydrological residence time (see Bennett *et al.* 2008). It is nevertheless chemically comparable to other cored sites which do not show acidification (Tab. 2), e.g., SM6 (core ALB04), SM8 (core ALB03) and WF3 (core ALB11). Instead, these three sites which, like NE7, have  $\text{pH} < 6$  and alkalinity  $< 100 \mu\text{eq L}^{-1}$ , show nutrient enrichment according to the diatoms and indeed have higher measured values of TDN and TDP (Tab. 2).

The acidity change in lake NE7 shows that a small pH decline possibly began in the 19<sup>th</sup> Century but a

marked decline occurred after about 1970 when acid indicating species, particularly *Actinella punctata*, began to increase strongly in abundance. Increasing abundances of this and other acidophilous species have been observed in sediment cores elsewhere in Canada (e.g., Dixit & Dickman 1986) where acid deposition has been identified as the cause of lake acidification. Hence, the recent pH history of NE7 seems to be compatible with an acid deposition explanation. There is no evidence of catchment disturbance and possible release of organic acidity from peaty deposits from around the lake and it is noteworthy that unacidified lake WF3 has similar chemistry but a higher mean DOC concentration than NE7. Furthermore, since NE7 is a small (at 11 ha it is the smallest in the data set), shallow, rapidly flushed lake with short residence time and small catchment, the lake system will have limited capacity for in-lake alkalinity generation. With its low alkalinity, all these characteristics make such sites very susceptible to the influence of atmospheric acid deposition (cf. Rudd *et al.* 1986; Kelly *et al.* 1987).

Measured acid deposition inputs to NE7 are however very low and dynamic acidification modelling shows no change in pH (Whitfield *et al.* 2010, this issue). Concentrations of dissolved organic carbon (DOC) in NE7 are amongst the highest of the sites studied leading to a relatively high acid neutralizing capacity (ANC) but low alkalinity (Tab. 2). Although DOC contributes organic buffering and acidity and climatic drivers of increasing DOC have been suggested by some studies (e.g., Freeman *et al.* 2001), there is a widespread trend across North America and northwestern Europe for acid sensitive lakes to show increasing values for both DOC and pH (Monteith *et al.* 2007). The marked pH decline in lake NE7 occurred since around 1970 and the timing is not consistent with changes in nutrient status of some other lakes which are possibly attributable to climatic change. In addition, various datasets from northern Canada show increasing temperatures, especially summer warming, since the 19<sup>th</sup> Century and palaeolim-

nological study of a lake in Wood Buffalo National Park found diatom community changes consistent with nutrient enrichment and alkalization over this period (Moser *et al.* 2002). Hence climate-induced increases in organic acidity are unlikely to account for the recent changes in DI-pH at lake NE7.

The main diatom assemblage changes observed in NE7 are coincident with the period of industrial development in the region. Fluxes of mercury to lake sediments at this site have increased in the last 20 years, again suggesting local inputs, but these could be driven by increases in sedimentation rates which, in turn, could have climatic or other drivers. Nevertheless, patterns of Hg accumulation in lake sediments of the Oil Sands Region could warrant further investigation. SCP analysis indicates that there are no major local sources, suggesting that coal and fuel oil combustion are not locally important or if they are used, flue gas emissions are effectively scrubbed of particulates.

#### 4.2. Other drivers of change in lakes in the Oil Sands Region

In most of the lakes studied, diatom analysis indicates increasing pH/alkalinity and/or increasing nutrient enrichment. Six of the 12 lakes appear to have experienced increases in DI-pH, including all four lakes west of Fort McMurray and in the Caribou Mountains (Tab. 4). The timing of these increases in DI-pH varies from pre-industrial to very recent. Even more widespread are the increases in nutrient enrichment suggested by the diatoms, observed at all lakes except SM3, NE2 and the acidified site NE7.

Switches to more negative (isotopically lighter)  $\delta^{13}\text{C}$  values are generally indicative of an increase in or greater abundance of dissolved inorganic carbon (DIC) in the epilimnion, arising from the stronger discrimination against  $^{13}\text{C}$ , leading to more negative  $\delta^{13}\text{C}$  values in algal organic matter. Enriched  $\delta^{13}\text{C}$  values have been observed with increasing pH associated with a decrease in dissolved  $\text{CO}_2$  and increased bicarbonate (e.g., Smith & Walker 1980). Loss of alkalinity associated with atmospheric deposition should lead to the reverse, i.e. more depleted  $\delta^{13}\text{C}$  values, and the observed  $\delta^{13}\text{C}$  trend in NE7 matches closely with the observed acidification at this site. Increased delivery of isotopically light DIC/DOC to those lakes exhibiting depletion trends in  $\delta^{13}\text{C}$  would also result in the observed patterns. However, the changes in  $\delta^{13}\text{C}$  are small and within the expected depletion (1.4‰) in  $\delta^{13}\text{C}$  due to fossil fuel combustion (the Suess effect) (Schelske & Hodell 1995).

