Inferring past trends in lake-water organic carbon concentrations in northern lakes using sediment spectroscopy

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ABSTRACT

Changing lake-water total organic carbon (TOC) concentrations are of concern for lake management because of corresponding effects on aquatic ecosystem functioning, drinking water resources and carbon cycling between land and sea. Understanding the importance of human activities on TOC changes requires knowledge of past concentrations; however, water-monitoring data are typically available for the past few decades only, if at all. Here, we present a universal model to infer past lake-water TOC concentrations in northern lakes across Europe and North America that uses visible-near-infrared (VNIR) spectroscopy on lake sediments. In the orthogonal partial least squares model, VNIR spectra of surface-sediment samples are calibrated against corresponding surface-water TOC concentrations (0.5–41 mg L^{-1}) from 345 Arctic to northern temperate lakes in Canada, Greenland, Sweden and Finland. Internal model-cross-validation resulted in a R^2 of 0.57 and a prediction error of 4.4 mg TOC L^{-1}. First applications to lakes in southern Ontario and Scotland, which are outside of the model's geographic range, show the model accurately captures monitoring trends, and suggest that TOC dynamics during the 20th century in these regions were primarily driven by changes in atmospheric deposition. Our results demonstrate that the lake-water TOC model is not geographically restricted, nor biased by post-depositional diagenesis, allowing the identification of past TOC variations in northern lakes of Europe and North America over timescales of decades to millennia.

Introduction

Changing total (or dissolved) organic carbon (TOC/DOC) concentrations have been monitored in many lakes across the northern hemisphere over the past decades, with increasing trends in most regions but also declines in some areas[1-3]. TOC in inland waters is an important component of the global carbon (C) cycle, as the pathway between the terrestrial environment and the ocean, lakes and rivers contribute to greenhouse gas emissions and sequester C in their sediments[4-5]. In the functioning of aquatic ecosystems, TOC concentrations play a fundamental role by influencing physical and chemical water properties, and consequently the structure of biological communities[6]. For example, TOC affects water acidity[7], dissolved oxygen levels[8-9], water color and thus light and heat penetration[10-11], which in turn regulate the development of thermal stratification and hypoxia/anoxia. TOC is also strongly bound to nutrients, and together these factors influence species distributions and habitat availability for primary producers (bacteria, algae) to fish and thus the productivity of aquatic ecosystems[12-16]. Furthermore, TOC affects the transport and sequestration of metals and organic pollutants[17], the development of toxic algal blooms[18] and associated costs for drinking water treatment[19-20].

Increasing TOC trends in Europe and NE North America have largely been attributed to reduced sulfate deposition and the subsequent recovery of soils from acidification, which increases organic matter solubility and thus TOC export from terrestrial to aquatic environments[1]. Following such a recovery, future TOC dynamics in these and other regions will be dominated by other stressors (e.g., changes in land use, nitrogen deposition, climate change) that affect the composition and size of the terrestrial TOC pool as well as the transport of TOC between terrestrial and aquatic environments. For example, over the next few decades climate-mediated changes in hydrology and land cover are projected to alter C cycling and TOC levels in lakes across boreal, subarctic and Arctic landscapes[21-25]. To provide realistic scenarios for these future changes in TOC concentrations and their associated implications for aquatic ecosystems, it is crucial to understand the role of single natural and anthropogenic stressors and their individual contribution to current and past changes in TOC levels. Monitoring data are critical for analyzing current trends but are available for relatively few lakes and span a few decades at most.

