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Paleoecological evidence of major declines in total organic carbon concentrations since the 19th century in four nemoboreal lakes

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Abstract

A decade of widespread increases in surface water concentrations of total organic carbon (TOC) in some regions has raised questions about longer term patterns in this important constituent of water chemistry. This study uses near-infrared spectroscopy (NIRS) to infer lake water TOC far beyond the decade or two of observational data generally available. An expanded calibration dataset of 140 lakes across Sweden covering a TOC gradient from 0.7 to 24.7 mg l⁻¹ was used to establish a relationship between the NIRS signal from surface sediments (0–0.5 cm) and the TOC concentration of the water mass. Internal cross-validation of the model resulted in an R² of 0.72 with a root mean squared error of calibration (RMSECV) of 2.6 mg l⁻¹. The TOC concentrations reconstructed from surface sediments in four Swedish lakes were typically within the range of concentrations observed in the monitoring data during the period represented by each sediment layer. TOC reconstructions from the full sediment cores of four lakes indicated that TOC concentrations were approximately twice as high a century ago.

Introduction

In recent years, increasing concentrations of total organic carbon (TOC) have been observed in many rivers and lakes in Sweden (Erlandsson et al. 2008a), Norway (Skjelkvale et al. 2007; Hongve et al. 2004), Finland (Vuorenmaa et al. 2006) and the UK (Evans et al. 2005). Changes in TOC concentration can affect pH (Evans et al. 2007), water colour, and the penetration of both light and UV radiation (Schindler et al. 1997). Consequently changes in TOC affect the structure and functioning of lake ecosystems by altering the composition and productivity of biological communities. By influencing respiration of biological communities, changes in TOC can also affect the emission of carbon dioxide (CO₂) to the atmosphere (Kling et al. 1991; Cole et al. 1994). Sobek et al. (2003) demonstrated that the rate of CO₂ emissions is positively correlated to TOC concentrations in Swedish lakes. Increased TOC concentrations can therefore increase CO₂ emissions to the atmosphere and influence the carbon balance (Worral et al. 2007).

The cause(s) of the recent increases in TOC concentrations observed in lakes across Europe is still uncertain. A growing body of work links the recent increases in TOC to reductions in acid deposition (Monteith et al. 2007, Erlandsson et al. 2008a) however changes in precipitation and solar radiation (Hudson et al. 2003, Lepistö et al. 2008), temperature (Freeman et al. 2001), pH (De Wit et al. 2007) and CO₂ levels (Freeman et al. 2001) have also been suggested as potential drivers. This uncertainty restricts our ability to predict whether further increases in TOC concentration will occur, and the magnitude of any such increases. For example, if acidification recovery is the causal mechanism, then TOC concentrations are likely to stabilise in the foreseeable future (Erlandsson et al. 2008a). If however, climate change is the cause, then future increases are more likely.

One method of improving our understanding of this issue is to examine the past variability of TOC concentrations. Despite the recent attention given to TOC concentrations, little is known about the long-term variability within natural ecosystems. The longest records of TOC extend back only a few decades and there are only a few proxy records (such as color and chemical oxygen demand) which cover a longer time period. Thus it is difficult to resolve

the drivers of change, or even to know what the degree of variability in TOC was prior to this century's anthropogenic drivers.

Calibration models provide one means of assessing past concentrations of TOC in lake-water. Diatom-based calibration models for TOC generally show rather poor statistical performance (Rosén et al. 2000). Furthermore the performance of such models may be further reduced due to confounding by a stronger pH signal. Inference models derived from near infrared spectroscopy (NIRS) show better model performance (Nilsson et al. 1996; Rosén 2005; Rosén and Hammarlund 2007) and are not subject to confounding by pH. A 100 lake calibration dataset has previously been constructed for northern Sweden (Rosén 2005). This paper expands on this existing research by including an additional 40 lakes from southern Sweden and thus a broader range of the nemoboreal landscape. The aim of this research is to develop an inference model that can be applied across all of Sweden, enabling quantitative reconstructions of past concentrations of TOC in lake-water. The accuracy of these reconstructions is assessed via comparisons to measured data recorded by the Swedish environmental monitoring program over approximately 20 years (SLU Uppsala). The long-term reconstructions can then be used as a base-line against which recently observed increases in TOC can be compared. This was done for four of the 40 lakes from southern Sweden by examining the last two centuries of TOC as determined by the calibration model.

