1 **Title:** The relative importance of photodegradation and biodegradation of terrestrially derived
2 dissolved organic carbon across four lakes of differing trophic status
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Abstract

Outgassing of carbon dioxide (CO_2) from freshwater ecosystems comprises 12-25% of the total carbon flux from soils and bedrock. This CO_2 is largely derived from both biodegradation and photodegradation of terrestrial dissolved organic carbon (DOC) entering lakes from wetlands and soils in the watersheds of lakes. In spite of the significance of these two processes in regulating rates of CO_2 outgassing, their relative importance remains poorly understood in lake ecosystems. In this study, we used groundwater from the watersheds of one subtropical and three temperate lakes of differing trophic status to simulate the effects of increases in terrestrial DOC from storm events. We assessed the relative importance of biodegradation and photodegradation in oxidizing DOC to CO_2. We measured changes in DOC concentration, colored dissolved organic carbon ($SUVA_{320}$ and S_r), dissolved oxygen, and dissolved inorganic carbon (DIC) in short-term experiments from May-August, 2016. In all lakes, photodegradation led to larger changes in DOC and DIC concentrations and optical characteristics than biodegradation. A descriptive discriminant analysis showed that in brown-water lakes, photodegradation led to the largest declines in DOC concentration. In these brown-water systems, ~30% of the DOC was processed by sunlight and a minimum of 1% was photo mineralized. In addition to documenting the importance of photodegradation in lakes, these results also highlight how lakes in the future may respond to changes in DOC inputs.

Introduction

Lakes are closely linked to their surrounding terrestrial ecosystems. As the lowest point in the landscape, they receive a significant influx of terrestrially-derived dissolved organic carbon (DOC) and nutrients (Williamson et al., 2009; Wilkinson et al., 2013). Climate and land use changes are altering the link between lakes and their surrounding landscapes by strengthening the flow of material during extreme rain events and large wildfires, or weakening it during extended periods of drought (Strock et al., 2016; Williamson et al., 2016). Long-term changes in DOC concentrations are variable and appear to be regionally controlled. In northeastern North American and western European lakes, there has been as much as a doubling of DOC concentrations due to recovery from anthropogenic acidification and climate change (Monteith et al., 2007; Williamson et al., 2015; de Wit et al., 2016). However, DOC concentrations in Greenland lakes (Saros et al., 2015) and the Mississippi River (Duan et al., 2017) have been decreasing. A long-term study of the Florida Everglades showed that some study sites were decreasing in DOC concentration, but the majority of sites were not changing (Julian et al., 2017). As DOC inputs into aquatic ecosystems have increased, stabilized, or decreased, long-term studies have focused on understanding the mechanisms behind the change, but less research has addressed the fate of DOC once it enters a lake.

By attenuating light in the water column and also providing a source of energy, DOC serves an important role in lakes by regulating the balance between photosynthesis and respiration (Williamson et al., 1999), and thus the flux of CO_2 to the atmosphere (Cole et al., 1994). Previous studies indicated that most lakes are net heterotrophic, where the breakdown of organic carbon exceeds production (Kling et al., 1991; Cole et al., 1994). Estimates suggest that lakes respire about half of the annual 2 gigaton flux of carbon to the oceans each year as CO_2

91   (Cole et al., 1994; Tranvik et al., 2009; Tranvik, 2014). The traditional paradigm has been that

92   the dominant mechanism causing the release of excess CO_2 from lakes is bacterial respiration of

93   DOC (biodegradation), with photomineralization (conversion of DOC to CO_2) accounting for

94   only 10% of bacterial rates (Granéli et al., 1996; del Giorgio et al., 1997; Jonsson et al., 2001).

95   However, research on over 200 Arctic lakes, rivers, and streams revealed that sunlight dominated

96   the processing of DOC, and photomineralization rates were on average 5x greater than dark

97   bacterial respiration rates (Cory et al., 2014). In addition, the source of inland water CO_2 remains

98   uncertain, due in large part to a lack of measurements (Raymond et al., 2013; Lapierre et al.,

99   2013; Weyhenmeyer et al., 2015) and predicting DOC reactivity has been challenging (Evans et

100   al., 2017). Quantifying the dominant degradation pathways for terrestrial DOC from a range of

101   lakes will improve estimates of carbon fluxes, particularly mineralization rates that currently

102   have a high degree of uncertainty (Hanson et al., 2014).