Paleolimnological studies have shown that it is possible to reconstruct past trends in TOC/DOC concentrations in lakes from sediment records using inference models based on visible-near-infrared (VNIR) spectroscopy[26-29]. VNIR spectroscopy is a fast, inexpensive and non-destructive technique that is particularly sensitive to changes in organic matter quality. The technique is widely used for quality control in industrial processes but has also become an important tool in environmental and biological studies to determine, for example, plant and animal tissue composition[30], different soil constituents[31] and chlorophyll-*a* concentrations in sediments[32]. By employing a transfer function between VNIR spectra of lake-surface sediments, i.e., the most recently accumulated material, and corresponding TOC/DOC concentrations in the water column, the method allows for the reconstruction of long-term data from sediment cores on the scales of decades to millennia. These long-term data provide critical knowledge about TOC changes in response to past environmental change, natural long-term TOC variability and reference levels prior to human disturbances. For example, recent studies in southern and central Sweden showed that the current TOC increase was preceded by a long-term decline over the last 500 to 1000 years in response to increasing human land use[27-28, 33]. In southern Sweden, changes in acid deposition were identified as an important factor contributing to TOC dynamics during the 20th century[34-35]. In other studies, the technique has allowed the tracking of TOC/DOC variations throughout the Holocene in response to environmental changes that have included treeline migration, mire development and permafrost dynamics[26, 36-40].

The existing VNIR inference models for lake-water TOC/DOC are based on regional lake calibration sets from Sweden[26-28] and Canada[29]. However, first applications of these models to sediment records from outside their geographical calibration range suggest that the technique may not be geographically restricted[29, 39], and that it might be possible to develop a universal model for lakes across large environmental gradients. Such a supra-regional model would allow for the application of the technique in other regions without the time and expense required to generate a sufficiently large regional calibration set.

Here, we combine sediment and water chemistry data from 345 lakes from Canada, Greenland, Sweden and Finland to establish a universal VNIR lake-water TOC inference model for northern lakes in Europe and North America (hereafter referred to as Northern lake-water TOC model). The calibration lakes span large vegetation and climate gradients from the Arctic across the boreal forest to the northern temperate zone (Fig. 1). To evaluate the Northern lake-water TOC model's performance, we applied it to sediment records from lakes that are located a) within (boreal Sweden, subarctic Canada) and b) outside (United Kingdom, northern temperate Canada) the model's geographic calibration range, and compared sediment-inferred to monitored lake-water TOC/DOC trends. By applying the model to a series of annually laminated sediment cores collected from the same lake over a 27-year period[41-42], we assessed whether post-depositional (diagenetic) changes in the sediment composition distort the reconstructions of past TOC levels.

Materials and methods

Calibration samples. The Northern lake-water TOC model is based on surface-sediment samples and corresponding lake-water TOC measurements from 345 lakes covering a TOC range from 0.5 to 41 mg L^{-1}. The model includes samples from previously developed models for Sweden (n=146; 0.7–22 mg TOC L^{-1})[26-28] and Canada (n=142; 0.9–41 mg TOC L^{-1})[29] as well as additional samples from Finland (n=47; 0.5–18 mg TOC L^{-1}) and Greenland (n=10; 4.9–28 mg TOC L^{-1}). The study lakes span a large geographic and environmental gradient from the high Arctic to boreal and northern temperate zones and from western Canada across to eastern Fennoscandia, and vary in elevation from sea level to 1387 m above sea level (a.s.l.). The calibration set covers a climate range with mean July air temperature from 3.5 to 17.0°C and range in mean annual precipitation from <150 to 1900 mm. Catchment vegetation ranges from polar desert in the Canadian high Arctic through tundra and boreal coniferous forests to mixed coniferous and deciduous forest in southern Sweden. The lakes vary in depth from 2 to 49 m, and are relatively undisturbed by human activities, except for atmospheric deposition and some agriculture and infrastructure developments, predominantly in southern Sweden. Lake characteristics vary from (ultra)oligotrophic to eutrophic (TP: 0.1–68 µg L^{-1}) and from acidic to alkaline (pH 3.5–8.8) (Table S1).

Surface sediments (topmost 0.5 cm or 1.0 cm) for the calibration model were generally recovered from the deepest part of each lake using a gravity corer, except for high Arctic sites where samples were taken mostly at shallower near-shore sites (<1 m water depth). Surface water sampling (within uppermost 1 m of water column) and water chemistry analyses followed standard protocols. TOC concentrations used for the calibration are mostly based on single measurements, except for 47 Swedish reference lakes (http://miljodata.slu.se/mvm/), which were sampled at least four times per year and the average TOC concentrations over the 3 years prior to sediment sampling were used in model development. More information about lake characteristics and limnological variables can be found in Table S1 and in the respective regional model papers[26-27, 29]. The Northern lake-water TOC model is calibrated against TOC concentrations because these were quantified for all lakes in contrast to DOC. In lakes for which DOC and TOC were measured (n=241), DOC compromised on average 87% of the TOC pool.

