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**Abstract** Boreal and northern temperate lakes (hereinafter referred to as northern lakes) are sites of intense processing of dissolved organic carbon (DOC), which is reflected in part in the persistent CO$_2$ supersaturation of their surface waters. These ecosystems are subject to strong seasonal fluctuations in both irradiance and DOC amount and quality, which in turn should result in temporal shifts in the magnitude of DOC photodegradation. Here we explore the temporal patterns in the magnitude of water column DOC photomineralization and its potential contribution to pelagic CO$_2$ production in three northern lakes of different DOC content. We performed laboratory DOC photodegradation incubations and combined the resulting rates with field measurements and modeling to reconstruct the annual cycle in depth-integrated DOC photomineralization. We found that areal rates of DOC photomineralization were driven by both irradiance and intrinsic DOC photoreactivity, both of which showed seasonality. Over an annual cycle, depth-integrated DOC photomineralization rates were remarkably similar across lakes, averaging 4.4 (SD = 0.7) g C m$^{-2}$ yr$^{-1}$ and daily rates followed an apparent seasonal pattern. The contribution of DOC photomineralization to total pelagic CO$_2$ production (as the sum of respiration and DOC photomineralization) peaked after ice melt (up to 49%), averaging 14% for the entire open water season. Our study identifies potential hot periods of photochemical activity that result from the interplay between DOC properties and environmental conditions, which should be incorporated into models of lake functioning.

1. Introduction

It is now well established that inland waters emit significant amounts of CO$_2$ to the atmosphere [Cole et al., 2007; Raymond et al., 2013]. One potential source of these emissions is the intense processing of terrestrially derived organic carbon that occurs in these aquatic ecosystems [Algesten et al., 2003; Tranvik et al., 2009]. This terrestrial dissolved organic carbon (DOC) is mostly composed of colored, aromatic, and high molecular weight compounds, which render it highly photodegradable [Wetzel et al., 1995; Opsahl and Benner, 1998].

In the aquatic network of northern regions, lakes may be prime sites of DOC photochemical degradation due to the combination of dominance of terrestrially derived DOC [Wilkinson et al., 2013] and extensive exposure to sunlight resulting from longer water residence times. Although many studies have explored various aspects of DOC photodegradation in lakes, few have placed this process within the context of whole-lake CO$_2$ production [Granéli et al., 1996; Jonsson et al., 2001; Cory et al., 2014], and even fewer have explored its seasonal variation [Lindell et al., 2000; Koehler et al., 2014]. The latter is critical in northern lakes, which are subjected to strong seasonality in both DOC quantity and quality, and irradiance. Although irradiance is predictable, the temporal patterns in DOC photoreactivity and quantity may not only differ among different lakes, but more importantly, they may not necessarily covary with irradiance. There is thus a large degree of uncertainty regarding the relative contribution of photochemical DOC mineralization to pelagic CO$_2$ dynamics over an annual cycle, and this represents a large gap in our understanding of the regulation of CO$_2$ emissions from lakes.

There has been significant progress over the past decades in our understanding of DOC photoreactivity and photochemical degradation in aquatic systems. DOC can be photodegraded into smaller (low molecular weight) and often biolabile molecules [Lindell et al., 1995; Bertilsson et al., 1999; Scully et al., 2003; Anesio et al., 2005]. It can also be photomineralized into inorganic carbon species such as CO and CO$_2$ [Salonen and Vähäkärri, 1994; Granéli et al., 1996, 1998; Stubbins et al., 2008]. To understand the intrinsic photoreactivity...
of DOC, however, degradation rates must be normalized by the energy (or photons) absorbed by the sample. This is generally expressed as the wavelength-dependent apparent quantum yield (AQY), which is expressed as the moles of DOC mineralized per mol of photons absorbed by the total chromophoric dissolved organic matter (CDOM) pool [Zepp, 1978; Vähätalo et al., 2000]. The magnitude of this photomineralization efficiency is highly variable among freshwater and marine systems [Vähätalo et al., 2000; Johannessen and Miller, 2001; White et al., 2010; Koehler et al., 2014], but no clear and consistent drivers of this variability have been identified yet. In spite of some high AQY values reported in the open ocean [Johannessen and Miller, 2001], there is an overall inshore to offshore gradient of decreasing AQY, suggesting generally lower apparent DOC photomineralization efficiency toward the open ocean [White et al., 2010; Aarnos et al., 2012]. Moreover, a recent study in arctic aquatic systems showed high DOC photomineralization efficiency in permafrost-derived DOC [Cory et al., 2014]. Lapierre and del Giorgio [2014] have reported a disproportionate increase in photo reactive DOC in highly colored, head water streams relative to larger rivers and lakes. Collectively, this evidence suggests that the degree of connectivity to terrestrial sources of DOC may potentially determine cross-system patterns in the intrinsic photoreactivity of this carbon. The degree and nature of the connection between lakes and land also varies seasonally as a function of hydrological conditions, and it would thus be expected that the intrinsic photochemical reactivity of the DOC loaded to lakes would therefore also vary seasonally. The few studies to have explicitly addressed this question have indeed reported seasonal patterns in DOC photoreactivity in boreal lakes [Lindell et al., 2000; Gonsior et al., 2013; Groeneveld et al., 2015], boreal streams [Porcal et al., 2013], and a tropical humic lagoon [Suhett et al., 2007]. To our knowledge, however, information on how the seasonality of DOC photo-reactivity affects areal rates of DOC photomineralization and its contribution to the whole water column CO₂ production in lakes is lacking in the literature.

Determining the role and the relative importance of photochemical processes at the whole-lake scale requires integrating the photomineralization rates over depth. When light penetrates the water column of lakes, irradiance intensity and its spectral properties are selectively attenuated. Because of the spectral dependency of the AQY, this in turn will generate a vertical gradient of DOC photomineralization, with the highest rates at the near surface [Granéli et al., 1996; Vähätalo et al., 2000]. Information on spectral dependency of DOC photomineralization is needed to estimate depth-integrated rates, and only a handful of studies have reported such rates in lakes. These studies have usually been based on either in situ measurements at discrete depths [Granéli et al., 1996; Vähätalo et al., 2000; Soumis et al., 2008] or modeled as a function of AQY [Cory et al., 2014; Koehler et al., 2014], and have reported a wide range of values. As a result, the relative contribution of DOC photomineralization to the whole-lake CO₂ production appears to be highly variable across systems. For example, photochemical processing has been shown to dominate DOC degradation in some boreal and arctic lakes [Malot and Dillon, 1997; Cory et al., 2014], whereas other studies, also in boreal regions, have reported only a modest contribution of photochemical processes to the lake CO₂ budget compared to biological rates [Granéli et al., 1996; Jonsson et al., 2001; Soumis et al., 2007; Koehler et al., 2014]. This variability is, however, not surprising, since in situ biological and photochemical DOC degradation have different drivers (e.g., temperature versus light) and the availability of photochemical and biological reactive DOC may also have contrasting drivers [Lapierre and del Giorgio, 2014]. This would suggest that the relative contribution of photochemical DOC mineralization to the total pelagic CO₂ production may follow a seasonal cycle, where hot moments of photochemical activity would not necessarily coincide with hot moments of biological degradation. This potential seasonal succession in the relative contribution of depth-integrated DOC photomineralization to the whole lake CO₂ production remains largely unexplored.