Methods

The calibration datasets

The existing model for inferring TOC concentrations in lake water from using NIRS analysis of lake sediments has an $R^2 = 0.61$, and an RMSEP of 1.6 mg L^{-1} . The 100 lakes incorporated into this dataset consisted predominantly of small (less than 20 ha) headwater lakes from areas with low human impact, spanning a climatic and altitudinal gradient in northern Sweden (Figure 1) with a median TOC of 4.1 mg/L (max 14.2) (Rosén 2005). Approximately half of these lakes were in alpine catchments above the tree-line, with the remainder situated in birch or pine forest dominated catchments. A brief summary of some physical and chemical

properties of lakes from this northern dataset is given in Table 1. Further details on the characteristics of these lakes and a description of the sampling techniques are given in Bigler and Hall (2002). Water samples for TOC analyses were collected from 1 m water depth using a Limnos-type water sampler on the same day as the sediment samples. These samples were analyzed by an accredited laboratory (Miljölaboratoriet, Umeå) within 2 days of collection.

In order to broaden the applicability of this initial calibration dataset, the current study incorporated an additional 40, small forest lakes from southern Sweden. The lakes are all part of the national lake monitoring program with samples taken seasonally (at least four times per year). Overt human impact on the catchments of these lakes is limited to conventional forestry and long-range atmospheric deposition, although limited agriculture and infrastructure is present within most catchments. These lakes typically had higher TOC concentrations than the initial training set with a median TOC of 11.4 mg/L (max 30.8) (Table 1). The lakes span a 1000 km N-S swath of nemoboreal forest where mean air temperatures vary from approximately +7 to -4 °C. Sediment cores from the 40 southern lakes were collected using a kayak corer during July and August 2006. Samples were collected from the deepest point of each lake. Sediments were extruded in the field, at either 0.5 cm or 1 cm resolution, and stored in the dark, at below 4 °C. NIRS analyses were performed on the surface samples (0-0.5 cm) of all 40 lakes. In addition, all of the retrieved sediment profile from four lakes (Brunnsjön, Fjärasjön, Hjärtsjön and Rotehogstjärnen) were analysed and used for the reconstruction component of this project. Within the southern lake calibration dataset, the TOC concentrations used were the mean concentration of TOC measured for that lake at 0.5 m water depth, between February and August 2006. These values were collected as part of the Swedish national environmental monitoring program. TOC concentrations were determined with a Shimadzu TOC-5000 total organic carbon analyzer. The measured TOC concentrations exhibit a high degree of variability, both intra- and inter-annually. A natural log ($x+1$) transformation was therefore applied to the TOC data to obtain a normal distribution.

The reconstruction lakes

The four lakes used to reconstruct past TOC concentrations were all relatively small lakes (Table 2) which are frozen for a short period in winter. These lakes are relatively low-lying and have maximum depths between 4.3 and 10.6 m (Table 2). These four lakes are currently

subject to relatively few human impacts, and their catchments are predominantly forested with little agricultural activity (Table 2). None of the lakes have been limed although these lakes typically are slightly acidic (Table 3). Nutrient concentrations in these lakes are typically low (Table 3) but vary on a seasonal basis.

Historical maps (Lantmäteriet) indicate that ditching has been carried out within each catchment, probably around the start of the 20th century. There also appears to have been some more recent ditching within the catchment of Brunnsjön, which occurred sometime between 1942 and today. With the exception of Hjärtsjön, agricultural activity within the catchments appears to have remained relatively constant from the early 1800's until the 1940's or 1950's but has since decreased, with less open fields apparent on the modern maps. Hjärtsjön appears to have had similar levels of agricultural activity, based on the extent of open fields, from 1775 until today. Additional roads have been built near both Brunnsjön and Hjärtsjön within the last 60 years.

