Uncoupled organic matter burial and quality in boreal lake sediments over the Holocene

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Abstract Boreal lake sediments are important sites of organic carbon (OC) storage, which have accumulated substantial amounts of OC over the Holocene epoch; the temporal evolution and the strength of this Holocene carbon (C) sink is, however, not well constrained. In this study we investigated the temporal record of carbon mass accumulation rates (CMARs) and assessed qualitative changes of terrestrially derived OC in the sediment profiles of seven Swedish boreal lakes, in order to evaluate the variability of boreal lake sediments as a C sink over time. CMARs were resolved on a short-term (centennial) and long-term (i.e., over millennia of the Holocene) timescale, using radioactive lead (210Pb) and carbon (14C) isotope dating. Sources and degradation state of terrestrially derived OC were identified and characterized by molecular analyses of lignin phenols. We found that CMARs varied substantially on both short-term and long-term scales and that the variability was mostly attributed to sedimentation rates and uncoupled from the OC content in the sediment profiles. The lignin phenol analyses revealed that woody material from gymnosperms was a dominant and constant OC source to the sediments over the Holocene. Furthermore, lignin-based degradation indices, such as acid-to-aldehyde ratios, indicated that postdepositional degradation in the sediments was very limited on longer timescales, implying that terrestrial OC is stabilized in the sediments on a permanent basis.

1. Introduction

Inland waters are important components of the global carbon (C) cycle, and their interplay with climate has become a highly debated topic during the past two decades [Cole et al., 2007; Tranvik et al., 2009; Aufdenkamper et al., 2011]. The world’s freshwater systems, including lakes, reservoirs, rivers, and streams, act as a significant source of carbon dioxide (CO2) and methane (CH4) to the atmosphere and were recently estimated to outgas 2.1 Pg C yr⁻¹ in the form of CO2 [Raymond et al., 2013] and 103 Tg C yr⁻¹ in the form of CH4 [Bastviken et al., 2011]. The sediments of lakes and reservoirs, however, act simultaneously as an efficient long-term C sink, due to the accumulation and burial of incompletely degraded organic carbon (OC). The turnover time of OC stored in lake sediments has been estimated to be on the order of millennia [Cole et al., 2007], and permanent burial rates between 22 and 56 Tg C yr⁻¹ have been suggested on a global scale [Einsle et al., 2001; Kastowski et al., 2011].

Several regional scale studies of OC burial in lake sediments have been conducted in the recent past, in order to better quantify this C sink over the Holocene epoch [Kortelainen et al., 2004; Kastowski et al., 2011; Ferland et al., 2012]. These studies calculated OC burial as average values over long time periods, e.g., as a Holocene average or as averages over the past few centuries. However, sedimentation rates and OC burial likely varied over time as lake ecosystems are sensitive to environmental change [Ouellet et al., 2012]. A substantial increase in lake OC burial has, for instance, been observed in Minnesota lakes over the past 150 years as a result of land use change [Anderson et al., 2013]. Hence, the interplay of naturally occurring environmental change, i.e., climatic shifts over the Holocene [Seppä et al., 2005], together with intensified land use change over the more recent past, could have altered lake sedimentation and affected OC burial. Deviations of recent OC burial from long-term average OC burial may cause a substantial temporal mismatch when comparing OC burial to C fluxes which operate at a shorter temporal scale, such as greenhouse gas emission to the atmosphere [Kortelainen et al., 2013]. At present, however, systematic comparisons of the temporal variability of OC burial over both longer (e.g., Holocene) and shorter timescales (e.g., past century) are lacking.
When considering OC burial in lake sediments as a C sink, the source and stability of the accumulating organic matter must be regarded. The OC source is important to resolve since the burial of OC derived from decaying terrestrial plants represents a lateral displacement of soil OC, which is part of the terrestrial C balance, while the burial of OC derived from internal lake primary production by, e.g., phytoplankton represents a new C sink. In addition, the stability of the accumulating OC is important to understand in order to gauge the degree to which accumulating OC actually is buried, i.e., removed from the short-term C cycle. While there are indications that degradation rates of old sediment OC are very low [Middelburg et al., 1993], particularly if the OC is land derived [Sobek et al., 2009], assessments of the stability of lake sediment OC over long periods are rare [Hu et al., 1999].

This study focuses on the temporal variability of OC accumulation in boreal lake sediments on short-term (centennial) and long-term (millennial) scales and evaluates the efficiency of lake sediments as a long-term C sink by assessing OC quality (i.e., sources and degradation state). Based on the evidence outlined above, the two main hypotheses of this study are that (1) OC accumulation in boreal lake sediments is not constant over time but affected by land use and climate change and (2) OC quantity and quality vary little over time because the postdepositional degradation of terrestrial organic matter is limited.

2. Methods

2.1. Site Description

We studied the profiles of sediment cores from seven lakes in the Bergslagen region (approximately 59–61°N and 13–15°E) in south central Sweden, where deglaciation occurred approximately 9800 to 9600 years ago [Lundqvist, 1986]. The contemporary climate of the region is subarctic with an average annual air temperature of 5°C, and an average annual precipitation of 900 mm (average from 1961 to 1990, Swedish Meteorological and Hydrological Institute). The bedrock in this area consists of Paleoproterozoic gneiss that is locally covered by lime poor and less than 5 m thick soils (Bergsgrundskarta, 1:250,000, Sveriges geologiska undersökning; Geological Survey of Sweden). The landscape is characterized by boreal coniferous forest and has a high density of small to medium sized, oligotrophic lakes. The Bergslagen region evolved historically as a mining district, where the exploration for iron and other metal sulfides intensified between the seventeenth and nineteenth centuries [Eriksson, 1960; Ågren, 1998] but descended rapidly in the late nineteenth and early twentieth centuries [Alvstam and Korhonen, 1995].