103   Many past studies have focused on testing the effects of photodegradation and

104   biodegradation on DOC quantity individually, but they have not simultaneously evaluated how

105   these two processes alter the colored dissolved organic carbon (CDOM) (Granéli et al., 1996;

106   Koehler et al., 2014; Vachon et al., 2016a). CDOM is the fraction of dissolved organic matter

107   that is capable of absorbing light. The effects of sunlight on DOC are not isolated to only

108   increasing mineralization rates. Photodegradation can also decrease the color and molecular

109   weight of DOC, which can increase light availability and the subsequent bacterial respiration of

110   DOC (Bertilsson and Tranvik, 2000; Amado et al., 2003; Chen and Jaffé, 2016). Cory et al.

111   (2014) found the dominant degradation process for Arctic lakes to be partial photodegradation,

112   suggesting that in lakes, sunlight-driven changes in CDOM without undergoing complete

113   mineralization may dominate DOC processing.

114   Since light attenuation varies so strongly among lakes of differing trophic status, testing

115   the relative importance of DOC processing via photodegradation or biodegradation with

116   mechanistic experiments is needed. Previous research on DOC degradation has primarily

117   occurred in high DOC lakes, but in clear-water lakes, 1% of surface UV-A and

118   photosynthetically active radiation (PAR), which are the primary wavelengths active in

119   photodegradation (Osburn et al., 2001) can reach significant depths. In some oligotrophic lakes

120   UV-A may reach up to 7 m for UV-A and 14 m for PAR. In some of the clearest lakes in the

121   world, such as Lake Tahoe, PAR can reach depths > 45 m (Rose et al., 2009a; Rose et al.,

122   2009b). Geographic location and time of year influence the amount of solar radiation lakes

123   receive. In the subtropics, PAR and UV light have high intensity across the spectrum year-

124   around, whereas in temperate regions those wavelengths are strongest during the summer

125   months.

126   Watershed land use and lake trophic status have also been shown to influence DOC

127   composition and reactivity (Lu et al., 2013; Hosen et al., 2014; Larson et al., 2014; Evans et al.,

128   2017). DOC from forested systems was more reactive and had different CDOM properties when

129   compared to disturbed environments (Lu et al., 2012; Williams et al., 2015; Evans et al., 2017).

130   Studies examining how terrestrial DOC inputs are processed in lakes are needed, especially with

131   the increasing frequency of extreme rain events (Rahmstorf and Coumou, 2011; Westra et al.,

132   2014; Fischer and Knutti, 2015). Future climate change projections suggest that for northern

133   ecosystems a 10% increase in precipitation could lead to a 30% increase in the mobilization of

134   soil organic matter (de Wit et al., 2016). Extreme rain events deliver fresh DOC not exposed to

135   prior sunlight into lakes, which can lead to significant reductions in light availability, as well as

136   increases in thermal stability and lake heterotrophy (Jennings et al., 2012; Klug et al., 2012; de

137 Eyto et al., 2016; Zwart et al., 2016). As DOC concentrations change globally, understanding the

138 processes that determine the fate of DOC will help predict the systems most likely to release

139 more CO_2.

140   Here our aim was to 1) determine the relative importance of photodegradation and

141 biodegradation for altering terrestrial DOC quantity and CDOM from lakes of varying trophic

142 status, 2) quantify the percentage of the initial DOC pool that was photomineralized, partially-

143 photodegraded, biodegraded or remained unprocessed, and 3) compare the effects of

144 photodegradation on DOC quantity and CDOM across four lakes to understand differences in

145 how terrestrial DOC from the watersheds of different lake types responds to photodegradation.

146 Since lakes are closely linked to their surrounding landscape (i.e. soils and vegetation), we

147 collected terrestrial DOC from the watershed of three temperate lakes and one subtropical lake,

148 all varying in trophic status. This soil organic matter represents the current and future inputs of

149 organic material. We studied changes in the concentration of DOC, dissolved inorganic carbon

150 (DIC), and dissolved oxygen (DO) and measured changes in CDOM. We hypothesized that

151 photodegradation would be more important than biodegradation in all lakes, but the strongest

152 responses to sunlight would be observed in the brown-water lakes.

