J Paleolimnol
DOI 10.1007/s10933-011-9527-8

ORIGINAL PAPER

A model for inferring dissolved organic carbon (DOC) in lakewater from visible-near-infrared spectroscopy (VNIRS) measures in lake sediment

Alexandra Rouillard · Peter Rosén · Marianne S. V. Douglas · Reinhard Pienitz · John P. Smol

Received: 22 September 2010 / Accepted: 26 April 2011

Abstract We developed an inference model to infer dissolved organic carbon (DOC) in lakewater from lake sediments using visible-near-infrared spectroscopy (VNIRS). The inference model used surface sediment samples collected from 160 Arctic Canada lakes, covering broad latitudinal (60–83°N), longitudinal (71–138°W) and environmental gradients, with a DOC range of 0.6–39.6 mg L^{-1}. The model was applied to Holocene lake sediment cores from Sweden and Canada and our inferences are compared to results from previous multiproxy paleolimnological investigations at these two sites. The inferred Swedish and Canadian DOC profiles are compared, respectively, to inferences from a Swedish-based VNIRS-total organic carbon (TOC) model and a Canadian-based diatom-inferred (Di-DOC) model from the same sediment records. The 5-component Partial Least Squares (PLS) model yields a cross-validated (*CV*) $R^2_{CV} = 0.61$ and a root mean squared error of prediction ($RMSEP_{CV}$) = 4.4 mg L^{-1} (11% of DOC gradient). The trends inferred for the two lakes were remarkably similar to the VNIRS-TOC and the Di-DOC inferred profiles and consistent with the other paleolimnological proxies, although absolute values differed. Differences in the calibration set gradients and lack of analogous VNIRS signatures in the modern datasets may explain this discrepancy. Our results corroborate previous geographically independent studies on the potential of using VNIRS to reconstruct past trends in lakewater DOC concentrations rapidly.

Keywords Visible-near-infrared spectroscopy · Dissolved organic carbon · Arctic · Paleolimnology · Paleo-optics · Carbon cycling

Electronic supplementary material The online version of this article (doi:10.1007/s10933-011-9527-8) contains supplementary material, which is available to authorized users.

A. Rouillard (✉) · J. P. Smol
Paleoecological Environmental Assessment and Research Laboratory, Department of Biology, Queen's University, Kingston, ON K7L 3N6, Canada
e-mail: alexandra.rouillard@uwa.edu.au

J. P. Smol
e-mail: smolj@queensu.ca

P. Rosén
Climate Impacts Research Centre, Umeå University, 981 07 Abisko, Sweden
e-mail: peter.rosen@emg.umu.se

M. S. V. Douglas
Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB T6G 2E1, Canada
e-mail: marianne.douglas@ualberta.ca

R. Pienitz
Aquatic Paleoecology Laboratory, Centre d'Études Nordiques (CEN), Université Laval, Québec, QC G1V 0A6, Canada
e-mail: reinhard.pienitz@cen.ulaval.ca

Published online: 25 May 2011

Introduction

Changes in global climate are expected to alter dissolved organic carbon (DOC) export to freshwater systems at high latitudes. The combined effects of modifications in growing season length, frequency of extreme climatic events and precipitation patterns on hydrology, permafrost thawing, mire dynamics, as well as vegetation composition are already being observed (ACIA 2005). Increasing DOC levels are being recorded in some regions in North America and northern Europe, and have been associated with climate warming, but may also be linked to chemical recovery from acid deposition and catchment changes (Monteith et al. 2007). DOC levels in high-latitude freshwaters have a strong influence on both microbial (Jansson et al. 2008) and global (Cole et al. 2007) carbon dynamics. Variations in DOC, as an estimate for chromophoric dissolved organic matter (CDOM) that originates largely from terrestrial environments (e.g. humic substances), have a major influence on the optical environment and ecosystem structure and functioning for aquatic organisms (ACIA 2005; Karlsson et al. 2009). Changes in attenuation of ultraviolet (UV) light and photosynthetically available radiation (PAR) (Leavitt et al. 2003), together with recent increases in UV penetration during spring, associated with the detrimental effect of chlorofluorocarbons (CFCs) on stratospheric ozone, could further amplify the consequences of climate warming on polar limnetic systems (ACIA 2005).

Historical reconstructions are needed to adequately address the impacts of ongoing changes in watershed processes affecting freshwater DOC levels in relation to the carbon cycle and paleo-optical variables. The multi-proxy approach is now recognized as essential in paleolimnological investigations (Birks and Birks 2006), but is challenging because of limited sediment availability as well as the costly and time-intensive analyses it requires. Diatom-based models have been used to infer quantitative measures of lakewater DOC (Fallu and Pienitz 1999; Curtis et al. 2009) and TOC (Rosén et al. 2000a) from lake sediment in northern regions of North America and Europe. Such reconstructions may not be robust for all lake ecosystems because of the confounding effect of other water chemistry variables, such as lake pH or nitrate, on siliceous algae assemblages (Curtis et al. 2009). In the last two decades, reflectance spectroscopy has become an important paleolimnological tool because it is a rapid, inexpensive and non-destructive method to obtain information on the composition of sediment organic materials (Korsman et al. 2001)—such as chlorophyll-*a* (Chl *a*) (Michelutti et al. 2010)—and other biogeochemical properties of sediment (Rosén et al. 2010).

Measurement of the absorbance of the visible-near-infrared wavelengths (400–2,500 nm) is done frequently in industry and provides information on the chemical composition of organic materials. Visible-near-infrared spectroscopy (VNIRS) has been used in paleolimnological studies to infer limnological variables such as total phosphorus (TP), pH and elemental C, N, P using inference models (Korsman et al. 1992). The VNIRS signal from subarctic lake sediment has also been linked to recent and long-term climate changes through their influences on watershed processes (Rosén et al. 2000b, 2001). VNIRS-based models were recently developed from a northern Swedish surface sediment training set, and later extended to more southern latitudes (Cunningham et al. 2011) for inferring past lakewater total organic carbon (TOC) (Rosén 2005). This allowed further exploration of past environmental effects on aquatic systems. Changes in mire dynamics, tree-line location, vegetation composition, fire regimes and precipitation patterns were shown to be tracked by the VNIRS-TOC reconstructions (Rosén 2005; Rosén and Hammarlund 2007; Kokfelt et al. 2009; Cunningham et al. 2011). The potential of the VNIRS technique for inferring lakewater organic carbon content has not yet been explored in North America, and very little is known about the geographic limitations of existing inference models.

The goals of this paper were to determine: (1) if predictive inference models can be established between sediment VNIRS spectral signatures and lakewater DOC from northern boreal to Arctic Canadian lakes, and (2) if lakewater DOC can be reconstructed from paleorecords at the Holocene scale using the developed model. In this study, a modern Canadian Arctic Calibration Set (CACS) of lake surface sediment, ranging from the boreal forest to high Arctic polar desert sites, was used to develop a model relating the VNIRS signal from lake surface sediments to lakewater DOC concentrations, following methods described by Rosén (2005). The Canadian model was applied to two well studied Holocene lake sediment profiles from a Canadian and a Swedish lake at the tree line. The VNIRS-based technique has the potential to become a time- and cost-effective geochemical proxy for studying several processes, including the C cycle between terrestrial and aquatic environments, and variability of underwater light regimes.

Materials and methods

A Canadian Arctic calibration set

Study area

The 160 lakes included in the calibration set encompass broad latitudinal (60–83°N) and longitudinal (65–138° W) gradients in northern Canada (Fig. 1). Most of the sites were included in previously published paleolimnological surveys (diatom calibrations sets), and the different regions are described elsewhere in greater detail (Table 1). This vast study area spans large environmental gradients with respect to bedrock geology, permafrost, soil development, vegetation, climate and limnological variables. The major part of the area covered by the CACS is located within the Arctic Archipelago and is underlain by sedimentary rocks of Phanerozoic age, with some Precambrian igneous intrusions. The most southern parts are underlain by the granite and gneiss of the Canadian Precambrian Shield (Thorsteinsson and Tozer 1970). The landscape features (permafrost and vegetation) were obtained using Arc-GIS Desktop ver. 9.2. The hydrological features displayed on the CACS map (Fig. 1) were obtained from the National Hydro Network (NHN) (GeoBase 2007)

