Removal of chromophoric dissolved organic matter under combined photochemical and microbial degradation as a response to different irradiation intensities

Theis Kragh[1],*, *Kaj Sand-Jensen*[2], *Emil Kristensen*[1,2], *Ole Pedersen*[2], *Mikkel Madsen-Østerbye*[2]

[1] *Department of Biology, University of Southern Denmark, Syddanmark 5230, Denmark*
[2] *Freshwater Biological Laboratory, Department of Biology, University of Copenhagen, Copenhagen 2100, Denmark*

ARTICLE INFO

ABSTRACT

Throughout the freshwater continuum, Dissolved Organic Carbon (DOC) and the colored fraction, Chromophoric Dissolved Organic Material (CDOM), are continuously being added, removed, and transformed, resulting in changes in the chromophoricity and lability of organic matter over time. We examined, experimentally, the effect of increasing irradiation-intensities on the combined photochemical and microbial degradation of CDOM and DOC. This was done by using a simulated mixed water column: aged water from a humic lake was exposed to four irradiation-intensities – representing winter, early and late spring, and summer conditions (0.10, 0.16, 0.36, and 0.58 W/m^2) – and compared with dark controls over 37 days. We found a linear relationship between CDOM degradation and irradiation-intensities up to 0.36 W/m^2; the degradation rate saturated at higher intensities, both at specific wavelengths and for broader intervals. After 37 days at high irradiation-intensity, CDOM absorption of irradiation at 340 nm had been reduced by 41%; 48% of DOC had been removed and DOC degradation continued to increase. Aromaticity (SUVA$_{254}$) declined significantly over 37 days at the two lowest but not at the two highest UV- intensities; levels in unexposed control water remained constant. Direct observations of the humic lake showed that CDOM absorption of irradiation (340 nm) declined by 27% from winter to summer. A model based on hydrological CDOM input and CDOM degradation calculated from field measurements of UV-radiation and experimental CDOM degradation with UV-exposure from sunlight accurately predicted the annual course as observed in the lake. With no external CDOM input, 92% of the CDOM could be degraded in a year. The results support the notion that combined photochemical and microbial CDOM degradation can be remarkably higher in lakes than previously thought and that humic lakes retain their color due to light absorption by ongoing CDOM input.

* Corresponding author.
  E-mail: tkragh@biology.sdu.dk (T. Kragh).

Introduction

Dissolved organic matter (DOM) is the largest dynamic pool of organic carbon in both marine and freshwater ecosystems. It is quantified as the concentration of dissolved organic carbon (DOC) (Benner, 2002; Cole et al., 2007). DOC concentrations in lake and stream surface waters have increased over the past 30 years in many parts of the Northern Hemisphere (Monteith et al., 2007). This DOC increase has been accompanied by a parallel increase in Chromophoric Dissolved Organic Material (CDOM, also known as Gelbstoff), since CDOM in lakes commonly constitutes 50%–70% of DOC (Aiken et al., 1985). CDOM mainly comprises complex refractory substances of partially degraded cellulose, hemicellulose, and lignin, which entered the watercourse from the terrestrial environment. The process of increasing light absorption by CDOM is often referred to as browning or brownification of the water (Kritzberg and Ekstrom, 2012; Roulet and Moore, 2006).

Increasing DOC concentrations and light absorption by CDOM have been attributed mainly to a combination of four factors (Clark et al., 2010): (i) warmer climate (Pagano et al., 2014) and the associated increased precipitation and runoff from land (Fasching et al., 2016; Weyhenmeyer et al., 2012); (ii) ecosystem recovery from decades of acidification in the 1970–1980s, now resulting in higher pH and increased DOC mobility in the catchment soils (Ekstrom et al., 2011; Monteith et al., 2007); (iii) changes in catchment vegetation driven both by climate-induced "greening" (Finstad et al., 2016) and afforestation (Kritzberg, 2017); and (iv) carbon-iron interactions and rising iron concentration in surface waters (Kritzberg and Ekstrom, 2012; Weyhenmeyer et al., 2014). The importance of each factor on increasing brownification is hard to separate because all four coincide and interact within the ecosystems (Clark et al., 2010; Roulet and Moore, 2006).

The presence of DOC and CDOM in lakes can profoundly affect ecosystem structure and function. Brownification impairs the water's light climate and thus reduces the primary production potential and the distribution of submerged aquatic plants in the affected lakes (Karlsson et al., 2009; Sondergaard et al., 2013). Increasing DOC input also increases the inorganic nutrient pool through photochemical and microbial DOC degradation (Berggren et al., 2015). Given the fundamental ecological influence of brownification on environmental conditions, metabolism, and food webs (Jansson et al., 2007; Sand-Jensen and Staehr, 2007), it is imperative to understand the processes behind the internal chromophoric removal in lakes and wetlands.

In the recent past, freshwaters were considered to be passive systems that transported DOC to the ocean. More recently, however, it has been recognized that a major fraction of the organic carbon exported from land is processed and lost on its way through the freshwater conduit (Battin et al., 2009; Cole et al., 2007; Tranvik et al., 2009), a finding that emphasizes the important but hitherto unacknowledged role played by inland waters in the global carbon cycle (Tranvik et al., 2009). As an example, Catalán et al. (2016) document a much shorter half-life of organic carbon in freshwater than in terrestrial soil and marine water.

Two fundamental processes remove or transform DOC in inland waters. Part of the DOC is degraded microbially and converted to carbon dioxide, which is released into the atmosphere (Fasching et al., 2014; Lapierre et al., 2013), while another part forms into aggregates that sink to the lake sediment and become buried (Cole et al., 2007). The latter process can contribute to the removal of up to 30% of DOC (Vachon et al., 2017). The remaining DOC, which is not processed in freshwater, is transported to the coastal water and the sea.

Degradation processes in the water are accelerated by UV-radiation, which can play an essential role in DOC mineralization – particularly in shallow streams and lakes, in which UV-impacted surface water represents a high proportion of the total water volume (Cory et al., 2014; Koehler et al., 2014). The UV-mediated degradation, also referred to as photobleaching, transforms CDOM into more-labile non-chromophoric DOC compounds, which are more easily remineralized by bacteria (Del Vecchio and Blough, 2002; Moran and Zepp, 1997). UV-radiation can open chemical structures (e.g. double bonds in phenolic ring structures) and bacteria can subsequently break down the new chemical substances and gain energy for their metabolism and molecules for their growth (Lanzalunga and Bietti, 2000). The presence of reactive oxygen species (ROS) generated by UV-exposure can impede bacterial DOC degradation to some extent (Scully et al., 2003). The actual concentration of DOC in lakes is thus influenced by a combination of four factors: in-lake processes related to the variable magnitude and the composition of DOC input, lake depth, and water retention time (Kohler et al., 2013).

Bacteria use the non-chromophoric, labile DOC fraction and, over time, the lake water is left with increasingly high proportions of recalcitrant and chromophoric DOC. Studies have shown that exposing these chromophoric compounds to UV transforms them into more-labile compounds, which bacteria can degrade (Del Vecchio and Blough, 2002; Helms et al., 2008; Madsen-Østerbye et al., 2018; Moran et al., 2000; Vachon et al., 2017). This suggests that sunlight and particularly UV-exposure of CDOM is the main factors in the degradation and removal of chromophoric compounds (Cory et al., 2014).

