Biogeosciences
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Discussions

Depth-dependent molecular composition and photoreactivity of dissolved organic matter in a Boreal Lake under winter and summer conditions

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Abstract

Transformations of dissolved organic matter (DOM) in boreal lakes lead to large greenhouse gas emissions as well as substantial carbon storage in sediments. Using novel molecular characterization approaches and photochemical degradation experiments
5 we studied how seasonal patterns in water column stratification affected the DOM in a Swedish lake under late winter and early summer conditions. Dissolved organic carbon (DOC) concentrations were consistently higher above the sediment when compared to surface waters. Solely photobleaching could not explain this difference in DOC because the lake was covered by 40 cm thick ice during late winter sampling and still
10 showed the same DOC trend. The differences in the molecular diversity between surface water DOM in winter and summer were consistent with summertime photobleaching/decarboxylation reactions and a possible bacterial consumption of photo-products. Additional photodegradation experiments using simulated sunlight showed a production of highly oxidized organic molecules and low molecular weight compounds in all
15 late winter samples and also in the deep water sample in summer. In the surface summer DOM sample, few such molecules were produced during the photodegradation experiments confirming that DOM was already photobleached prior to the experiments. This study suggests that photobleaching, and therefore also the ice cover during winter plays a central role in surface DOM structural dynamics with important differences in
20 the molecular composition of DOM between surface and deep boreal lake waters. The release of DOC from boreal lake sediments likely also contribute to this pattern. Photochemical degradation of DOM may be more extensive following ice-out and water column turnover when non-light exposed and thereby photosensitive DOM is photo-mineralized. Hence, the yearly DOM photo-mineralization may be greater than inferred
25 from studies of recently light exposed DOM.

1 Introduction

It is becoming increasingly clear that processes in freshwaters play a key role for global carbon cycling and in particular for the fate of the organic matter (OM) exported from soils. Large amounts of OM are decomposed to carbon dioxide and methane in lakes and emissions of these gases correspond to 80 % of the continental uptake of carbon dioxide equivalents (Bastviken et al., 2011). At the same time OM can also flocculate, sink, and become buried and preserved in sediments (von Wachenfeldt and Tranvik, 2008; Sobek et al., 2012). Recent estimates are that sediments harbor 98 % of the boreal lake OM (Einola et al., 2011), and that the yearly sedimentary burial of OM in lakes exceed the burial in the oceans (Tranvik et al., 2009). The remainder will be transported downstream towards the ocean. The processes behind these different fates are driven by interactions between the quantity and quality of the OM, microbial metabolism, and abiotic processes such as photochemistry and the balance between flocculation and dissolution of OM. However, the relative magnitude and the regulation of OM fates are still unclear in most systems.

There have been numerous short term incubation studies of microbial and photo-chemical interactions with dissolved OM (DOM) degradation in lake waters (e.g. Moran and Zepp, 1997). It has been shown that the combination of initial photochemical degradation of the DOM form smaller molecules and that they are more accessible to microbial degradation. This is also important for the total OM mineralization (Bertilsson and Allard, 1996; Tranvik and Bertilsson, 2001; Anesio et al., 2005). When expanding these findings from short-term incubations over time and space, large seasonal differences in lake OM cycling should be expected in stratified and ice covered systems where different proportions of the OM are exposed to light during different seasons. Given that 51 % of the global lake area is situated north of 48° latitude (Downing and Duarte 2009), and that chromophoric DOM (CDOM) typically dominates the DOM pool in these lakes, such seasonal effects could actually be a major determinant of the fates of OM in lakes. It is well established that during summer stratification in dimictic lakes,

the CDOM concentration in the surface layer (epilimnion) is decreased due to photo-bleaching when compared to the deeper waters below the thermocline (hypolimnion) (Bracchini et al., 2006). As a result photobleaching is a significant and major player in molecular alteration of lake DOM. Modeling attempts stressed that 50 % of the CDOM light absorption within the entire water column in lakes can be lost in 18–44 days under summer conditions due to photobleaching (Reche, Pace and Cole, 2000). However this model did not take into account that different CDOM components are likely to degrade at different time scales. For example, it is likely that at the onset of sunlight exposure a preferential loss of highly photosensitive components of CDOM occurs and that slower photodegrading CDOM constituents are relatively increased but continue to photode-grade at slower rates. Seasonal stratification and the change in redox conditions may also be important for a relatively neglected process in lake carbon cycling studies – re-dissolution of particulate OM from lake sediments (Skoog and Arias-Esquivel, 2009). During stratification periods near-bottom water layers often become anoxic which af-fect all redox sensitive equilibria and processes as well as e.g. pH and this could affect OM solubility. The re-dissolution can be important for assessments of OM stability and burial in lake sediments.

We addressed the hypotheses that seasonal patterns in water column stratification are important for lake carbon cycling by constraining photodegradation and by inducing bottom water conditions that enhance the re-dissolution of sedimented particulate OM. To do this, a series of photochemical experiments in-line with the measurements of opti-cal properties such as ultraviolet/visible (UV/Vis) spectroscopy and excitation emission matrix (EEM) fluorescence spectroscopy were undertaken and combined with ultrahigh resolution electrospray ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-MS) to assess how the quality and characteristics of OM changed between winter and summer conditions and within the water column.