The study lakes (Table 1) are located within an area of 180 km² around the village Kloten, at altitudes between 135 and 284 m above sea level. They cover surface areas between 0.007 and 1.72 km², and have maximum water column depths between 6 and 32 m. The catchment areas range between 1 and 17 km², whereby the smaller lakes have higher catchment-to-lake area ratios than the larger lakes. The lake water is characterized by low pH values and high concentrations of dissolved organic carbon (DOC; Table 1). Several historic mines are located in the watersheds of the two largest study lakes; two in close vicinity (<0.5 km) to Lake Övre Skärsjön and one mine in about 1 km distance to Lake Dagarn. There are no mines located within the watersheds of any of the other lakes (National Atlas of Sweden; Sveriges Nationalatlas).

2.2. Sediment Sampling

We sampled sediment cores for the determination of short-term carbon mass accumulation rates (CMARs), i.e., accumulation rates over the past 100 years, and cores for the determination of long-term accumulation
rates, i.e., accumulation rates on millennial timescales. Sampling was carried out in 2007, 2010, and 2011, using a gravity corer for short sediment cores (30–50 cm of sediment), and a Livingstone corer for long cores (1 m sections of sediment) [Livingstone, 1955]. One undisturbed short core per lake was taken from the deepest point in the lakes and immediately sliced after sampling into 0.5 cm sections within the top 10 cm and into 1 cm sections between 10 and 20 cm depth. The long cores were taken in overlapping 1 m sections from deep areas of the lakes, where the sediment thickness was highest. These sampling locations were chosen according to lake maps showing sediment thickness across the basin, which were created by acoustic sub-bottom profiling (M.-È. Ferland et al., Cross-regional patterns in carbon accumulation in boreal and temperate lakes, unpublished manuscript, 2013). In total, one vertical sediment profile covering the entire organic-rich sediment bed (between 1.5 and 3 m), including the interface between organic-rich sediment and postglacial clay deposits, was obtained from each lake. One exception was the sediment core from Lake Gäddtjärn, where the transition to clay could not be sampled due to practical problems during the sampling procedure. All samples were stored dark at 4°C until further analysis.

2.3. Sediment Analyses and Calculations of CMARs

The sediment samples were analyzed for short-term and long-term CMARs calculated according to the equation:

$$\text{CMAR} = \rho_{\text{dry}} \times \text{CC} \times \text{SR}$$

where $\rho_{\text{dry}}$ is the dry bulk density (in g cm$^{-3}$) of the sliced sediment samples, CC is the C content (in %), and SR are the sedimentation rates (in cm yr$^{-1}$), calculated from lead ($^{210}$Pb) dating of short core samples and radiocarbon ($^{14}$C) dating of long core samples, respectively.

The dry bulk density of short cores was calculated from the dry weight of sediment samples sliced at defined depth intervals (see above). Long cores were first scanned at every 2.5 cm depth for wet density by measurements of gamma ray attenuation using a Multi Sensor Core Logger (GEOTEK) at the Department of Geological Sciences at Stockholm University (for further method description see Weber et al. [1997]). After scanning, the cores were split lengthways and sliced according to their lamination or into 5 cm intervals if no lamination was visible. All samples were freeze dried, and the dry bulk density was calculated from the wet density and the dry mass of the samples. C and nitrogen (N) contents were measured on dry samples after homogenization with a mortar, on an element analyzer system (ECS 4010 Elemental Combustion System, CHNS-O). Absence of inorganic C was confirmed by acidifying samples with 10% hydrochloric acid (HCl).

Short-term sedimentation rates were determined from $^{210}$Pb dating of the sliced short cores (M.-È. Ferland et al., unpublished manuscript, 2013). The activity of $^{210}$Pb was measured by gamma spectrometry on dry bulk sediment samples, and sedimentation rates were determined by using the Constant Rate of Supply model, which assumes a constant supply of unsupported $^{210}$Pb to the sediment [Appleby and Oldfield, 1978].

Long-term sedimentation rates were derived from $^{14}$C dating of organic macrofossils, such as gymnosperm needles (Picea abies and Pinus sylvestris), birch leaves (Betula) and wood fragments, and in the absence of macrofossils of bulk sediment samples. Between four and eight samples were chosen throughout each long core profile, starting at a few centimeters above the transition of organic-rich sediment to glacial clay. The samples were chemically processed and analyzed for $^{14}$C at the Ångström Laboratory, Uppsala University. Sample pretreatment followed the acid-alkali-acid method and iron-catalytic graphitization [Vogel et al., 1984]. Briefly, all samples were treated with 1% HCl, heated to 80°C, and kept for 10 h to remove potential carbonates. NaOH (0.5%) was subsequently added and the mixtures heated to 80°C again for 1 h. The alkaline-soluble parts were precipitated by the addition of concentrated HCl. The washed and dried precipitates were combusted to CO$_2$ and converted to graphite, using a Fe catalyst. The $^{14}$C ages of the catalyst fraction were determined by accelerated mass spectrometry [Possnert, 1990] and calibrated with the program OxCal v3.10, using the IntCal09 calibration curve [Reimer et al., 2009].