Traditionally, CDOM degradation experiments have consisted of a single-dose UV treatment followed by incubation of the treated water in darkness, after which the extent of bacterial degradation in the dark conditions is measured (Del Vecchio and Blough, 2002; Helms et al., 2008; Moran et al., 2000; Vachon et al., 2017). This approach enables an examination of first-order degradation kinetics. However, emerging studies address the importance of combining exposure to irradiation with microbial degradation in a circulating water column (Jones et al., 2016; Madsen-Østerbye et al., 2018). Intuitively one might expect that the coupled irradiation-exposure and microbial degradation may increase the degradation of organic matter, particularly of the most recalcitrant fractions. A tight coupling may be established between the UV-mediated opening of firm chemical structures and the continued enzymatic degradation by the bacteria. If this is so, then an experimental application that couples irradiation-exposure with microbial degradation would enable us to obtain a more realistic measure of the potential reduction of CDOM light absorption and the ensuing lake brownification as it takes place in nature.

Few studies have addressed the direct effect of irradiation-intensity on the loss of CDOM in an experiment that simulates a circulating water column. Madsen-Østerbye et al. (2018) show a linear CDOM degradation over time under simulated natural conditions with coupled irradiation-exposure and microbial degradation. However, the influence of increasing irradiation-intensity on CDOM lability and chromophoric removal in a circulating water column experiment is not known.

Weishaar et al. (2003) looked for an operational way to study the ratio between labile and non-labile DOC compounds. They show that UV-absorption at a wavelength of 254 nm, when normalized to the DOC concentration, correlates strongly ($r^2 > 0.97$) with a carbon aromaticity parameter named specific UV-absorbance ($SUVA_{254}$). In addition to aromaticity, the change in the $SUVA_{254}$ ratio reflects which organic fractions are mainly utilized by bacteria over time. An increase in the ratio reflects a higher loss of non-chromophoric DOC compared to chromophoric DOC, and *vice versa*. Thus, the $SUVA_{254}$ ratio offers a proxy for assessing both chemical (Weishaar et al., 2003; Westerhoff et al., 2004) and biological reactivity in the natural DOC pool (Asmala et al., 2013; Berggren et al., 2009).

Here, we introduce a new experimental approach in order to quantify the coupled degradation of DOC and CDOM by irradiation and microbial degradation over week-long periods. Our previous work shows that photobleaching's direct effect represents a small fraction, compared to chromophoric removal when water was continuously circulated between irradiation-exposure and microbial degradation in the dark (Madsen-Østerbye et al., 2018).

In the present study, we used an experimental system to quantify the degradation of DOC and CDOM as well as to unravel the possible shifts in aromaticity as organic molecules are degraded and transformed over time. We then constructed a model to estimate the degradation and the resulting decline of CDOM absorption coefficients. Finally, we evaluated the ecosystem relevance of our results by comparing our estimates with CDOM absorption coefficients measured over a year in the humic lake that was the source of the water used in our experiments.
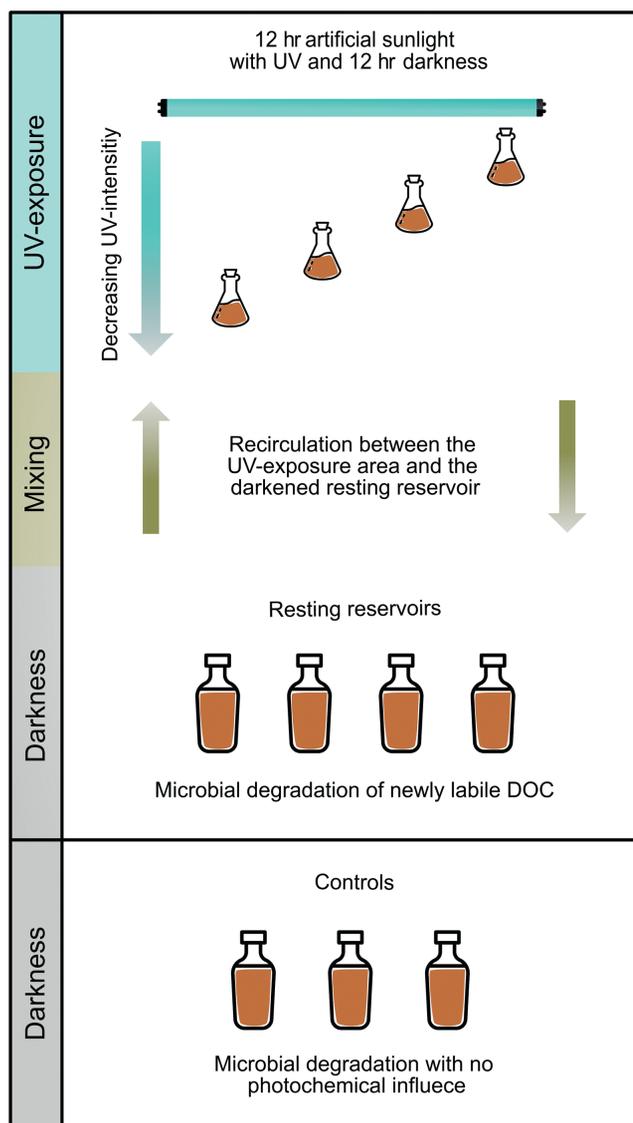

Fig. 1 – The experimental setup where the water was exposed to radiation in one part and transported into larger water reservoirs in darkness. The controls were kept in darkness.

1.   Materials and methods

In order to quantify the combined effects of irradiation-exposure and microbial-mediated degradation of CDOM and DOC, we conducted an experiment in which lake water was subjected to four irradiation-intensities (0.1 to 0.58 W/m^2) and then to darkness control while maintaining ongoing microbial degradation. The experimental setup was designed to mimic the slow vertical mixing of a natural water column in which only organic matter in near-surface water is exposed to UV-radiation (Morris et al., 1995), after which this water is transported to deeper layers, where it undergoes microbial degradation (Fig. 1). The circulating system adopted the design introduced by Madsen-Østerbye et al. (2018)) and consisted of three replicates and one control at each irradiation-intensity.

1.1.   *Sample water*

Water was collected in February 2017 from 2 m depth in humic Lake Tvorup, located in Thy National Park in northwest Jutland, Denmark (56°91′N, 8°46′E). The lake has a maximum depth of 5.4 m and an average depth of 2.7 m. Like many humic lakes in the Scandinavian boreal zone, Lake Tvorup is surrounded by conifer plantations and heathland (Algesten et al., 2004; Verpoorter et al., 2012). After collection, we aged the lake water in darkness for six months at 4°C. This was done to remove all labile compounds in the water, leaving only recalcitrant compounds that can be transformed by solar radiation into labile DOC that subsequently can be microbially degraded. The composition of organic material in the aged water probably resembles that in the lake's incoming groundwater,

which had been in the dark and exposed to bacterial decomposition in the soil for such a long time that no further degradation could occur before the water is exposed to irradiation (Madsen-Østerbye and others 2018).

Before starting the experiment, all equipment was acid rinsed. 90% of the initial water volume was passed through a Whatman GF/F filter (nominal pore size 0.7 µm) to remove all particles, heterotrophic flagellates, and microalgae. The remaining 10% of the water volume was passed through a GF/C filter (nominal pore size 1.2 µm) to maintain the bacteria in the water that would be used as an inoculum, while removing larger heterotrophic flagellates and microalgae. Previously, it has been shown that bacteria from an inoculum of this filtered size range can rebuild their biomass within 0–7 days in similar experimental setups (Kragh et al., 2008; Risse-Buhl et al., 2013). Thus, samples for bacterial counts were taken out at T_0 and T_{37}, stored at -20°C, and counted microscopically according to Kragh et al. (2008).