Key to reconciling these reported differences in photochemical rates is to understand the variability and the relative contribution of the three main components involved in determining total DOC photomineralization in lakes: irradiance, DOC amount, and DOC reactivity, all of which are highly variable not only across lakes of different regions but also within a single lake throughout the seasons [Lindell et al., 2000; Gonsior et al., 2013]. Here we reconstructed the annual cycle of depth-integrated photomineralization of DOC in three limnologically distinct northern lakes, explicitly incorporating seasonal shifts in DOC reactivity, DOC amount, and irradiance. We further place these photomineralization rates in the context of the seasonal variation in the measured pelagic respiration rates. Our aim was to quantify the overall contribution of photochemical degradation of DOC to the water column CO₂ production and to identify potential hot moments in this contribution and assess how these may vary across lake types.
2. Methods

2.1. Site Description and Sampling

The study lakes are located in the temperate and boreal regions of Québec (Canada) and were sampled monthly or biweekly during at least one annual cycle (between 2010 and 2012). General lake characteristics are presented in Table 1. Lac Hébécourt (273 m altitude, 48.51°N, 79.38°W) is the shallowest but the largest of the studied lakes and is situated in the Lac Duparquet Research and Teaching Forest, a managed mix forest dominated by balsam fir (Abies balsamea) and white birch (Betula papyrifera) settled mainly on glaciolacustrine clays. The lake has five major river/stream inputs, four of which are heavily dammed by beavers (Castor canadensis). Lac Simoncouche has a pristine watershed dominated by black spruce (Picea mariana) and balsam fir (Abies balsamea) settled on podzolic soils (347 m altitude, 48.23°N, 71.25°W). The lake has two major inlet streams (each having an upstream lake) and several headwater ephemeral streams that only flow after heavy rains. The southern part of the lake has extensive development of aquatic macrophytes (Brasenia schreberi) from June to October (covering up to about 10–15% of total lake area). Lac Croche is a headwater lake surrounded by a pristine watershed dominated by maple (Acer saccharum) and yellow birch (Betula alleghaniensis) settled on well-drained Ferro-humic podzols (365 m altitude, 45.99°N, 74.00°W).

Lake water was collected at 0.5 m depth at the deepest location of the lake. Samples were immediately brought back to the lab for photochemical DOC mineralization and dark biological respiration incubations, and for further chemical analyses. Additionally, we carried out vertical profiles (each meter) of temperature, dissolved oxygen, conductivity, and pH using a multiparameter probe (Yellow Spring Instruments, USA). Chlorophyll samples were analyzed spectrophotometrically following filtration with Whatman (GF/F) filters and hot ethanol (90%) extraction. DOC concentration was measured on 0.45 μm filtered water samples on an OI-1010 TIC-TOC Analyzer (OI Analytical, College Station, TX, USA) using wet persulfate oxidation. Total phosphorus was analyzed spectrophotometrically after persulfate digestion.

2.2. DOC Light Absorptivity and Photoreactivity

We assessed lake DOC photoreactivity by determining the magnitude of DOC light absorption and the DOC mineralization during light incubations. After filtering lake water (0.45 μm), light absorption by DOC was measured in the laboratory with an ultraviolet-visible Ultrospec 2100 spectrometer (Biochrom, Cambridge, UK). Absorbance of colored dissolved organic matter (A\textsubscript{CDOM}) was measured over the range of 280–800 nm and then expressed as the Neperian absorption coefficient (a\textsubscript{CDOM}; m\textsuperscript{-1}) according to Beer-Lambert’s law:

\[
a_{\text{CDOM},\lambda} = \ln(10) \times \frac{A_{\text{CDOM},\lambda}}{L},
\]

where L is the path length of the spectrophotometer cell in meters, and the factor ln(10) converts from \text{log}_{10} to ln. As the absorption coefficient typically decreases with increasing wavelength, we fit the absorption spectrum for each sample to a decreasing exponential function described as:

\[
a_{\text{CDOM},\lambda} = a_{\text{ref}} \times e^{(\lambda_{\text{ref}} - \lambda)} + K,
\]

Table 1. General Characteristics of the Three Study Lakes

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Lac Hébécourt</th>
<th>Lac Croche</th>
<th>Lac Simoncouche</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake area (ha)</td>
<td>775.0</td>
<td>18.1</td>
<td>86.1</td>
</tr>
<tr>
<td>Watershed area (ha)</td>
<td>2800</td>
<td>88</td>
<td>2633</td>
</tr>
<tr>
<td>Mean depth (m)</td>
<td>2.2</td>
<td>5.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Mean annual air temperature (°C)</td>
<td>NA\textsuperscript{d}</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Ice-free period (days)</td>
<td>193</td>
<td>217</td>
<td>225</td>
</tr>
<tr>
<td>Water residence time (years)</td>
<td>0.48</td>
<td>1.10</td>
<td>0.09</td>
</tr>
<tr>
<td>DOC (mg C L\textsuperscript{-1})</td>
<td>9.9 ± 0.8</td>
<td>4.6 ± 0.5</td>
<td>6.9 ± 0.9</td>
</tr>
<tr>
<td>Absorption coefficient at 440 nm (m\textsuperscript{-1})</td>
<td>2.2 ± 0.6</td>
<td>0.8 ± 0.2</td>
<td>1.9 ± 0.5</td>
</tr>
<tr>
<td>UV light extinction coefficient (m\textsuperscript{-1})</td>
<td>18.9</td>
<td>10.6</td>
<td>19.7</td>
</tr>
<tr>
<td>Chlorophyll a (μgL\textsuperscript{-1})</td>
<td>5.7 ± 3.5</td>
<td>1.4 ± 0.7</td>
<td>1.7 ± 0.8</td>
</tr>
<tr>
<td>Total phosphorus (μgL\textsuperscript{-1})</td>
<td>27.6 ± 4.7</td>
<td>4.0 ± 1.2</td>
<td>10.0 ± 2.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Measured in 2011.\textsuperscript{b}Annual average.\textsuperscript{c}Ice-free season average ± standard deviation.\textsuperscript{d}NA = not available for the whole year.
where \( a_{\text{ref}} \) is the absorption coefficient at the reference wavelength (here 290 nm) \( (\text{m}^{-1}) \), \( S \) is the curve shape parameter \( (\text{nm}^{-1}) \), \( \lambda_{\text{ref}} \) is the reference wavelength, and \( K \) is the background scattering constant \( (\text{m}^{-1}) \).