Diagenesis series. Nylandssjön (62° 57′ N, 18° 17′ E; 34 m asl) is a 17.5 m deep, mesotrophic boreal-forest-lake with a surface area of 0.28 km^2 located at the coast of the Gulf of Bothnia in northern Sweden. Since the beginning of the 20th century when the lake culturally eutrophied, hypolimnetic hypoxia has occurred regularly during the summer and winter, leading to the formation of annually laminated (varved) sediment. The varved character of the sediment enables accurate subsampling of individual years, and sediment cores have been repeatedly recovered from Nylandssjön over the past four decades using a freeze corer[41-42]. In this study, we used sediment cores recovered in 1983, 1985, 1989, 1992, 1993, 1997, 2002, 2004, 2006, 2007 and 2010. This core series allows tracking the influence of post-depositional, diagenetic processes on the composition of sediment that accumulated in the 1982 varve (surface varve of 1983 core) after 2, 6, 9, 10, 14, 19, 21, 23, 24 and 27 years.

Long-term TOC reconstruction lakes. We applied the Northern lake-water TOC model to sediment records from six lakes, with three each located within and outside the model's geographical calibration range (Fig. 1). The lakes located within the geographic range of the model include Långsjön (60° 43′60″ N, 16° 25′46″ E; 239 m a.s.l.; Z_{max} = 6 m; area = 0.07 km^2) and Gipsjön (60° 39′01″ N, 13°37′23″ E; 376 m a.s.l.; Z_{max} = 14 m; area = 0.67 km^2). Both of these are humic, naturally acidic (pH = 6.1/5.5 in 2010–2012) lakes located in the spruce and pine-dominated boreal forest of south-central Sweden, and have been part of the Swedish freshwater monitoring program since 1987[28]. Slipper Lake (64°35′65″ N, 110°50′07″ W; 460 m a.s.l.; Z_{maz} = 17 m, area = 1.9 km^2) is a slightly acidic (pH = 6.4), oligotrophic tundra lake in the central Canadian subarctic, located ~50 km north of the current treeline[29, 43].

Lakes located outside of the geographic limits of the model include Heney Lake (45° 23′ N, 79° 07′ W; 351 m a.s.l.) and Eagle Lake (44° 40′19″ N, 76° 40′26″ W; 198 m a.s.l.), which are oligotrophic lakes surrounded by mixed coniferous and broad-leaved forests in south-central/southern Ontario, Canada. Heney Lake is a relatively small (0.21 km^2) acidic lake (pH = 5.9 in 2010–2012), with a maximum depth of 6 m, and has been regularly sampled for DOC and other lake-water variables since 1978 as part of the Ontario Ministry of the Environment and

Climate Change's long-term monitoring program at the Dorset Environmental Science Centre. Eagle Lake is a slightly alkaline (pH = 7.9), comparatively large (6.65 km^2) and deep (31 m) lake, and DOC concentrations have periodically been measured since 2001[44]. Round Loch of Glenhead (55°5' N, 4°25'W; 298 m a.s.l.) is an oligotrophic moorland lake in south-west Scotland, United Kingdom. The lake has a surface area of 0.13 km^2, a maximum depth of 14 m[45] and is part of the United Kingdom Upland Waters Monitoring Network (UWMN), formerly the UK Acid Waters Monitoring Network, with data extending back to 1988. The lake acidified following atmospheric acid deposition during the last century and is currently recovering, with a pH of 5.3 in 2011–2013[46].