2.4. Molecular Lignin Analyses

The molecular composition of lignin, which in general constitutes 25–30% to the vascular plant biomass [Hedges et al., 1997; Bianchi and Canuel, 2011], was analyzed in dry sediment samples of the long cores, in order to characterize sources and degradation state of terrestrially derived OC over the Holocene. Eleven phenolic monomers, belonging to the four groups of vanillyl phenols (V), syringyl phenols (S), cinnamyl phenols (C), and $p$-hydroxyl phenols (P), were extracted from sediment samples by the cupric oxide (CuO) oxidation
method, developed by Hedges and Ertel [1982]. Ten to twelve sediment samples were chosen throughout each long core profile and analyzed for their phenolic composition at the laboratory of the Research Group for Marine Geochemistry at the University of Oldenburg (Germany). Briefly, aliquots of dry sediment corresponding to 250 mg of OC were treated with sodium hydroxide (NaOH) solution (4 mol L\(^{-1}\)) and ferrous ammonium sulfate hexahydrate (Fe(NH\(_4\))\(_2\)(SO\(_4\))\(_2\) · 6H\(_2\)O) solution (6 g L\(^{-1}\)) in an argon atmosphere. The samples were subsequently heated to 155°C for 3 h and cooled for 90 min in Teflon vials. After cooling, samples were adjusted to pH 2 by additions of HCl and phosphoric acid (H\(_3\)PO\(_4\)). The samples were analyzed on an ultra performance liquid chromatography system (Waters Acquity UPLC), using a modified method after Lobbes et al. [1999], where the 11 phenols were identified by their retention times and absorbance spectra. For calibration, standard solutions containing all 11 phenols were used in different dilutions. A set of parameters used in recent literature [Dittmar and Lara, 2001; Tareq et al., 2004; Bianchi and Canuel, 2011] were calculated to assess the sources and the extent of diagenetic alteration of sedimentary organic matter (Table 2). \(X_{\text{lignin}}\) and \(\Lambda_8\) were used as quantitative indicators of OC present in the form of lignin. To further distinguish between lignin-containing and lignin-free plants, the ratio of \(p\)-hydroxyacetophenone to-total \(p\)-hydroxyl phenols (PON/P) was calculated. PON is primarily derived from lignin, whereas lignin-free materials primarily release \(p\)-hydroxybenzaldehyde and \(p\)-hydroxybenzoic acid [Benner et al., 1990]. S/V ratios were determined to differentiate between the inputs of angiosperm and gymnosperm plants, since solely angiosperm lignins contain the syringyl phenol group. CV ratios were used to distinguish between woody and nonwoody plant tissues, as cinnamyl phenols are not abundant in woody plant material. In addition, the Lignin Phenol Vegetation Index (LPVI) was calculated according to Tareq et al. [2004] (Table 2). The LPVI is a more sensitive approach for the identification of different plant sources, because it accounts for the fact that cinnamyl phenols are more prone to degradation compared to vanillyl and syringyl phenols. LPVI values between 1 and 27 generally reflect gymnosperm plant material, whereby woody material generates the value 1 and nonwoody tissues LPVI values between 12 and 27 [Tareq et al., 2004]. During degradation of lignins, acids are transferred to aldehydes as a consequence of propyl side chain oxidation. The degradation state of OC was therefore characterized through the determination of acid-to-aldehyde ratios (Ad/Al) within the vanillyl phenol group, the syringyl phenol group, and the \(p\)-hydroxyl phenol group [Ertel and Hedges, 1984]. In addition, the ratio of nonmethoxylated phenols to methoxylated phenols \(P/(V + S)\) was calculated to assess the diagenetic alteration stage [Dittmar and Lara, 2001], as the \(p\)-hydroxyl phenols are more resistant to degradation than the other phenols.

### 3. Results

#### 3.1. OC Content and Molar C:N Ratios

The vertical sediment profiles of OC content and molar C:N ratio are shown in Figure 1. The OC content in the sediment cores varied between 1 and 35% of the dry weight. The two smallest lakes, Svarttjärn and Gäddtjärn, had on average the highest OC contents of 28.3 ± 6.8% (mean ± standard deviation) and 25.4 ± 2.3%, respectively, whereas the lowest OC contents were found in the sediments of the two largest lakes.
Óvre Skärsjön and Dagarn (15.0 ± 2.8% and 10.1 ± 3.9%, respectively). The OC content varied to different degrees within the top 20 cm; however, no common trend was apparent. Between 20 cm from the top and 10 cm above the clay, i.e., over most of the sediment profiles the OC content varied very little with depth, except for lakes Grästjärn and Dagarn, which displayed a decrease in OC content over depth. At the transition from lacustrine organic-rich sediment to glacial clay deposits, the OC content decreased rapidly to relatively low values (<10%) in most cores, except for lakes Gäddtjärn and Oppsveten where the OC content decreased less pronouncedly. For Lake Gäddtjärn this can be attributed to the fact that the transition from OC-rich layers to clay deposits was not sampled, due to problems during the sampling procedure.

Molar C:N ratios ranged in total between 8.4 and 26.4 and were on average highest in the sediments of the two smallest lakes Svarttjärn and Gäddtjärn (19.3 ± 2.2 and 19.4 ± 1.7 respectively) and lowest in the largest lakes Óvre Skärsjön and Dagarn (16.0 ± 1.6 and 15.3 ± 1.4). In all the cores the vertical sediment profiles exhibited a low variability of C:N ratio over depth but decreased in general at the transition to clay deposits (Figure 1).