2   Methods

2.1   Sampling

One liter water samples were collected at 0.5 m depth (surface) and just above the sed-
iment at 7 m depth in April, and June 2011 in Lillsjön (58°39′33.05″ N, 16°8′34.81″ E)
a lake located in Östergötland, Sweden. During the first sampling in April, the lake was
still covered by 40 cm thick ice that started to form in November 2010. Dissolved oxy-
gen and temperature profiles were measured during sampling using a hand-held probe
(Hach HQ40d).

All water samples were directly filtered through Whatman GF/F glassfiber filters and
acidified after filtration to pH 2 using ultrapure concentrated HCl (Sigma Aldrich 32 %,
puriss. p.a.). 800 mL of each water sample was then solid-phase extracted (SPE) as
described elsewhere (Dittmar et al., 2008). Briefly, Agilent Bond Elut PPL solid-phase
extraction cartridges, filled with 1 g of the PPL resin (a styrene-divinylbenzene polymer
that has been modified with a proprietary non-polar surface), were pre-conditioned
with methanol, rinsed with acidified (pH 2) Milli-Q water and then the water sample
was gravity-fed through it. Dissolved organic carbon (DOC) was measured on acidified
samples before and after the SPE extraction using a Shimadzu 5000 TOC analyzer
and carbon extraction efficiencies ranged between 58 and 64 %. The absorbance of
the samples before and after SPE extraction was also measured using a (Ultraspec
2100 Pro, scan over 190–700 nm) and showed an average recovery of the CDOM of
63 %. The SPE-extracts were eluted with methanol and stored at −20 °C in a freezer
prior to photochemical experiments.

2.2   Photochemical Experiments.

After completely drying of 1 mL of each SPE-DOM sample under nitrogen gas and
the re-dissolution in 40 mL high purity water (LC-MS grade water, Chromasolv, Sigma-
Aldrich), the sample pH was close to the original water sample at pH 6.5. This was

important to avoid changes in the pH dependent shift in absorbance and photobleaching as described elsewhere (Pace et al., 2012; Janot et al., 2010).

The samples were then divided and half of the sample (20 mL) was continuously pumped through a custom-built photo reactor cell made out of Tefzel tubing for 24 h. A 10 mL gas equilibrator was also attached in-line to allow saturation of air gases at any given time. The flat coiled cell was exposed to simulated sunlight (SolSim Luzchem) that closely matched the intensity of one sun at a solar zenith angle of $z = 48.2°$ (1.5 AirMass filter) corresponding to temperate latitudes in summer and an intensity of 870 W m^{-2}. The Tefzel polymer (ethylene tetrafluoroethylene) has excellent light transmitting properties with > 90 % at 300 nm. This system has several advantages including minimizing inner filtering effects (due to the very short path length of 1 mm), avoiding starvation of air gases (gas equilibrator) and being a closed system avoiding contamination during extended sunlight exposure times.

Dark controls were stored in the dark at similar temperature maintained within the ventilated solar simulator chamber. All samples (irradiated and dark controls) were diluted with 50 % LC-MS methanol and analyzed by negative mode electrospray FT-MS.

2.3 Measurements of Optical Properties.

Absorbance measurements were undertaken on all samples before and after exposure to simulated sunlight using a Cary Bio100 Spectrophotometer with 1 cm quartz cuvettes. Excitation emission matrix (EEM) fluorescence spectra were recorded using a Horiba Fluoromax 4 Spectrofluorometer at 5 nm excitation intervals between 240–500 nm and an emission range of 290–600 nm at 2 nm intervals. Scatter-correction and normalization to quinine sulfate equivalency was performed similar to the procedure described elsewhere (Zepp et al., 2004).

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2.4 Ultrahigh Resolution Mass Spectrometric Analysis

A Bruker Solarix QE 12 Tesla FT-MS with negative mode electrospray ionization located at the Helmholtz Center for Environmental Health, Munich, Germany was used to analyze the SPE- DOM samples from the lake after a dilution of 1 : 100 and all samples before and after photochemical degradation experiments at similar dilution. Electrospray is a soft ionization technique that creates largely intact molecules (no fragmentation) with a single charge and the ultrahigh resolution (mass error < 0.2 ppm and mass resolution > 400 000 at mass 400) allows to unambiguously assign molecular formulae from all m/z peaks (Stenson, Marshall and Cooper, 2003). The accuracy of the used FT-MS is high enough to distinguish masses with a difference of less than an electron and hence multiply charged ions can be distinguished and are rarely observed due to their much weaker ionization efficiencies when compared to their singly charged counterparts. The following chemical elements were allowed to calculate molecular formulae: $^{12}C_{0-\infty}$, $^{1}H_{0-\infty}$, $^{16}O_{0-\infty}$, $^{14}N_{0-5}$ and $^{32}S_{0-2}$ as well as the $^{13}C_{0-1}$ isotopomer. Unambiguous molecular formula assignments are now possible up to 800 Dalton due to the mass accuracy of less than 0.2 ppm. Further information how to accurately assign molecular formulae to ultrahigh resolution FT-MS data is given elsewhere (Dittmar et al. 2007, Schmitt-Kopplin and Hertkorn 2007). Briefly, the mass spectra were calibrated across the observed mass range (150–700 Da) using internal standards of high relative abundance exact mass peaks with known molecular formulas that have been previously found in all DOM samples. External pre-calibration prior to mass spectrometric analyses were undertaken using arginine standards. The reproducibility of the SPE method in conjunction with the same mass spectrometer used in this study has been previously described on triplicate samples (Shakeri Yekta et al., 2012). The reproducibility of the relative abundances of mass peaks was good and showed in average less than 4 % variability but maximum differences of 10 % of high abundance mass peaks may occur; hence we only considered changes in relative abundance that exceeded 10 % relative difference. Usually 20–30 % of the mass peaks have low enough