To determine DOC photoreactivity, we performed irradiation experiments in the laboratory. Water was filtered (2.7 \( \mu \text{m} \) nominal pore size GF/F Whatman filter) and then exposed to artificial light in a solar simulator (Q-sun Xe-1, Q-Lab; light intensity of 0.68 W m\(^{-2}\) at 340 nm) in borosilicate vials (O.D. \( \times \) L: 24.8 \( \times \) 83 mm; Volume = 40 ml) at controlled temperature (24°C). Vials (between 4 and 20 in each incubation) were randomly positioned flat on the tray in the irradiation chamber to ensure uniformity in irradiation intensity and spectra to all the vials. The irradiated surface area was then assumed to be equivalent to the inner diameter multiplied by the length of the vial. No dark controls were incubated in the irradiation chamber. DOC photomineralization \( (\text{mg} \text{ C L}^{-1} \text{ d}^{-1} \text{ or } \text{mol} \text{ m}^{-3} \text{ d}^{-1}) \) was measured as the differences in DOC and DIC concentrations between time = 0 (unexposed) and at \( t = 24 \text{ h} \). Filtration through 2.7 \( \mu \text{m} \) may have left the part of the bacterial community in the vial prior of the light incubation, we further discuss the reason to use this filter and how we accounted for potential bacterial activity in the vials by correcting for dark controls in the supporting information Text S1.

2.3. AQY Estimation

We estimated the wavelength-integrated AQY \( (\text{wAQY}) \) for each sample by dividing the DOC loss (and DIC production) during the incubation \( (\text{mol} \text{ C}) \) by the photons absorbed by CDOM \( (\text{mol} \text{ photon}) \), accounting for self shading and glass vial transmittance. First, the quantum density flux \( (Q_{\text{abs}}) \) absorbed in each sample was estimated from the following equation:

\[
Q_{\text{abs}} = \text{bleach} \times A \times T \int_{\lambda=280}^{\lambda=600} \frac{I_0}{E_\lambda} \times (\text{glass trans})_\lambda \times \tau_{\text{CDOM,} \lambda},
\]

where \( Q_{\text{abs}} \) is the total photons absorbed by CDOM in the vial \( (\text{mol} \text{ photons} \text{ d}^{-1}) \), bleach is the average proportion of initial absorption coefficient lost at 375 nm due to bleaching during the incubation. We chose this particular wavelength because it is around 375 nm that we found the maximum irradiance energy absorbed (irradiance multiplied by DOC absorption) normally peaks between 350 and 400 nm. \( A \) is the surface of the vial exposed to light \( (0.0018 \text{ m}^2, \text{estimated as the inner diameter multiplied by the length of the vial}) \), \( T \) is the total time of the incubation \( (\text{s}) \), \( I_0 \) is the lamp irradiance for a specific wavelength \( (\text{Js}^{-1} \text{ m}^{-2} \text{ or } \text{W} \text{ m}^{-2}) \).

Assessing the exact light absorption in cylindrical vials can be highly uncertain; thus a sensitivity analysis was performed to further test the effect of varying the surface area of exposure on the resulting rates of photomineralization (see supporting information Text S1 and Table S1). We divided the lamp energy by \( E_\lambda \) \( (\text{J mol photon}^{-1}) \), which is the energy per mol of photons at a specific wavelength \( (\text{defined as nhc} / \lambda_c, \text{where } n \text{ is the number of photon in one mol, } h \text{ is the Planck’s constant, and } c \text{ is the speed of light}) \). (Glass trans), is the wavelength-specific fraction of light that reaches the water sample (supporting information Figure S1).

The mean wavelength-specific fraction of light absorbed in the vial \( \tau_{\text{CDOM,} \lambda} \) was computed to account for self shading [Hu et al., 2002] using the diameter of the vial as the pathlength. Considering the lamp output \( (750 \text{ W m}^{-2}) \) and light absorption by the glass in the vial, we estimated that all water samples received a total of approximately 650 W m\(^{-2}\) of radiation \( (280–800 \text{ nm}) \). Detailed information on the spectral characteristics of the light source and the spectral transmittance of the incubation vials (see supporting information Figure S1).

Our incubation yielded information on the total DOC mineralization per total amount of photons absorbed within the whole UV-visible range. It has been well established that the apparent quantum yield \( (\text{AQY}) \) is not constant along the spectrum, but rather peaks in the UV range and decreases exponentially with increasing wavelength [Vähätalo et al., 2000; Johannessen and Miller, 2001; Stubbins et al., 2011]. It is therefore necessary to estimate the spectral dependency of the DOC photomineralization for each sample. In this regard, we can express the total DOC mineralization for a given sample as the sum of the DOC loss rates at each wavelength, which is itself the product of the AQY and the amount of light absorbed by the sample at each wavelength:

\[
\text{Total DOC mineralization} = \sum_{\lambda=280}^{\lambda=600} Q_{\text{abs},\lambda} \times \text{AQY}_{\lambda},
\]

where \( \text{AQY}_\lambda \) is the wavelength-specific AQY, and \( Q_{\text{abs},\lambda} \) is the wavelength-specific photon absorbed by the CDOM during the incubation, corrected for self shading [Hu et al., 2002]. The spectral dependency of AQY
(AQY$_X$) can be described as an exponential declining function [Vähätalo et al., 2000; Aamos et al., 2012; Cory et al., 2014]:

$$\text{AQY}_X = c \times e^{-d \lambda}$$ \hspace{1cm} (5)

where $c$ (dimensionless) and $d$ (nm$^{-1}$) are constants, and $\lambda$ is the wavelength in nanometers (nm). Merging equations (4) and (5) results in

$$\text{Total DOC mineralization} = \sum_{\lambda = 280}^{\lambda = 600} \text{Q}_{\lambda} \times \left( c \times e^{-d \lambda} \right).$$ \hspace{1cm} (6)