All sediment cores were radiometrically dated by analyzing ^{210}Pb, ^{226}Ra (via its granddaughter isotope ^{214}Pb), ^{137}Cs, and ^{241}Am using gamma spectrometry. Resulting age-depth relationships for the past 100-150 years were calculated using the constant rate of ^{210}Pb supply (CRS) dating model[47]. For Gipsjön, Långsjön and Slipper Lake, sediment ages beyond the dating range of ^{210}Pb were constrained by accelerator mass spectroscopy (AMS) radiocarbon ages determined on terrestrial macrofossils and bulk sediments. Deeper sediments from Heney Lake, Eagle Lake and Round Loch of Glenhead were not radiocarbon dated and sediment ages beyond the ^{210}Pb dating range were estimated based on linear extrapolations of the ^{210}Pb chronologies. Additional information regarding site descriptions, sampling and dating techniques can be found in detailed studies of the sediment records from Långsjön and Gipsjön[28], Slipper Lake[29, 43], Heney Lake[48], Eagle Lake[44], and in the SI for Round Loch of Glenhead (Fig. S1).

Because of the potential mobility of sulfur in sediments, we used total lead (Pb) concentrations in the sediment records from Heney Lake, Eagle Lake and Round Loch of Glenhead as indicator for increased deposition of atmospheric pollutants in the respective areas. Similar to sulfur dioxide, Pb emissions increased following industrialization in response to the increased ore smelting, combustion of coal and later leaded gasoline, and peaked in the 1970's[49-51]. In the Canadian lakes, Pb was measured on freeze-dried powdered sample material by wavelength dispersive X-ray fluorescence using a Bruker S8 Tiger spectrometer, while a Spectro XLAB2000 X-ray fluorescence spectrometer was used for Round Loch of Glenhead.

VNIR spectroscopy and model development. Prior to spectroscopic analyses, sediment samples were freeze-dried and subsequently sieved (125 μm mesh) or ground to a fine powder to remove the effects of water and particle size on the VNIR signal. VNIR spectra were recorded with a FOSS XDS Rapid Content Analyser in diffuse reflectance mode. Each sediment sample spectra represents a mean of 32 scans at 2-nm resolution in the wavelength range from 400 to 2500 nm. The measured diffuse reflectance (R) of light in the VNIR region was transformed to apparent absorbance (A) following the equation: $A = \log(1/R)$. Orthogonal Partial Least Squares (O-PLS) regression modelling[52] was used to establish the calibration model between the VNIR spectral information of the surface sediments and the corresponding measured TOC concentration in the surface water. Prior to numerical analysis, VNIR spectra were centered, while TOC concentrations were standardized and square-root transformed. To evaluate the model performance, we used the cross-validated (CV) coefficient of determination (R^2_{cv}) and the root mean square error of cross-validation ($RMSE_{CV}$) (in mg TOC L^{-1}) resulting from seven-fold cross-validation. PLS modeling and lake-water TOC reconstruction were performed using SIMCA 14.0 (Umetrics AB, Umeå, Sweden).

Results and discussion

Northern lake-water TOC model. The calibration between 345 surface sediment VNIR spectra and corresponding measured lake-water TOC concentrations resulted in a 7-component OPLS model with an R^2_{cv} of 0.57 and $RMSE_{CV}$ of 4.4 mg L^{-1} (10.9% of TOC gradient) (Fig.2, Table S2).

The internal performance of the Northern lake-water TOC model is slightly less accurate but comparable to the previously published regional TOC/DOC models for Sweden and Arctic Canada (R^2_{cv} = 0.61–0.72; $RMSE_{CV}$ = 1.6–4.4 mg L^{-1} (10.8–11.3% of TOC/DOC gradient)[26-27, 29]. Part of the discrepancy between sediment-inferred and measured TOC concentrations results from the fact that most lake-water TOC concentrations used for the calibration are based on single measurements (n=291), which do not account for inter and intra-annual TOC variability, which can be large in lakes with low residence time, and/or high mean concentrations. For example, in the 47 Swedish reference lakes, the only lakes in the calibration set with multiple measurements ($n \geq 4$ per year), TOC varied substantially over the 3 years preceding sediment sampling, with an average standard deviation of 2.0 (0.5–6.1) mg L^{-1} (18.5% (6.1–58.0%) of the mean TOC content) across all lakes. High TOC concentrations are less accurately inferred and commonly underestimated (Figs. 2 and S2), which is likely a consequence of having few lakes with high TOC in the calibration set (13 lakes with TOC >20 mg L^{-1}).