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intensity to be either above or below the set signal to noise ratio in replicate samples. This can cause a large variability between replicates for such low intensity mass peaks. (Shakeri Yekta et al., 2012). Correspondingly, an analysis to find unique mass peaks in each sample revealed that unique mass peaks showed always very low abundances indicating that they were likely not unique but just had an intensity above the signal to noise ratio in some samples. To avoid any artifacts of the data, we only considered mass peaks that were commonly found in all samples of the same treatment. Van Krevelen diagrams where the elemental ratios of oxygen to carbon (O/C) are plotted against the hydrogen to carbon (H/C) ratios of each individually assigned molecular formula are particular useful to visualize FT-MS data and to show the chemical space of a DOM sample occupied in this specific elemental plot (Kim et al., 2003; Hertkorn et al., 2008) and were used throughout the study.

Another useful visualization tool is the Kendrick diagram, where the Kendrick mass defect (KMD) is plotted against the nominal mass (Kendrick 1963, Wu, Rodgers and Marshall 2004, Hertkorn et al. 2008). The Kendrick mass (KM) is essentially a normalization of the IUPAC mass to the mass of CH_2 groups ($m = 14.01565$) and the KMD is the difference between nominal mass (NM) and KM.

$$KM = \text{IUPAC mass} \times (14.000000/14.01565) \tag{1}$$

$$KMD = NM - KM \tag{2}$$

All homologues of CH_2 would have the same KMD and therefore it can be used to distinguish CH_2 homologues common in FT-MS data of DOM. A second independent parameter (z^*) was used to assign homologues as previously suggested (Hsu et al., 1992; Stenson et al., 2003):

$$z^* = (\text{mod}[NM/14]) - 14 \tag{3}$$

The modulus (mod) function returns the remainder after the NM is divided by 14 (Stenson et al., 2003). Here, we used a modified Kendrick plot where the ratio of the KMD

is divided by z^* and then plotted against the mass to show accurately unambiguous homologous series in one plot (Shakeri Yekta et al., 2012).

3 Results and discussion

During the April sampling, the dissolved oxygen saturation was 59 % just underneath the ice and decreased rapidly with depth to low oxygen levels (1 %) at 0.5 m above the sediment (Fig. 1). However, the bottom water had probably been oxic until just before the sampling as indicated by previous oxic profiles taken in the month of March (data not shown).

In June, the lake was strongly stratified with 100 % oxygen saturation at 0.5 m depth decreasing with depth to about 18 % at 0.5 m above sediment (Table 1 and Fig. 1). At both sampling periods, the DOC concentrations were consistently higher 0.5 m above sediment than at 0.5 m below the surface. The DOC concentration was highest in the deep sample under ice followed by the surface sample under ice, the deep sample in summer, and the surface sample in summer (Table 1). This indicated either a source of DOM to the bottom water and/or a DOC dilution/depletion at the surface both under ice and during summer. Under the winter conditions with the existing ice cover and frozen soils, it seemed unlikely that the surface water was diluted (rain, runoff etc.). The most likely reason for the higher DOM concentrations in the bottom water is release from sediment. A change in the redox potential at the sediment surface caused by switching from aerobic to anaerobic conditions has previously been reported to cause a high release of DOC at the onset of anoxia (Skoog and Arias-Esquivel, 2009). In our case, this may have occurred in the month before the April sampling. Other alternative explanation could be higher microbial mineralization in the surface water, but it is difficult to find good arguments for this given the slightly lower winter temperatures in the surface water and that most parts of the hypolimnion were oxic during the winter.

In June, the even higher difference between surface and deep DOC values could be due to the additional effect of photobleaching in the surface water that was not

effective in April under ice. Additional DOM sources that may have influenced the DOC concentrations cannot be ruled out but the months of April, May and June 2011 were particularly dry in this region and large amounts of leaching from forest soils after spring mixing was unlikely.

To test the hypothesis that DOM is released from sediments, photochemical experiments were undertaken to evaluate if differences existed between the photochemical reactivity (photobleaching) of DOM between surface and deep water as a function of season and a comparison between ice-covered and light protected surface waters in late winter with surface water in summer after exposure to sunlight during the dry and sunny spring of 2011. If a release of DOM from sediments occurred and the significant differences in DOC concentrations between surface and deep waters are not primarily related to photobleaching, than there should not be a great difference between photobleaching in surface and deep waters under winter conditions and during ice-cover. Indeed photochemical degradation of solid-phase extracted DOM (SPE-DOM) in April at the surface and just above the sediment after the exposure to 24 h simulated sunlight was substantial but revealed only small changes between depths (Figs. 2, 3 and 6). In contrast, the same photochemical experiments undertaken on water sampled in June showed much less photobleaching at the surface when compared to deep water SPE-DOM. This indicates that a significant amount of the surface CDOM had already been photobleached by natural sunlight prior to additional laboratory-based photobleaching experiments (Figs. 2, 3 and 6). Thus the observed consistent differences between surface and deep water DOC concentrations were likely caused by a combination of DOC released from sediments and photobleaching/microbial degradation of DOM at the surface in summer and mainly driven by DOM fluxes from sediments in winter.