1.2.   *Experimental design*

The experimental system was divided into two parts. In one part, water was transported into small quartz vials (0.05 L), where it was exposed to radiation. In the other part, water was returned to a larger water reservoirs (1 L), where microbes degraded the organic matter in total darkness (Fig. 1). Transportation between the two parts occurred via inert PTFE Teflon tubing in a closed circuit driven by a BT100-L multi-channel peristaltic pump (Langer Instruments, USA). The rate of water flow corresponded to 100% of water circulation every 24 hr. Samples were removed for analysis every seven days. Each sampling slightly reduced the water volume, and the flow rate was adjusted to maintain an unaltered exposure time to radiation. Previous tests (Kragh et al., 2008) have shown no bottle effect; that is, degradation rates and bacterial cell numbers were shown to be constant regardless of bottle size, including 1 l. The lack of bottle effect is in accordance with Hammes et al. (2010). We also performed a full experimental run using only MQ water samples, which did not lead to increases in DOC. For these reasons, we are confident that our experimental setup did not bias our results.

As water circulated through the quartz vial, it was exposed to radiation in a cycle with 12 hr of exposure and 12 rh of darkness. A Q-Panel UVA-340 lamp (Q-LAB, USA) provided a spectral composition similar to natural sunlight in the wavelength region 295–365 nm (Q-lab 2019).

Quantum yields for DOC photodegradation are highest in the high-energy UVB portion of the spectrum (Mopper and Kieber, 2000). However, depending on location (lat/long), date, time, and sky conditions, more than 10 times as much visible light than UV can reach the water surface; thus, the action spectrum of DOC photodegradation can be quantitatively dominated by visible light, not UV. The water circulated from the light chamber to the larger water reservoir, which was kept in complete darkness for microbial degradation of labile compounds produced by radiation. Thus, 5% of the total water volume was exposed during the 12 hr of radiation, corresponding to a circulating water column in which the upper 5% near the surface receives radiation during the day. The experiment was conducted at 20°C.

Water was exposed to four irradiation-intensities: 0.58 W/m², 0.36 W/m², 0.16 W/m², and 0.01 W/m² at 340 nm. The choice of irradiation-intensities in the experiment was based on field measurements using a Black Comet UV-VIS spectrometer model CXR (StellarNet Inc., USA). From field measurements between sunrise and sunset on sunny days, we validated the spectrum of the experimental light source and the spectrum of the sunlight at the field site. We then established the relationship between UV-intensity measured with the Black Comet UV-VIS and PAR-intensity as measured by HOBO PAR sensor (400–700 nm): (S-LIA-M003, Onset Computers). Having established this relationship, we could calculate the daily irradiation-intensity for the entire year based on PAR-measurements alone. The PAR measurements were taken continuously at the lake site. The highest measured summer radiation of 0.62 W/m² at 340 nm was close to the maximum intensity (0.65 and 0.68 W/m²) used in previous experimental studies (Kragh et al., 2008; Vachon et al., 2017). However, our experimental lamp and design restricted maximum UV-exposure to 0.58 W/m² at 340 nm. The highest (0.36) and lowest (0.16 W/m²) UV-radiation measurements during spring were used. The lowest UV-intensity of 0.1 W/m² in the experiments corresponded to winter radiation. A setup of triplicates was kept in complete darkness during the experiments to measure microbial degradation without exposure to irradiation.

An experiment with photodegradation only was performed to measure the extent of photodegradation without bacteria. The water received a irradiation-dose of 0.58 W/m², corresponding to the accumulated irradiation-dose received over 37 days in the experimental design. Prior to incubation, all the water was GF/F filtered twice to minimize the number of bacteria.

1.3.   *Sampling and analyses*

The experiment lasted for 37 days. Water samples were retrieved every week, filtered through pre-combusted GF/F filters, and analyzed for DOC and CDOM. Before each collection and filtration of samples, all experimental incubating bottles were checked visually for flocculation and homogenized to minimize particles' effects. The GF/F filters were analyzed for flocculates of particulate organic carbon (POC), following Kragh et al. (2008). Observed minute amounts of POC were accounted for in the calculations of DOC degradation (POC < 0.3%).

DOC samples were conserved with 150 µL 2 mol/L HCL per 15 mL sample and measured on a Total Organic Carbon Analyzer (Shimadzu instruments, USA), as introduced by Kragh and Sondergaard (2004). DOC was measured by the non-purgeable organic carbon (NPOC) method with a 3-point calibration curve ($r^2 = 0.998$) and with at least three technical replicates/injections of each DOC sample to ensure statistical confidence. Standard series and blanks were included for each experimental run and showed that the analytical method had an accuracy of ±1%. All DOC samples were treated in an ultrasonic bath and whirl mixed to separate flocculation induced by the pH reduction used for preservation (Kragh et al., 2008).

CDOM absorbance of light was measured on a UV-1800 spectrophotometer (Shimadzu instruments, USA) fitted with
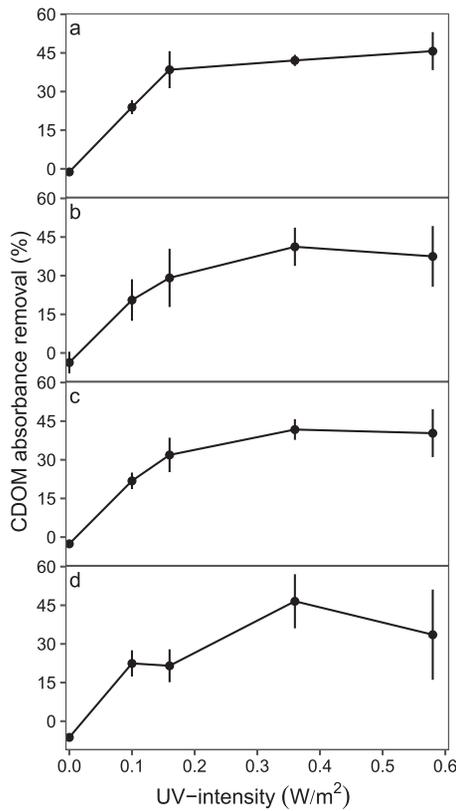
Fig. 2 – CDOM removal after 37 days as a percentage of the initial values *versus* daily UV-intensity (W/m^2) at two specific wavelengths (a) 340 nm and (b) 440 nm and two intervals (c) 400–700 nm and (d) 300–700 nm. Mean values (± standard error of the mean, SEM, n = 3). Saturation curve analysis showed $r^2 > 0.969$ for the two specific wavelengths (a and b), $r^2 = 0.824$ for 400–700 nm (c) and $r^2 = 0.978$ for 300–700 nm (d).

ground constant (m^{-1}) that accounts for scattering produced in the cuvette by small particles or bubbles, and S is the spectral slope parameter (nm^{-1}) that describes the approximate exponential decrease in absorption with increasing wavelength.

1.4.   *Field measurements and modeling*

In order to evaluate whether the degradation rates found in the experiment followed natural conditions, we monitored Lake Tvorup closely for a year. A meteorological station was established 15 m from the shore, 2 m above the lake surface. The station was equipped with a sensor for daily radiance (HOBO PAR sensor (400–700 nm): S-LIA-M003, Onset Computers), a data logger (HOBO micro station, H21-002, Onset Computers) and a tipping bucket for precipitation measurements (HOBO rain gauge data logger: RG3, Onset Computers) with a recorder (H07-002-04, Onset Computers). Every week, water samples were collected at one-meter depth from the deepest part of the lake and analyzed for CDOM (as described above) to document the *in situ* development of CDOM absorption coefficients. The daily solar PAR-radiation between 9 a.m. and 3 p.m. was used to estimate the average UV-radiation in the daily window when UV-radiation is sufficiently high to stimulate a reduction of CDOM absorption. The average daily radiation was used to calculate the reduction of CDOM absorption according to the experiments' mean values over 37 days.