Overall, the isotope and C/N ratio profiles for the study sites do not show any systematic changes in the biogeochemistry of the lakes that can be attributed to recent Oil Sands activities related to the extraction of oil. Whilst many of the cores show changes in the  $\delta^{13}\text{C}$  values and C/N ratios in particular, the timing of these

changes pre-dates the late 19<sup>th</sup> Century when emissions of N compounds to the atmosphere were on the increase in the northern hemisphere. The source of organic matter to the lakes has originated, progressively, from greater contributions of aquatic algae. This could be interpreted as a productivity response and is in agreement with observations from the diatom analysis in several of the sites, though there are no signs of increased productivity in the  $\delta^{13}\text{C}$  values, which would be expected to increase as greater productivity drew down the DIC pool of the lakes. The declining  $\delta^{13}\text{C}$  values do not preclude an increase in productivity if greater inputs of inorganic carbon to the lakes occurred that were sufficient to offset the draw down of the DIC pool associated with increased productivity. Further work will be required to determine whether this is a plausible scenario.

Changes in sediment  $\delta^{15}\text{N}$  are inconclusive. Bulk deposition and throughflow samples showed values of  $\delta^{15}\text{N}\text{-NO}_3^-$  and  $\delta^{15}\text{N}\text{-NH}_4^+$  in the range  $-3.3$  to  $+1\%$  (B. Mayer, unpublished data). Increasing in-lake utilisation of these N sources might therefore be expected to result in a decline in lake sediment  $\delta^{15}\text{N}$  from the pre-industrial values of *ca*  $+1$  to  $+3.5\%$ , ignoring possible in-lake fractionation effects. However, only a few lakes show declines in bulk sediment  $\delta^{15}\text{N}$  and several show increases. Most of these changes commenced in the 19<sup>th</sup> Century and cannot be attributed to N emissions associated with industrial activities in the Oil Sands Region.

The widespread increases in pH/alkalinity and nutrient status suggested by the diatoms and, to a lesser degree the stable isotopes and C:N ratios, are in agreement with earlier observations made by Hazewinkel *et al.* (2008). Possible sources of increasing nutrients are from industrial atmospheric pollution, forest fires or release from soils in the lake catchments. If the latter is shown to be case then it may be that climate warming is having a greater effect on these wilderness lakes than is industrial activity in the region (cf. Moser *et al.* 2002), but the relative importance of climatic change and anthropogenic pollution is not yet known.

## 5. CONCLUSIONS

The various palaeolimnological analyses described here indicate that acidification does not appear to be a widespread problem in northern Alberta and largely support the conclusions of Hazewinkel *et al.* (2008). However, we do present the first evidence for one site with a significant, recent acidification (lake NE7). This is one of the smallest and shallowest of the sites studied with a peaty catchment, and it is possible that lakes of a similar type are the most vulnerable to the potentially acidifying impacts of deposition arising from the Oil Sands extraction activities.

In addition to identifying the first clearly acidified lake in the region, a key finding from this work concerns the evidence for widespread nutrient enrichment

in the region's lakes. While some changes in the sedimentary diatom records are indicative of nutrient enrichment that began in the early 19<sup>th</sup> Century, suggesting longer-term drivers such as climate, stronger enrichment signals were recorded for the last 20–30 years. Diatom analysis of the twelve cores clearly indicates that the majority of lakes investigated are far from stable and are currently undergoing ecological changes as a result of 20<sup>th</sup> Century processes.

The causes of lake ecosystem instability in the region are currently unclear. Climate change and nutrient enrichment are probably involved as well as air pollution. Separating species responses to climate warming and air pollution is difficult due to interactions of both potential drivers of lake ecosystem change, but different components of lake communities may show distinctive responses to both drivers. Given the relatively high phosphorus concentrations in some of the region's lakes, it remains a possibility that NO<sub>x</sub> emissions and N deposition could also be resulting in changes to lake nutrient status which merit further study. An assessment of the nutrient limitation characteristics of the region's lakes, especially in terms of phytoplankton productivity and diatom species changes, could provide vital information on lake vulnerability to eutrophication caused by N deposition. Furthermore, separating the relative importance of climatic change and anthropogenic pollution in causing some of the changes in unacidified lakes requires further study of other components of lake biota with distinctive sensitivities to climate or nutrient dynamics.

#### ACKNOWLEDGMENTS

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