Impact of diagenesis on lake-water TOC reconstruction. The Northern lake-water TOC model infers an average TOC concentration of 7.6±0.3 mg L^{-1} (n = 11) for the sediment varve from Nylandssjön that formed in 1982 and which has been repeatedly sampled from sediment cores that were recovered over the following 27 years (Fig.3). No relationship was found between sediment aging and inferred lake-water TOC content ($R^2 = 0.003$; $p = 0.87$). Previous studies have shown that sediments in Nylandssjön undergo strong early diagenetic changes in the first three decades after sediment deposition (but especially in the first 5–10 years), altering the organic matter quantity and quality (e.g., C and nitrogen (N) content, C and N isotopes, specific biomarkers). For example, post-depositional changes led to an average total C loss of 23%, a total nitrogen loss of 35% and consequently an increase in C/N ratios from ~10 to ~12[41-42, 53]. Despite these diagenetic changes, sediment-inferred lake-water TOC concentrations remain unaltered, which demonstrates that sediment ageing, during the early critical years when diagenetic alterations are greatest and thus likely also over longer timescales, does not bias the reconstruction of lake-water TOC dynamics using VNIR spectroscopy.

Sediment-inferred long-term trends. Långsjön, Gipsjön (Sweden) and Slipper Lake (Canada) are located within the Northern lake-water TOC model's calibration range (Fig.1). Inferred lake-water TOC concentrations for these lakes match previously published long-term trends based on the regional Swedish and Canadian TOC/DOC models, respectively, as well as available monitoring trends for the past three decades (Fig.4). As shown previously with the regional Swedish model, the universal Northern lake-water TOC model shows a long-term declining trend since the 17th century (Fig.4a-b) for Långsjön and Gipsjön, which has been attributed to human landscape alteration through early forest grazing and farming in central Sweden[28]. Compared to the regional model, the universal Northern lake-water TOC model somewhat underestimates absolute values during the monitoring period for Långsjön, but with a closer match in Gipsjön. This demonstrates that the model's reduced site-specificity compared to the regional model does not affect the ability to predict past TOC trends but may lower the accuracy of the approach. When applied to Slipper Lake (Canada) the Northern lake-water TOC model closely reproduces the dynamics inferred by the Canadian DOC model[29] (Fig.4c).

Heney Lake, Eagle Lake (Canada) and Round Loch of Glenhead (Scotland, UK) are located outside of the Northern lake-water TOC model's geographical calibration range (Fig.1). Inferred TOC trends for the three lakes are in good agreement with monitoring data and capture the ongoing TOC increase (Fig.5). While sediment-inferred absolute TOC values match measured DOC concentrations in Heney Lake and Eagle Lake, the Northern lake-water TOC model slightly overestimates (~2 mg L^{-1}) DOC concentrations monitored in Round Loch of Glenhead. The better fit between measured and inferred values for Heney Lake and Eagle Lake might be explained by the larger mesh size used for filtration of water samples from the two Canadian lakes (80 µm) compared to samples in the UK UWMN (0.45 µm), which would reduce the difference between the different C pools (DOC vs. TOC) in the Canadian lakes.

Long-term TOC reconstructions for the three lakes show a similar pattern, with higher TOC levels prior to a pronounced decline during the 20th century followed by the currently observed TOC increase (Fig.5). Prior to ~1900 C.E., TOC values were relatively stable in Heney Lake (6.8±0.5 mg L^{-1}) and Eagle Lake (6.1±0.4 mg L^{-1}), while past dynamics in Round Loch of Glenhead were more complex, with inferred values around 5–7.5 mg L^{-1} during ~1500–1700 C.E. followed by elevated values around 8–10 mg L^{-1} during ~1700–1850 C.E. By the late-19th to early-20th century, TOC decreased in all lakes by 50–70%, from concentrations in the range of 6–7.5 mg L^{-1} to minimum values of 2–3.5 mg L^{-1} during the mid-20th century. Recovery of TOC levels started in the 1980's and 1990's in Heney Lake and Eagle Lake, and by the 1970's in Round Loch of Glenhead, with inferred concentrations for the topmost samples of 4.6, 4.7 and 7.0 mg L^{-1}, respectively.