3.2. Radiocarbon and Lead Age Chronologies

The results of the radiocarbon analyses are presented as calibrated 14C ages (in years B.P.) with 2σ uncertainty ranges. Further details on calibrated and uncalibrated 14C results can be obtained from the supporting information (Table S1). Basal 14C ages, derived from organic macrofossils and bulk sediment at about 10 cm above clay deposits, ranged from 9790 years B.P. (10,150–9550 years B.P.) in Lake Lilla Sångaren to 8255 years B.P. (8350–8060 years B.P.) in Lake Övre Skärsjön. The core from Lake Gäddtjärn had the youngest basal 14C age of 7530 years B.P. (7630–7430 years B.P.), which was most likely related to the lack of bottom material in the sediment core due to problems during the sampling procedure. For Lake Dagarn no basal age could be determined since the macrofossil sample dissolved during analysis. However, as Lake Dagarn is located in regional proximity (9 km) to Lake Övre Skärsjön, we assumed a similar basal age of about 8250 years B.P. Generally, the calibrated 14C ages of consecutive samples followed chronological order; however, one age in the profile of Lake Dagarn and in the profile of Lake Övre Skärsjön were younger than the two embracing ages, presumably related to coring artifacts, and therefore, these data were removed. Two ages from the profile of Svarttjärn were removed as well, since the small amount of sample material caused high uncertainties in these ages.

The 210Pb dating revealed ages with chronological order in all sediment profiles. For the calculations of short-term CMARs we considered the period of the last 100 years, i.e., approximately from the year 2007 and 2010 to the year 1900 A.D., due to high uncertainty errors in older layers. The date 1900 A.D. was in most profiles found at depths between 7 and 10 cm, except in the Lake Lilla Sångaren profile where it was located between 3 and 3.5 cm.

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Figure 1. Vertical sediment profiles of the seven study lakes, showing OC content in % dry weight (dark circles) and molar C:N ratios (grey circles). Lakes are in order of increasing surface area. SV = Svarttjärn, GD = Gäddtjärn, GR = Grästjärn, LS = Lilla Sångaren, OP = Oppsveten, OV = Övre Skärsjön, and DA = Dagarn.
3.3. Short-Term and Long-Term CMARs

Both short-term and long-term CMARs varied substantially over time and across all studied lakes (Figures 2 and 3). Short-term accumulation rates during the past 100 years ranged between 0.9 and 16.7 g C m\(^{-2}\) yr\(^{-1}\) and were on average highest in the lakes Grästjärn (8.9 ± 0.9 g C m\(^{-2}\) yr\(^{-1}\); mean ± standard error) and Gäddtjärn (7.8 ± 1.5 g C m\(^{-2}\) yr\(^{-1}\)). The lowest average rate of 3.5 ± 0.9 g C m\(^{-2}\) yr\(^{-1}\) was found in the sediment short core from Lake Svarttjärn. Generally, mean short-term CMARs over the past 100 years were in all lakes, except Lake Svarttjärn, significantly (up to 4 times) higher than mean long-term rates, i.e., CMARs calculated for the entire period of OC accumulation during the Holocene (Figure 3).

CMARs between \(^{14}\)C-dated samples in the long cores ranged from 0.6 to 9.5 g C m\(^{-2}\) yr\(^{-1}\). The two smallest lakes Svarttjärn and Gäddtjärn had the highest mean long-term rates (4.9 ± 1.1 g C m\(^{-2}\) yr\(^{-1}\) and 5.3 ± 1.0 g C m\(^{-2}\) yr\(^{-1}\), respectively), whereas sediment cores from the other lakes revealed lower mean long-term CMARs (<3 g Cm\(^{-2}\) yr\(^{-1}\)). Calculated areal C stocks were consequently about twice as high (45.8 and 40.6 kg C m\(^{-2}\)) in the two smallest lakes compared to the areal C stocks in the larger lakes of this study (16.0–24.5 kg C m\(^{-2}\)).
Results of the Lignin Phenol Analysesa

Table 3.