153

154 **1. Methods**

155 **1.1** *Study Sites and Samplers*

156   Groundwater samples were collected from the watersheds immediately adjacent to four

157 lakes used in this study (Table 1). All of the lakes are small, with a surface area ≤ 0.48 km^2 and a

158 maximum depth ranging from 12.5 m in Lake Waynewood to 24 m in Lake Giles. The three

159 temperate lakes (Giles – oligotrophic; Lacawac – brown-water; Waynewood – eutrophic) are in

160   close proximity, located on the Pocono Plateau in northeastern Pennsylvania. Lake Annie

161   (brown-water) is a subtropical, sinkhole lake located on the Lake Wales Ridge in south-central

162   Florida. These lakes were selected because of their variability in the dominant vegetation types

163   in their watersheds that lead to differences in DOC concentration and quality (Table 1). Annie,

164   Giles, and Lacawac are all seepage lakes within protected watersheds, and there have been no

165   significant changes in land use or land cover over the past thirty years. The watersheds of Giles

166   and Lacawac have > 90% cover of mixed and northern hardwood-conifer forests, with oak trees

167   dominating the watershed at Giles, while hemlocks represent the highest proportion of

168   Lacawac's watershed (Moeller et al., 1995). Annie is surrounded by well-drained sandy soils and

169   the major vegetation types include a mixed-scrub community, pinelands, and oak forests (Gaiser,

170   2009). Both Annie and Lacawac are brown-water lakes with moderate DOC concentrations and

171   lower transparency (Table 1). A higher percentage of wetlands (7% for Annie and 25% for

172   Lacawac) in their watersheds likely contribute to their darker color compared to the other lakes

173   (Moeller et al., 1995; H. Swain *unpublished data)*. Waynewood is the most eutrophic lake and

174   has the largest watershed with runoff from dairy farms upstream that feeds into the lake through

175   an inlet stream. The forest surrounding Waynewood is similarly dominated by oak and hemlock

176   trees, but there is overall less total forest cover in the watershed than Lacawac and Giles, and

177   there are more homes adjacent to the lake (Moeller et al., 1995). Detailed information about lake

178   residence time calculations and annual precipitation trends can be found for the Pocono lakes

179   (Moeller et al, 1995) and Lake Annie (Swain, 1998; Sacks et al, 1998).

180

Table 1. Summary characteristics of the four study lakes in May-August 2013–2016 (mean ± SD). Abbreviations: Chl-*a* (chlorophyll-a), DOC (dissolved organic carbon), GW DOC (initial groundwater DOC), PAR (photosynthetically active radiation, 400-700 nm), UV-A (ultraviolet A radiation, 380 nm), UV-B (ultraviolet B radiation, 320 nm), RT (residence time).

Lake	Lat. (°)	Long. (°)	Lake area (km²)	Max. depth (m)	Chl-*a* (µg L⁻¹) ± (SD)	Lake DOC (mg L⁻¹) ± (SD)	GW DOC (mg L⁻¹) ± (SD)	pH ± (SD)	1% UV-B depth (m) ± (SD)	1% UV-A depth (m) ± (SD)	1% PAR depth (m) ± (SD)	RT (yr)
Lacawac	41° 22′ N	75° 17′ W	0.21	13	1.9 (1.4)	5.2 (0.8)	59.4 (6.1)	6.6[+]	0.4 (0.1)	0.9 (0.2)	5.7 (0.6)	3.3
Annie	27° 12′ N	81° 20′ W	0.36	20.7	4.0 (1.5)	9.4 (2.5)	20.7 (0.5)	5.5 (0.3)	0.5*	1.3*	4.5 (1.6)	2
Wayne-wood	41° 23′ N	75° 21′ W	0.28	12.5	5.3 (3.7)	6.4 (1.0)	7.6 (0.3)	7.5[+]	0.3 (0.1)	0.7 (0.2)	4.3 (0.9)	0.42
Giles	41° 22′ N	75° 5′ W	0.48	24	1.1 (0.7)	2.3 (0.3)	6.0 (0.6)	6.2[+] (0.3)	2.0 (0.5)	4.7 (1.2)	14.4 (2.1)	5.6

*Indicates estimates from a single profile in March 2012. [+]pH data in Lacawac and Waynewood are from 2015 only and from 2015-2016 in Giles.

Samplers were used to collect groundwater as a proxy for terrestrial DOC runoff entering the lakes. Storm events have been shown to mobilize DOC from shallow groundwater pools into aquatic ecosystems (Boyer et al, 1997). The samplers were installed in close proximity to the Pocono lakes near small inlet streams in sandy or bog areas on 6 July 2015 (~1 year prior to experiments). The groundwater sampler consisted of 1m sections of 7.6cm diameter PVC pipe installed to a depth of 60-81cm below ground. 0.5cm holes were drilled in the sides with a fine mesh covering the holes to let shallow groundwater in but exclude large particulates. At Lake Annie, a groundwater sampler was installed on 17 March 2016 on the south side of the lake near a small, intermittent inlet stream. The groundwater sampler near Lake Annie was a 3m section of PVC pipe installed slightly deeper to 2m below ground to allow continuous access to groundwater during the dry season.