All the parameters in equation (6) are known, except for parameters $c$ (dimensionless) and the slope parameter $d$ (nm$^{-1}$). Unfortunately, because two parameters ($c$ and $d$) are unknown, it is impossible to solve equation (6), as it results in infinite combinations. Having information on one of these two unknowns, however, allows us to back-calculate the other. Whereas parameter $c$ (in equations (5) and (6)) represents the intercept of the relationship between AQY and wavelength, parameter $d$ describes the shape of the spectral slope, which allows to weigh the relative importance of each wavelength on DOC photo-mineralization. For the purpose of this study only, we assumed that parameter $d$ in equations (5) and (6) can be replaced by parameter $S$ in equation (2) that describes the absorption spectrum. We base this assumption on previous studies that have shown strong relationships between measured AQY and the absorption coefficient of DOC across wavelengths [Xie et al., 2009; Stubbins et al., 2011]. Since the quantum yield of DOC mineralization for a given sample is a function of its absorption coefficient, it follows that the spectral slope of the AQY for a given sample should closely follow its absorption spectrum, and this in turn implies that the parameter $d$ of the AQY spectral model (equations (5) and (6)) should be analogous to coefficient $S$ of the absorption spectrum model (equation (2)). Here we have used this potential equivalence to apportion the total DOC mineralization that we measured in the incubation across the spectrum. We thus replaced parameter $d$ by parameter $S$ in equation (6), and we iteratively fit parameter $c$ by solving equation (6) (“fzero” function in MATLAB 7, MathWorks). Now having parameters $c$ and $S$ (or $d$), the spectral AQY could then be estimated using equation (5). It is important to note that this potential equivalence between CDOM absorption and AQY slopes is an assumption, and although our field comparison of the output of this model with actual DOC photodegradation supports this assumption (supporting information Text S1), it should be further tested with direct measure of AQY spectra (e.g., using cutoff filters) in future studies. Further details and implication on using this slope parameter, as well as a full sensitivity analysis are presented in the supporting information Text S1 and Table S2.

### 2.4. Water Column Irradiance

For each sampling day, we estimated the water column irradiance at each depth by combining modeled incident irradiance corrected for cloud cover and surface reflectance and measurements of diffuse vertical attenuation coefficients ($K_d$). Hourly data (0:00 to 23:00) of direct and diffuse surface downwelling irradiance were modeled using the Tropospheric Ultraviolet Visible (TUV) model [Madronich and Flocke, 1997] for each sampling date and location, under clear sky conditions and total ozone content retrieved from OMI-AURA [Ozone Monitoring Instrument (OMI) Science Team, 2012]. To convert to daily integrated just-below-surface downwelling scalar irradiance ($Q_{0-}$), global (direct + diffuse) irradiance from the TUV model was corrected for cloud cover and transmittance at the surface of the lake and converted to scalar irradiance using the average underwater cosine, following Fichot and Miller [2010]. We first performed a cloud correction on modeled irradiance using OMI-AURA daily radiative cloud fraction (0–1) on each site [OMI Science Team, 2012], and we parameterized a correction factor using measurements of in situ irradiance just over the lake (see supporting information Text S2). Transmittance at the air-water interface for every hour was computed separately for diffuse and direct fractions of irradiance using zenith solar angle and following Fresnel’s law [Fichot and Miller, 2010]. Finally, conversion to scalar irradiance was computed using the estimated average underwater cosine for downwelling irradiance, also following Fichot and Miller [2010]. Hourly underwater irradiance was interpolated (cubic) to a 1 s time resolution to yield daily integrated just-below-water scalar downwelling irradiance ($Q_{0-}$).

Water column irradiance attenuation was calculated from in situ measurements of underwater cosine-corrected downwelling irradiance using a UV-visible profiler (PUV-2545, Biospherical Instrument Inc., San Diego, USA) at five different wavelengths (313, 320, 340, 443, and 550 nm) [Frenette et al., 2006]. Ten
measurements per second were recorded as the probe was slowly deployed through the whole water column. Attenuation coefficients ($K_{\text{DOM}}$) were computed for each measured wavelength ($\lambda$). For sampling dates for which we did not have the UV profiler, $K_{\text{DOM}}$ were estimated using empirical linear models based on our own measurements using DOC or $a_{\text{CDOM}}$ as independent variables (see supporting information Text S3 for details and empirical equations). Attenuation coefficients for each wavelength (1 nm resolution) from 280 to 600 were then estimated by fitting our measured (or estimated) $K_{\text{DOM}}$ following a model described earlier [Markager and Vincent, 2000]. The daily spectral scalar irradiance at each depth ($\lambda$) ($Q_{0-\lambda \rightarrow \lambda} \text{ mol photons \text{ m}^{-2} \text{ h}^{-1}}$) was determined following the equation

$$Q_{0-\lambda \rightarrow \lambda} = Q_{0-\lambda} \times e^{-K_{\text{DOM}} \lambda d}$$

where $Q_{0-\lambda}$ is the cloud-corrected just-below-surface scalar downwelling irradiance (mol photons m$^{-2}$ m$^{-2}$ d$^{-1}$), and $K_{\text{DOM}}$ is the spectral specific vertical irradiance attenuation coefficient.

### 2.5. Areal DOC Photomineralization Rates

The areal DOC photomineralization rate (PM, mg C m$^{-2}$ d$^{-1}$) at each sampling date and lake was calculated as the sum of the volumetric photomineralization rates ($PM_{z}$) at each (0.01 m) depth interval, multiplied by the strata volumes derived from lake bathymetry (for each 0.01 m depth interval, in m$^3$), and divided by lake surface area (m$^2$). Volumetric DOC photomineralization rates at each depth and each hour can be described as follows:

$$PM_{z} = \int_{\lambda=280}^{\lambda=600} Q_{0-\lambda \rightarrow \lambda} \times a_{\text{CDOM}}, \lambda \times AQY_{\lambda},$$

where $PM_{z}$ is the daily photomineralization at depth $z$ (mol C m$^{-3}$ d$^{-1}$), $Q_{0-\lambda \rightarrow \lambda}$ is the spectral scalar irradiance at depth $z$ (mol photons m$^{-2}$ d$^{-1}$), $a_{\text{CDOM}}, \lambda$ is the wavelength-specific absorption coefficient of DOC (m$^{-1}$), and $AQY_{\lambda}$ is the estimated wavelength-specific quantum yield of DOC mineralization (mol DOC loss · mol photons$^{-1}$) estimated for each specific date and lake. A sensitivity analysis revealed that varying the wavelength-specific AQY spectral slope ($d$) used in equation (5) over the entire range of values that were measured resulted in a total variation of PM of no more than 10% (see supporting information Text S1 for complete sensitivity analysis). Moreover, to validate the model, modeled rates of $PM_{z}$ were compared to measured rates in quartz vials during two days in July 2015 in Lac Croche (see supporting information Text S4 for details on results and the methods). We further estimated the average annual photodegradation in each lake by recalculating the monthly averaged PM rates and using the natural cubic spline function to integrate over the whole open-water period on each lake. Average monthly PM rates were calculated from monthly averaged AQY, cloud cover, and irradiance following the same steps as described previously.