NIRS analyses

The frozen sediment samples were freeze-dried and ground to a fine powder, to reduce grain-size effects. Samples were placed in the same room as the analytical equipment the night prior to analysis, to avoid any temperature effects. NIR spectra were recorded using a NIRSystems 6500 instrument (FOSS NIRSystems Inc., USA). The instrument measures diffuse reflectance (R), which is then transformed to apparent absorbance values (A) using the equation $A = \log(1/R)$. Data were collected at 2-nm intervals between 400 and 2500 nm yielding 1050 data points per sample. Spectral variation arising from varying effective path lengths and particle size was removed using multiplicative signal correction (MSC) prior to development of the calibration dataset (Geladi et al. 1985). This removes noise and maximizes the remaining signal, which results from compositional differences of the samples.

Principal component analyses and regression analyses (partial least squares) were used to develop inference models based on the 140 lake calibration dataset, using the statistical package SIMCA (Umetrics, Sweden). Internal cross validation (based on a leave 10% out

protocol) was performed during model development to assess performance of the models. The calibration model was then applied to sediment cores from four lakes, thus allowing past TOC concentrations of lake water to be inferred.

SCP dating

Concentrations of spheroidal carbonaceous fly ash particles (SCP) were used to infer approximate dates of recent sediment samples following standard procedures (Wik and Renberg 1996). This dating method uses two markers to infer the age of recent sediments. The first marker is a rapid increase in SCP concentrations, which corresponds to the increase in fossil fuel combustion following the Second World War (c. 1950 A.D.). The second marker is the maximum SCP concentration, which corresponds to the peak in oil consumption in the early 1970s. SCPs were typically counted at 1 cm intervals over the top 10 cm of the four sediment cores used for the reconstructions. If no SCPs were recorded in two consecutive samples, then counting was stopped.

Results

SCP dating

Total concentrations of SCPs were several times higher in Fjäräsjön and Rotehogstjärnen than in Brunnsjön and Hjärtsjön. Variations in SCP concentrations were also more pronounced in the first two lakes (Figure 2). Hjärtsjön, Fjäräsjön and Rotehogstjärnen all had relatively straightforward SCP profiles. The 1970's peak was visible in the different cores at depths between 2.5 and 4 cm. The depth at which the 1950's increase occurred also differed between cores, varying between 5 and 7 cm in depth. From these data, we can infer sediment accumulation rates between 0.07 and 0.11 cm per year in the top sediments. The surface samples (0 – 0.5 cm) for Fjäräsjön and Rotehogstjärnen therefore represent approximately 4.5 years of sediment accumulation whilst Hjärtsjön represents approximately 6 years of sediment

accumulation. The SCP results indicate higher sedimentation rates between 1950 and the 1970's, varying between 0.10 and 0.15 cm per year. Based on these results, each of these three sediment cores probably represents 200 years or more.

The SCP profile of Brunnsjön is quite irregular within the top section and suggests that there has been disturbance within the sediments since the 1950's. Given the steepness of the SCP curve below 10 cm, these sediments are not believed to be disturbed. Within this core, the change in SCP accumulation at approximately 13 cm is interpreted as representing the 1950's increase. It is likely that the peak at 10 cm represents the 1970's peak although, given the disturbance of sediments, this is not certain. Previous work on an earlier core from this lake, also suggested a maximum concentrations of SCPs occurred at 10 cm (Ek & Korsman 2001). As a result of the disturbed sediments seen in the core used within the current study, interpretation of the upper section must be considered tentative at best. The results suggest a high sedimentation rate of 0.27 cm/year since the 1970's with a lower rate (0.15 cm/year) before this. Extrapolation of the second sedimentation rate suggests that the core covers the last 150 years.

Model performance

An initial PCA analysis of the spectral data did not reveal any outliers, therefore all samples were retained. A transfer function based on all wavelengths showed good results ($R^2 = 0.72$, RMSEP= 2.6 (8.7% of the gradient)). Despite the good performance overall, high TOC concentrations were less accurately inferred (Figure 3). This possibly reflects the reduced number of samples (20) within the calibration dataset that had TOC values above 10 mg L⁻¹. The surface samples from the four lakes selected for reconstructions (Hjärtsjön, Fjärasjön, Rotehogstjärnen and Brunnsjön) were compared to recent monitoring data to ascertain the accuracy of the inference model (Figure 4). Predicted TOC concentrations for Fjärasjön and Rotehogstjärnen are in good agreement with the monitoring data. Predicted values for the surface sample are almost identical to the average value of the measured data for the time period represented by the surface sediments. The three other sediment samples that span the observational record from both these lakes are also similar to the monitored values. The