199   On 7 May 2016, 10 L of water was collected using a peristaltic pump from the

200   groundwater samplers at all of the Pocono lakes in acid-washed 18 L bottles. Groundwater

201   samples from Annie were collected from the sampler monthly (25 April, 31 May, 27 June, and 1

202   Aug 2016) prior to starting the experiments and shipped overnight on ice to Pennsylvania. All

203   groundwater samples were kept cold (4 °C) and dark until filtered to avoid sunlight exposure

204   prior to the start of the experiments. Samples for the May experiments were filtered on May 8,

205   2016 through pre-combusted (450 ℃) 0.7 µm Whatman GF/F filters. The remaining 8 L of

206   groundwater for the June, July, and August experiments for each Pocono lake were filtered in a

207   similar manner over the next 14 days. Samples were kept cold and dark until the experiments

208   started. Samples for June, July, and August were re-filtered with a pre-combusted 0.7 µm

209   Whatman GF/F filter prior to the start of those experiments. The initial DOC concentration of the

210   groundwater for each lake varied at the start of each experiment, but it was always higher than

211   the in-lake DOC concentration (Table 1).

212

213   **1.2 *Sampling Design and Variables Analyzed***

214   To determine the relative importance of photodegradation and biodegradation for

215   processing DOC, we designed three treatments in a manner similar to Cory et al., (2014): 1)

216   photodegradation only, 2) biodegradation only, and 3) control. From each treatment, five

217   different variables were measured including DOC concentration, DIC concentration, DO

218   concentration, $SUVA_{320}$, and S_r. The different variables measured in each treatment required the

219   use of different containers for the sample water. Samples for DOC analysis (concentration and

220   CDOM) were deployed in acid-washed, muffled 35 mL quartz tubes sealed with silicone

221   stoppers. The quartz tubes had an average transmittance of 96% of solar UV-A and 87% of solar

222 UV-B, which allowed for an accurate representation of *in-situ* solar radiation levels (SFig. 1,

223 Morris and Hargreaves, 1997). However, the quartz tubes were not gas tight, so samples for

224 dissolved inorganic carbon (DIC) and dissolved oxygen (DO) analysis were deployed in gas tight

225 borosilicate exetainer vials (138W; Labco, Ceredigion, UK). The borosilicate vials had a volume

226 of 12 mL but were filled to 10 mL (i.e. 2 mL of headspace) due to safety concerns with mercury

227 chloride (see below). A clean 10 mL pipette was used to carefully transfer water into the

228 borosilicate vials. Borosilicate glass has a sharp cut-off at 320 nm and transmits <5% UV-B, but

229 it transmits an average of 63% of UV-A radiation and 90% of PAR (SFig. 1, Reche et al., 1999).

230   Water samples for all of the treatments were initially filtered through pre-combusted 0.7

231 µm Whatman GF/F filters one day prior to the start of each monthly experiment. For the

232 photodegradation and control treatments detailed below, samples for DO and DIC analysis were

233 treated with 0.35 mL of 1% mercury chloride ($HgCl_2$) to kill the microbial community. Samples

234 for DOC concentration and CDOM analysis ($SUVA_{320}$ and S_r) for the same treatments were

235 sterile filtered with a 0.2 µm membrane filter (Sterivex MilliporeSigma, Burlington, MA USA)

236 pre-rinsed with 100 mL of DI water and 50 mL of sample water instead of using $HgCl_2$ because

237 adding $HgCl_2$ altered the optical scans. Sterile filtering has previously been shown to remove the

238 majority of microbes present, and water samples remained sterile for one week following this

239 procedure (Moran et al., 2000; Fasching and Battin, 2011). For the biodegradation treatment,

240 water samples were inoculated with 100 µL of unfiltered groundwater that was collected 1 day

241 prior to the start of each monthly experiment. By adding a fresh inoculum of groundwater each

242 month, we aimed to re-stimulate the microbial community and assess the short-term response of

243 biodegradation. In the biodegradation treatments, we did not correct for differences in vial size