To estimate CDOM degradation in a closed system with no hydrological CDOM input, we calculated CDOM degradation in the humic Lake Tvorup day-by-day for the entire year. To model an open system in which CDOM in natural groundwater enters a lake, where it is degraded, we calculated CDOM light absorption every day and summed them in 14-day intervals over the year for comparison with the measured CDOM absorption. In order to compare seasonal degradation with seasonal measurements of CDOM, we used a CDOM absorption coefficient in the inflow of 1.37 m^{-1} at 340 nm and a mean water retention rate (WRR) of one lake volume per year, based on direct measurements in Lake Tvorup (Kristensen et al., 2018). Given the mean WRR value, the seasonal variation of water inflow was assumed to follow the 14-day moving average of precipitation throughout the year, which we had measured directly at the site. Precipitation varies extensively from day to day, while groundwater inflow is smoothed over time by gradual changes of the groundwater table. For that reason, we used accumulated precipitation over 14 days as a proxy measure for groundwater input. The modeled CDOM absorption coefficient at 340 nm is described by the following difference equation (Eq. (2)):

$$\frac{\Delta a}{\Delta t} = a_{prv} - a_{degra} + a_{in} \qquad (2)$$

where the change in CDOM absorption coefficient over time ($\Delta a / \Delta t$) is determined by the previously estimated CDOM absorption coefficient (a_{prv}), the fraction of degradation based on average irradiation-intensity, and the CDOM-irradiation-degradation experiments multiplied by the total CDOM pool (a_{degra}) and the inflow of CDOM (a_{in}). Given that our measurements showed annual inflow to be equal to lake water volume, we could estimate inflow over 14-day intervals (Inflow$_{14\ days}$)

a 1 cm quartz cuvette across the spectrum 300–750 nm with scanning intervals of 1 nm. Absorbance values were converted into Napierian absorption coefficients (αCDOM (λ) by multiplying the absorbance at wavelength λ (nm) by 2.303 (i.e., ln(10)) and dividing by the cuvette path length (Stedmon and Markager, 2001). CDOM absorption is presented at 340 and 440 nm (Fig. 2), which corresponds to the highest UV-intensity at 340 nm, while 440 nm is often used as a reference wavelength of water color and chromophoric content (Cuthbert and Del Giorgio, 1992). CDOM absorption was also calculated for the photosynthetically active spectrum (PAR, 400–700 nm) and the entire analyzed spectrum, 300–700 nm.

DOC and CDOM data were used to assess CDOM aromaticity by normalizing the CDOM absorption coefficients at 254 nm to the DOC concentration, as described in Weishaar et al. (2003). Absorption spectra were modeled down to 254 nm, according to Eq. (1) (Bricaud et al., 1981; Stedmon and Markager, 2001):

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0)e^{-S(\lambda-\lambda_0)} + K \qquad (1)$$

where a_{CDOM} is the absorption coefficient (m^{-1}), λ is the wavelength (nm), λ_0 is a reference wavelength (nm), K is a back-

as the proportion of precipitation in each 14-day interval relative to annual precipitation, multiplied by lake water volume. The inflow of CDOM over each 14-day can thus be understood to be the proportional water inflow multiplied by mean CDOM in groundwater.

1.5.   *Statistical analysis*

All statistical analyses and graphs were made using the GraphPad Prism 7 software package (GraphPad Software, San Diego, CA, USA) or R (R Core Team, 2017). Extrapolation of CDOM light absorption down to 254 nm was made using the *cdom* R package (Massicotte and Markager, 2016). The saturation of CDOM degradation and DOC removal at increasing irradiation-exposure was estimated using the non-linear regression analysis of *one site-specific binding* in GraphPad prism. Differences between SUVA$_{254}$ at different UV-intensities was made for all sampling over time using 2-way ANOVA followed by Dunnett's multiple comparisons test in GraphPad prism. Figures show the mean $\pm$ SEM (standard error of the mean) unless specified otherwise.

2.   Results

2.1.   *CDOM response*

CDOM degradation over 37 days measured at 340 nm and 440 nm and at two wavelength intervals (300–700 nm and 400–700 nm) followed a saturating function with time (Fig. 2). To test the effects of varying irradiation-intensities on CDOM degradation, we subjected the water to four irradiation-intensities. Degradation increased from 24% ($\pm$ 5%, SEM) when the light was presented at an irradiation-intensity of 0.1 W/m^2 to 46% ($\pm$ 10%, SEM) at an irradiation-intensity of 0.58 W/m^2. Between irradiation-intensities of 0 to 0.36 W/m^2, CDOM degradation followed a linear pattern; CDOM degradation saturated somewhere between 0.36 and 0.58 W/m^2. Along the entire interval of visible light, 400–700 nm, CDOM light absorption remained constant between irradiation-intensities of 0.1 and 0.16 W/m^2, thereafter increasing and reaching maximum degradation (46%) at 0.36 W/m^2. No results at different irradiation-intensities showed that the degradation rate moved from a linear decay towards first-order decay with decreasing carbon degradation and, thus, carbon limitation of decay after 37 days.

2.2.   *DOC response*

DOC degradation increased at higher irradiation-intensities (Fig. 3). Compared with zero intensity, degradation of DOC subjected to irradiation-intensity of 0.16 W/m^2 was modestly higher. After 37 days, 13% of the initial DOC pool had been removed, corresponding to a concentration reduction of 1.05 mg C/L. At 0.36 W/m^2, DOC degradation increased to 48% of the initial DOC pool (ca. 7.15 mg C/L). At an even higher irradiation-intensity of 0.58 W/m^2, 55% of the initial DOC pool was degraded over the course of the 37-day experiment (ca. 8.41 mg C/L). At this highest exposure, the DOC level approached but never reached a plateau. The percentage of DOC
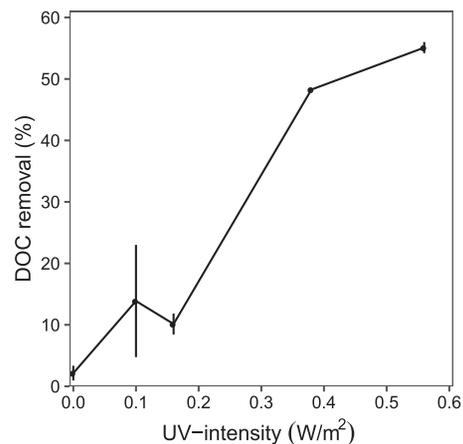

Fig. 3 – DOC removal after 37 days as a percentage of the initial concentration *versus* daily UV-intensity (W/m^2). Mean values ($\pm$ standard error of the mean, SEM, n = 3).

removed at high irradiation-intensity surpassed the percentage of degradation of CDOM absorption. In contrast, at low irradiation-intensities, the decrease of CDOM exceeded that of DOC (Figs. 2 and 3). Similar to CDOM, no experiments of DOC degradation over time indicated a first-order decay. The experiment with irradiation-intensity of 0.58 W/m^2 showed hardly any bacterial degradation (GF/F filtrated twice) over the course of the experiment; only 8% of the initial DOC pool was degraded by photochemical processes alone.

2.3.   *Bacterial response*

Initial bacterial counts were 1.85×10^5 cells/mL($\pm 0.47 \times 10^5$, SEM).

The DOC source used in the experiment was aged, recalcitrant, and did not support more than 2.68×10^5 cells/mL ($\pm 0.77 \times 10^5$, SEM) at the end of the experiment when no exposure to simulated sunlight was applied. Exposure to 0.01 and 0.16 W/m^2 increased the bacterial count to 2.28×10^6 cells/mL ($\pm 0.85 \times 10^6$, SEM) and 2.42×10^6 cells/mL ($\pm 0.39 \times 10^6$, SEM). The highest exposures of 0.36 and 0.58 W/m^2 increased bacterial numbers to 6.34×10^6 cells/mL ($\pm 0.71 \times 10^6$, SEM) and 6.58×10^6 cells/mL ($\pm 0.29 \times 10^6$, SEM), respectively.