predicted TOC concentrations for Brunnsjön and Hjärtsjön were both lower than the average values observed for the time period of each sample (Figure 4), although the values from Hjärtsjön remain within the model error. A number of the measured values from Brunnsjön exceed the range incorporated into the calibration dataset, which may partly explain why the model underestimates values within this lake. The observed bias against higher values may also contribute to underestimation of values from Brunnsjön. Furthermore, the uncertainty of the dating may also contribute to the observed discrepancy between measured and inferred values. Overall, it was decided that, given the time-span that each sediment sample represented, the inferred values, and thus the inference model itself, were sufficiently accurate to undertake long-term reconstructions.

Long-term trends in TOC

Reconstructions of TOC concentrations in lake water from the four lakes all show relatively similar trends (Figure 5). TOC was much higher in the deepest samples, typically about double the current concentrations. Large decreases were then observed, however the timing and nature of this decrease varied between lakes. A relatively constant decrease in TOC concentrations is observed throughout the core from Hjärtsjön. Fjäråsjön initially decreased very gradually, until an abrupt drop in concentrations occurred towards the end of the 19th century. After this abrupt drop, concentrations continued to decrease on a more gradual basis until the present day. Both Rotehogstjärnen and Brunnsjön showed a pronounced decrease in concentrations, which peaked at around 1930 after which concentrations have remained relatively constant, or increased slightly.

Discussion

Our results clearly demonstrate the applicability of NIRS for reconstructing past TOC concentrations in lake water. The initial model of 100 lakes from northern Sweden had a $R^2 = 0.61$. Incorporating 40 additional lakes from southern Sweden not only expanded the range of TOC concentrations within the model, but also improved model performance by reducing the

error from 11.3% of the gradient to 8.6%. The accuracy of the model decreased at higher concentrations. This is possibly due to the fact that only twenty samples had TOC concentrations greater than 10 mg L⁻¹. When a similar number of samples with low TOC concentrations were randomly selected from the calibration dataset, the correlation between observed and predicted values was also reduced. It is likely that further increasing the number of samples with high TOC used within the calibration dataset could further improve model performance.

The reconstructed values showed a good agreement with the corresponding values in the contemporary surface water monitoring record, particularly for Fjäräsjön and Rotehogstjärnen. Values for Hjärtsjön were slightly less accurate, but were still within the model error. The ability of the model to infer measured TOC values in three different lakes, once averaged across the appropriate time period, indicates that the model is adequately inferring TOC concentrations. TOC concentrations were not accurately inferred in Brunnsjön, however, and may reflect disturbance within the catchment or the lake sediments. Despite this, the SCP profiles suggest that there has been minimal disturbance prior to 1970's, and certainly prior to the 1950's, thus the reconstructed TOC values should be valid prior to this point. Further support for reconstructed TOC values is derived from diatom studies which show a similar pattern in the relative abundances of the two dominant diatom species, namely that they gradually decreased from the late 1800's until ~1950, after which their relative abundances have remained relatively constant (Ek & Korsman 2001).

The most striking feature of the reconstructions is how much higher the TOC concentrations were 100-200 years ago, compared to recent times. In each of the four lakes, current TOC concentrations are approximately 50% lower than concentrations from approximately 100 - 200 years ago. The early values of TOC concentrations observed in several lakes are close to the limits of the model, and in the case of Brunnsjön, exceed the model range. Given this, and the fact that model performance was reduced at high concentrations, these high values should be regarded as indicative only. It is also possible that the model is influenced by the type of TOC present within the sediments. Although NIRS predominantly reflects the molecular vibrations of compounds within the sediment, it is possible that coloured TOC may potentially have a different spectral signature than non-coloured TOC due to different molecular structures. Thus the NIRS could potentially reflect

the colour, rather than the amount of TOC present within the sediments. This could potentially influence model performance, particularly within the sites with more agriculture or urban areas where non-coloured organic matter and/or particulate organic carbon is likely to comprise a larger proportion of the TOC. A significant correlation exists between TOC and water colour (measured as filtered absorbance at 420 nm) in rivers from southern Sweden (Erlandsson et al. 2008b). A similarly strong relationship was observed between these variables, when the 40 lakes from southern Sweden were considered overall ($R^2 = 0.68$). When the relationships were examined over time, within individual lakes, the correlations were reduced, with the R^2 values for these variables within the four reconstruction lakes varying between 0.17 and 0.53 (unpublished data, SEPA). This implies that changes in the colour of the TOC have occurred during the last twenty years. The relatively low correlations between TOC and colour, combined with the good relationships observed between observed and inferred TOC suggest that NIRS model probably reflects TOC quantity and not colour.