The ultrahigh resolution negative electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-MS) was used (Fig. 4) to allow for unambiguous assignments of molecular formulae to each exact mass peak in each sample. Only masses containing C, H and O atoms were used in further analysis because nitrogen-

and sulfur-containing molecular formulas were assigned but showed low abundances in negative electrospray mass spectrometry (Fig. 4).

The comparison between surface and deep SPE-DOM under winter conditions collected in April 2011 showed that the relative abundance of highly oxidized organic compounds (O/C ratio between 0.50–0.87) was slightly decreased in the surface compared to deep SPE-DOM, whereas the less oxidized organic compounds (O/C ratio < 0.45) showed a small increase in the surface relative to deep SPE-DOM (Fig. 5). One explanation could be that more oxidized DOM is often also more water soluble and therefore is preferentially released from sediments. This would increase the relative abundance of more oxidized DOM in the bottom water.

In June 2011, differences between surface and deep water were primarily associated with increased abundances of mass peaks assigned to relatively low H/C and high O/C ratio lower molecular weight compounds in the surface SPE-DOM sample (Fig. 5). Interestingly, those highly oxidized molecular formulas appeared in even higher relative abundances after light treatment in our photochemical degradation experiments (Figs. 6 and 7). This indicates that these molecules were photochemical products that are labile and depleted by either microbial degradation or additional photochemical decarboxylation (Xie et al., 2004; Xu and Wan, 2000) and likely resulted in the production of carbon mono- and dioxide and other small carboxylic acids (Bertilsson and Tranvik, 1998). Microbial decarboxylation seemed to be an effective pathway based on dark incubation of water from the same lake in a previous study and the loss of about 7 % of the initial DOC within 147 days at 15 °C (Bastviken et al., 2004). However, assuming initial surface water DOC concentrations of $22 \, \mathrm{mg \, L^{-1}}$, negligible input of water and DOC from land, and dark respiration rate of $1.7 \, \mathrm{mg \, L^{-1}}$ (Bastviken et al., 2004), the direct or indirect photochemically induced DOC degradation in the surface water over 2 months (between the samplings in April and June) would be at least $1.1 \, \mathrm{mg \, L^{-1}}$ or 40 % of the total DOC loss (Table 1). This is accounting for the same dark microbial decomposition during two months as observed experimentally during 5 months at similar

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temperatures and it is therefore likely that the photochemical contribution to the surface water DOC loss were greater.

The limited photoreactivity measured by optical properties (Figs. 2 and 3) of the June 2011 SPE-DOM sample already indicated that photo-active components in this SPE-DOM were largely degraded prior to photobleaching experiments. As a result, the photobleaching demonstrated by changes in optical properties should be also reflected in the ultrahigh resolution mass spectrometric data and a different effect of photobleaching on molecular diversity was expected in the June surface DOM sample when compared to all others. Indeed, all the other samples, including the surface and deep SPE-DOM sample collected in April 2011 together with the deep sample from June 2011, showed a similar photochemical behavior with a production of highly oxidized and high O/C ratio molecules (Figs. 6 and 7). Additionally, a shift to lower molecular weight and a significant increase in relative abundance of these low molecular weight mass peaks was observed in all those samples. The photo production of highly oxidized compounds can be explained with reaction of reactive oxygen species, such as the hydroxyl radical ($\cdot$OH), super oxide (O_2^-) and hydrogen peroxide (H_2O_2). A photochemically induced depolymerization and a decrease in molecular weight of DOM have also been suggested previously (Thomson, Parkinson and Roddick 2004).

The consistent decrease following light exposure in all samples, including the summer surface sample, of mass peaks associated with H/C ratios below 0.8 of associated molecular formulae and throughout a broad range of O/C ratios as demonstrated with the June surface and deep samples (Fig. 7, black circles), is indicative for a large pool of presumably aromatic CDOM components that are photosensitive (Table 2) and present throughout the study periods in surface and deep samples. The high double bond equivalency (DBE, number of double bonds and rings) and the DBE divided by the carbon number (DBE/C) values are indicative of unsaturated compounds (Table 2). However, the June bottom water SPE-DOM (and all April samples) showed an additional pool of more saturated low oxygen-containing compounds that were photobleached (Fig. 7, red circle and Table 2). These were presumably the precursors for

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the highly oxidized low molecular weight compounds photochemically-produced in the experiment in all April and the June bottom water samples (Figs. 6 and 7). The DBE and DBE/C values are a lot lower and in conjunction with the relatively high H/C ratios, are indicative for the much more saturated nature of this component (Table 2).

The lack of these photo reactive and more saturated precursor DOM components in the June surface sample and the lack of highly oxidized photochemically-formed compounds in the same sample and after the light treatment of this sample strongly support a direct linkage between low O/C, relatively saturated precursors, and their highly oxidized and lower mass photo products. These results suggest the existence of two distinctly different CDOM components, where one is very photo-reactive and is quickly completely degraded/phototransformed even in highly absorbing boreal lake surface waters in spring and one that is more persistent but still undergoes photo-chemical transformation throughout spring and summer. Both components are part of the molecular weight fraction ≥ 300 Da and are responsible for the photochemical pro-duction of lower molecular weight compounds (Fig. 7).

The FT-MS data is consistent with the observations of changes in optical properties. Data from both these approaches indicate that the photochemical reactivity of the June surface SPE-DOM sample was significantly reduced due to natural photobleaching that had already occurred during spring in 2011 and the complete loss of a distinct pool of photo reactive mostly saturated compounds.