2.4.   *Aromaticity-SUVA$_{254}$*

In the dark, aromaticity measured as SUVA$_{254}$ remained constant over time (Fig. 4). At the two lowest irradiation-intensities, SUVA$_{254}$ decreased gradually yet significantly over time and, after 21 days at 0.16 and after 28 days at 0.1 W/m^2 was significantly lower than SUVA$_{254}$ values in water kept in darkness (2-way ANOVA, Dunnet's Multiple Comparison Test, $P < 0.001$–0.05). In contrast, at the two highest irradiation-intensities, there were significant increase of SUVA$_{254}$ ratio compared to dark samples (2-way ANOVA, Dunnet's Multiple Comparison Test, $P < 0.001$).
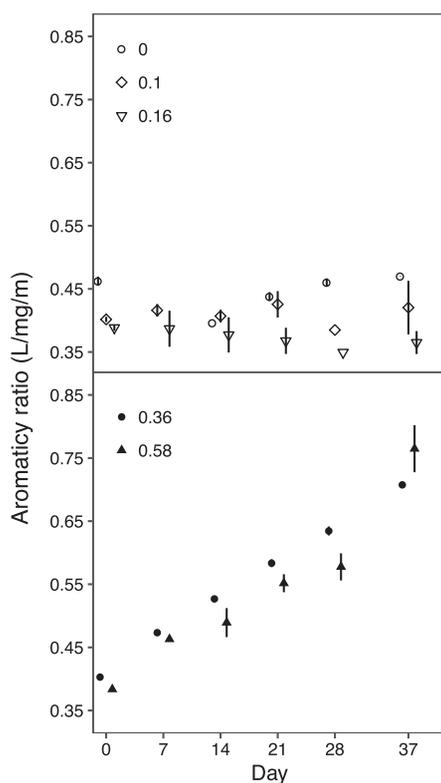
Fig. 4 – Calculated aromaticity, SUVA$_{254}$ ((L/mg DOC/m)) as a function of time up to 37 days for each experimental UV-intensity (W/m^2) and in darkness as indicated for the different symbols. Mean values (± standard error of the mean, SEM, $n = 3$). In several instances, SEM did not extend outside the size of symbols. Samples at zero irradiation-intensity on day seven were lost.

2.5.   *Field measurements and model estimations*

Daily measurements in 2015 at Lake Tvorup show that UV-intensities in the winter were too low to support photochemically induced organic degradation, and our experiments at UV-intensities similar to natural winter intensities support this finding. The winter period included 125 days, or 34% of the year, primarily between 13 November and 1 February. Twenty-five additional days with low radiation and no photochemical degradation were scattered after 1 February, and 21 days were prior to 13 November. In contrast, 109 days, or 30% of days in the year, had irradiation-intensities that supported the highest photochemically induced degradation rates. Finally, 98 days exhibited intermediate photochemical induced degradation and 33 days supported the lowest measurable photochemically induced degradation. Using the 2015 radiation field data and the experimental relationship of CDOM degradation to UV-intensity, 91.7% of the initial CDOM absorption at 340 nm would be degraded within a year.

Overall, observed and modeled seasonal changes of CDOM light absorption accounting for input and degradation followed the same annual course (Fig. 5). Weekly water samples show a 27% CDOM reduction from winter to summer, while
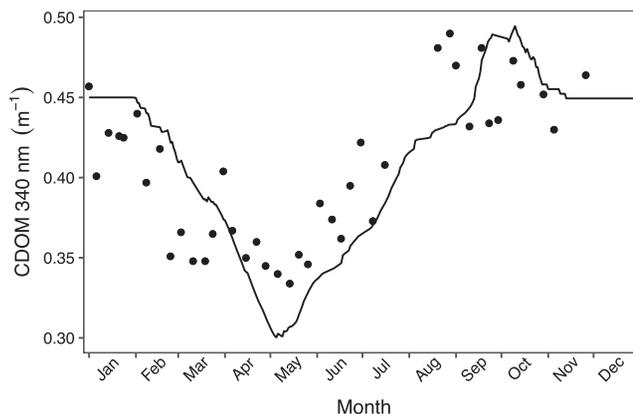

Fig. 5 – Temporal changes of measured and modeled CDOM absorption at 340 nm over a year in Lake Tvorup. The filled circles represent *in situ* samples. The solid line represents modeled data accounting for the inflow of new material and light-induced degradation according to *in situ* light-intensity and experiments on degradation as a function of light-intensity.

model calculations predict a slightly larger chromophoric loss (33%, Fig. 5).

3.   Discussion

3.1.   *CDOM and DOC degradation*

Our observed general reduction of CDOM absorption and DOC concentrations as a response to irradiation-exposure complies well with previous studies (Cory et al., 2014; Del Vecchio and Blough, 2002; Koehler et al., 2014). However, our new experimental setup, which mimics the continuous mixing of the water column, clearly shows a saturation point in CDOM degradation as a response to increasing irradiation-intensities. Initial CDOM degradation at increasing but still-low irradiation-intensity may be consistent with previous studies that indicated prolonged duration of a single initial UV-exposure: a higher combined UV-dose resulted in a higher CDOM transformation to more labile compounds that could be further degraded by bacteria (Kragh et al., 2008; Moran et al., 2000). The irradiation-saturated component of CDOM degradation at exposure to high irradiation-intensity might suggest that at some late point in time, no labile CDOM remains and what is left is non-degradable. It is important to note that this point was not reached in our experiments and would never be reached in nature, where the open system continuously adds new CDOM. Results for the full 37-day experiment showed a more or less linear reduction of light absorption by CDOM throughout. However, we expect that a more extended experimental duration would find that CDOM and DOC degradation slowly become exhausted; any further degradation would follow another pattern.

The accumulated irradiation-dose over 37 days in our 0.36 W/m^2 experiment corresponded to the single-dose experiment used in a previous study by Kragh et al. (2008). Com-

pared to that study, which found a total DOC loss of 27%, we found a remarkably higher loss: more than 47% at 0.36 W/m^2. The result may arise from differences in the constituent elements of each experiment's DOC. However, this explanation does not seem likely because both experiments used water from the same humic lake that had been aged in the dark for six months at 4°C prior to the experiments. The aged lake water has already lost a very high proportions of labile DOC by slow passage through the soils, retention in the lake before sampling and six months storage prior to experimental use. It is more likely that higher DOC turnover arises from differences in the new experimental setup, which mimics natural conditions more comprehensively. As its name implies, earlier studies exposed all water to solar irradiation and then placed all water in the dark for a certain period of time in order to measure the impact of a single dose of radiation on degradation. By contrast, our experiment was designed to mimic more precisely the behavior of water in nature, where organic products produced by irradiation-exposure and microbial degradation over time are continuously re-exposed to radiation, which could and apparently did stimulate ongoing degradation of DOC and also be more representative of processes that happen in nature. It is even more likely that ongoing irradiation-exposure facilitates a more substantial decline of CDOM because re-exposure of initially recalcitrant organic matter to radiation may prepare the organic molecules for subsequent microbial degradation. The notion that the decrease in CDOM and DOC is mainly caused by microbial degradation is supported by the bacterial counts, which in general increased with increasing irradiation. However, we do not know the turnover rate or the proportion of damaged bacteria, which has been shown to increase with increased exposure to irradiation (Maranger et al., 2002). Concurrent to our results, Corin et al. (1998) have shown that the number of colony forming units increased with increasing exposure to irradiation (24–168 hr). Thus, our current finding buttresses findings from our earlier work (Madsen-Østerbye et al., 2018), which showed that a single-dose experiment using forest groundwater resulted in a 1.5% decline of light absorption by CDOM at 340 nm, a parallel experiment using forest groundwater registered a decline of only 2.7%, and a third experiment using lake water saw a decline of 5.8%. By stark contrast, the CDOM decline in our experiments, which coupled irradiation-exposure with microbial degradation, reduced CDOM absorption by a remarkable 87% in heathland groundwater and 20% in forest and lake water. Both results strongly support the notion that irradiation-induced CDOM degradation can be much higher in lake water than previously assumed from single-dose experiments.