244 (i.e. 100 µL was added to both the 12 mL vials and the 35 mL tubes). Treatments were deployed

245   in triplicate for each lake (i.e. 3 DOC quartz tubes, 3 DO borosilicate vials, and 3 DIC

246   borosilicate vials for each treatment). Here, we included a summary of the three experimental

247   treatments that were designed as follows:

248   a) *Photodegradation Only*: Water for DOC concentration and CDOM analysis (SUVA$_{320}$

249   and S$_r$) was sterile filtered and stored in quartz tubes (n = 3 replicates). Water for DIC

250   and DO analysis was treated with 1% HgCl$_2$ and stored in borosilicate vials (n = 6

251   replicates; 3 replicates for DIC and 3 replicates for DO analysis).

252   b) *Biodegradation Only*: Water for all analyses was inoculated with 100 μL of unfiltered

253   groundwater. Water samples for DOC concentration and CDOM analysis were stored in

254   quartz tubes (n = 3 replicates). Water samples for DIC and DO analysis were stored in

255   borosilicate vials (n = 6 replicates; 3 replicates for DIC and 3 replicates for DO analysis).

256   Both the quartz tubes and borosilicate vials were wrapped with multiple layers of

257   aluminum foil to eliminate light exposure.

258   c) *Control*: Water for DOC concentration and CDOM analysis was sterile filtered and

259   stored in quartz tubes (n = 3 replicates). Water for DIC and DO analysis was treated with

260   1% HgCl$_2$ and stored in borosilicate vials (n = 6 replicates; 3 replicates for DIC and 3

261   replicates for DO analysis). All samples were wrapped in aluminum foil (dark).

262

263   The experimental treatments for each lake were deployed for seven days at the surface of

264   Lake Lacawac in May, June, July, and August of 2016 (for exact sampling dates see SI, Table 1).

265   Mean surface lake temperature for each experiment are reported in SI Table 1. Samples were

266   kept at the lake surface using floating racks, and samples from each lake were randomly

267   distributed across the racks. The deployment design ensured that samples stayed at the surface

11

268   and dipped no deeper than 2 cm in the water column. After the one-week exposure, racks were

269   collected from the surface of Lake Lacawac and samples were immediately transferred into

270   coolers and returned to the lab. We assessed the response of terrestrially derived DOC to

271   photodegradation and biodegradation by measuring changes in the concentrations of DOC, DIC,

272   and DO, and the absorbance properties ($SUVA_{320}$ and S_r) of the CDOM. All samples were

273   analyzed within 72 hours of collection.

274   Dissolved organic carbon concentrations and standards were analyzed using a Shimadzu

275   TOC-V_{CPH} Total Organic Analyzer with an ASI-V auto sampler. External acidification was used

276   for each sample and triplicate measurements were performed following the methods of Sharp

277   (1993). Diluted 50 ppm DOC standards (Aqua Solutions) were used to calibrate the TOC

278   Analyzer and standards were regularly analyzed with the samples. Dissolved inorganic carbon

279   concentrations (as CO_2) were measured with a Shimadzu GC-8A Gas Chromatograph using

280   helium as the carrier gas. Samples were acidified using 0.1 N H_2SO_4 and then stripped with

281   nitrogen gas prior to injection. Dissolved oxygen was measured using a modified Winkler

282   titration (Parson et al., 1984). Samples for gas measurements (DO and DIC) were kept in a 21°C

283   water bath for 30 minutes prior to analysis. These samples were well mixed just prior to analysis.

284   The absorbance properties of CDOM were analyzed using a Shimadzu UV 1800 scanning

285   spectrophotometer at 25°C. Raw absorbance scans were generated from 800 to 200 nm using a 1

286   cm cuvette and were blank corrected with ultra-pure DI water. From the absorbance scans, the

287   spectral slope ratio (S_r; 275-295 : 350-400 nm) was calculated following Helms et al. (2008).

288   The DOC specific ultraviolet absorbance at 320 nm ($SUVA_{320}$) was calculated following

289   methods in Williamson et al., (2014). S_r can be used as a proxy for the molecular weight of the

290 DOC, while $SUVA_{320}$ can be used as a proxy for DOC color and aromatic carbon content (Helms

291 et al., 2008, Williamson et al., 2014).