<table>
<thead>
<tr>
<th>Lake</th>
<th>$X_{\text{lignin}}$ (%)</th>
<th>$\Lambda_X$ (%)</th>
<th>PON/P</th>
<th>S/V</th>
<th>C/V</th>
<th>LPVI</th>
<th>P/(V + S)</th>
<th>(Ad/Al)p</th>
<th>(Ad/Al)v</th>
<th>(Ad/Al)s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Svarttjärn</td>
<td>12.3 ± 2.1</td>
<td>1.0 ± 0.2</td>
<td>0.32 ± 0.04</td>
<td>0.28 ± 0.09</td>
<td>0.17 ± 0.03</td>
<td>2.0 ± 0.4</td>
<td>0.93 ± 0.18</td>
<td>0.63 ± 0.12</td>
<td>0.65 ± 0.17</td>
<td>0.29 ± 0.06</td>
</tr>
<tr>
<td>Gäddtjärn</td>
<td>13.8 ± 3.0</td>
<td>1.8 ± 0.6</td>
<td>0.30 ± 0.03</td>
<td>0.21 ± 0.03</td>
<td>3.1 ± 0.9</td>
<td>0.83 ± 0.15</td>
<td>0.58 ± 0.09</td>
<td>0.64 ± 0.11</td>
<td>0.33 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Grästjärn</td>
<td>9.6 ± 2.0</td>
<td>1.3 ± 0.3</td>
<td>0.22 ± 0.04</td>
<td>0.23 ± 0.08</td>
<td>0.29 ± 0.05</td>
<td>2.6 ± 0.6</td>
<td>1.24 ± 0.40</td>
<td>0.34 ± 0.08</td>
<td>0.61 ± 0.17</td>
<td>0.34 ± 0.04</td>
</tr>
<tr>
<td>Lilla Sångaren</td>
<td>13.8 ± 5.0</td>
<td>1.9 ± 0.9</td>
<td>0.25 ± 0.04</td>
<td>0.17 ± 0.05</td>
<td>4.3 ± 2.7</td>
<td>0.77 ± 0.36</td>
<td>0.43 ± 0.07</td>
<td>0.69 ± 0.12</td>
<td>0.30 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>Oppsveten</td>
<td>12.6 ± 1.8</td>
<td>1.7 ± 0.3</td>
<td>0.28 ± 0.02</td>
<td>0.16 ± 0.05</td>
<td>3.8 ± 0.7</td>
<td>0.67 ± 0.11</td>
<td>0.50 ± 0.06</td>
<td>0.86 ± 0.11</td>
<td>0.41 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>Övre Skärsjön</td>
<td>6.6 ± 1.5</td>
<td>1.0 ± 0.2</td>
<td>0.26 ± 0.01</td>
<td>0.15 ± 0.06</td>
<td>0.52 ± 0.22</td>
<td>2.3 ± 0.4</td>
<td>1.55 ± 0.75</td>
<td>0.43 ± 0.02</td>
<td>0.87 ± 0.17</td>
<td>0.36 ± 0.07</td>
</tr>
<tr>
<td>Dagarn</td>
<td>10.3 ± 2.3</td>
<td>1.9 ± 0.4</td>
<td>0.28 ± 0.02</td>
<td>0.26 ± 0.11</td>
<td>0.38 ± 0.17</td>
<td>3.8 ± 0.8</td>
<td>0.99 ± 0.49</td>
<td>0.45 ± 0.03</td>
<td>0.70 ± 0.15</td>
<td>0.36 ± 0.04</td>
</tr>
</tbody>
</table>

Numbers denote mean values ± standard deviation of each lignin phenol parameter, calculated for the long core profiles of the lakes Svarttjärn ($n$ = 14), Gäddtjärn ($n$ = 11), Grästjärn ($n$ = 14), Lilla Sångaren ($n$ = 14), Oppsveten ($n$ = 16), Övre Skärsjön ($n$ = 9), and Dagarn ($n$ = 10).

Minimum and maximum long-term CMARs for each lake varied around the long-term mean CMAR roughly by a factor of 2. For example, the mean CMAR for Lake Gäddtjärn was 5.3 g C m⁻² yr⁻¹, compared to a minimum CMAR of 3.6 g C m⁻² yr⁻¹ and a maximum CMAR of 9.5 g C m⁻² yr⁻¹. The temporal trend in CMARs showed individual patterns in each lake (Figure 2) and was closely linked to sediment accumulation rates, rather than to the OC content. The four largest lakes displayed the lowest CMAR during the initial few thousand years of organic sediment accumulation, while the three smaller lakes showed no common general temporal pattern. Mean long-term CMARs calculated for the late Holocene period (0–4200 years B.P.) were on average slightly higher (1 g C m⁻² yr⁻¹; Figure S1 in the supporting information), however, not significantly different from mean long-term CMARs calculated for the mid Holocene period (4200–7500 years B.P.; t test, $p < 0.01$; $n = 7$). These two periods differed from each other in climate, with more dry and warmer conditions during the earlier period and cooler and moister conditions during the later period [i.e., Seppä et al., 2005].

The variability in short-term CMARs had a similar magnitude as the variability in long-term CMARs in two of the smallest lakes. However, this was not the case in the largest lakes where the variability in short-term CMARs was higher than the variability in long-term CMARs (Figure 2). Accordingly, while the variability in millennial CMARs was negatively correlated to lake size (regression of lake area against standard deviations of CMARs; $R^2 = 0.63$; $p < 0.01$; $n = 7$; data not shown), there was no such correlation at a centennial scale. Comparatively, very low rates between 0.9 and 3.1 g C m⁻² yr⁻¹ were observed in the profile from Lake Svarttjärn during the first half of the twentieth century. Conversely, CMARs increased rapidly in the more recent time after 1960 A.D., reaching again the average Holocene rate of 4.9 g C m⁻² yr⁻¹ (Figure 2). The sediment profiles from the other six lakes exhibited short-term CMARs higher than mean rates calculated over the entire period of Holocene OC accumulation (1.9 to 5.3 g C m⁻² yr⁻¹). In Lake Gäddtjärn CMARs oscillated slightly over time around a mean of 7.8 g C m⁻² yr⁻¹. The sediment profile from lake Grästjärn showed a relatively early (1897–1937 A.D.) and stepwise increase in CMARs from 3.6 to 10.0 g C m⁻² yr⁻¹. From 1937 A.D. to the recent past values remained rather constant at comparable high rates between 9.4 and 13.3 g C m⁻² yr⁻¹. Short-term CMARs in the four largest lakes increased over time, starting from values close to the Holocene mean CMARs in the early twentieth century. This increase was mostly pronounced in the sediment core from Lake Övre Skärsjön, where values increased about fourfold from 3.7 g C m⁻² yr⁻¹ between 1903 A.D. and 1937 A.D. to 16.7 g C m⁻² yr⁻¹ between 2007 A.D. and 2010 A.D. CMARs in the sediment core from Lake Lilla Sångaren, in contrast, displayed only a minor increase from 2.2 to 4.4 g C m⁻² yr⁻¹ within the covered period of 1913 A.D. to 2007 A.D.