### 2.6. Whole-Lake Pelagic Respiration

Pelagic respiration rates were derived from changes in oxygen concentration in unfiltered water samples incubated in 500 mL Erlenmeyer at near in situ temperature in the dark for 48 h [Marchand et al., 2009]. Briefly, $O_{2}$ concentrations were measured using an optode system, consisting of oxygen-sensitive optical sensors and a fiber optic meter (Fibox 3, PreSens, Regensburg, Germany), except for Lac Croche samples, where $O_{2}$ was measured using a dual-inlet mass spectrometer [Guillemette and del Giorgio, 2011]. All samples showed linear decreases of $O_{2}$, and respiration rates were derived as the slope of the $O_{2}$ concentration versus time plots. All pelagic respiration rates were then converted into C units assuming RQ of 1. It has been previously reported that the bacterial RQ measured in similar systems varies as a function of system trophic status and size, from less than 0.7 to over 1.6 [Berggren et al., 2012]. Although the reported average lake bacterial RQ was in the order of 1.2, the predicted RQ for our lakes based on their average chlorophyll and DOC concentrations was somewhat lower, in the order of 0.90 to 1.1, and we have therefore assumed an average RQ of 1 for our three lakes. There was a strong relationship between our measured respiration rates and both DOC and water temperature (see section 3 for details), and we used the resulting multivariate regression model to estimate the areal rates of respiration using depth volume-weighted temperature (as $\Sigma(V_{Z} \times T_{Z})$/ LV, where $V_{Z}$ is the volume of each strata, $T_{Z}$ is the temperature at the corresponding depth, and LV is the lake volume) and DOC as independent variables, multiplied by the lake mean depth.
from variability in the sample replicates and the uncertainties associated with bleaching during incubations in the solar simulator (see supporting information Text S2 for further details). For predicted pelagic respiration values (equation (11)), we used a delogging correction factor (1.33) calculated from the standard error of the estimate [Sprugel, 1983] to remove the bias introduced by the logarithmic transformation [Baskerville, 1974]. We calculated the 95% confidence interval around the predicted values in the software R [R Development Core Team, 2008]. We evaluated the potential uncertainties in the relative contribution of PM by performing a Monte Carlo simulation using the slope parameter errors in the multiple regression predicting pelagic respiration (equation (11)) and uncertainties from PM. As a result, this allowed us to have an additional uncertainty estimation for the pelagic respiration itself. To assess the importance of each component in the calculation of PM rates, we used partial regression analysis (JMP 7.0, SAS Institute). Variables used in the multiple regression analysis for the pelagic respiration itself. To assess the importance of each component in the calculation of PM
terms, we ran Monte Carlo simulations for each sample (999 iterations), in which each parameter in the calculation is randomly picked from a normal distribution around its mean value. Parameters selected to induce potential uncertainties in the resulting AQY (and thus PM) were related to uncertainties in DOC mineralization resulting from variability in the sample replicates and the uncertainties associated with bleaching during incubations in the solar simulator (see supporting information Text S2 for further details). For predicted pelagic respiration values (equation (11)), we used a delogging correction factor (1.33) calculated from the standard error of the estimate [Sprugel, 1983] to remove the bias introduced by the logarithmic transformation [Baskerville, 1974]. We calculated the 95% confidence interval around the predicted values in the software R [R Development Core Team, 2008]. We evaluated the potential uncertainties in the relative contribution of PM by performing a Monte Carlo simulation using the slope parameter errors in the multiple regression predicting pelagic respiration (equation (11)) and uncertainties from PM. As a result, this allowed us to have an additional uncertainty estimation for the pelagic respiration itself. To assess the importance of each component in the calculation of PM rates, we used partial regression analysis (JMP 7.0, SAS Institute). Variables used in the multiple regression analysis were log10-transformed to adjust to a normal distribution. We compared CDOM (a440), respiration, AQY, PM, and proportion of PM to total CO2 production values between lakes and seasons (values were clustered by season according to sampling date with n of 2–4 per season) using two-way (with interaction) ANOVA with weighted response when possible (1/variance) using JMP 7.0 statistical software (SAS Institute). Spring refers to measurements made between ice melt until the beginning of June, summer refers to samples taken between late June to late September, and fall refers to samples taken during October until the lake is covered with ice (i.e., late November to early December).

3. Results
The concentration of DOC and CDOM in the surface waters of the three lakes are presented in Table 1. CDOM, measured as absorbance at 440 nm, was significantly different among lakes (see supporting information Figure S5 for the range in absorption coefficient spectra) but did not show significant seasonal variation (two-way ANOVA). CDOM also directly affected the light penetration in the water column, and the light extinction coefficients (Kd,λ) at different wavelengths were strongly related to CDOM (Table S3 in the supporting information). The average lake UV light extinction coefficient (Kd320) was 18.9, 19.7, and 10.6 m−1 for Lac Hébécourt, Simoncouche, and Croche, respectively.

3.1. DOC Photoreactivity and Photochemical CO2 Production
The intrinsic photoreactivity of DOC was estimated using standardized laboratory incubations under simulated sunlight. Average DOC mineralization (as DOC loss and DIC production) during light incubation was 0.41 mg C L−1 d−1 (ranging from 0.06 to 1.12 mg C L−1 d−1) and was weakly but significantly positively related to the initial CDOM (lognormal linear regression, r² = 0.18, p = 0.03). DOC and DIC concentrations after 24 h of irradiance were generally significantly different from the initial concentration (p < 0.05, t test). We further corrected the DOC loss per amount of photons absorbed in the vial (i.e., wiAQY as mol C loss per mol photon absorbed), which yielded an average wiAQY of 0.00026 ± 0.00016 (mean ± SD). The average wiAQY for Lac Croche (0.00019) and Lac Simoncouche (0.00020) were very similar, whereas Lac Hébécourt showed lower (significantly different, two-way ANOVA, p = 0.04) average wiAQY (0.00008). Although wiAQY seemed to
follow a seasonal pattern, being generally higher in spring and autumn and lower in the middle of the summer (Figure 1), this was not statistically justified by the two-way ANOVA test ($p > 0.05$). Figure 2 further shows the AQY spectra grouped by periods, where the average spectral AQY for all three lakes peaked after ice melt and was higher than the summer and fall averages.