This study suggests that seasonal molecular changes in SPE-DOM can be explained by a synergy between photochemical degradation (including a likely microbial decar-boxylation of highly oxidized photo-products) and a possible release of DOM from sedi-ments. Photobleaching can also be considered to play a major role in altering the DOM molecular composition in surface boreal lake waters far beyond the limited attenuation of light, due to a water column mixing by wind including seasonal lake circulations. This study further suggests a pool of highly photosensitive relatively saturated CDOM that can be efficiently removed through photobleaching in the surface of highly absorbing

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boreal lake waters, e.g. following lake water turnover in spring, and another CDOM pool showing much slower photobleaching behavior.

Altogether the results based on FT-MS analyses of SPE-DOM and laboratory-based photochemical experiments suggest periods with extensive photo-mineralization after ice-out and lake turnover when DOM from dark parts of the water column (under ice or in the hypolimnion) becomes exposed to light (Fig. 8). Therefore photomineralization may not be uniform over the year but show a distinct seasonal pattern and may be greater over the whole year than inferred from studies of previously light exposed DOM.

To summarize the presented results we developed a conceptual framework (Fig. 8) that emphasizes the observed trends in this study and underlines the importance of seasonal photobleaching differences.

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Table 1. Temperature, dissolved oxygen saturation and DOC concentrations during sampling of Lillsjön, a boreal lake.

Sample Lillsjön	Depth (m)	Sampling 1 April 2011			Sampling 28 June 2011		
		Temperature (°C)	Oxygen saturation (%)	DOC (mg L^{-1})	Temperature (°C)	Oxygen saturation (%)	DOC (mg L^{-1})
surface	0.5	2.1	59	22.7 ± 0.3	19.4	100	18.7 ± 0.2
bottom	7	4	1	25.0 ± 0.2	4.7	18	21.5 ± 0.2

Table 2. The ten most abundant mass peaks and their associated molecular formulae of each of the two distinctly different pools of (1) aromatic and (2) more saturated/aliphatic photosensitive CDOM components analyzed by FT-MS.

Formulae	Exact neutral mass	Rel. abundance before irradiation	Rel. abundance after irradiation	Change (%)	O/C ratio	H/C ratio	DBE[*]	DBE/C
10 highly photo-degraded members of the aromatic CDOM component								
C21H14O5	346.0841	4.7	1.5	−37.5	0.24	0.67	15	0.71
C20H12O6	348.0634	7.5	2.0	−40.4	0.30	0.60	15	0.75
C21H14O6	362.079	6.8	1.9	−37.7	0.29	0.67	15	0.71
C21H12O7	376.0583	8.4	1.9	−41.7	0.33	0.57	16	0.76
C22H12O7	388.0583	7.1	1.1	−46.5	0.32	0.55	17	0.77
C22H10O8	402.0376	5.5	1.0	−44.4	0.36	0.45	18	0.82
C23H14O7	402.074	5.0	1.1	−47.2	0.30	0.61	17	0.74
C23H12O8	416.0532	6.1	1.2	−44.2	0.35	0.52	18	0.78
C24H14O15	542.0333	5.2	2.2	−32.7	0.63	0.58	18	0.75
C24H14O16	558.0282	2.9	1.0	−39.4	0.67	0.58	18	0.75
10 highly photo−degraded members of the more aliphatic/saturated CDOM component								
C29H38O8	514.2567	3.3	1.3	−46.5	0.28	1.31	11	0.38
C30H40O9	544.2672	4.2	1.7	−45.7	0.30	1.33	11	0.37
C20H26O4	330.1831	5.5	2.3	−42.2	0.20	1.30	8	0.40
C17H26O4	294.1831	4.7	2.2	−38.3	0.24	1.53	5	0.29
C26H36O7	460.2461	4.3	2.0	−37.7	0.27	1.38	9	0.35
C28H42O9	522.2829	3.5	1.6	−37.3	0.32	1.50	8	0.29
C28H36O8	500.2410	4.8	2.3	−37.1	0.29	1.29	11	0.39
C28H40O8	504.2723	5.3	2.5	−36.4	0.29	1.43	9	0.32
C30H38O10	558.2465	4.0	1.9	−35.8	0.33	1.27	12	0.40
C25H30O7	442.1992	4.5	2.2	−35.8	0.28	1.20	11	0.44