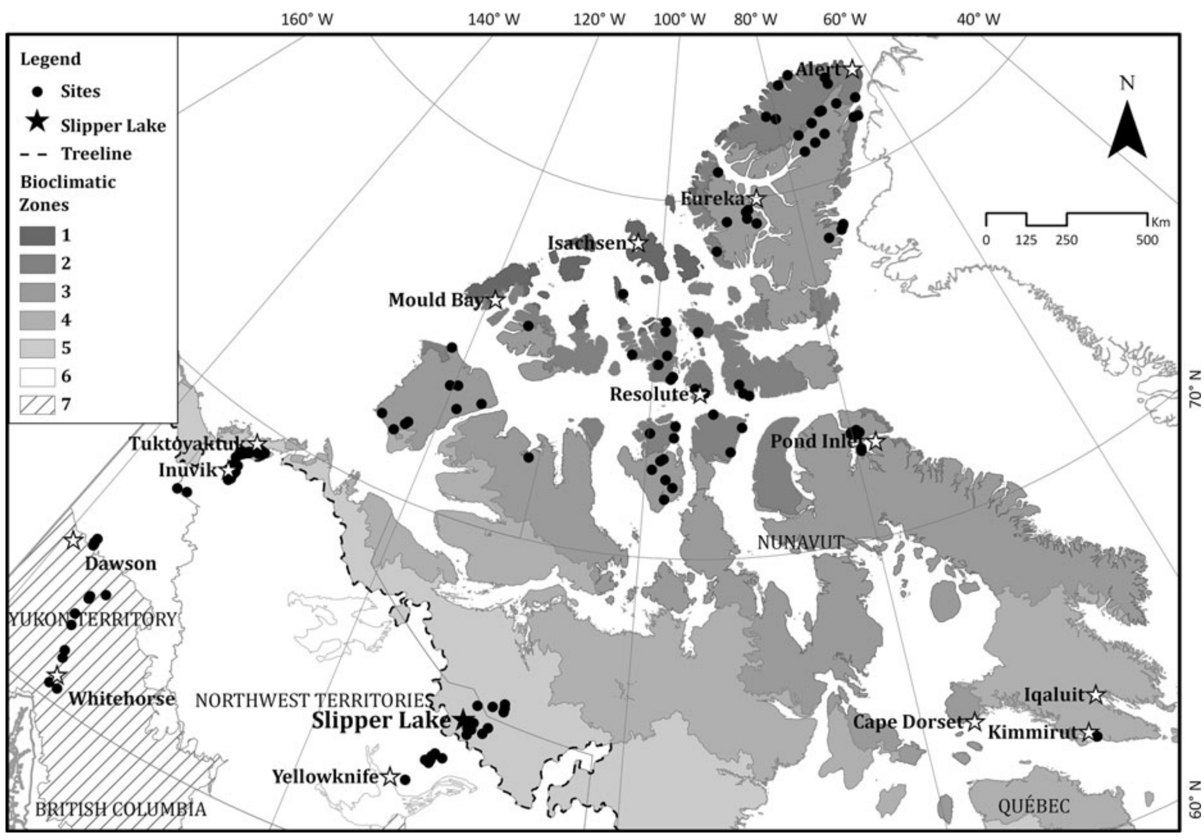

Fig. 1 Map of the Canadian Arctic Calibration Lakes Set (CACS) (*filled circle*) distributed along seven bioclimatic zones as defined by the CAVM (2003) and the Ecological Working group (2002), ranging from boreal forest to high Arctic polar desert (60–83°N and 64–138°W) (see legend), including major towns (*empty stars*), tree line (*dashed line*) and Slipper Lake (NWT) (*filled star*). Generated with Arc-GIS Desktop ver. 9.2

Table 1 Canadian Arctic lakes calibration set (CACS) regions, with the names and number of sites (*n*), sampling years and reference for full water chemistry and/or lakes description

Region	Collection year (s)	n	Sites #ref	Publication
Northern Ellesmere Island and Oasis (EP)	2003	18	Appleby, D, F, G, "Lake A", "Lake C2", P, R, S, Nan, W, X, Skeleton, AB, AC, 10, Hazen, 24	Keatley et al. (2007a)
Axel Heiberg Island (AX)	1998	7	Q, Y, Z, AI, AJ, Buchanan, Colour	Michelutti et al. (2002a)
Cape Herschel (CH) and Pim Island (P)	2007	3	Elison Lake, Proteus, "Greely"	Douglas and Smol (1994); Unpub.
Central Ellesmere Island (E)	2004	1	Rock Basin Lake	Michelutti et al. (2006)
Lougheed Island (LO)	2005	1	A	Unpub.
Bathurst Island (B)	1994, 2005	9	C, G, H, M, N, Y, AE, AJ, AT	Lim et al. (2001); Unpub.
Devon Island (DV)	2001	4	E, F, H, I	Lim and Douglas (2003)
Melville Island (MV)	2002	1	AE	Keatley et al. (2007b)
Cornwallis Island	1993	2	12 Mile, Trafalgar	Michelutti et al. (2007)
Banks Island (BK)	2000	9	A, Shoran, R, T, U, Y, Swan, AH, AI	Lim et al. (2005)
Somerset Island (S)	1994, 1996	3	AP, AQ, AS	Unpub.
Prince of Wales (W)	1995	9	E, G, L, N, Q, W, Fisher, AG, AK	Unpub.
Bylot Island (BI)	2005, 2006	16	1, 2, 4, 5, 7–11, 17, 20–22, 25, 26, 28	Côté et al. (2010)
Wynniatt Bay (Victoria Island) (V)	1997	1	G	Michelutti et al. (2002b)
Southern Baffin Island	2008	1	JUET-2	Unpub.
Yukon (U)	1990	44	2, 5–12, 18–23, 25–29, 31, 32, 34, 36–46, 49–50, 52, 54–56, 58, 59	Pienitz et al. (1997a)
Mackenzie Delta (Inuvik, NWT) (IK)	2009	17	C8, C23, DEM2, DEM4-5, I3, I8, I11, I17, I20, I23A, I25B, 5B, 7B	Kokelj et al. (2005); Unpub.
Yellowknife (Central NWT) (Y)	1991	19	1, 3–14, 16–20, 21, 23	Pienitz et al. (1997b)

available at *Geobase* (www.geobase.ca). The majority (79%) of the sites are located in continuous permafrost, and only 10 and 2.5% are on discontinuous and sporadic permafrost in more southerly locations, respectively (GSC 2002a, b). Surface materials in the CACS lakes catchments are mostly unconsolidated materials such as glacial deposits, sands, soils and organic terrains, but also include bedrock and bedrock outcrops (GSC 1973). The various types of cryosolic, brunisolic (south of tree line only) and rock-dominated soils covering the catchments of the CACS sites (Soil Landscapes of Canada Working Group 2006) have substrate chemistry ranging from acidic (pH < 5.5) to mineral-rich circumneutral (pH 5.5–7.2) and carbonate-rich (pH > 7.2) (CAVM 2003).

The surface sediment dataset has an altitudinal gradient from sea level to 1,387 m a.s.l. and extends from subarctic boreal forest in the south to polar desert on the most northerly main Canadian island, Ellesmere Island. The bioclimatic zones (Fig. 1) are based on the Circumpolar Arctic Vegetation Map Team (CAVM 2003) classification north of the tree line as well as on the Ecological Working Group classification in EcoZones (2002) south of the tree line. Seventy-four percent of the CACS lakes are located above the tree line (CAVM 2003). The cover of vascular plants in the polar desert (Zone 1), i.e. cushion forbs in favourable microsites, is <5%, and mosses and lichens can cover up to 40% of lake catchments, forming an open and patchy vegetation. As one proceeds further south, the temperature and the growing season lengthen, allowing the mosses and herbaceous layers to thicken and become taller. Woody prostrate dwarf shrubs (Zone 2) progressively increase in stature to become hemiprostrate (Zone 3) and are eventually replaced by krummholz tree forms (Zone 4), reaching up to 2 m above ground at tree line (Zone 5). The number of species and overall cover of vascular plants increase from north to south to occupy 80–100% of lake catchment areas at tree line (CAVM 2003). South of the tree line, the taiga ecosystem (Zone 6) was originally classified into three EcoZones from west to east, and are namely, the Taïga Cordillera, Plains and Shield (Ecological Working Group 2002), that are grouped here into a subarctic transition zone characterized by a forest-tundra vegetation. The southernmost sites in the Yukon are located in the conifer-dominated Boreal Forest (Zone 7), and six of these sites are located in alpine settings (Pienitz et al. 1997a). At these high latitudes, peatland is present in patches throughout the landscape, but it occupies a larger proportion of the catchment at the southernmost sites (GSC 2002a).

The annual precipitation and snowfall, as well as mean July and January air temperatures for the different zones, are averages of the available data from the closest possible meteorological stations to the study sites and cover the CACS 1990–2009 collection period (Table 2). Generally colder seasons, drier conditions and a higher proportion of snowfall are observed at higher latitudes. The study sites are located in remote areas and are not affected by direct anthropogenic disturbances, with the exception of seven Inuvik sites that have small sumps for drilling mud and waste (mostly KCl) disposal in their catchment, which should not affect the VNIRS signal in the lake sediment.