Given the magnitude of the decreases in TOC reported here, a brief discussion on the issue of sediment “aging” of TOC seems warranted. Rosén et al. (2000) demonstrated that there was no detectable alteration of the sedimentary NIRS spectra between 0-1 cm and 1-2 cm samples, from 56 lakes in northern Sweden. Furthermore, previous NIRS based reconstructions of TOC concentrations in northern Sweden have shown varying trends in TOC concentrations among different lake types (Rosén 2005; Rosén and Hammarlund 2007). If the decrease observed within the current study were an artefact of sediment “aging”, then one would logically expect all sediment cores to show a similar trend. Instead, these previous studies clearly demonstrate that TOC concentrations are related to past environmental conditions around individual lakes. In particular, reconstructions from alpine lakes showed relatively constant TOC concentrations over several millennia (Rosén 2005), thus providing supporting evidence that sediment aging does not affect the NIRS signal with regard to TOC models. Similarly, if aging were an issue, the effects of this would also be most pronounced within the top five cm, which is not observed in the current study. It can therefore be concluded that the decrease in TOC over the past hundred years or so, observed within this study, is real, and not an artefact of sediment “aging”.

As stated above, our results clearly show that large decreases in TOC have occurred over the past century. Although it is possible that the major anthropogenic drivers currently

being discussed with regards to recent TOC increases, namely acidification and climate change, caused the observed decreases, this seems unlikely given the time-frame of these changes. Diatom reconstructions in this region indicate that modern acidification due to atmospheric deposition began in the post-second world war period even though pH has changed substantially over a thousand years earlier, probably due to human induced catchment changes (Renberg et al. 1993). Long-term decreases in the pH of many lakes have previously been demonstrated for southern Sweden, both in relation to historical activities over several centuries (Ek and Renberg 2001) and acid deposition over the last century (Bindler et al. 2002; Bindler et al. 2008). Sulphur deposition, a precursor to acidification that has been linked to TOC changes, as well as many other pollutants, had begun to reach Sweden over a century ago, with lead arriving in Roman times. Olsson et al. (1997) demonstrated that the rate of sulfur accumulation in sediments of a Swedish lake increased dramatically around 1800 and remained high until the late 20th century. Such changes in sulfur deposition and accumulation may have affected TOC concentrations. Thus it is possible that the long-term decrease in TOC which we observed may be caused by sulfur deposition over the past two centuries. However, the magnitude of early sulphate deposition is small compared to that of the last century. If sulphate deposition was the cause of the observed TOC decrease, a second, larger decrease in TOC would have been expected to occur around the 1970's. Given that this is not observed in any of the cores, it seems likely that another factor was responsible for the large decrease in TOC observed during the 19th century.

Climatic variables such as temperature, radiation and precipitation can also influence TOC concentrations in lakes (Hudson et al. 2003; Hongve et al. 2004). It is therefore possible that the observed long-term decrease in TOC might also be related to climatic parameters. Long-term temperature data shows a gradual increase of 1.4 °C in spring temperatures in Stockholm and Uppsala between the period of 1861-1990 and the most recent period (1966-1995) (Moberg and Bergstrom, 1997). It is possible that spring temperatures may have affected snow melt, run-off and thus influenced TOC concentrations within these lakes, however, changes in spring temperature have been most pronounced in the last 3 decades which is not reflected in the TOC profiles. Small increases in summer and annual mean temperature were also observed during this time, but of a much smaller magnitude. Improved sediment dating and higher resolution studies would be required for further investigations of potential relationships between long-term trends in TOC and climatic data.