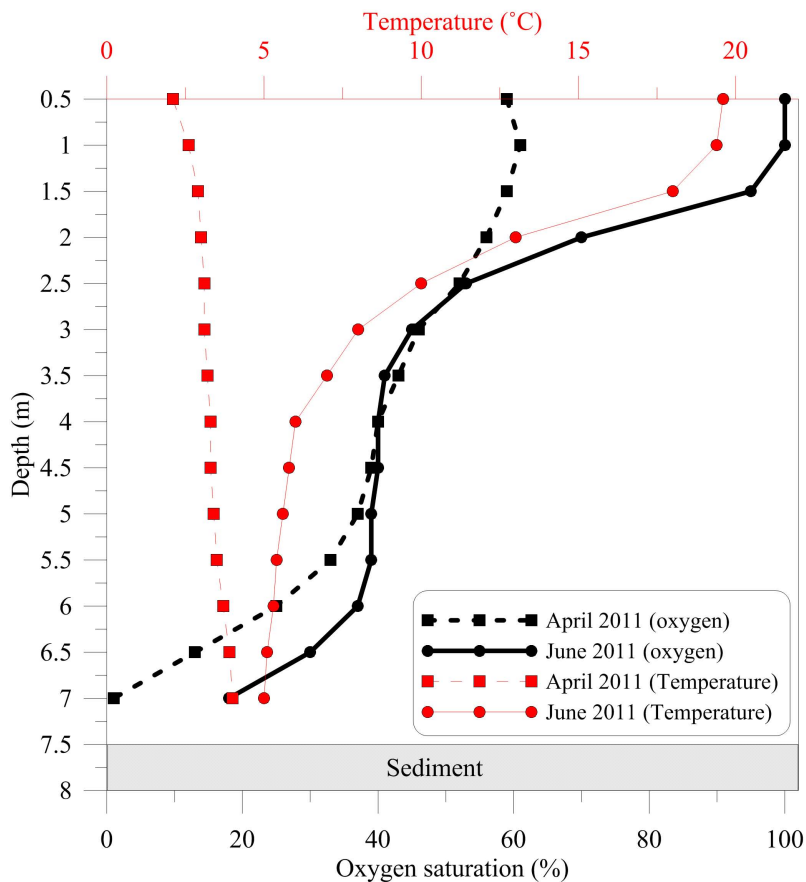[*] DBE is the double bond equivalency that represents all carbon-carbon and carbon-oxygen double bonds.

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Fig. 1. Temperature and dissolved oxygen saturation profiles of Lillsjön Lake in April and June 2011.

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

BGD

10, 8949–8975, 2013

Boreal DOM molecular composition and photoreactivity

M. Gonsior et al.

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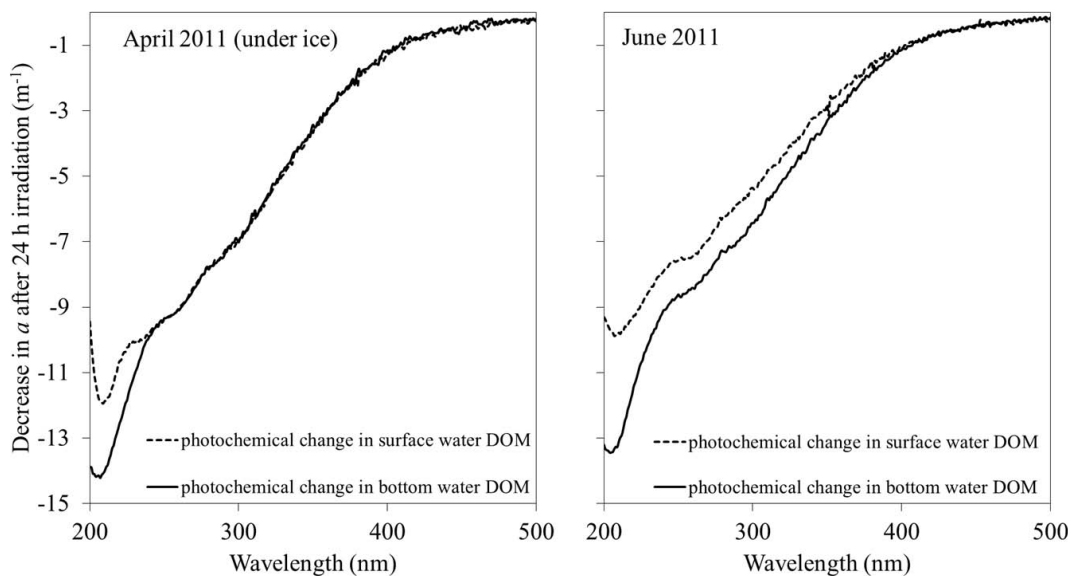
Fig. 2. Depth-dependent seasonal changes in the photochemical degradation patterns after 24 h exposure to simulated sunlight of lake SPE-DOM and analyzed by UV/V is absorption spectroscopy.
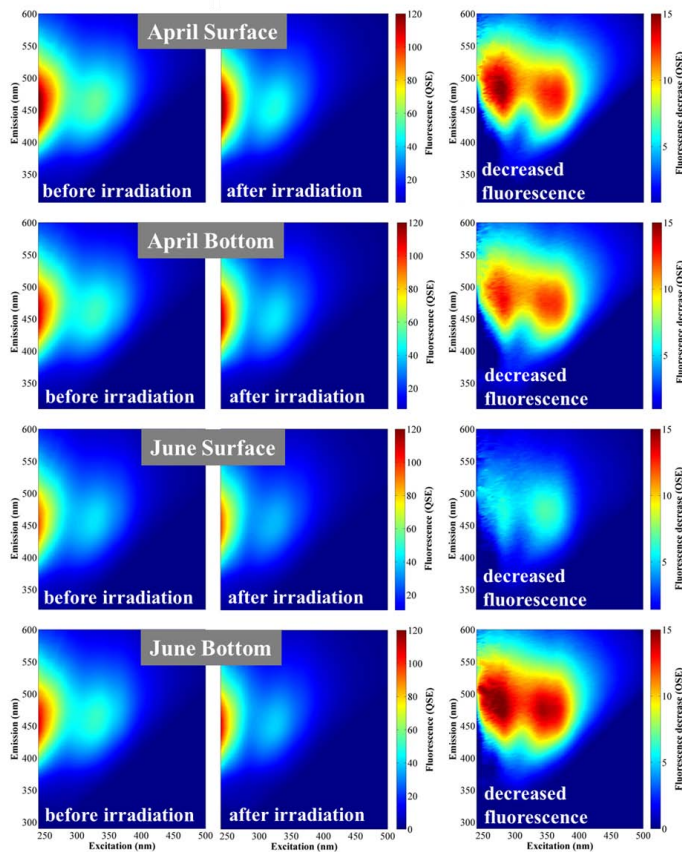
Fig. 3. Excitation emission matrix fluorescence of surface and deep SPE-DOM collected in April and June 2011 before and after exposure to simulated sunlight including a differential plot of the decreased fluorescence after irradiation. Note: SPE-DOM was dried and then re-dissolved in pure water at pH 6.5.
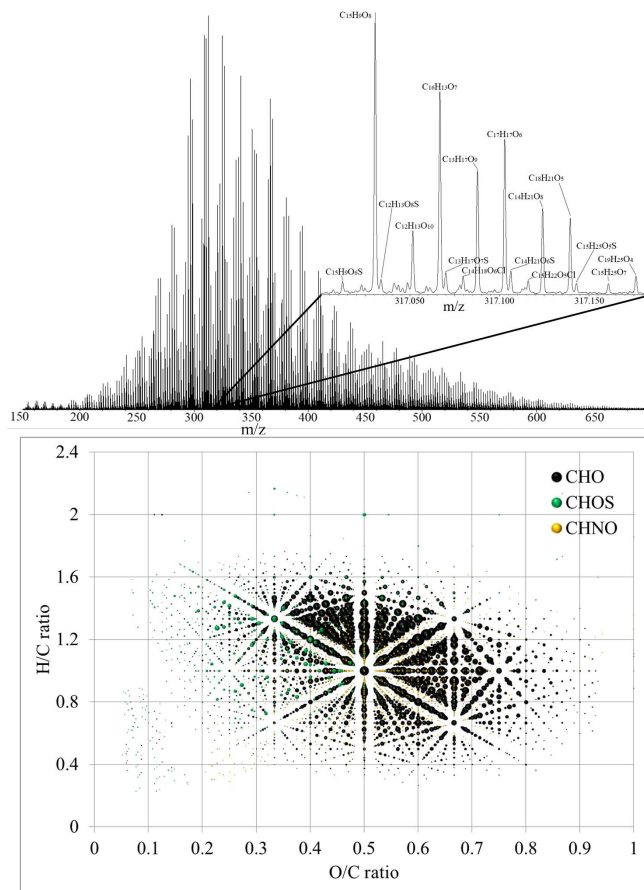
Fig. 4. Ultrahigh resolution mass spectrum of SPE-DOM extracted from a boreal lake at the surface in April 2011 in Sweden (Lillsjön) and the van Krevelen diagram of CHO, CHOS and CHNO formulae. Note: size of bubbles represent relative abundances of associated mass peaks.