The subset of the CACS water chemistry and other important limnological variables in Table 3 encompasses the typical environmental gradients observed in the Canadian Arctic (Vincent and Laybourn-Parry 2008). Most of the lakes in the CACS are relatively shallow (mean = 7.6 m), with summer water temperatures that increase from north (mean = 5.6°C in Zone 1) to south (mean = 7.7°C in Zone 7) and a pH range between 3.5 and 8.8, the most acidic sites being found in Zones 1 and 3. The sites are generally oligotrophic (mean total phosphorus, unfiltered (TPU) = 8.6 μg L^{-1}, Chl *a*, uncorrected (Chl*a*U) = 1.1 μg L^{-1}, total nitrogen (TN) = 0.3 mg L^{-1}), but mesotrophic and even slightly eutrophic sites are also present across the set. While TN levels seem to increase between bioclimatic zones from north to south, TPU and Chl*a*U do not follow an equally clear trend. The systems are dilute on average (specific conductance = 126 μS cm^{-1}, dissolved inorganic carbon (DIC) = 12.8 mg L^{-1}, major ions <21 mg L^{-1}), but individual values vary and cover wide ranges. As reported elsewhere (Pienitz and Smol 1993), a large gradient (0.6–39.6 mg L^{-1}) of generally decreasing DOC was recorded from southern Yukon to northern Ellesmere Island, about a ten-fold difference between the means, following changes in bioclimatic and permafrost zones. Most sample sites are located in non-forested catchments (74%), where lakes typically display low DOC values. The particulate organic carbon (POC) accounts for up to 38% of the TOC, with no clear trend between the zones.

Sample collection

Water and surface sediment samples for this calibration set were collected in summer months (July and August) during previous paleolimnological investigations between 1990 and 2009. Sampling was conducted following the standard methods used in our other Arctic studies (Douglas and Smol 1994). At subarctic latitudes and, when possible, further north, the sediment was collected from the deepest part of the lake using a gravity corer. In high Arctic

Table 2 Averaged meteorological data (1990–2009) (mean July and January temperature, mean annual precipitation and snowfall portion of the mean total precipitation) available for the seven bioclimatic zones (Zone) covering the CACS, with the number of sites (*n*) (Environment Canada 2010)

Bioclimatic zone	n	Meteorological stations	Mean july temp (°C)	Mean jan temp (°C)	Mean annual snow (% tot prec)	Mean annual prec (mm)
1	2	Alert	3.5	−32.3	85	148
2	32	Resolute Bay	4.2	−32.2	62	169
3	50	Eureka, Nanisivik, Sachs Harbour, Tuloyoak	6.5	−32.1	62	175
4	1	Kimmirut, Pangnirtung	8.8	−23.8	62	377
5	33	Kugluktuk, Rankin Inlet, Tuktoyaktuk	11.0	−28.2	41	245
6	33	Inuvik, Yellowknife	17.0	−25.8	39	283
7	9	Mayo, Whitehorse	15.4	−20.2	37	295

Table 3 Select lake water chemistry variables of the CACS ponds in the seven bioclimatic zones

Variable	Unit	1	2	3	4	5	6	7	Tot
Depth	m	–	3.6(2–6.9)	10.2(2.1–80)	8.5	6.1(2–20)	5.9(2–18.5)	14.4(3–49)	7.6(2–80)
Temp	°C	6.0(4.5–7.5)	6.3(1.5–12.0)	8.3(1.5–15.4)	21.0	12.9(7.5–18.0)	16.2(11.5–20.3)	20.8(17.0–23.0)	11.2(1.5–23.0)
pH		5.6(3.5–7.7)	8.1(6.8–8.7)	7.4(3.6–8.8)	7.0	7.8(6.2–8.6)	7.6(5.9–8.8)	8.5(7.8–8.8)	7.7(3.5–8.8)
Cond	μS cm^{-1}	170(30–309)	147(10–780)	124(4–500)	48	97(8–343)	68(0–153)	331(49–1,500)	126(0–1,500)
Chl*a*U	μg L^{-1}	0.6(0.6–0.6)	0.7(0.05–2.7)	0.9(<0.1–3.2)	2.9	1.1(<0.1–2.6)	1.7(0.4–10.5)	1.2(0.05–2.8)	1.1(<0.1–10.5)
TPU	μg L^{-1}	15.3(7.4–23.2)	6.2(1.1–21.8)	9.6(0.1–34.3)	8.1	6.9(0.006–20.8)	10.1(0.01–43.9)	10.8(4.9–15.8)	8.6(0.006–43.9)
DIC	mg L^{-1}	1.7(0.6–2.8)	14.5(1.1–26.6)	12.7(0.3–59.5)	2.2	11.5(0.1–35.2)	6.1(0.3–20.5)	40.7(3.8–134)	12.8(0.1–134)
DOC	mg L^{-1}	1.7(0.9–2.4)	2.0(0.8–6.9)	3.5(0.6–18.5)	2.9	7.9(1.6–26.7)	12.3(3.1–39.6)	16.7(8.4–35.1)	6.6(0.6–39.6)
POC	mg L^{-1}	0.3(0.1–0.4)	0.3(0.09–0.7)	0.4(0.2–1.0)	0.3	0.5(0.2–1.0)	0.6(0.2–1.5)	0.8(0.3–3.3)	0.5(0.1–3.3)
PON	mg L^{-1}	0.02(0.02–0.02)	0.02(0.001–0.05)	0.04(0.01–0.09)	0.03	0.07(0.02–0.1)	0.08(0.03–0.20)	0.11(0.04–0.4)	0.1(0.001–0.4)
TN	mg L^{-1}	0.05(0.03–0.07)	0.2(0.05–0.9)	0.3(0.03–1.2)	0.2	0.4(0.1–0.9)	0.5(0.1–0.9)	0.7(0.3–1.6)	0.3(0.03–1.6)
SiO_2	mg L^{-1}	3.9(0.2–7.7)	0.4(0.05–1.3)	1.1(0.06–4.6)	0.5	0.4(0.08–1.5)	1.1(0.1–3.3)	5.5(0.2–9.3)	1.1(0.05–9.3)
Ca^{2+}	mg L^{-1}	8.6(3.2–13.9)	20.5(0.4–43.7)	16.7(0.1–71.8)	2.1	16.6(0.5–59.6)	12.3(1.1–39.2)	30.1(7.8–50.3)	17.1(0.1–71.8)
Mg^{2+}	mg L^{-1}	3.7(0.7–6.6)	5.0(0.4–20.3)	6.9(0.1–57.3)	1.4	8.6(2.2–16.7)	4.7(2.2–10.9)	–	6.1(0.1–57.3)
Na^+	mg L^{-1}	13.5(0.7–26.3)	8.7(0.2–153)	4.1(0.1–42.8)	7.1	5.3(0.4–33.4)	2.7(0.2–13)	25.8(0.7–187)	6.3(0.1–187)
K^+	mg L^{-1}	1.3(0.07–2.5)	0.6(0.1–5.7)	1.2(0.1–8.5)	0.5	1.2(0.3–6.7)	0.9(0.1–2.1)	4.9(0.6–29.9)	1.2(0.07–29.9)
Cl^-	mg L^{-1}	16.7(1.2–32.1)	16.1(0.2–278)	6.2(0.2–63.5)	9.8	10.1(0.5–75.2)	2.1(0.0–6.1)	4.0(0.6–24.5)	8.2(0.04–278)
SO_4^{2-}	mg L^{-1}	60.8(1.5–120)	6.9(0.2–39.7)	18.9(0.3–182)	3.1	5.6(0.3–51.0)	12.4(0.3–72.0)	161(0.5–1,242)	20.8(0.2–1,242)
NO_2NO_3	mg L^{-1}	0.006(<0.005–0.009)	0.02(<0.005–0.1)	0.009(<0.005–0.079)	<0.005	0.006(<0.005–0.02)	0.01(<0.005–0.04)	0.006(<0.001–0.02)	0.01(<0.005–0.1)
NO_2^+	mg L^{-1}	<0.002	0.002(0.0005–0.007)	0.002(<0.002–0.006)	<0.002	0.001(<0.0002–0.007)	0.003(<0.0002–0.03)	0.0005(<0.0002–0.001)	0.002(<0.0002–0.03)
NH_3^+	mg L^{-1}	0.009(0.008–0.01)	0.008(<0.005–0.04)	0.01(0.002–0.04)	0.02	0.01(<0.005–0.056)	0.01(<0.005–0.1)	0.009(<0.005–0.031)	0.01(0.002–0.1)