Although much of the literature has focused on relationships between TOC concentrations, acid deposition and climate in the 20th century, this study clearly demonstrates that the changes in TOC pre-date this. Accordingly, other factors operating further back in time also need to be considered. Land use change provides a plausible explanation for the major changes in TOC which occurred approximately a century ago. Factors which could have contributed to this include drainage, lowering of lake levels, the harvesting of peat for fuel and clear-felling of forests. Given that Sweden's extensive drainage started before the 1920's, ditching operations may well explain some of the observed TOC decrease. Historical maps indicate ditching has been carried out between the late 19th and mid 20th centuries, within each catchment area. Historical records also support this, with two proposals for ditching around Brunnsjön submitted in 1900 and 1912. Based on the maps, additional ditching has been carried out in the vicinity of Brunnsjön since the 1940's. Ditching operations can reduce TOC input into drains (Åström et al. 2001), and subsequently, the lakes into which the drains flow. This may explain some of the observed decreases in TOC. For example, the step-like decrease in Fjärasjön in the late 1800's could result from ditching, however, the only time line we currently have for the ditching operations within this catchment is that they occurred sometime between 1872 and 1954. Thus, potential relationships between ditching and TOC concentrations remain purely speculative, unless more exact dates of such events can be obtained.

Certainly there have been great pressures put on Sweden's landscapes which may have affected TOC concentrations. Further investigations of how different factors have influenced TOC concentrations in the past may be necessary if we are to understand more recently observed increases. Whatever the underlying cause of the TOC decreases, our results indicate that the variability of TOC is much greater than had previously been thought. These results also call into question the validity of using late 20th century conditions as reference values.

Conclusions

Our results showed a strong relationship between NIRS spectra and TOC concentrations in lake water, using a 140 lake calibration dataset from across Sweden. Predicted results

compared well with monitoring data. Reconstructions of past TOC concentrations clearly demonstrate that large decreases in TOC concentrations having occurred over the past two centuries. Much of these decreases occurred before the 1920's which is when S deposition began to increase most strongly. It is therefore speculated that decreasing TOC levels may be related to land use changes, however, further work would be required to verify this.

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Figure 1 Map showing location of lakes from the initial dataset from northern Sweden (▲) and the additional 40 lakes (●) included as part of this project. The four lakes used for TOC reconstructions are labeled (●).

Figure 2 Concentrations of spheroidal carbonaceous fly ash particles (SCPs) used to assign approximate ages to the sediment samples. The 1970's peak is indicated by a dashed line, whilst the 1950's increase is indicated by a dotted line. Note that different scales are used.

Figure 3 Comparison of measured and NIRS inferred TOC concentrations in lake water.

Figure 4 Comparison of inferred TOC values (—) with the median value of available monitoring results for the equivalent time period is shown as (—). Monitoring results from 0.5 m depth (□) are combined with data from 2 m water depth (△), to extend the time period covered. The sediment samples used to infer the TOC concentrations represent between 1.8 and 6 years of sediment accumulation (see text for details), as indicated by the continuous black line. The average measured TOC concentrations over the same time period are shown by the dashed line. Note that different scales are used on the Y axis.

Figure 5 NIRS inferred reconstructions of TOC concentrations in lake water for four lakes in southern Sweden. Approximate dates based on SCP results are shown by the vertical lines, with 1970 indicated by a light grey line and 1950 indicated by a black line, The dashed line indicates 1900, as extrapolated from the sedimentation rates determined from SCP results. Note that different scales are used on the Y axis.

Tables

Table 1 Summary of selected chemical and physical properties of the (a) initial 100 lake calibration dataset and (b) the additional 40 lakes included within this study. Values for (a) are based on single measurements taken at the time of sediment collection; values for (b) are based on regular monitoring results collected between February and August 2006.