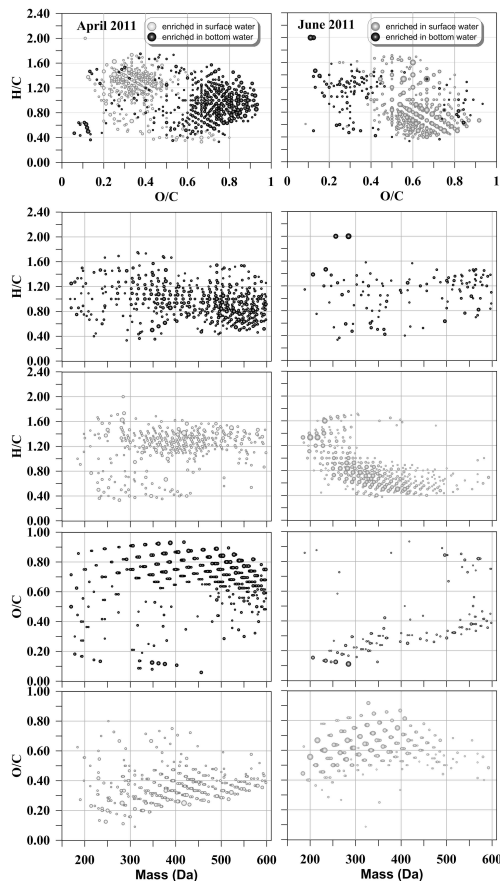**Fig. 5.** Van Krevelen, H/C and O/C versus mass diagrams of relative differences in mass peak abundances between surface and deep SPE-DOM in April and June 2011. Note: the bubbles represent the relative abundances greater 10 %.
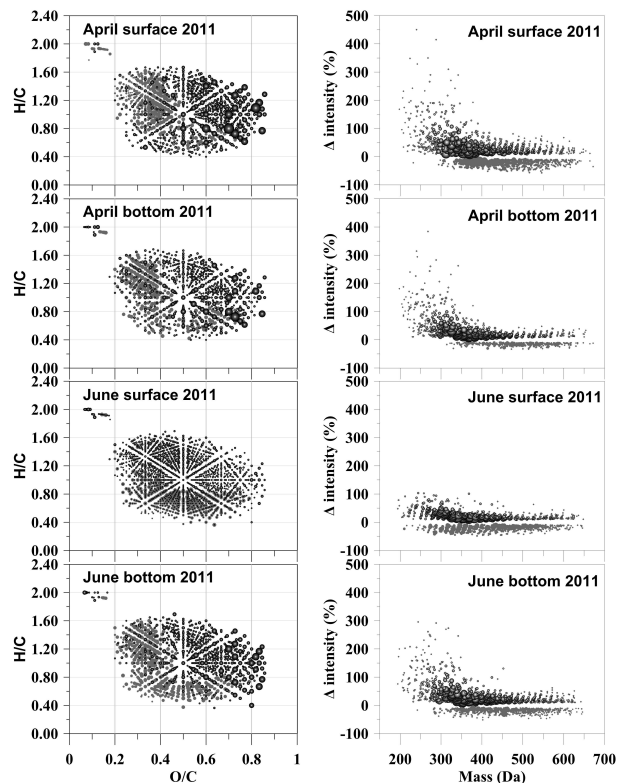
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Fig. 6. Photochemically-induced changes in the molecular composition of a boreal lake SPE-DOM at the surface and bottom in late winter (ice covered) and at the surface and bottom in summer shown in van Krevelen diagrams and the observed relative changes in intensity for all mass peaks, respectively. (Note: black bubbles represent molecular formulae with an increase greater 10 % in associated relative abundances of the mass peaks after 24 h solar simulated irradiation and grey bubbles with a decrease greater 10 %, respectively.)