i.e. Chlorophyll-*a* uncorrected (Chl*a*U), total phosphorus unfiltered (TPU), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON), total nitrogen (TN), silica (SiO_2), ions of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chlorine (Cl^-) and sulfate (SO_4^{2-}), as well as nitrogen pentoxida (NO_2NO_3), nitrites (NO^{2+}), and ammonium (NH_3^+), and other important limnological variables (elevation (Elev), lake depth, water temperature (Temp), pH, conductivity (Cond)) for the 160 CACS lakes summarized by bioclimatic zonations (Zone). The mean values are presented with the zone range in parentheses locations, the top cm of sediment was typically collected from <1 m water depth by walking out as far from the shore as possible. Most sediment samples were stored in the dark at 4°C, except samples from Bylot Island, which were kept freeze-dried. Water collection and chemical analyses were performed according to standard protocols described in the publications related to each sample region (Table 1). The vast majority of the samples were sent to the National Laboratory for Environmental Testing (NLET) at the National Water Research Institute in Burlington, Ontario, for major and minor ions, phosphorus, nitrogen, carbon, and Chl *a*. Protocols for bottling and filtering, and methods for chemical analyses can be found in Environment Canada (1979, 1994a, b) for all sites sampled. Trace metals in the Inuvik samples were analysed at the Taïga Laboratory (Yellowknife, NWT). Given the logistical constraints of Arctic research, only a single DOC surface water measurement was performed for each site. Water temperature, pH and conductivity were measured on location. The suite of limnological variables available for each site is provided in Appendix 1 (Electronic Supplementary Material).

Spectral analysis and model development

About 0.5 mL of freeze-dried sediment for each sample was sieved through a mesh size of 710 µm, hand-ground in a mortar and run for spectral analyses using a NIRSystems 6500 instrument (FOSS NIRSystems Inc., Silver Spring, MD, USA). A few ($n = 22$) samples with high sand content were ground for 30 s using a planetary mill. Interactions between the light in the VNIR region and the sediment sample organic components are reported by the instrument as apparent absorbance wavelength and intensity values (A), according to $A = log(1/R)$, in which R is the measured diffuse reflectance. The sediment apparent absorbance spectrum (VNIRS "signature") for each sample is formed by 1,050 data points collected between 2,500 and 400 nm at 2-nm intervals, thus capturing the spectral sensitivity to Chl *a* and its derivatives in the visible light (400–700 nm) (Michelutti et al. 2010). All samples utilized in the present study were run in a two-week time frame and standard samples were included at the start and end of each session to prevent potential instrument drift.

Development of the calibration model followed the typical procedure of diffuse reflectance spectral calibration using multivariate statistics, and is largely based on Rosén (2005). Ponds, i.e. waterbodies that freeze to the bottom during winter (typically <2 m depth), were removed from the initial set of 427 sites for numerical analyses, resulting in a calibration set of 161 lakes. Outliers were detected using a principal components analysis (PCA) of the VNIRS spectra. Only one lake, which was outside the 95% root mean square error of the PCA, was removed from the analysis prior to modelling. This lake, which was artificially dammed, heavily influenced the model fit. The transfer function was developed with a partial least squares regression (PLS) of the centred VNIRS spectra with standardized and square-root-transformed lakewater DOC. The square root of lakewater DOC was used to attain a normal distribution because the CACS contained a higher number of sampled lakes with DOC values <10 mg L^{-1}. A multiplicative scatter correction (MSC), a linear transformation for which the mean VNIRS signature of the calibration set is subtracted from the spectral signature of every site, was also applied to the spectral data prior to performing multivariate analyses to remove noise effects caused by particle size, as well as varying effective path length and measurement conditions (Geladi et al. 1985). All multivariate statistics were performed using SIMCA-P + ver. 12.0.1 (Umetrics AB, SE-907 91 Umeå, Sweden). The model chosen had the highest coefficient of determination between the observed and the predicted values and the lowest root mean squared error of prediction assessed by internal ten-fold cross-validation (R^2_{CV} and $RMSEP_{CV}$). The $RMSEP_{CV}$ was calculated from the measured and back-transformed predicted DOC values.

Downcore application

Slipper Lake, Canada

The CACS VNIRS-DOC model was applied to a Holocene sediment core from Slipper Lake (64° 35.65′N, 110° 50.07′W; 460 m a.s.l.), an oligotrophic tundra lake located approximately 50 km north of tree line in the Northwest Territories (NWT), Canada. Slipper Lake is a moderately deep lake (maximum depth = 17 m) located in a remote area within the

CACS geographical coverage (Fig. 1). Previous studies from this lake included the application of diatom-based models for DOC (Di-DOC), dissolved inorganic carbon (Di-DIC) and total nitrogen (Di-TN) (Rühland 2001; Rühland and Smol 2002) to two dated sediment cores, a main core (45.5 cm), and a replicate core (17.5 cm) collected through ice in March, 1997 (Rühland and Smol 2005). In addition, cladoceran assemblage changes were examined from the shorter core (Sweetman et al. 2008). As there was insufficient sediment available from the top 23.5 cm of the main Slipper Lake core, the shorter core had to be used to represent the most recent history of this lake. Thus, 25 samples from the shorter core represent the top section (0–17.0 cm) and 10 samples from the main core represent the bottom section analysed in this study (23.5–42.5 cm). Bulk sediment from the deepest part of the main core (43.5–44.5 cm) was dated with accelerator mass spectrometry (AMS) at 4,760 ± 70 radiocarbon years before present (^{14}C yr BP), thus the period covered by the records does not encompass the entire Holocene history of Slipper Lake, i.e. since deglaciation. Site description details as well as sampling and dating techniques can be found in Rühland and Smol (2005).

The weighted-averaging (WA) diatom-based DOC inference model (Di-DOC) used for Slipper Lake was developed from a 67-lake training set in the central Canadian Arctic tree line region (Rühland and Smol 2002) and applied to the sediment cores (Rühland and Smol 2005). The Di-DOC model had a bootstrapped coefficient of determination (r^2_{boot}) of 0.49 and a root mean squared error of prediction ($RMSEP_{boot}$) of 0.28 Log (DOC + 1.45) mg L^{-1}. Diatom assemblages in Slipper Lake were relatively stable for the first five millennia, with the largest change occurring in the last *ca*. 150 years (~5.0 cm). Rühland and Smol (2005) concluded that the substantial taxonomic shifts in the diatom flora to a more planktonic assemblage were largely due to 19th century warming (longer ice-free period) and associated changes to water column properties, e.g. prolonged thermal stratification. The pronounced taxonomic shifts in diatoms were not matched in the diatom-inferred model reconstructions for DOC, DIC or TN, suggesting that changes other than these reconstructed variables, e.g. aquatic habitat shifts, were the main drivers of the diatom changes. Loss-on-ignition (LOI) measurements were stable in the record until they experienced a slight decrease from 25 to 15 cm, after which they increased until recent times (Rühland and Smol 2005). No substantial changes were observed in cladoceran assemblages throughout the shorter sediment core (Sweetman et al. 2008).

Seukokjaure, Sweden

The CACS DOC-VNIRS model was also applied to a well studied Swedish lake sediment core to assess how well the Holocene reconstruction based on the Canadian model matches an independent reconstruction based on the VNIRS-TOC model developed by Rosén (2005). A sediment profile was obtained from Seukokjaure (67° 46′N, 17° 31′E; 670 m a.s.l.), a small, relatively shallow (max depth = 6.1 m), oligotrophic tree line lake located in northern Sweden in an area with low human impact. The AMS radiocarbon date on terrestrial macrophyte and aquatic moss remains established that the age at 132 cm was 9,070 ± 75 ^{14}C years BP. This lake has been investigated for long-term environmental changes using multiple sediment variables, and detailed site information as well as sampling and dating descriptions are available elsewhere (Rosén et al. 2003, 2010; Rosén and Persson 2006; Reuss et al. 2010). Transfer functions were developed for pollen, diatom and chironomid assemblages to infer July air temperature over the Holocene (Rosén et al. 2003). Loss-on-ignition (Rosén et al. 2003) and Fourier transform infrared spectroscopy (FTIRS) (Rosén and Persson 2006) were also performed and used to reconstruct the tree line history of the lake catchment and to infer lakewater TOC. In addition, conventionally-measured and FTIRS-inferred LOI, biogenic silica, pigments, δ^{13}C and δ^{15}N profiles were shown to support the interpretations of tree line changes from previous papers (Reuss et al. 2010; Rosén et al. 2010).

Based on a 99-lake set from northern Sweden, the Swedish four-component PLS model used has a R^2_{CV} of 0.63 and a root mean squared error of prediction by cross-validation ($RMSEP_{CV}$) of 1.7 mg L^{-1} that represents 11% of the TOC gradient. Details of sample preparation and model development, using the original 100-lake calibration set, are described in Rosén (2005). According to the comparative analysis of the proxies for Seukokjaure, the lake catchment started to become forested about 600 years after deglaciation, about 9,500 calibrated years BP or ~130 cm sediment depth, and became alpine again from 850 cal years BP (~15 cm) until present (Reuss et al. 2010). A similar pattern of Holocene change was observed in Di-inferred DOC reconstructed for Queen's Lake (NWT, Canada), currently located at northern tree line (Pienitz et al. 1999).