a	Max	Min	Mean	Median	SD
maximum lake depth (m)	17	2	6	5	3
pH	8.1	5.8	6.7	6.2	0.4
conductivity ($\mu\text{S/m}$)	12.8	0.6	2.1	1.6	1.7
Ca (meq/L)	1.03	0.01	0.10	0.07	0.12
Mg (meq/L)	0.18	0.01	0.04	0.03	0.04
Na (meq/L)	0.11	0.01	0.04	0.03	0.02
SO ₄ (meq/L)	0.36	0.01	0.04	0.03	0.05
Cl (meq/L)	0.10	0.01	0.03	0.02	0.02
Si (mg/L)	3.06	0.01	0.79	0.72	0.68
TOC (mg/L)	14.9	0.7	4.1	3.3	2.7

b	Max	Min	Mean	Median	SD
maximum lake depth (m)	25.3	1.6	10.6	9.8	6.5
pH	8.1	4.5	6.2	6.3	0.8
conductivity ($\mu\text{S/m}$)	66.6	0.6	6.1	4.7	8.29
Ca (meq/L)	3.82	0.02	0.25	0.13	0.48
Mg (meq/L)	1.28	0.01	0.12	0.07	0.16
Na (meq/L)	1.65	0.01	0.20	0.17	0.21
SO ₄ (meq/L)	2.75	0.01	0.15	0.09	0.34
Cl (meq/L)	1.47	0.01	0.16	0.13	0.20
Si (mg/L)	5.11	0.09	1.76	1.70	1.20
TOC (mg/L)	30.6	0.8	11.3	10.3	5.6

Table 2 Geographical characteristics of the four lakes used for TOC reconstructions

	Brunnsjön	Fjärasjön	Hjärtsjön	Rotehogstjärnen
Lake depth (m)	10.6	4.3	6.4	9.4
Altitude (m asl)	98	237	276	121
Lake area (km ²)	0.1	0.3	1.3	0.2
Catchment (km ²)	3.4	2.6	6.6	3.8
% Forest	96.7	86.7	72.1	93.2
% Open Vegetation	0.0	0.0	0.7	2.1
% Water	3.1	12.6	19.5	4.4
% Mire	0.0	0.0	1.4	0.0
% Agriculture	0.1	0.6	3.6	0.5
Precipitation (mm/yr)	750	650	750	950

Table 3 Summary of selected chemical and physical properties for each of the four lakes used for TOC reconstructions within this study. Values shown are based on monitoring data collected on 4-8 occasions between February and October 2006.

Brunnsjön					
	Max	Min	Mean	Median	SD
Water Temp (°C)	22.5	0.5	13.3	15.7	8.5
pH	5.8	4.9	5.5	5.6	0.3
Conductivity (µS/m)	6.0	5.2	5.6	5.5	0.3
TN (µg/L)	736	464	584	581	83
TP (µg/L)	14.0	8.0	11.0	11.0	2.2
Si (mg/L)	5.1	2.6	3.6	3.5	0.9
TOC (mg/L)	23.4	18.4	20.6	20.7	1.6
Fjäråsjön					
	Max	Min	Mean	Median	SD
Water Temp (°C)	19.9	0.8	10.0	9.7	8.0
pH	7.0	6.4	6.7	6.7	0.3
Conductivity (µS/m)	6.2	5.6	5.9	5.9	0.3
TN (µg/L)	509	318	399	385	88
TP (µg/L)	10.0	7.0	8.8	9.0	1.3
Si (mg/L)	2.6	0.8	1.4	1.1	0.8
TOC (mg/L)	10.1	9.1	9.5	9.3	0.5
Hjärtsjön					
	Max	Min	Mean	Median	SD
Water Temp (°C)	19.8	0.7	11.2	12.1	7.9
pH	5.6	5.3	5.4	5.4	0.1
Conductivity (µS/m)	3.9	3.5	3.7	3.6	0.2
TN (µg/L)	443	263	335	316	86
TP (µg/L)	5.0	4.0	4.8	5.0	0.5
Si (mg/L)	0.9	0.2	0.7	0.8	0.3
TOC (mg/L)	5.5	4.0	4.6	4.4	0.7
Rotehogstjärnen					
	Max	Min	Mean	Median	SD
Water Temp (°C)	21.3	0.3	12.8	14.5	8.2
pH	6.1	4.6	5.4	5.4	0.4
Conductivity (µS/m)	5.2	3.5	4.1	4.0	0.5
TN (µg/L)	504	218	381	411	89
TP (µg/L)	16.0	9.0	12.1	11.5	2.4
Si (mg/L)	2.8	0.4	1.3	1.2	0.8
TOC (mg/L)	17.0	10.3	13.1	12.2	2.2

Brunnsjön

Fjäråsjön

Hjärtsjön

Rotehogstjärnen