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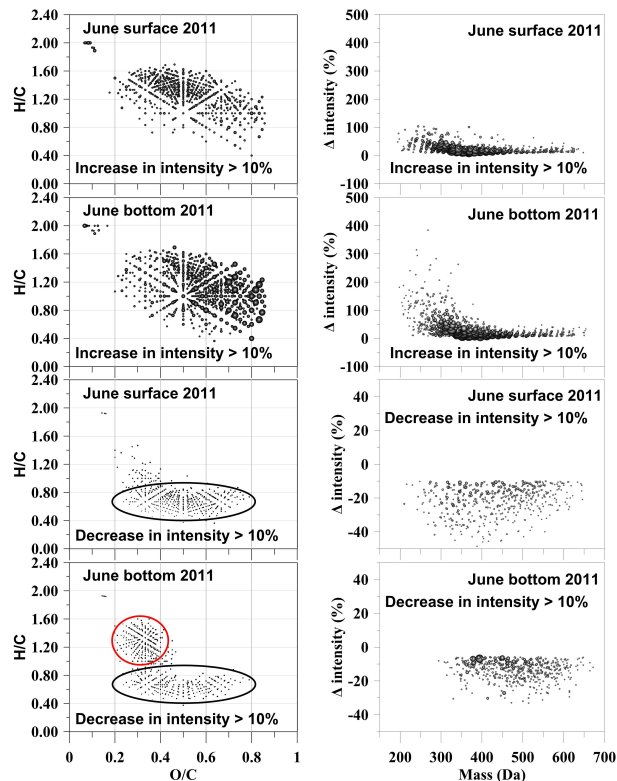Printer-friendly Version

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Fig. 7. Photochemically-induced changes in the molecular composition of a boreal lake SPE-DOM at the surface and bottom in summer and its associated increase in intensity of mass peaks that showed more than 10 % change and a decrease of more than 10 %, respectively. Results are illustrated using van Krevelen diagrams and diagrams where the relative change in intensity is plotted against mass. Note: The bubble size in the van Krevelen diagrams correspond to the relative intensity change after irradiation, whereas the bubble size in the mass diagram corresponds to relative abundance of a mass peak.

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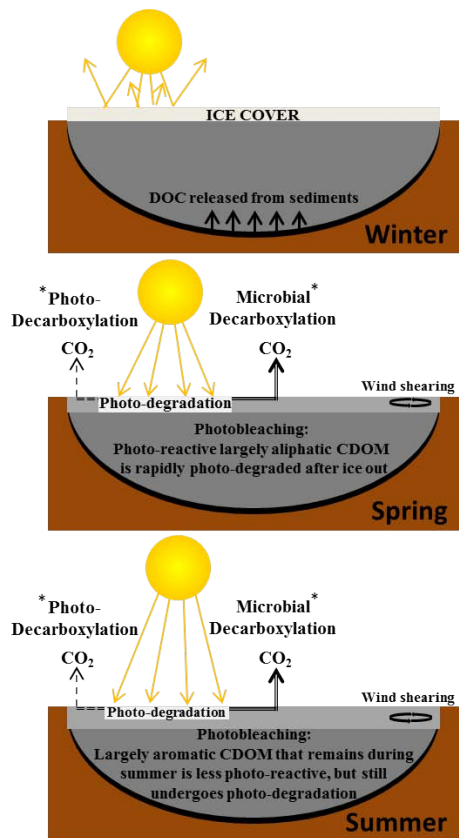Abstract | Introduction

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ICE COVER

DOC released from sediments

Winter

*Photo-Decarboxylation

Microbial* Decarboxylation

CO_2

CO_2

Wind shearing

Photo-degradation

Photobleaching:
Photo-reactive largely aliphatic CDOM
is rapidly photo-degraded after ice out

Spring

*Photo-Decarboxylation

Microbial* Decarboxylation

CO_2

CO_2

Wind shearing

Photo-degradation

Photobleaching:
Largely aromatic CDOM that remains during
summer is less photo-reactive, but still
undergoes photo-degradation

Summer

*Note: Microbial and photo-decarboxylation are known processes for partial mineralization of DOM but were not directly measured in this study and hence it was not possible to distinguish between these two pathways.

Fig. 8. Conceptual framework of (C)DOM transformation in a boreal lake based on FT-MS analysis of SPE-DOM and photochemical degradation experiments.