Canadian and Swedish dataset signatures versus VNIRS profiles

PCA was used to explore changes in the VNIRS spectra through time. Sample scores from both reconstruction lakes were compared with sample scores from the Canadian and the Swedish calibration set to assess how downcore VNIRS spectra in Slipper Lake and Seukokjaure compare to the surface sediment spectra from lakes with different catchment vegetation. Slipper Lake and Seukokjaure are particularly well suited for this evaluation because they both have a detailed environmental history using multi-proxy paleolimnological studies. Furthermore, the two sites are currently both located within the geographical boundaries and environmental gradients encompassed by the Canadian and Swedish training sets, allowing for meaningful comparison. This test also shows whether downcore samples have analogues in the calibration set (Rosén and Persson 2006).

Results

Model performance

The model fit and predictive abilities of our VNIRS-DOC model were similar to those obtained for previous VNIRS-based models for TOC inference developed in Sweden (Fig. 2). A 4.4 mg L^{-1} $RMSEP_{CV}$ of calibration (11% of the calibration gradient) with an R^2_{CV} of 0.61 was obtained for a 5-component PLS model ($RMSEP_{CV}$ and R^2_{CV} for first four components: 4.8, 4.8, 4.8, 4.5 mg L^{-1} and 0.52, 0.53, 0.55, 0.60, respectively). Considering the influence of the larger gradient covered by the CACS (0.6–39.6 mg L^{-1}) on the $RMSEP_{CV}$, the model fit and predictive abilities are comparable to those obtained for the Swedish 99 and 100-lake TS (present study; Rosén 2005) and the extended set (Cunningham et al. 2011) with, respectively, an R^2_{CV} of 0.61 and 0.72 and an $RMSEP_{CV}$ of 1.6 and 2.6 mg L^{-1} representing 10.8 and 11.2% of the gradient. The CACS-based inference model did not predict values as high as the ones observed in the lake dataset (maximum predicted DOC = 26 mg L^{-1}) (Fig. 2), which highlights the model limitations for inferring high DOC values quantitatively. Because most of the sites (76%) have DOC concentrations <10 mg L^{-1}, higher levels of reconstructed DOC should be interpreted with caution as reported elsewhere (Cunningham et al. 2011). Integrating more lakes with higher DOC values would allow us to account for a greater diversity of organic compounds in the model and probably improve predictive ability in the higher range of DOC. Further investigations of how the different regions of the VNIRS spectra influence the PLS analysis to infer lakewater DOC could also improve the model's performance, as well as reduce its complexity.

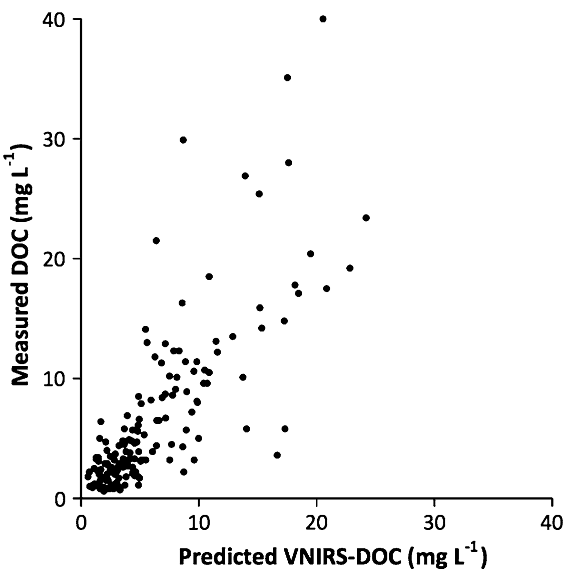

Fig. 2 Observed lake water dissolved organic carbon (DOC) versus near-infrared spectroscopy (VNIRS)-predicted lake water DOC (mg L^{-1}) from the CACS with the model's fit (R^2_{CV}) and the root mean squared error of prediction as assessed by cross-validation ($RMSEP_{CV}$)

Discussion

Slipper Lake

Similar inferred patterns of lakewater DOC values were obtained for the Slipper Lake paleorecord by the VNIRS and diatom-based DOC models, although absolute values differed slightly (Fig. 3). The Di-DOC model recent estimate (5.0 mg L^{-1}) is closer to the present-day DOC reported in Rühland and Smol (2005), i.e. 5.0 mg L^{-1} in 1996 and 4.5 mg L^{-1} in 1997, measured from water sampled in the winter through the ice, than to the VNIRS-DOC estimate (2.9 mg L^{-1}). However, the VNIRS-DOC reconstruction appears less noisy with more stable inferences between the intervals than the Di-DOC profile. Reconstructed DOC from 5.5 cm to the top of the core followed a subtle decreasing trend, which would be in agreement with the effects of climatic warming as suggested by the other sediment variables analysed (Rühland and Smol 2005; Sweetman et al. 2008). Considering the models' prediction errors, however, no major trends in inferred lakewater DOC were observed in either profile at the Holocene scale.

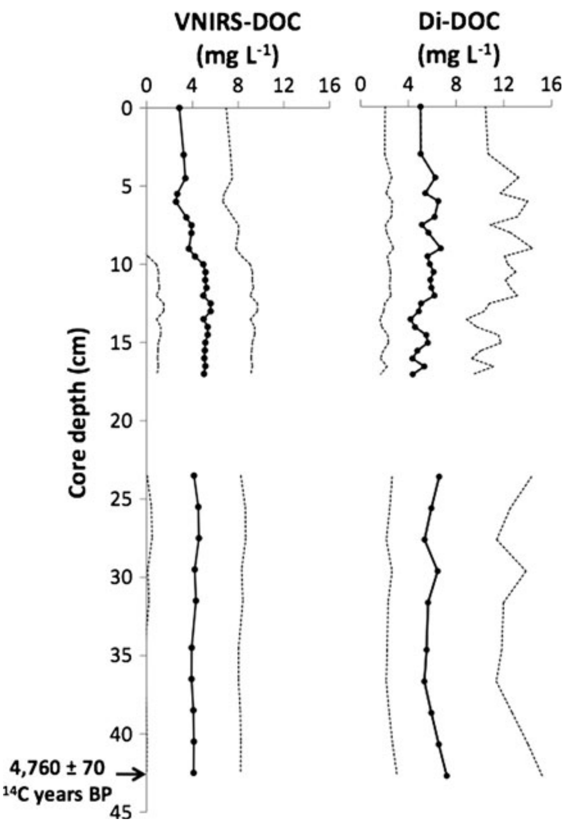

Fig. 3 Reconstructions of past lakewater DOC from Slipper Lake (NWT, Canada), inferred using a partial least squares analysis (PLS) VNIRS-based (VNIRS-DOC) and a weighted-averaging (WA) diatom-based (Di-DOC; Rühland 2001: Fig. 6, Appendix 5.5) model applied to a Holocene sediment profile with bottom (23.5–42.5 cm) and top (0–17.5 cm) segments. $RMSEP_{CV}$ and back-transformed sample-specific bootstrapped errors ($RMSEP_{boot}$) are included for the VNIRS-DOC and Di-DOC reconstructions, respectively

Apart from a similar recent slight decline, nearby Toronto Lake (63°43′N, 109°21′W) similarly did not reveal major fluctuations in diatom-inferred DOC levels over the Holocene despite larger variations in LOI (Pienitz et al. 1999). Even though the lake is located at the tree line and pronounced changes in diatom-inferred DOC over the Holocene were observed at nearby Queen's Lake (64°07′N, 110°34′W) (Pienitz et al. 1999), it is possible that Slipper Lake and its catchment have not undergone major changes affecting lakewater DOC levels over the last few millennia. In fact, present-day measurements still display low DOC levels. Additionally, if tree line migrated northward onto the site during the Holocene Thermal Maximum, approximately 5,000 years BP, it may not have been captured in this lake record because the full Holocene history of the lake was not covered in the 45.5 cm core.

Degradation processes could have caused the most recent slight decline in the VNIRS-DOC profile. However, previous studies suggest that sediment degradation has only a minor effect on the VNIRS signal compared to the effect from environment (Rosén et al. 2000b; Rosén 2005). Although we cannot assess if, or to what extent degradation could have influenced the VNIRS-measured products in the calibration set or in the Holocene sediment records, the good match with biological proxies supports our conclusions.