We combined the estimated spectral AQY, ambient irradiance and water column irradiance extinction, to estimate the photochemical DOC mineralization. The modeled volumetric rates ($PM_z$) were in reasonable agreements with in situ measurements of volumetric photomineralization rates (see supporting information Figure S4). Morphometry-weighted estimates of areal DOC photomineralization (PM) averaged 23.8 mg C m$^{-2}$ d$^{-1}$ (ranging from 2.5 to 104.2 mg C m$^{-2}$ d$^{-1}$) and were not significantly different between lakes (two-way ANOVA, $p = 0.92$). On an annual basis, PM averaged 4.4 ± 0.7 g C m$^{-2}$ yr$^{-1}$, and was 4.9, 3.6, and 4.7 g C m$^{-2}$ yr$^{-1}$ for Lac Hébécourt, Lac Croche, and Lac Simoncouche, respectively (see supporting information Figure S6 for the annual integration from monthly rates). PM also followed an apparent seasonal pattern, which was consistent between the different lakes, being typically higher in spring (averaged measured rates of 39.2 mg C m$^{-2}$ d$^{-1}$), and decreasing during the summer to rates around 18.3 mg C m$^{-2}$ d$^{-1}$ (Figure 3a). However, no statistical difference was found between seasons ($p = 0.19$). There were deviations from this pattern in PM in Lac Simoncouche, where PM peaked in June–July rather than right after ice-out. We performed a series of multiple regression analysis to assess the relative

![Figure 2](image-url)

*Figure 2.* Estimated apparent quantum yield spectra based on the assumption that the slope parameter corresponds to the spectral slope of the absorbance spectrum. "Ice-out" is the (three lakes) average of the values recorded immediately after ice-out ($n = 3$), "Mid-summer" is the (three lakes) average of July and August values ($n = 6$), and "Fall" spectrum (orange line) is the (three lakes) average of September, October, and November samples ($n = 6$). The grey area represents the range of measured AQY spectra ($n = 5$) reported in Koehler et al. [2014], and the grey dashed line is the fitted AQY spectrum reported in Vähätalo et al. [2000].

![Figure 3](image-url)

*Figure 3.* (a) The areal photochemical DOC mineralization (mg C m$^{-2}$ d$^{-1}$) and (b) the areal pelagic respiration (mg C m$^{-2}$ d$^{-1}$) from lakes Hébécourt (orange circles), Croche (green circles), and Simoncouche (blue circles). Error bars for photomineralization are the standard deviation around the average values, computed from error in the DOC degradation during the incubation and the uncertainties in the light absorption in the vial (see section 2 for details on the calculations). Error bars on the pelagic respiration are the standard deviation around the average values, computed from the slope parameter error of the multiple regression model (see section 2). We additionally plotted the lower and upper 95% confidence interval (matching color bars). Note that all measurements from various years are presented on the same time line.
The relative contribution of PM to whole-lake pelagic CO2 production (photo + respiration) averaged 14% (range 1%–49%) across all our samples, and followed a seasonal pattern similar to that of PM (Figure 4), where spring contribution was the highest. The contributions were statistically different between lakes (p = 0.04; two-way ANOVA) and seasons (p = 0.01; two-ANOVA).

### 3.3. Relative Importance of Photochemical DOC Mineralization to Lake Pelagic CO2 Production

The relative contribution of PM to whole-lake pelagic CO2 production (photo + respiration) averaged 14% (ranging from 1% to 49%) across all our samples, and followed a seasonal pattern similar to that of PM (Figure 4), where spring contribution was the highest. The contributions were statistically different between lakes (p = 0.02; two-way ANOVA) and seasons (p = 0.02; two-way ANOVA), even if there were large uncertainties.
associated with the spring values. During spring, all lakes showed a greater average contribution of PM relative to PR (around 26% on average), and the average contribution declined abruptly during the summer to around 7.5%. In all three lakes, there was a slight increase in the contribution of PM of up to 12% on average toward the fall period. This seasonal pattern in the relative contribution of PM to whole water column CO₂ production was partly driven by strong shifts in the magnitude of water column respiration (Figure 5).

4. Discussion
4.1. Variability in Intrinsic DOC Photoreactivity
We carried out incubations with lake water surface samples under simulated sunlight to determine DOC photomineralization and to estimate the wavelength-integrated apparent quantum yield (wiAQY). Predictably, samples with higher initial CDOM had the highest absolute DOC mineralization rate during light exposure. The relationship between the absolute photomineralization and CDOM, however, was weaker ($r^2 = 0.18$) than the one reported by Lapierre et al. [2013], which used the same approach but worked at the whole network scale, and thus had a much larger DOC and CDOM range. This would suggest that over very large gradients, the absolute amount of photodegradable DOC broadly tracks the bulk DOC [Lapierre et al., 2013]. At the scale of individual lakes, however, the temporal variation in the intrinsic properties of the DOC, reflected in seasonal shifts in the apparent quantum yield of this DOC, overshadowed the temporal patterns in the concentration of DOC or CDOM.

In this regard, our results show temporal shifts and an apparent seasonal pattern in the DOC photoreactivity (reflected as the wiAQY; Figure 1). The lowest values were usually recorded in midsummer, presumably because DOC has already undergone significant photochemical processing and there are low inputs of new DOC during this period. Accordingly, photoreactivity tends to be not only lower but also less variable within and between lakes during the summer period (Figure 1). After ice melt and during fall, however, the DOC photoreactivity tended to depart from this range (Figures 1 and 2), which correspond to periods when DOC, which has been relatively photoprotected either under the ice or in the hypolimnion, is brought to the surface and exposed to sunlight. Our results are however partly blurred by the uncertainties in some samples, thus further measurements in time would be needed to statistically prove the existing seasonal pattern. Nevertheless, the observed apparent seasonal trend agrees with previous studies that have reported enhanced photoreactivity of DOC in spring in both lakes [Lindell et al., 2000; Gonsior et al., 2013] and streams [Porcal et al., 2013]. Relatively high DOC photoreactivity values in fall were also reported in a small boreal lake in Sweden [Groeneveld et al., 2015]. The high values in DOC photoreactivity recorded in late summer and fall (Figures 1 and 2) are likely associated to either the mixing of highly photoreactive hypolimnetic DOC [Gonsior et al., 2013] or from the loading of highly reactive soil DOC following heavy rain events that typically occur in the fall [Raymond and Saiers, 2010]. These periods of intense rain result in an increase in both the lake flushing rate and the input of terrestrial DOC that may be fresher and more photosensitive, driving an overall increase in photoreactivity and therefore also in the production and emission of CO₂ [Vachon and del Giorgio, 2014]. This may suggest potential hysteresis in intrinsic DOC photoreactivity, wherein water residence time correlates to the loading of fresh DOC and also determines the light exposure history of DOC, which in turn shapes its residual photosensitivity. We suggest that events that affect water residence time of lakes, such as major storms and the spring freshet, may modulate the dynamics of photomineralization in lakes, although this direct link is still to be demonstrated.
Lakes had similar temporal patterns in DOC photoreactivity (Figure 1), except in Lac Simoncouche, where the spring peak in wiAQY was delayed compared to the other two lakes. In particular, we observed relatively low DOC photoreactivity value in Simoncouche after ice melt (Figure 1), which suggests that either photoreactive DOC had already been photodegraded by the time we sampled or that it had been diluted by the spring freshet hydrologic load, since both CDOM and DOC also significantly decreased during that period (data not shown). The peak in DOC photoreactivity in Lac Simoncouche came in late spring (Figure 1), when external inputs were already low, suggesting that photoreactive DOC could have been generated within the lake. Macrophyte-derived DOC leachates have been shown to be highly colored [Lapierre and Frenette, 2009] and photoreactive [Anesio et al., 1999]. Since nearly 15% of Lac Simoncouche was covered by macrophytes, we suggest that macrophyte leachates could have represented a potential source of photoreactive DOC in this particular lake, although this hypothesis should be further tested.