3.4. Lignin Biomarker

The results of the lignin phenol analyses are presented in Table 3 and illustrated in Figures 4 and 5. The source parameters indicated that terrestrial organic matter contributed significantly to the OC delivered to the lakes and that woody tissues from gymnosperms have been the dominant and constant source of terrestrial OC over the Holocene. The parameter $X_{\text{lignin}}$, which was calculated to determine the amount of OC present in the form of lignin (mmol C/OC in sample), ranged in total from 4.7‰ to 27.9‰. Mean values for each sediment profile ranged from 6.6 ± 1.5‰ (mean ± standard deviation) in Lake Övre Skärsjön to 13.8 ± 3.0‰ in the lakes Gäddtjärn and Lilla Sångaren (Table 3). $X_{\text{lignin}}$ exhibited in most profiles very little variability with depth; however, in the sediment profile from Lake Gäddtjärn the $X_{\text{lignin}}$
values oscillated slightly and in the sediment profile from Lake Lilla Sångaren a local maximum with the highest measured value of 27.9‰ was found at 17.5 cm depth (Figure 4). Λ₈ values showed similar patterns to Χ_lignin, with values ranging from 0.7% to 4.5%. PON/P values, which were calculated to indicate the relative input of lignin-containing to lignin-free plants, varied very little with depth around mean values between 0.22 ± 0.04 (Lake Grästjärn) and 0.32 ± 0.04 (Lake Svarttjärn; Figure 4). S/V and C/V values were generally low (<0.5) and mostly constant in the sediment profiles (Figure 4). Albeit, the sediments from the two largest lakes, Övre Skärsjön and Dagarn, displayed slightly higher C/V values up to 0.93 within the upper 30 cm, possibly reflecting increased inputs of nonwoody plant tissues and grasses to these lakes. The LPVI displayed values at the lower range close to 1 (1.7 to 5.9) and patterns over depth similar to the parameter Χ_lignin, except for a maximum value of 12.3 at 17.5 cm depth in the sediment from Lake Lilla Sångaren (figure not shown).

The parameters considered to assess the diagenetic state of terrestrial OC indicated that degradation was rather limited in all of the sediment profiles. The Ad/Al values of the different phenol groups exhibited in general low values <1, and did not show any clear trends over depth. Ad/Al values of the vanillyl group were on average slightly higher than the ratios of the p-hydroxyl and the syringyl group (Table 3), and oscillated strongly with depth (Figure 5). There was no evidence for an increase in degradation state with depth, as it would be indicated by an increase in the Ad/Al values. Similarly, the parameter P/(V + S) did not show any consistent trend with depth in the profiles (Figure 5). However, some of the profiles exhibited locally very high P/(V + S) values, e.g., a maximum value of 2.67 was found at the bottom sample from Lake Övre Skärsjön and comparatively high values in a few samples from the sediment profiles of the lakes Dagarn and Grästjärn.
4. Discussion

4.1. Temporal Variability in CMAR

This study shows that OC accumulation rates in lake sediments varied substantially over the Holocene (Figure 2) and that many lakes display the highest CMARs during the last 100 years (Figure 4). On average, CMARs varied by a factor of 2 around the long-term mean CMAR. In contrast to these findings, OC accumulation in lake sediments is quantitatively often described by one value of average OC accumulation, covering the entire period of the past 10,000 years [e.g., Campbell et al., 2000; Ferland et al., 2012; Kortelainen et al., 2013]. In some lakes, the use of a Holocene average for determining long-term CMARs may be warranted, as indicated by the lack of systematic difference between early Holocene CMARs and late Holocene CMARs in West Greenland lakes [Anderson et al., 2009]. On the other hand, CMARs found at 20 cm core depth, corresponding to about 200 years of age, were on average twice as high as the Holocene average CMAR (5.6 g C m$^{-2}$ yr$^{-1}$) in 66 European lakes [Kastowski et al., 2011]. Our study confirms that for boreal lakes in Sweden, the assumption of a uniform Holocene CMAR is generally not valid.

Our results show that OC accumulation in boreal lake sediments varied in magnitude on both centennial and millennial timescales. CMARs showed individual patterns on long-term scales, whereas a similar trend of increasing CMARs could be observed in most lakes for the more recent period of the last 100 years. The increase in short-term CMARs is a commonly observed phenomenon and mostly attributed to man-made modifications of the environment, such as changes in hydrology, erosion rates, and nutrient input to lakes [e.g., Mulholland and Elwood, 1982; Kastowski et al., 2011; Anderson et al., 2013]. In our case, mean short-term CMARs for the past 100 years were between 1 and 7 g C m$^{-2}$ yr$^{-1}$ higher than the mean long-term rates in six of the studied lakes. A recent study of CMARs in boreal lakes of Quebec, in contrast, found that short-term and long-term CMARs were almost identical in the investigated region [Ferland et al., 2014]. However, this
diverging finding might be related to the different methodological approaches in calculating CMARs. Ferland et al. [2014] resolved CMARs spatially and calculated basinwide average short-term and long-term accumulation rates, in order to correct for sediment focusing. We did not correct for sediment focusing in this study, since we were interested in resolving the temporal variability in OC accumulation at a particular location in each lake, i.e., the deepest point. Our values therefore likely represent maximum accumulation rates and are not representative of the entire lake area.