Seukokjaure

The Canadian and Swedish VNIRS-based models produced similar trends in inferred lakewater DOC and TOC for Seukokjaure over the Holocene, but similar to the Canadian example, the absolute values differed (Fig. 4). Both the VNIRS-inferred DOC and TOC profiles show an initial increase towards a plateau that lasts until ~15 cm (850 cal years BP), after which the levels decrease almost to initial values. The reconstructed values varied beyond the model predictive range of the DOC and the TOC model, ranging

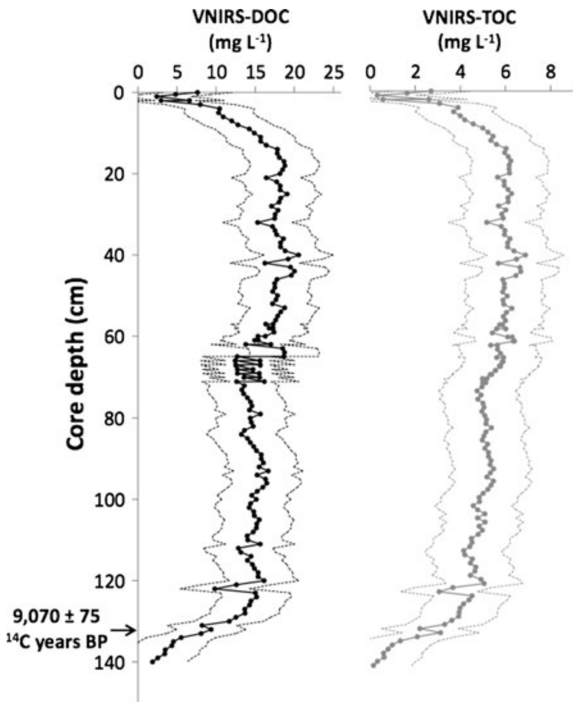

Fig. 4 Reconstruction of past lake water DOC and TOC (mg L^{-1}) from Seukokjaure (Sweden) Holocene sediment core, inferred using a VNIRS-based model developed from the CACS (*black*) and the 99 Swedish lakes (*grey*), respectively

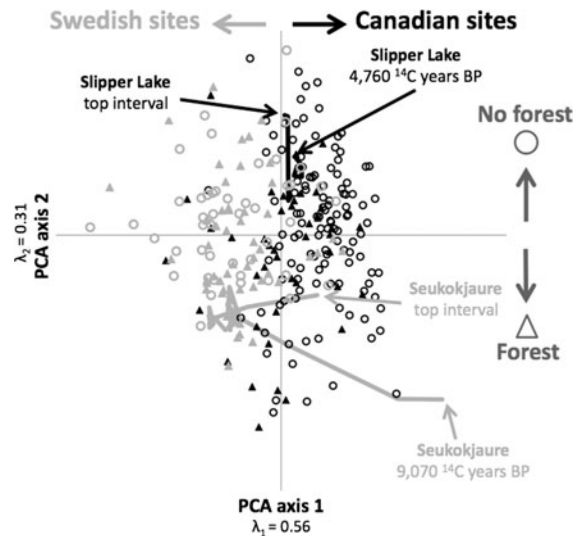

Fig. 5 Principal components analysis (PCA) of the VNIRS signatures in the surface sediment training set of 160 Canadian lakes (*black*) and 99 Swedish lakes (*grey*). Sites located in forested catchments are displayed as *filled triangles*, whereas those in non-forested catchments are shown as *empty circles*. The 5-pt running means of the VNIRS spectra from downcore Slipper Lake (*black line*) and Seukokjaure (*grey line*) were plotted passively to the PCA. The weight on axis 1 and 2 are 0.56 and 0.31, respectively. All spectra were centred and MSC-filtered prior to analysis

respectively from 1.9 to 20.6 mg L^{-1} and from 0.15 to 6.9 mg L^{-1}. Early establishment of soil after deglaciation, recorded by an increase in VNIRS-DOC, and the relatively recent switch from a lake in a forested zone to an alpine lake, recorded by a decrease in VNIRS-DOC, is tracked by other proxies (Rosén et al. 2003; Rosén and Persson 2006; Reuss et al. 2010) and similarly tracked by both models in a qualitative way. The timing and trends are the same, but the magnitude/amplitude is much greater in the Canadian model. Because the TOC from the Swedish 99-lake training set is almost entirely made of DOC (Rosén 2005), quantitative estimates from the models should be comparable. A preliminary CACS VNIRS-TOC model yielded poor performance, probably due to the more variable particulate organic carbon (POC) fraction at these sites, up to 38%.

Catchment influence on the VNIRS signatures

The PCA of the VNIRS measurements of the Canadian and the Swedish sediment sets allow an interpretation of the relationship between the sets and the downcore applications, independent from associated DOC levels and from a catchment point of view (Fig. 5). The variation accounted for by the first two components is 56 and 31%, respectively. The VNIRS signatures of surface lake sediment from the Swedish and the Canadian sets are distributed along axis 1, with some overlap. The resemblance between the VNIRS signatures of the two sediment sets can be attributed to the overall similar characteristics of Arctic environments and may partly explain the surprisingly high agreement between the DOC and TOC trends inferred from the Seukokjaure record. Indeed, several differences in the sampling and handling techniques as well as in the dataset characteristics between the two sets could have created more disagreement in the outputs (Cunningham et al. 2011).

There are variations in permafrost extent, bedrock geology, and soil and vegetation composition that could also explain the observed distribution of sites along axis 1. While more than 75% of the Canadian sites are located on permafrost (GSC 2002b), few of the Swedish sites were located on frozen ground

(Rosén 2005). The influence of permafrost on DOC export to aquatic systems is well documented (Frey and McClelland 2009). The soil types and bedrock geology are also much more diverse along the major geographical transect covered by the CACS than within the smaller area covered by the Swedish set (CAVM 2003; Rosén 2005). Additionally, the high-latitude, forested catchments of the Swedish sites are dominated by deciduous birch trees (Rosén 2005), while no such vegetation type is found in the Canadian coniferous-dominated boreal forest (Ecological Working Group 2002). Differences in quality and quantity of allochthonous organic carbon input can be expected from a deciduous versus conifer forest (Rinnan et al. 2008). Finally, polar desert sites found in the high latitudes of the Canadian Arctic Archipelago are not represented in the Swedish dataset.

The VNIRS signatures from the two datasets are also distributed along a forested to non-forested gradient on axis 2. For the Swedish and the Canadian sets, respectively, 46 and 74% of sites were in non-forested catchments, while 54 and 26% were located in forested catchments, above and below tree line. This distribution pattern suggests that the VNIRS signature reflects both quantitative and qualitative properties of organic material transported into the aquatic system, which is then preserved in the sediment. This correlation between the VNIRS signature and catchment vegetation was shown before in the Swedish subarctic region (Rosén et al. 2000b, 2001). It may, in part, be related to increasing ecosystem primary production with decreasing latitude. In fact, the sedimentary Chl *a* signal, shown to track past primary production (Michelutti et al. 2010), was inferred from visible reflectance spectra between 650 and 700 nm, a zone that is included in the signatures plotted here.

It is clear that the VNIRS signature is complex, and the factors influencing the suite of organic compounds present in the DOC are far from well understood. In the present study, there was no statistically significant relationship between the VNIRS signatures and DOC when the ponds (<2 m deep) of the original calibration set were included in analyses. The light- and oxygen-enhanced presence of epipelic living material at the sediment/water interface of ponds with a different VNIRS signal may help explain the absence of correlation (den Heyer and Kalff 1998). Also, larger and deeper water masses of bigger systems may display different deposition-diagenesis of organic matter compared to processes in smaller waterbodies. A better understanding of the biogeochemical processes affecting lakewater DOC through time during deposition in the water column, at the sediment/water interface and deeper in the paleo-record, may provide insights into the mechanisms relating DOC to VNIRS signatures.

Downcore VNIRS patterns are consistent with the modelled DOC reconstructions for both Slipper Lake and Seukokjaure. The Slipper Lake VNIRS profile varies slightly along axis 2 and groups with non-forested Swedish alpine lakes and Canadian alpine and Arctic tundra lake sites, consistent with a DOC profile experiencing only minor variations (Fig. 3). In contrast, Seukokjaure's profile displays a much wider variation along axis 1, in agreement with the reconstructed DOC and lake history (Fig. 4). Early Holocene (>9,500 cal years BP) values cluster outside the range of the Canadian set, towards polar desert sites, and the profile then shifts rapidly towards forested Swedish sites for most of the period investigated. Finally, the most recent intervals (<200 cal years BP) cluster towards the Canadian Arctic tundra and forest-tundra lakes after another rapid transition. Our results correspond well with the observation that the lake is situated at the present tree line with only a few scattered trees in the catchment. The position of the Seukokjaure VNIRS profile at the overlap between the Swedish and the Canadian datasets on the PCA biplot may help explain the similar inference trends yielded by the two geographically independent models.