Our estimated wiAQYs were well within the values reported for boreal lakes in Scandinavia [Vähätalo et al., 2000; Koehler et al., 2014; Groeneveld et al., 2015], yet our estimated rates of wiAQY immediately after ice melt were in the upper range (Figure 2). This highlights the fact that within a given lake and over an annual cycle, there is considerable variability in wiAQY [Groeneveld et al., 2015]. Our highest spring AQY were nevertheless well below the range of values reported by Cory et al. [2014] for arctic lakes and rivers that are influenced by permafrost, which are among the highest ever reported.

4.2. Depth-Integrated DOC Photomineralization

By combining estimates of water column irradiance and DOC properties, we have been able to model the DOC photomineralization rates in three northern lakes for the whole open-water season. The in situ measurements of volumetric DOC photomineralization performed in July 2015 in Lac Croche further agreed with the modeled rates, thus validating our methods (see supporting information Text S4 for complete results). The estimated PM ranged from 2.5 to 104.2 mg C m$^{-2}$ d$^{-1}$, which covers well the averaged measured depth-integrated CO$_2$ production in boreal lakes in Québec [Soumis et al., 2007], in Swedish [Granéli et al., 1996; Vähätalo et al., 2000; Koehler et al., 2014] as well as arctic lakes [Cory et al., 2014] (Table 2). On an annual basis, the average PM of the three study lakes was almost identical as the annual average reported by Koehler et al. [2014]. Taking only the summer rates, the average PM in our three lakes was 18.3 mg C m$^{-2}$ d$^{-1}$, which is very close to previous estimates for that period of the year [Vähätalo et al., 2000; Koehler et al., 2014], whereas our average spring rates (39.2 mg C m$^{-2}$ d$^{-1}$) was more similar to estimates from other boreal and arctic lakes (Table 2). Similar to seasonal variability in DOC photoreactivity, PM estimated in three lakes thus covered almost the whole range reported in the literature, although a portion of the reported cross-lake variability in PM may be due to differences in the approaches (i.e., measured versus modeled).

<table>
<thead>
<tr>
<th>Study</th>
<th>Study Period</th>
<th>Photomineralization (mg C m$^{-2}$ d$^{-1}$)</th>
<th>Pelagic Respiration (mg C m$^{-2}$ d$^{-1}$)</th>
<th>Ratio of Photomineralization to biomineralization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granéli et al. [1996]</td>
<td>summer, boreal</td>
<td>51.2 ± 5.6$^a$</td>
<td>618.3 ± 224.1$^{a,b}$</td>
<td>0.08</td>
</tr>
<tr>
<td>Vähätalo et al. [2000]</td>
<td>summer, boreal</td>
<td>11.9 ± 4.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Jonsson et al. [2001]</td>
<td>summer, boreal</td>
<td>23.8</td>
<td>161.9</td>
<td>0.15</td>
</tr>
<tr>
<td>Soumis et al. [2007]</td>
<td>summer, boreal</td>
<td>74.8 ± 17.2</td>
<td>187.0$^c$</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>summer, temperate</td>
<td>74.5 ± 17.2</td>
<td>496.7$^d$</td>
<td>0.15</td>
</tr>
<tr>
<td>Cory et al. [2014]</td>
<td>Arctic lake (Toolik)</td>
<td>50.9 ± 13.8</td>
<td>77.2 ± 17.4$^d$</td>
<td>0.66</td>
</tr>
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<td></td>
<td>Coastal arctic lakes</td>
<td>109.8 ± 60.0</td>
<td>24.0 ± 3.2$^d$</td>
<td>4.58</td>
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<td>Koehler et al. [2014]</td>
<td>annual, boreal</td>
<td>16.4 ± 0.2$^e$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>This study</td>
<td>all samples$^f$</td>
<td>23.8 ± 22.6</td>
<td>188.6 ± 126.3</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>summer$^f$</td>
<td>18.3 ± 15.7</td>
<td>244.2 ± 115.1</td>
<td>0.07</td>
</tr>
</tbody>
</table>

$^a$Average of all the lakes, excluding lake Stråken.
$^b$Epilimnetic rates.
$^c$Back calculated from ratio.
$^d$Bacterial respiration only.
$^e$Annual rates divided by 232 of ice free days.
$^f$Average of all (or only summer) samples of the three lakes.

Table 2. Summary of Published (and Original) Values of Photochemical DOC Mineralization and Pelagic Respiration (Average ± Standard Deviation) and the Resulting Ratio of Photochemical DOC Mineralization to Biological Rates
The apparent seasonal trends in areal rates of lake photochemical processes (Figure 3a) resulted from a combination of the seasonal pattern in irradiance and the temporal shifts in DOC photoreactivity. This pattern was coherent across the different lakes, in spite of major differences in their morphometry and hydrology. Despite the uncertainties and large variability between the rates, we observed an important shift that occurred in spring, which could be explained by the combination of greater irradiance and higher photoreactivity of DOC. There is also a question of scale involved: at very large spatial scales, the gradients in both the amount of CDOM [Lapiere et al., 2013] and of irradiance may overwhelm local differences in DOM reactivity [Koehler et al., 2014], but our results strongly suggest that both irradiance and DOC photoreactivity are key factors driving ecosystem scale photomineralization.