We acknowledge that micro-stratification of the water column may develop on extremely calm, sunny days in humic lakes and reduce vertical mixing (Solomon et al., 2015). However, this should have no major influence on CDOM degradation because UV-penetration is confined to the upper few centimeters of the water column in humic lakes (Graneli et al., 1996; Groeneveld et al., 2016; Koehler et al., 2014; Vahatalo et al., 2000), as well as in our experimental setup. The depth of light penetration is shallow because CDOM is absorbing light and undergoing photodegradation (i.e., rates of photodegradation are fast, even if occurring in just the top few cm

of the water column). Thus, even during micro-stratification, mixing will go much deeper than the UV-influenced subsurface water. On the other hand, the rate and extent of degradation may depend on the composition of organic matter undergoing decomposition. Our results are more susceptible to this concern, as our experiments analyze only one water type, from a single sample taken from a specific lake.

In contrast to the positive effect of radiation on bioavailability of CDOM and DOC, which results in higher bacterial utilization of the organic carbon, some studies have reported a negative effect of solar radiation on bacterial growth with DOC in marine water (Benner and Biddanda, 1998; Obernosterer et al., 1999). This difference in response to UV-exposure between marine and freshwater is reported to result from DOC quality and the concentration of humic compounds (Tranvik and Bertilsson, 2001). The level of recalcitrant DOC correlates directly with the humic content of the water. The recalcitrant DOC pool responds to UV-exposure, resulting in transformation into more-labile compounds that are available for bacterial degradation. In contrast, water that is more dilute in humic substances but high in labile DOC responds to irradiation-exposure, which transforms a higher proportion of labile compounds to more refractory compounds (Scully et al., 2003; Vähätalo, 2010).

Besides UV-radiation, the increased production of free oxygen radicals at high UV-intensities could limit bacterial activity (Blough and Zepp, 1995). While free oxygen radicals have a negative effect on bacterial growth, their reactions with recalcitrant non-chromophoric DOC can transform it into more-labile components (Vähätalo, 2010).

3.2. Changes of aromaticity with increasing UV

Degradation of CDOM absorption and DOC concentration was negligible in the aged lake water placed in the dark, and aromaticity described by SUVA$_{254}$ remained constant. At the two lowest UV-intensities, SUVA$_{254}$ declined linearly over time, reflecting both more substantial degradation of CDOM absorption compared with DOC and, presumably, the transformation of chromophoric DOC to non-chromophoric DOC of higher degradability. In contrast, at the two highest CDOM absorption remained constant while DOC removal continued to increase resulting in higher SUVA$_{254}$-ratios over time. Thus, the response of CDOM and DOC removal and SUVA$_{254}$ is dependent on UV-intensity. The distinct increase of SUVA$_{254}$ over time at the two highest UV-intensities reflects a higher loss of non-chromophoric DOC compared to chromophoric DOC. Apparently high UV-intensities of high photon energy have the potential to facilitate a stronger bacterial degradation of non-chromophoric than chromophoric DOC in aged water sampled from the humic lake. A finer chemical analysis of molecule composition in the water is needed to explain the detailed responses to coupled UV-exposure and bacterial degradation over time.

We may speculate that co-metabolism could also contribute to the higher DOC removal rates at increasing UV-dosage as opposed to CDOM removal. Co-metabolism is reported from terrestrial environments (Fontaine et al., 2007) and occurs when an increase in substrate availability for microbial degradation induces enzyme production or increased

enzyme activity, which leads to higher DOC decomposition rates (Kuzyakov, 2010).

Lake studies have typically shown an increase in the aromaticity ratio $SUVA_{254}$ from the low-UV winter season to the high-UV summer season (Porcal et al., 2013). In large lakes with a long water retention time, a distinct decrease in $SUVA_{254}$ from the inlet to the outlet reflects a reduction of the aromatic content and a decrease in humification of dissolved organic matter as water is exposed to combined UV-exposure and bacterial and degradation over several years (Aullo-Maestro et al., 2017). This development may be parallel to the time course of $SUVA_{254}$ in our experiments at the two lowest irradiation-intensities. At high irradiation-intensities, the change in $SUVA_{254}$ remains open to discussion. It may result from a complex mixture of direct UV-mineralization, direct bacterial degradation, co-metabolism, and, perhaps, mutual transformations between chromophoric and non-chromophoric compounds.

3.3. CDOM degradation in humic lakes

Implications of the measured degradation rates in the present study were made by relating them to *in situ* measurements of CDOM in the lake from which the samples originated. Firstly, we evaluated degradation in a setup where no new CDOM was added. We estimated that some 92% of the chromophoric substances are removed during the year as a response to coupled irradiation-induced and microbial degradation. The high removal illustrates how extensive the removal can be if no new CDOM is received. In a more realistic scenario, with the input of new CDOM from the catchment, accounting for CDOM absorption and amount of inflowing water, lake water retention time, and irradiation-mediated degradation, we could closely predict the temporal course of light absorption by CDOM in the lake over the year. Small differences between observed and predicted values were likely related to variable wind-induced mixing, as well as temperature effects on microbial degradation that are not included in our model.

We are aware that our model is built on data from a particular humic lake and one type of water, sampled at a specific time and subsequently aged for 6 months. The aged water mimics the composition and degradability of groundwater inflow, which underwent further degradation only after the influence of irradiation-exposure. The date or even season when we took the sample likely had a limited impact, as we then aged the water for 6 months; variations in the presence of phytoplankton-generated labile pools disappear under all circumstances after 6 months of aging. Although the possible influence of sampling in different seasons has not been tested, the relatively close match between measured and modeled CDOM absorption suggests that the combination of experiments and simple modeling offers a suitable description of the main determinants. Thus, it may be more profitable to apply our approach to other humic lakes with different sources of CDOM rather than testing the seasonal aspect in a single lake.

We found that low UV-intensities during the winter months in Lake Tvorup did not support photochemical degradation. Together with higher precipitation and intensified groundwater input and surface runoff from the catchment, winter is often characterized by a net input of new organic material, leading to higher in-lake CDOM concentration (Fasching et al., 2016; Weyhenmeyer et al., 2012). Previous studies have shown a higher photodegradation in early spring (Gonsior et al., 2013) as also supported by our *in situ* CDOM samples in Lake Tvorup. Because no photodegradation takes place during winter, there is an accumulation of otherwise photo-labile CDOM. Consequently, the same irradiation-intensities can result in more degradation in spring compared to summer, simply because more degradable CDOM is present in springtime water. Still, more CDOM is degraded during summer, when irradiation-intensities are highest.

In both the lake itself and in the experiment, the chromophoric loss corresponded with the removal range of 25%–50% estimated by Muller et al. (2014). However, the higher CDOM loss in our combined laboratory-field model study, compared to *in situ* chromophoric loss with CDOM replenishment, indicates that lakes are much more dynamic regarding CDOM degradation than previously assumed. *In situ,* chromophoric degradation is masked by the constant input of new material in volumes that can be linked with rain events (Raymond and Saiers, 2010). In addition, a lake such as Lake Tvorup is highly susceptible to major water pulses due to the short water retention time, which means that a high proportion of the CDOM pool is renewed over a short period of time (Berggren et al., 2018). Such water pulses adding new material to the lake could account for some of the observed temporal variation of CDOM absorption coefficients in the collected water samples.