Absolute values and model performance enhancement

Because most of the Slipper Lake and Seukokjaure VNIRS profiles fall within the boundaries of the Canadian set distribution on the PCA, we are confident that analogous VNIRS signatures were included in the model to infer past lakewater DOC levels. This supports the validity of our reconstructions. The Seukokjaure profile from the PCA (Fig. 5), however, shows that the organic compounds of the early Holocene sediment intervals (>9,500 cal years BP) recorded within the VNIRS signal share more similarities with those characterizing modern high Arctic Canadian lakes. The closest sites are Canadian polar desert lakes from Northern Ellesmere Island (EPF and Nan Lake) and Axel Heiberg Island (Buchanan and Colour Lakes), Colour Lake being the most similar. These four waterbodies are dilute, ultra-oligotrophic lakes of various sizes (7–1,800 ha) and pH (3.6–8.8), with low DOC (1–5 mg L^{-1}). They may represent the conditions in the Seukokjaure catchment in the early Holocene. Although within the error bars of both models, the difference between the reconstructed Swedish and Canadian values is greater for the early Holocene period (73–93%) compared to an average of 65% difference during the forested period (9,500–850 cal years BP). Because the best analogues are found among high Arctic lakes in Canada, the VNIRS-inferred DOC values for the early period in Seukokjaure are probably reconstructed more reliably by the Canadian model. Similarly, the most recent intervals, i.e. the last ~200 cal years of the alpine lake record have better analogue sites within the Canadian set (Arctic-tundra lakes), as shown by the PCA clustering, and the difference in absolute values inferred by the two models is also high, up to 80–87%. On the other hand, the PCA shows that the Swedish model probably reconstructs the most reliable values in the forested period of Seukokjaure, because only a few VNIRS signatures from Canadian lakes "surround" the 9,500–200 cal years BP intervals, compared to a majority of forested Swedish lakes that display very similar VNIRS signals. Birch-dominated subarctic Swedish catchments are not represented in the Canadian set, and this difference could be driving the spectral composition.

As mentioned, quantitative inferences remain an issue for applications of VNIRS-based models. Here, the large difference between the absolute values and amplitudes of trends in the Canadian and the Swedish reconstructions of Seukokjaure, is likely due to differences in environmental gradients of the datasets and lack of modern analogues in the calibration sets. The remarkably similar trends observed between the Seukokjaure inferences of this study and the outcomes obtained through models developed from geographically independent lake sets, suggest that application of VNIRS to lake sediments to infer past DOC levels qualitatively is robust and potentially without major geographic restrictions at high latitudes. Additionally, our data suggest that larger calibration sets could be preferable for DOC reconstructions to provide analogous VNIRS signatures in areas that are expected to have undergone large environmental fluctuations over the time frame studied, such as high-latitude lakes over the Holocene. The combination of the Swedish and the Canadian datasets, and further additions of southern Canadian lakes to the model could benefit the model's performance and reliability by including a wider variety of signals (Cunningham et al. 2011). Further, extending the calibration to latitudes farther south in Canada and applying the model to sediment cores from the temperate region could help answer important questions regarding the timing and causes of increasing DOC trends observed in recent years (Monteith et al. 2007).

Conclusions

We developed a lakewater-DOC inference model based on VNIRS from a Canadian Arctic lake surface-sediment calibration set. The Canadian model yielded similar statistical performance to the Swedish VNIRS-TOC inference models, and allowed us to reconstruct Holocene lakewater DOC levels qualitatively from paleolimnological records of two northern tree line lakes. Our results suggest that the history of lake catchment changes is partly preserved in sediment cores in the form of a geochemical "fingerprint" that can be recorded using VNIRS and modelling approaches. Our analyses also suggest that VNIRS-based models used to infer trends in past lakewater DOC have no major environmental limitation at high latitudes, and thus offer a wide scale of applicability. Uncertainties remain regarding absolute values reconstructed using the Canadian set. Nevertheless, improvement of the calibration set may be achieved by providing additional analogues and gaining further understanding of the mechanisms linking lakewater DOC and the VNIRS. Furthermore, implementing the technique for wavelength weight on multivariate analyses should improve the overall reliability of VNIRS-based models. Most importantly, the indirect model developed here allows the rapid reconstruction of overall trends in lakewater DOC from lake sediment records, highlighting the usefulness of VNIRS as a time- and cost-effective tool for the investigation of long-term changes in the optical environment and C cycle of freshwater ecosystems.

Acknowledgments This study was funded by the NSERC (Ottawa, Canada), CIRC, Umeå University and through the CGS-MSFSS program. We thank J. Thienpont, M. Pisaric and S. Kokelj for providing the Inuvik sediments, as well as the many field crews who assisted in various sampling programs. We also thank K. Rühland for sharing data and knowledge on Slipper Lake, A. Holmgren for her help with the VNIRS analyses in Umeå, C. Grooms for his technical assistance, N. Michelutti and the PEARL, CEN, CIRC and EMG research groups for their support, as well as B. F. Cumming and S. Lamoureux and two anonymous reviewers for their constructive comments on the manuscript.

References

ACIA (2005) Arctic climate impact assessment. Cambridge University Press, Cambridge

Birks HH, Birks HJB (2006) Multi-proxy studies in palaeolimnology. Veg Hist Archaeobot 15:235–251

CAVM Team (2003) Circumpolar arctic vegetation map. Conservation of Arctic Flora and Fauna (CAFF) Map No. 1 [map]. 1:7,500,000. US Fish and Wildlife Service, Anchorage, USA

Cole JJ, Prairie YT, Caraco NF, Mcdowell WH, Tranvik LJ, Striegl RG, Duarte CM, Kortelainen P, Downing JA, Middelburg JJ, Melack J (2007) Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. Ecosystems 10:172–185

Côté G, Pienitz R, Velle G, Wang X (2010) Impact of Geese on the Limnology of Lakes and Ponds from Bylot Island (Nunavut, Canada). Intern Rev Hydrobiol 95:105–129

Cunningham L, Bishop K, Mettävainio E, Rosén P (2011) Paleoecological evidence of major declines in total organic carbon concentrations since the nineteenth century in four nemoboreal lakes. J Paleolimnol 45:507–518

Curtis CJ, Juggins S, Clarke G, Battarbee R, Kernan M, Catalan J, Thompson R, Posch M (2009) Regional influence of acid deposition and climate change in European mountain lakes assessed using diatom transfer functions. Freshw Biol 54:2555–2572

den Heyer C, Kalff J (1998) Organic matter mineralization rates in sediments: a within-and among-lake study. Limnol Oceanogr 43:695–705

Douglas MSV, Smol JP (1994) Limnology of high arctic ponds (Cape Herschel, Ellesmere Island, N.W.T). Arch Hydrobiol 131:401–434

Ecological Working Group (2002) The State of Canada's ecosystems in maps [map]. 1:2,500,000. Ecological Mapping Analysis and Protocols, Government of Canada, Ottawa, Canada

Environment Canada (1979) Analytical methods manual. Inland Waters Directorate, Water Quality Branch, Ottawa, Canada

Environment Canada (1994a) Manual for analytical methods, vol 1-major ions and nutrients. National Laboratory for Environmental Testing, Canadian Centre for Inland Waters, Burlington

Environment Canada (1994b) Manual for analytical methods, vol 2-trace metals. National Laboratory for Environmental Testing, Canadian Centre for Inland Waters, Burlington

Fallu M, Pienitz R (1999) Diatomées lacustres de Jamésie-Hudsonie (Québec) et modèle de reconstitution des concentrations de carbone organique dissous. Écoscience 6:603–620

Frey KE, McClelland JW (2009) Impacts of permafrost degradation on arctic river biogeochemistry. Hydrol Process 23:169–182

Geladi P, Macdougall D, Martens H (1985) Linearization and scatter-correction for near-infrared reflectance spectra of meat. Appl Spectrosc 39:491–500

GeoBase (2007) National hydro Network (NHN) [web database]. 1:50,000. Centre for Topographic Information, Geomatics Canada, Earth Sciences Sector, Natural Resources Canada, Sherbrooke, Canada

Geological Survey of Canada (GSC) (1973) Surface Materials [map]. 1:15,000,000. The National Atlas of Canada. Surveys and Mapping Branch, Department of Energy, Mines and Resources, Ottawa, Canada, pp 37–38

Geological Survey of Canada (GSC) (2002a) Canadian peatland database [web database]. 1:6,500,000. Earth Sciences Sector, Terrain Sciences Division, Natural Resources Canada, Ottawa, Canada

Geological Survey of Canada (GSC) (2002b) Canadian permafrost thickness [web database]. Earth Sciences Sector, Natural Resources Canada, Ottawa