4.3. Importance of DOC Photomineralization at the Whole-Lake Scale

Having well-constrained estimates of depth-integrated DOC photomineralization and assessing its temporal patterns is necessary to adequately quantify the importance of photochemical processing of DOC relative to the other C fluxes in lakes. As irradiance and temperature closely track each other on an annual cycle, it could a priori be expected that water column respiration and photomineralization should follow the same overall seasonal pattern. This hypothesis, assumes that photomineralization is driven entirely by irradiance. We, however, found an apparent seasonal decoupling in water column CO₂ production by biological and photochemical processes. Photochemical mineralization was enhanced episodically in spring and fall, whereas respiration followed a smoother seasonal pattern (Figure 3). As a consequence of the temporal decoupling between respiration and photomineralization, the relative contribution of photochemical process to the whole water column CO₂ production (as the sum of photochemical and biological processes) also showed a clear seasonal pattern (Figure 4), despite the large uncertainties in the spring values. The cold water found in the water column after ice-out combined with the availability of highly photoreactive DOC rendered photomineralization equally important with respiration as CO₂ contributor in early spring. As the water warms up and the DOC becomes photobleached and less photoreactive, pelagic respiration becomes the main source of CO₂ production in the lake water column in summer (Figure 4). It should be pointed out that chemical CO₂ production (i.e., calcite precipitation) is not a significant process in any of these lakes.

Although there was a large temporal variability in PM within a given lake, the average open water seasonal values were not significantly different between our study lakes (two-way ANOVA, p > 0.05), despite significant differences in bulk DOC and CDOM concentrations (see section 3). This low interlake variability in PM probably reflects the interplay between DOC concentration and light penetration. Because of the rapid absorption of UV light by DOC in the water column, rates of DOC photomineralization declined rapidly with depth. We evaluated that on average, about 40%, 80%, and 90% of the photomineralization occurred in the top 0.1, 0.5, and 1 m, respectively. This depth dependency of photomineralization is similar to that reported by Koehler et al. [2014], who estimated that 95% of the mineralization in boreal lakes occurred in the top 0.8 m. Because our lakes are deeper than 2 m on average, most of the UV light is absorbed by both water and mostly DOC, resulting in a reduced influence of morphometry and DOC content on the depth-integrated DOC photomineralization across our lakes. In contrast, despite the sometimes large uncertainties around the predicted respiration rates, there was a larger difference in the amplitude of areal water column respiration rates between the lakes relative to that in PM, mostly due to lake depth and DOC concentration. As Lac Hébécourt and Lac Simoncouche are both shallow, the difference in amplitude is mainly explained by the DOC concentrations. For Lac Croche, in spite of its oligotrophic condition, its deeper basin results in areal respiration rates that are intermediate between two other lakes (Figure 3b), suggesting that deep oligotrophic lakes may still be important sites of biological CO₂ production. It is however important to mention that as respiration rates were measured using surface water samples, extrapolating hypolimnetic rates can be problematic, which is particularly the case in a well-stratified water column like in Lac Croche (see supporting information for vertical profiles data). However, the smaller volume in the deeper layers (about 30% of the whole lake volume in Lac Croche) together with lower respiration rates because of the lower temperature results in a relatively small contribution of hypolimnetic respiration at the whole lake scale (less than 10% in the case of Lac Croche). As a result, using models derived from surface waters to extrapolate areal respiration rates is unlikely to yield overly biased estimates, and we maintain that the resulting temporal patterns are robust. Nonetheless, because there were still large uncertainties around the predicted values (Figure 3b), individual areal respiration rates must be interpreted with caution.
The overall annual contribution of photochemical DOC mineralization to the total water column CO₂ production averaged 14% for all three lakes combined (Figure 4). Although PM rates were similar between the different lakes, the relative contribution of PM was slightly more variable across lakes: PM in shallow and unproductive Lac Simoncouché contributed to 17% of the total water column CO₂ production, whereas in productive Lac Hébécourt and deep Lac Croche PM contributed to about 12–13%. This range was mainly due to cross-lake differences in areal pelagic respiration rates, which were significantly different despite their sometimes large uncertainties. Our findings are not incompatible with other studies that have also compared rates of photochemical with biological processes. For example, Cory et al. [2014] reported a very high contribution of DOC photochemical mineralization in subarctic rivers and lakes (sometimes over 100%), and that pattern was a combination of highly reactive DOC in these systems with consistently low respiration rates due to low temperature. In contrast, Granéli et al. [1996] reported a relatively modest contribution (around 8%) of photochemical DOC mineralization relative to respiration in Swedish boreal lakes. The cross-system variation in the relative contribution of photochemical mineralization reported in these previous studies follows a gradient in pelagic respiration (Figure 5), which seems to stabilize at a minimum of around 0.1 (i.e., photochemical mineralization is 10% of biological respiration). The underlying reasons are not clear, however, because in our study, periods of low respiration coincided with peaks in photochemical activity and vice versa. Having considered the entire ice-free period, however, allowed us to capture both temporal shifts in DOC photoreactivity and water temperature that affect DOC processing (biological and photochemical) differently, highlighting the importance of spring and fall periods (as well as cold water systems, i.e., left part of Figure 5) when DOC processing is not expected to be intense, with implications on our understanding of lake C cycling.

We have shown here, like other studies, that photochemical DOC mineralization represents a significant C flux in these northern lakes and thus potentially a significant component of the CO₂ budget in these lakes. Previous studies have reported relatively high spring emissions from northern lakes, presumably due to the release of CO₂ accumulated under the ice in boreal and subarctic regions [Karlsson et al., 2013; Ducharme-Riel et al., 2015]. Combining our results of PM with the annual CO₂ cycle for these lakes reported by Ducharme-Riel et al. [2015] suggests that photochemical mineralization of photosensitive DOC could contribute around 20% of spring CO₂ emissions. We can further express the role of PM in terms of its potential to sustain ambient CO₂ concentrations in lake surface waters. We estimate that CO₂ photoproduction could potentially contribute to the equivalent of 28 µatm on average and up to 50–150 µatm during peak production in early spring, once gas exchange has been factored in [Vachon and Prairie, 2013]. These results suggest that although photomineralization cannot by itself sustain the systematic CO₂ supersaturation that has been observed across these temperate and boreal lakes, which typically ranges from 450 to over 1000 µatm [Lapiere and del Giorgio, 2012; Rosilo et al., 2014], it is nevertheless a significant contributor to this phenomenon.

Acknowledgments
We would like to thank Alice Parkes, Annick St-Pierre, Mathieu Dumais, and Jean-Philippe Desinées for field and laboratory assistance. We also thank Sara Mercier-Blais for providing complementary data on Lac Croche, Philippe Massicotte for useful comments on previous version of the manuscript, Drs. J.-J. Frenette and R. Carignan for help with the PUV measurements and Y.T. Prairie for help with statistical analyses. We thank two anonymous reviewers for their constructive and helpful comments. This project was part of the large-scale research program of the Industrial Research Chair in Carbon Biogeochemistry in Boreal Aquatic Systems (CarBAS), cofunded by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Hydro-Québec. NSERC doctoral scholarship and UQAM-FARE scholarship was also attributed to DV. Data are available on request from DV.

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