Another explanation for regional differences in short-term and long-term CMARs could be related to differences in environmental change. The investigated lakes in Ferland et al. [2014] are located in a region with very low population density (<1 person km$^{-2}$, The Atlas of Canada), where the major anthropogenic impacts are the creation of a hydroelectric reservoir [Teodoru et al., 2012] and mining activities in the recent past (see the Clearwater project; http://www.eastmain.com/projects). The Bergslagen region in Sweden, in contrast, experienced several centuries of intensive mining activities related to the industrial revolution in Europe [Ågren, 1998]. Several iron forges, a blast furnace and a steam-powered saw mill were established in the Bergslagen region between the seventeenth and nineteenth centuries, and the landscape was modified through clear cutting of forest due to growing demands for timber and charcoal [Eriksson, 1957, 1960]. The impact of the metal industry on the lakes in the Bergslagen region, i.e., heavy metal deposition and acidification through airborne pollution, was shown by paleolimnological studies of lakes near the Falun copper mine, located approximately 80 km north of our study area [Ek and Renberg, 2001; Hammarlund et al., 2007]. It was previously suggested that atmospheric deposition of acids affects the solubility of organic matter in soils, as lower soil pH inhibits the dissolution of soil organic carbon from the solid phase [Clark et al., 2006]. In the Bergslagen region, the mining industry started to decline from the end of the nineteenth century, yet, many mining enterprises did not close until about 1950 A.D. [Eriksson, 1957]. Hence, the progressive increase in our short-term CMARs during the twentieth century might to some degree reflect the recovery of aquatic and terrestrial ecosystems from acidification, following the strong reduction of sulfur emissions in this area. A higher export of OC from soils in the recent past due to increasing soil pH [Bragée et al., 2015] could potentially be reflected by increased CMARs.

The temporal variability in CMARs in our data set is mostly explained by the variability in sedimentation rates, as sedimentation rates and CMARs follow almost identical patterns over time. The OC content only slightly modifies the temporal trend in CMARs. At the base of the OC sediment layers in two lakes, Svartrjarn and Grästjarn, OC contents are low probably because of a high share of inorganic particles that eroded from poorly developed soils during the early Holocene. Here high sediment accumulation compensates for the low OC content, resulting in CMARs comparable to those of low-accumulating but OC-rich layers. The strong control of sedimentation rates on carbon burial has been observed by several other studies [Sobek et al., 2009; Kastowski et al., 2011]. For instance, Kastowski et al. [2011] found that in European lakes the strong increases in CMARs were mainly linked to increasing sedimentation rates. Similarly, Anderson et al. [2013] showed that recent increases in CMAR in Minnesota lakes were largely related to increased agricultural land use, resulting in both increased soil erosion and enhanced lake productivity, both leading to increased sedimentation. Possibly, the reason for high sediment deposition leading to high OC accumulation in our lakes may be that higher sedimentation rates enhance the burial efficiency of OC. Fast sedimentation promotes fast isolation of OC from oxygen, which lowers mineralization rates of organic matter in the sediment. It has been shown that short oxygen exposure times greatly enhance the OC burial efficiency, particularly for land-derived OC [Sobek et al., 2009]. In general, the OC burial efficiency is likely to be variable over time since it is sensitive to environmental conditions such as oxygen concentration, temperature, OC source, and sedimentation rate [Sobek et al., 2009].

4.2. Variability in CMAR Across Lakes

Long-term CMARs vary individually in each lake, such that it is difficult to link temporal trends to environmental change on a broader scale. However, a few common features can be discussed in regard to changes in the Holocene climate. Mean CMARs calculated for the mid Holocene were lower than mean CMARs calculated for the late Holocene (Figure S1 in the supporting information). The mid Holocene Thermal Maximum led to a relatively warm and dry climate in central Sweden, while the late Holocene, in contrast, experienced a cooling trend and moister conditions [Seppä et al., 2005; Brown et al., 2011]. Higher precipitation and reduced evaporation have likely resulted in increased runoff, leading to more erosion and leaching of soils and hence an increased supply of sediment and OC loads to lakes. However, these overall long-term trends could not be
seen in the two small lakes, Svarttjärn and Gäädtjärn, probably since the broad-scale effects of climate are modulated by local conditions such as catchment characteristics and hydrological flow paths. The smallest lakes had on average twice as high CMARs compared to the other lakes, related to both higher sedimentation rates and higher OC contents in the sediment profiles. The temporal variability in CMARs was also much higher in the smaller lakes.