Jansson M, Hickler T, Jonsson A, Karlsson J (2008) Links between terrestrial primary production and bacterial production and respiration in lakes in a climate gradient in subarctic Sweden. Ecosystems 11:367–376

Karlsson J, Byström P, Ask J, Ask P, Persson L, Jansson M (2009) Light limitation of nutrient-poor lake ecosystems. Nature 460:506–509

Keatley BE, Douglas MSV, Smol JP (2007a) Limnological characteristics of a high arctic oasis and comparisons across northern Ellesmere Island. Arctic 60:294–308

Keatley BE, Douglas MSV, Smol JP (2007b) Physical and chemical limnological characteristics of lakes and ponds across environmental gradients on Melville Island, Nunavut/NWT, High Arctic Canada. Fundam Appl Limnol 168:355–376

Kokelj S, Jenkins R, Milburn D, Burn C, Snow N (2005) The influence of thermokarst disturbance on the water quality of small upland lakes, Mackenzie Delta Region, Northwest Territories, Canada. Permafr Periglac Process 16:343–353

Kokfelt U, Rosén P, Schoning K, Christensen T, Förster J, Karlsson J, Reuss N, Rundgren M, Callaghan T, Jonasson C, Hammarlund D (2009) Ecosystem responses to increased precipitation and permafrost decay in sub-arctic Sweden inferred from peat and lake sediments. Glob Chang Biol 15:1652–1663

Korsman T, Nilsson M, Ohman J, Renberg I (1992) Near-infrared reflectance spectroscopy of sediments—a potential method to infer the past pH of lakes. Environ Sci Technol 26:2122–2126

Korsman T, Renberg I, Dabakk E, Nilsson MB (2001) Near-infrared spectrometry (NIRS) in palaeolimnology. In: Last WM, Smol JP (eds) Physical and geochemical methods. Kluwer, Dordrecht, pp 299–317

Leavitt P, Cumming BF, Smol JP, Reasoner M, Pienitz R, Hodgson D (2003) Climatic control of ultraviolet radiation effects on lakes. Limnol Oceanogr 48:2062–2069

Lim DSS, Douglas MSV (2003) Limnological characteristics of 22 lakes and ponds in the Haughton Crater region of Devon Island, Nunavut, Canadian High Arctic. Arct Antarct Alp Res 35:509–519

Lim DSS, Douglas MSV, Smol JP, Lean DRS (2001) Physical and chemical limnological characteristics of 38 lakes and ponds on Bathurst Island, Nunavut, Canadian High Arctic. Int Rev Hydrobiol 86:1–22

Lim DSS, Douglas MSV, Smol JPS (2005) Limnology of 46 lakes and ponds on Banks Island, NWT, Canadian Arctic Archipelago. Hydrobiologia 545:11–32

Michelutti N, Douglas MSV, Lean DRS, Smol JP (2002a) Physical and chemical limnology of 34 ultra-oligotrophic lakes and ponds near Wynniatt Bay, Victoria Island, Arctic Canada. Hydrobiologia 482:1–13

Michelutti N, Douglas MSV, Muir D, Wang X, Smol JP (2002b) Limnological characteristics of 38 lakes and ponds on Axel Heiberg Island, High Arctic Canada. Int Rev Hydrobiol 87:385–399

Michelutti N, Douglas MSV, Wolfe AP, Smol JP (2006) Heightened sensitivity of a poorly buffered high arctic lake to late-Holocene climatic change. Quat Res 65:421–430

Michelutti N, Douglas MSV, Smol JP (2007) Evaluating diatom community composition in the absence of marked limnological gradients in the high Arctic: a surface sediment calibration set from Cornwallis Island (Nunavut, Canada). Polar Biol 30:1459–1473

Michelutti N, Blais JM, Cumming BF, Paterson AM, Rühland KM, Wolfe AP, Smol JP (2010) Do spectrally inferred determinations of chlorophyll a reflect trends in lake trophic status? J Paleolimnol 43:205–217

Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Høgåsen T, Wilander A, Skjelkvåle BL, Jeffries DS, Vuorenmaa J, Keller B, Kopácek J, Vesely J (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450:537–540

Pienitz R, Smol JP (1993) Diatom assemblages and their relationship to environmental variables in lakes from the boreal forest-tundra ecotone near Yellowknife, Northwest-Territories, Canada. Hydrobiologia 269:391–404

Pienitz R, Smol JP, Lean DRS (1997a) Physical and chemical limnology of 24 lakes located between Yellowknife and Contwoyto Lake, Northwest Territories (Canada). Can J Fish Aquat Sci 54:347–358

Pienitz R, Smol JP, Lean DRS (1997b) Physical and chemical limnology of 59 lakes located between the southern Yukon and the Tuktoyaktuk Peninsula, Northwest Territories (Canada). Can J Fish Aquat Sci 54:330–346

Pienitz R, Smol JP, Macdonald GM (1999) Paleolimnological reconstruction of Holocene climatic trends from two boreal treeline lakes, Northwest Territories, Canada. Arct Antarct Alp Res 31:82–93

Reuss NS, Hammarlund D, Rundgren M, Segerström U, Eriksson L, Rosén P (2010) Lake ecosystem responses to Holocene climate change at the subarctic tree-line in Northern Sweden. Ecosystems 13:393–409

Rinnan R, Michelsen A, Jonasson S (2008) Effects of litter addition and warming on soil carbon, nutrient pools and microbial communities in a subarctic heath ecosystem. Appl Soil Ecol 39:271–281

Rosén P (2005) Total organic carbon (TOC) of lake water during the Holocene inferred from lake sediments and near-infrared spectroscopy (NIRS) in eight lakes from northern Sweden. Biogeochemistry 76:503–516

Rosén P, Hammarlund D (2007) Effects of climate, fire and vegetation development on Holocene changes in total organic carbon concentration in three boreal forest lakes in northern Sweden. Biogeosciences 4:975–984

Rosén P, Persson P (2006) Fourier-transform infrared spectroscopy (FTIRS), a new method to infer past changes in tree-line position and TOC using lake sediment. J Paleolimnol 35:913–923

Rosén P, Hall R, Korsman T, Renberg I (2000a) Diatom transfer-functions for quantifying past air temperature, pH and total organic carbon concentration from lakes in northern Sweden. J Paleolimnol 24:109–123

Rosén P, Dabakk E, Renberg I, Nilsson M, Hall R (2000b) Near-infrared spectrometry (NIRS): a new tool for inferring past climatic changes from lake sediments. Holocene 10:161–166

Rosén P, Segerström U, Eriksson L, Renberg I, Birks HJB (2001) Holocene climatic change reconstructed from diatoms, chironomids, pollen and near-infrared spectroscopy at an alpine lake (Sjuodjljaure) in northern Sweden. Holocene 11:551–562

Rosén P, Segerström U, Eriksson L, Renberg I (2003) Do diatom, chironomid, and pollen records consistently infer Holocene July air temperature? A comparison using sediment cores from four alpine lakes in northern Sweden. Arct Antarct Alp Res 35:279–290

Rosén P, Vogel H, Cunningham L, Reuss N, Conley DJ, Persson P (2010) Fourier transform infrared spectroscopy, a new method for rapid determination of total organic and inorganic carbon and biogenic silica concentration in lake sediments. J Paleolimnol 43:247–259

Rühland KM (2001) Diatom Assemblage shifts relative to changes in environmental and climatic conditions in the circumpolar treeline regions of the Canadian and Siberian Arctic. PhD thesis, Department of Biology, Queen's University, pp 124–150

Rühland KM, Smol JP (2002) Freshwater diatoms from the Canadian Arctic treeline and development of paleolimnological inference models. J Phycol 38:249–264

Rühland KM, Smol JP (2005) Diatom shifts as evidence for recent subarctic warming in a remote tundra lake, NWT, Canada. Palaeogeogr Palaeoclimatol Palaeoecol 226:1–16

Soil Landscapes of Canada Working Group (2006) Soil landscapes of Canada, v3.1 [map]. 1:1,000,000. Agriculture and Agri-Food Canada, Ottawa, Canada

Sweetman JN, Laface E, Rühland KM, Smol JP (2008) Evaluating the response of cladocera to recent environmental changes in lakes from the Central Canadian Arctic treeline region. Arct Antarct Alp Res 40:584–591

Thorsteinsson R, Tozer ET (1970) Geology of the Arctic Archipelago. In: Douglas, RJW (ed) Geology and economic minerals of Canada. Geological Survey of Canada, Economic Geology Report, Ottawa, pp 547–590

Vincent WF, Laybourn-Parry J (2008) Polar lakes and rivers: limnology of Arctic and Antarctic aquatic ecosystems. Oxford University Press, Oxford