The three lakes are located in areas with notable acid deposition during the past century, and soils and surface waters in these areas are currently recovering from the effects of acidification[2]. For example, diatom-based pH reconstructions showed a distinct pH decline from 5.5 to 4.8 in Round Loch of Glenhead following industrialisation[45, 54]. In all lakes, sediment-inferred TOC dynamics closely follow changes in sulfate deposition and mirror the increase in sulfur dioxide emissions in the late 19th to early 20th century, as well as emissions reductions since the 1970's[50, 55-56] (Fig. 6). The concurrent changes strongly suggest that TOC dynamics in these lakes were mainly driven by changes in deposition chemistry during the 20th century. These data support the assumption that the currently observed TOC increase in these former high deposition areas is largely a response to reduced acid deposition, promoting TOC export from catchment soils to the lakes[1]. All three of these study lakes record inferred TOC decreases in concert with the rise of total Pb concentrations (a robust proxy for increased deposition of atmospheric pollutants, including sulfur, following industrialization) in the sediments, which emphasizes their common response to acid deposition (Fig 6).

Current TOC concentrations remain beneath inferred pre-industrial levels in the two Canadian lakes, which suggests the potential for TOC to increase further by an order of ~2 mg L^{-1} in the latter phase of recovery from acidification. However, human activities (road and cottage development, forestry, mining) over the past 150 years have altered the lakes' catchment characteristics such as vegetation cover and composition, complicating the identification of appropriate TOC reference levels, such as seen in the long-term land-use driven changes in south-central Sweden[28]. In addition, other concurrent environmental changes in response to climate change or atmospheric N deposition may have further shifted the post-acidification TOC baseline[57]. For Round Loch of Glenhead, the identification of pre-industrial TOC levels is more difficult because of the landscape's long history of anthropogenic disturbance, including land clearance, burning, and grazing, over several millennia. Elevated TOC levels prior to the TOC decline coincide with a period of increased blanket peat erosion around the lake[45, 58], which would have increased the input of terrestrial-derived organic matter and thus elevated the lake's TOC load. Inferred TOC for this period may therefore overestimate pre-industrial reference conditions, suggesting that current TOC concentrations in Round Loch of Glenhead might have already returned to, or possibly exceeded, pre-industrial levels.

The strong agreement between monitored and sediment-inferred TOC/DOC trends, as well as the consistent response to a common environmental stressor (i.e., acid deposition) for lakes in different geographic regions, demonstrates that the Northern lake-water TOC model can accurately infer past lake-water TOC trends, even in regions outside of its geographic coverage. With its wide applicability across large environmental gradients, the universal Northern lake-water VNIR-TOC model is a powerful tool for the fast, cost-efficient reconstruction of long-term TOC dynamics in northern lakes across Europe and North America, and potentially also in other northern regions for which regional calibration sets do not yet exist. Application of the technique can provide new insights into long-term C cycling in inland waters, help to identify the confounding effects of concurrent changes in TOC when interpreting biotic changes in aquatic community structures, and to determine appropriate reference conditions for drinking water management. Knowledge about past TOC variations will help to refine process-based TOC/DOC models[34, 59-60], and thus better predict future changes in surface-water chemistry.

ASSOCIATED CONTENT

Supporting Information. Summary of mean lake-water chemistry for the regional calibration sets (Table S1), Measured and sediment-inferred TOC concentrations for lakes included in the Northern lake-water TOC model (Table S2), ^{210}Pb chronology for Round Loch of Glenhead (Figure S1) and difference between measured and sediment-inferred TOC versus measured TOC concentrations (Figure S2).

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