4.   Conclusion

In conclusion, catchment vegetation and water retention time that influence input and degradation of CDOM, respectively, are essential when forecasting future CDOM levels and optical conditions in lakes (Madsen-Østerbye et al., 2018). Establishing a precise response of CDOM and DOC degradation to UV-radiation is another crucial step towards improved modeling of carbon dynamics in aquatic systems. Moreover, further work on the combined effect of water column mixing and temperature on CDOM degradation can increase our understanding of the carbon cycle in humic lakes. Overall, we find that chromophoric removal could be markedly higher than earlier studies have indicated because of irradiation-exposure directly coupled to microbial degradation. Thus, large proportions of organic carbon are processed and lost during transport through freshwater systems.

Ph.D. study. We are indebted to insightful comments on the manuscript and proofreading by David Stuligross.

REFERENCES

Aiken, G.R., McKnight, D.M., Wershaw, R.L., MacCarthy, P.E., 1985. Humic Substances in Soil, Sediment, and Water-Geochemistry, Isolation and Characterization. Wiley.

Algesten, G., Sobek, S., Bergstrom, A.K., Agren, A., Tranvik, L.J., Jansson, M., 2004. Role of lakes for organic carbon cycling in the boreal zone. Glob. Chang. Biol. 10, 141–147.

Asmala, E., Autio, R., Kaartokallio, H., Pitkanen, L., Stedmon, C.A., Thomas, D.N., 2013. Bioavailability of riverine dissolved organic matter in three Baltic Sea estuaries and the effect of catchment land use. Biogeosciences 10, 6969–6986.

Aullo-Maestro, M.E., Hunter, P., Spyrakos, E., Mercatoris, P., Kovacs, A., Horvath, H., et al., 2017. Spatio-seasonal variability of chromophoric dissolved organic matter absorption and responses to photobleaching in a large shallow temperate lake. Biogeosciences 14, 1215–1233.

Battin, T.J., Luyssaert, S., Kaplan, L.A., Aufdenkampe, A.K., Richter, A., Tranvik, L.J., 2009. The boundless carbon cycle. Nat. Geosci. 2, 598–600.

Benner, R., 2002. Chemical composition and reactivity. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Academic Press, San Diego, CA, pp. 59–90.

Benner, R., Biddanda, B., 1998. Photochemical transformations of surface and deep marine dissolved organic matter: Effects on bacterial growth. Limnol. Oceanogr. 43, 1373–1378.

Berggren, M., Klaus, M., Selvam, B.P., Strom, L., Laudon, H., Jansson, M., et al., 2018. Quality transformation of dissolved organic carbon during water transit through lakes: contrasting controls by photochemical and biological processes. Biogeosciences 15, 457–470.

Berggren, M., Laudon, H., Jansson, M., 2009. Aging of allochthonous organic carbon regulates bacterial production in unproductive boreal lakes. Limnol. Oceanogr. 54, 1333–1342.

Berggren, M., Sponseller, R.A., Alves Soares, A.R., Bergström, A.K., 2015. Toward an ecologically meaningful view of resource stoichiometry in DOM-dominated aquatic systems. J. Plankton Res. 37, 489–499.

Blough, N.V., Zepp, R.G., 1995. Reactive oxygen species in natural waters. In: Active Oxygen in Chemistry. Springer, pp. 280–333.

Bricaud, A., Morel, A., Prieur, L., 1981. Absorption by dissolved organic-matter of the sea (yellow substance) in the UV and visible domains. Limnol. Oceanogr. 26, 43–53.

Catalán, N., Marcé, R., Kothawala, D.N., Tranvik, L.J., 2016. Organic carbon decomposition rates controlled by water retention time across inland waters. Nat. Geosci. 9, 501–504.

Clark, J., Bottrell, S., Evans, C., Monteith, D., Bartlett, R., Rose, R., et al., 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. Sci. Total Environ. 408, 2768–2775.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., et al., 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems 10, 171–184.

Corin, N., Backlund, P., Wiklund, T., 1998. Bacterial growth in humic waters exposed to UV-radiation and simulated sunlight. Chemosphere 36, 1947–1958.

Cory, R.M., Ward, C.P., Crump, B.C., Kling, G.W., 2014. Sunlight controls water column processing of carbon in arctic fresh waters. Science 345, 925–928.

Cuthbert, I.D., Del Giorgio, P., 1992. Toward a standard method of

measuring color in fresh-water. Limnol. Oceanogr. 37, 1319–1326.

Del Vecchio, R., Blough, N.V., 2002. Photobleaching of chromophoric dissolved organic matter in natural waters: kinetics and modeling. Mar. Chem. 78, 231–253.

Ekstrom, S.M., Kritzberg, E.S., Kleja, D.B., Larsson, N., Nilsson, P.A., Graneli, W., et al., 2011. Effect of acid deposition on quantity and quality of dissolved organic matter in soil-water. Environ. Sci. Technol. 45, 4733–4739.

Fasching, C., Behounek, B., Singer, G.A., Battin, T.J., 2014. Microbial degradation of terrigenous dissolved organic matter and potential consequences for carbon cycling in brown-water streams. Sci. Rep. 4 (1), 1–7.

Fasching, C., Ulseth, A.J., Schelker, J., Steniczka, G., Battin, T.J., 2016. Hydrology controls dissolved organic matter export and composition in an Alpine stream and its hyporheic zone. Limnol. Oceanogr. 61, 558–571.

Finstad, A.G., Andersen, T., Larsen, S., Tominaga, K., Blumentrath, S., De Wit, H.A., et al., 2016. From greening to browning: catchment vegetation development and reduced S-deposition promote organic carbon load on decadal time scales in Nordic lakes. Sci. Rep. 6 (1), 1–8.

Fontaine, S., Barot, S., Barré, P., Bdioui, N., Mary, B., Rumpel, C., 2007. Stability of organic carbon in deep soil layers controlled by fresh carbon supply. Nature 450, 277.

Gonsior, M., Schmitt-Kopplin, P., Bastviken, D., 2013. Depth-dependent molecular composition and photo-reactivity of dissolved organic matter in a boreal lake under winter and summer conditions. Biogeosciences 10, 6945–6956.

Graneli, W., Lindell, M., Tranvik, L., 1996. Photo-oxidative production of dissolved inorganic carbon in lakes of different humic content. Limnol. Oceanogr. 41, 698–706.

Groeneveld, M., Tranvik, L., Natchimuthu, S., Koehler, B., 2016. Photochemical mineralisation in a boreal brown water lake: considerable temporal variability and minor contribution to carbon dioxide production. Biogeosciences 13, 3931–3943.

Hammes, F., Vital, M., Egli, T., 2010. Critical evaluation of the volumetric "bottle effect" on microbial batch growth. Appl. Environ. Microbiol. 76, 1278–1281.

Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J., Mopper, K., 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limnol. Oceanogr. 53, 955–969.

Jansson, M., Persson, L., De Roos, A.M., Jones, R.I., Tranvik, L.J., 2007. Terrestrial carbon and intraspecific size-variation shape lake ecosystems. Trends Ecol. Evol. 22, 316–322.

Jones, T.G., Evans, C.D., Jones, D.L., Hill, P.W., Freeman, C., 2016. Transformations in DOC along a source to sea continuum; impacts of photo-degradation, biological processes and mixing. Aquat. Sci. 78, 433–446.

Karlsson, J., Bystrom, P., Ask, J., Ask, P., Persson, L., Jansson, M., 2009. Light limitation of nutrient-poor lake ecosystems. Nature 460, 506–U80.

Koehler, B., Landelius, T., Weyhenmeyer, G.A., Machida, N., Tranvik, L.J., 2014. Sunlight-induced carbon dioxide emissions from inland waters. Glob. Biogeochem. Cycles 28, 696–711.

Kohler, S.J., Kothawala, D., Futter, M.N., Liungman, O., Tranvik, L., 2013. In-lake processes offset increased terrestrial inputs of dissolved organic carbon and color to lakes. PloS One 8, 8 e70598.