Several small-scale and a few large-scale studies have investigated the variability in OC accumulation across lakes and identified a variety of different factors controlling OC accumulation [Squires et al., 2006; Kastowski et al., 2011; Ferland et al., 2012]. These factors include, for instance, lake morphometric and landscape characteristics, such as elevation, basin depth, catchment-to-lake area ratio [Squires et al., 2006], catchment slope, the proportion of cropland [Kastowski et al., 2011], and the dynamic ratio (= √lake area/mean depth [Ferland et al., 2012]). It has previously been shown that small lakes, in general, tend to have higher mean CMARs and a larger variability [Kastowski et al., 2011]. Likewise, the two smallest lakes in this study display the highest variability in CMARs on a long-term scale. Nevertheless, in the more recent past all lakes exhibit a higher variability in CMARs. The high catchment-to-lake area ratios in small lakes may explain the higher variability of CMARs found in small lakes on long-term scales. (Table 1). Hence, compared to large lakes, changes in the local environment of small lakes are likely to result in a comparatively stronger alteration in sediment delivery which is diluted on a comparatively smaller sediment area. Local changes connected to forestry, ditching, mining, and the natural development of wetlands might give a stronger imprint in the sediment record in the small lakes compared to the larger lakes, even if the larger lakes will also be affected by local changes. In addition, the small lakes have no or only very few lakes upstream, and thus function as primary deposition sites of eroded sediment. This may explain both the higher magnitude of OC accumulation and the more pronounced dynamics in small lakes, since changes in catchment erosion and sediment transport are most likely to be recorded in lakes that represent the primary depositional environment.

4.3. Indicators of OC Source and Degradation State

The lignin phenol parameters and C:N ratios indicate a substantial share of terrestrial organic matter in the sediments of all seven investigated lakes, predominantly derived from woody tissues of gymnosperm plants. Furthermore, the profiles show that neither the quantity nor the composition of lignin phenols changed significantly over depth (Figures 4 and 5), indicating that the source of organic matter has been predominantly needle trees over the entire Holocene.

The $X_{\text{lignin}}$ values of about 11% and likewise the $\Lambda_{\Lambda}$ values of about 2%, which are indicative for the relative contribution of aquatic and terrestrial OC to the sediments, are fairly consistent over depth, and in a range comparable to $\Lambda_{\Lambda}$ values (0.8–2.3%) reported for recent sediments in Canadian boreal lakes [Teisserenc et al., 2010] and in the postglacial sedimentary record of an Alaskan lake (0.7 to 2.1%), [Hu et al., 1999]. Likewise, the homogenous downward trends of S/V and C/V values (Figure 4) and fairly stable LPVI values close to 1 (Table 3), altogether indicate woody gymnosperms as the dominant input of terrestrial organic matter to the sediments. Only two lakes (Övre Skärsjön and Dagarn) have temporarily slightly higher CV ratios, indicating small contributions of nonwoody plant material, probably related to historical human activities such as mining and deforestation close to Lake Övre Skärsjön and agriculture around Lake Dagarn.

The strength of the sediments acting as permanent C sink is reflected in the stable downward trend of OC content and C:N ratios (Figure 1), as well as mostly homogenous Ad/Al and P/$(V + S)$ values (Figure 5), indicating that postdepositional organic matter degradation has been very limited on long-term scales. C:N ratios have been found to change substantially on short-term scales, during the first years of deposition, due to preferential degradation of N-containing compounds during early diagenesis. For instance, investigations of C:N ratios in varved sediments over a period of 27 years, yielded losses of 23% in C, and 35% in N [Gälman et al., 2008]. However, in the study lakes, at the centennial scale we could not observe an increase in C:N ratios over depth with increasing age of the organic material. Even if both C and N were lost at the same rate, a decrease in their concentration should have appeared but this was not the case as stable OC content values were observed (Figure 1). Likewise the Ad/Al values and the parameter P/$(V + S)$ obscured any clear patterns that could indicate substantial diagenetic changes over depth. Within each group, values should increase with the degree of degradation [e.g., Opsahl and Benner, 1995], but this was not observed in any of the sediment profiles. However, comparing mean Ad/Al values within, for instance, the vanillyphenyl group (0.61–0.87) to values of fresh plant material of 0.1–0.3 [Hedges et al., 1988], suggests that the material has been altered to some degree, either
before or during early years after deposition. Since sediment pore water turns generally anoxic at a few millimeters depth, biologically driven processes change and degradation rates slow drastically down beneath the surficial sediment layers [e.g., Maerki et al., 2006; Sobek et al., 2009]. There was no systematic decrease with depth in $^{210}$Pb showing that lignin is not lost or altered to any detectable degree under anoxic conditions, even over timescales of thousands of years. Our results therefore emphasize that the breakdown of organic material might completely stop in deeper layers and that OC in sediments is stabilized already within the first century after deposition.

5. Conclusion

This study demonstrates that CMARs in boreal lakes varied substantially over the Holocene and that for six out of seven lakes the CMARs during the past century reached an all-time high. The variability in CMARs was most likely controlled by changes in sediment delivery rates from the catchment to the lake and by the limited degree of postdepositional degradation, but was not related to a shift in terrestrial organic matter sources. OC quantity as well as quality, derived from the C/N ratio and lignin phenols, remained stable over the Holocene, indicating little variability in OC sources and very limited long-term postdepositional degradation. Changing sedimentation rates on millennial timescales could potentially be linked to Holocene climate change and to very local changes in the close environments of the smallest lakes. Over the past century, human activities, such as mining and agriculture are likely to have affected the sediment supply to the lakes.

For perspective, however, it should be reiterated that CO$_2$ emission from lakes to the atmosphere is generally greater than OC burial in lakes, both on a global [Tranvik et al., 2009] and regional (e.g., boreal) [Kortelainen et al., 2013] scale. Since CO$_2$ emission is positively related to terrestrial OC inputs to lakes [Sobek et al., 2003], it is likely that periods of high terrestrial OC delivery were periods not only of elevated OC burial but also of high CO$_2$ emission. However, independent of trends in CO$_2$ emission, our study suggests that OC accumulation in boreal lake sediments represents a very stable long-term sink of mainly land-derived OC and that the strength of the sink has varied over time.

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