Kragh, T., Sondergaard, M., 2004. Production and bioavailability of autochthonous dissolved organic carbon: effects of mesozooplankton. Aquat. Microb. Ecol. 36, 61–72.

Kragh, T., Sondergaard, M., Tranvik, L., 2008. Effect of exposure to sunlight and phosphorus-limitation on bacterial degradation of coloured dissolved organic matter (CDOM) in freshwater. FEMS Microbiol. Ecol. 64, 230–239.

Kristensen, E., Madsen-Østerbye, M., Massicotte, P., Pedersen, O., Markager, S., Kragh, T., 2018. Catchment tracers reveal discharge, recharge and sources of groundwater-borne pollutants in a novel lake modelling approach. Biogeosciences 15, 1203.

Kritzberg, E.S., 2017. Centennial-long trends of lake browning show major effect of afforestation. Limnol. Oceanogr. Lett. 2, 105–112.

Kritzberg, E.S., Ekstrom, S.M., 2012. Increasing iron concentrations in surface waters-a factor behind brownification? Biogeosciences 9, 1465–1478.

Kuzyakov, Y., 2010. Priming effects: Interactions between living and dead organic matter. Soil Biol. Biochem. 42, 1363–1371.

Lanzalunga, O., Bietti, M., 2000. Photo- and radiation chemical induced degradation of lignin model compounds. J. Photochem. Photobiol. B: Biol. 56, 85–108.

Lapierre, J.F., Guillemette, F., Berggren, M., del Giorgio, P.A., 2013. Increases in terrestrially derived carbon stimulate organic carbon processing and CO2 emissions in boreal aquatic ecosystems. Nat. Commun. 4 (1), 1–7.

Madsen-Østerbye, M., Kragh, T., Pedersen, O., Sand-Jensen, K., 2018. Coupled UV-exposure and microbial decomposition improves measures of organic matter degradation and light models in humic lake. Ecol. Eng. 118, 191–200.

Maranger, R., Del Giorgio, P., Bird, D., 2002. Accumulation of damaged bacteria and viruses in lake water exposed to solar radiation. Aquat. Microb. Ecol. 28, 213–227.

Massicotte, P., Markager, S., 2016. Using a Gaussian decomposition approach to model absorption spectra of chromophoric dissolved organic matter. Mar. Chem. 180, 24–32.

Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Hogasen, T., et al., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450, 537–5U9.

Mopper, K., Kieber, D.J., 2000. Marine photochemistry and its impact on carbon cycling. In: The Effects of UV Radiation in the Marine Environment, 10. Cambridge University Press, pp. 101–129.

Moran, M.A., Sheldon, W.M., Zepp, R.G., 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. Limnol. Oceanogr. 45, 1254–1264.

Moran, M.A., Zepp, R.G., 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnol. Oceanogr. 42, 1307–1316.

Morris, D.P., Zagarese, H., Williamson, C.E., Balseiro, E.G., Hargreaves, B.R., Modenutti, B., et al., 1995. The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. Limnol. Oceanogr. 40, 1381–1391.

Muller, R.A., Kothawala, D.N., Podgrajsek, E., Sahlee, E., Koehler, B., Tranvik, L.J., et al., 2014. Hourly, daily, and seasonal variability in the absorption spectra of chromophoric dissolved organic matter in a eutrophic, humic lake. J. Geophys. Res. 119, 1985–1998 G Biogeosci.

Obernosterer, I., Reitner, B., Herndl, G.J., 1999. Contrasting effects of solar radiation on dissolved organic matter and its bioavailability to marine bacterioplankton. Limnol. Oceanogr. 44, 1645–1654.

Pagano, T., Bida, M., Kenny, J.E., 2014. Trends in levels of allochthonous dissolved organic carbon in natural water: a review of potential mechanisms under a changing climate. Water 6, 2862–2897.

Porcal, P., Dillon, P.J., Molot, L.A., 2013. Seasonal changes in photochemical properties of dissolved organic matter in small boreal streams. Biogeosciences 10, 5533–5543.

, 2017. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria, p. 2017 ISBN3-900051-07-0.

Raymond, P.A., Saiers, J.E., 2010. Event controlled DOC export from forested watersheds. Biogeochemistry 100, 197–209.

Risse-Buhl, U., Hagedorn, F., Dümig, A., Gessner, M.O., Schaaf, W., Nii-Annang, S., et al., 2013. Dynamics, chemical properties and bioavailability of DOC in an early successional catchment. Biogeosciences 10, 4751.

Roulet, N., Moore, T.R., 2006. Environmental chemistry-Browning the waters. Nature 444, 283–284.

Sand-Jensen, K., Staehr, P.A., 2007. Scaling of pelagic metabolism to size, trophy and forest cover in small Danish lakes. Ecosystems 10, 127–141.

Scully, N.M., Cooper, W.J., Tranvik, L.J., 2003. Photochemical effects on microbial activity in natural waters: the interaction of reactive oxygen species and dissolved organic matter. FEMS Microbiol. Ecol. 46, 353–357.

Solomon, C.T., Jones, S.E., Weidel, B.C., Buffam, I., Fork, M.L., Karlsson, J., et al., 2015. Ecosystem consequences of changing inputs of terrestrial dissolved organic matter to lakes: Current knowledge and future challenges. Ecosystems 18, 376–389.

Sondergaard, M., Phillips, G., Hellsten, S., Kolada, A., Ecke, F., Maemets, H., et al., 2013. Maximum growing depth of submerged macrophytes in European lakes. Hydrobiologia 704, 165–177.

Stedmon, C.A., Markager, S., 2001. The optics of chromophoric dissolved organic matter (CDOM) in the Greenland Sea: An algorithm for differentiation between marine and terrestrially derived organic matter. Limnol. Oceanogr. 46, 2087–2093.

Tranvik, L.J., Bertilsson, S., 2001. Contrasting effects of solar UV radiation on dissolved organic sources for bacterial growth. Ecol. Lett. 4, 458–463.

Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., et al., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. 54, 2298–2314.

Vachon, D., Prairie, Y.T., Guillemette, F., del Giorgio, P.A., 2017. Modeling allochthonous dissolved organic carbon mineralization under variable hydrologic regimes in boreal lakes. Ecosystems 20, 781–795.

Vahatalo, A.V., Salkinoja-Salonen, M., Taalas, P., Salonen, K., 2000. Spectrum of the quantum yield for photochemical mineralization of dissolved organic carbon in a humic lake. Limnol. Oceanogr. 45, 664–676.

Verpoorter, C., Kutser, T., Tranvik, L., 2012. Automated mapping of water bodies using Landsat multispectral data. Limnol. Oceanogr. Methods 10, 1037–1050.

Vähätalo, A., 2010. Light, photolytic reactivity and chemical products. In: Likens, G.E. (Ed.), Biogeochemistry of Inland Waters. Elsevier/Academic Press, Amsterdam, pp. 37–49.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37, 4702–4708.

Westerhoff, P., Chao, P., Mash, H., 2004. Reactivity of natural organic matter with aqueous chlorine and bromine. Water Res. 38, 1502–1513.

Weyhenmeyer, G.A., Froberg, M., Karltun, E., Khalili, M., Kothawala, D., Temnerud, J., et al., 2012. Selective decay of terrestrial organic carbon during transport from land to sea. Glob. Chang. Biol. 18, 349–355.

Weyhenmeyer, G.A., Prairie, Y.T., Tranvik, L.J., 2014. Browning of boreal freshwaters coupled to carbon-iron interactions along the aquatic continuum. PloS One 9, e88104.

Q-lab. Technical bulletin LU-8160: A choice of lambs for the QUV Accelerater Weathering tester, 2019. https://www.q-lab.com/documents/public/d6f438b3-dd28-4126-b3fd-659958759358.pdf?ReturnUrl=/resources/technical-bulletins.aspx.