292   Due to differences between the borosilicate vials and quartz tubes, the DIC and DO

293 samples were spectrally corrected for the amount of light they received (SI, SFig. 1). Total

294 cumulative energy exposure over the monthly incubations was calculated from a BSI Model

295 GUV-521 (Biospherical Instruments, San Diego, CA) radiometer with cosine irradiance sensors

296 that have a nominal bandwidth of 8 nm for 305 nm, 320 nm, 340 nm, 380 nm, and 400-700 nm

297 (PAR). Daily irradiance for UV-B, UV-A, and PAR were calculated using 15-minute averages of

298 1-second readings from a GUV radiometer located near Lake Lacawac over the 7-day

299 experiments. The area under the curve was calculated by multiplying the measurement frequency

300 (900 sec) by the average of two adjacent time step readings. These values were then summed

301 over the exposure period to calculate the total cumulative energy exposure for each sample.

302 Readings from a profiling BIC sensor (Biospherical Instruments, San Diego, CA) were then used

303 to calculate the percent of the deck cell at the surface rack incubation depth (0.02 m) in Lake

304 Lacawac.

305

306 **1.3 *Explanation of Calculations and Statistical Analysis***

307   To determine the fate of terrestrial DOC in the four lakes, we used the measured changes

308 (i.e. final – control) in DOC and DIC concentrations to identify four pools of DOC:

309 photomineralized, partially photodegraded, biodegraded, and unprocessed. The amount of carbon

310 photomineralized (converted to CO_2) was calculated as the concentration of DIC produced by

311 sunlight (i.e. carbon that was completely oxidized by sunlight). The amount of carbon partially

312 photodegraded represents the remainder of the carbon pool that was processed by sunlight (but

313 not completely oxidized to CO_2) and was calculated as the total DOC processed by sunlight

314 minus the amount photomineralized (Eq 1).

315 Equation 1. Partially Photodegraded = [Total Photodegraded – Photomineralized]

316 The amount of carbon biodegraded was calculated as the concentration of DOC lost in the

317 biodegradation treatments. The unprocessed carbon was calculated as the fraction of the carbon

318 pool that was not processed by either sunlight or microbes as shown in Eq. 2

319 Equation 2. Unprocessed = [Control DOC – Photomineralized – Partially Photodegraded –

320 Biodegraded].

321 Each process was determined for each lake and each month. Here we report the average response

322 across all four months for each DOC pool.

323 While we carried out monthly experiments (May-August), here we report the average

324 response across the open-water season (i.e. all four months) to provide a more complete picture

325 of DOC processing. The downside of this approach is that it potentially increases variation in

326 variables associated with DOC processing, since such processing may vary across the season.

327 However, there was not a strong seasonal response to photodegradation or biodegradation in all

328 of our study variables (SI Fig. 3). Furthermore, the majority of the terrestrial DOC was collected

329 on a single date and time (except for Lake Annie).

330 Final treatments were compared relative to the dark and killed (1% $HgCl_2$) control

331 treatments, as those samples were deployed at the surface of the lake with the photodegradation

332 and biodegradation treatments. We used a t-test to determine whether the photodegradation

333 samples for all of the variables were significantly different from the biodegradation samples (n =

334 12 for each treatment) in each lake (Table 2). Photodegradation and biodegradation samples were

335 analyzed separately using a one-way ANOVA to assess differences between lakes. A post-hoc

336   Tukey's multiple comparison test (Sigma Plot 14.0) was used to determine if there were

337   significant differences in the response variables between the lakes to the photodegradation and

338   biodegradation treatments (Fig 1). A descriptive discriminant analysis (DDA) was used to

339   classify the four lakes based on changes in DOC, DIC, DO, $SUVA_{320}$, and S_r measurements due

340   to photodegradation (Fig 3). Since these five measures are likely to be highly correlated with one

341   another, DDA is a good choice since it considers these relationships simultaneously in the

342   analysis (Sherry 2006). In this case, DDA, works by producing linear combinations of the five

343   measured variables (DOC, DIC, DO, $SUVA_{320}$, and S_r). The first linear combination provides the

344   best separation of the four lakes, followed by subsequent linear combinations for axes that are

345   orthogonal (Sherry, 2006). Linear combinations are weighted more heavily by variables that are

346   better able to discriminate between the lakes. In the figures and tables below, we report these

347   data as either average measured changes (i.e. concentrations) or average percent changes and

348   have indicated where appropriate. Data for this experiment were analyzed in either Sigma Plot

349   14.0 (Fig. 1, Table 2) or Systat version 10.2 (Fig. 4).

350

351   **2. Results**

352   Throughout the results and discussion, the use of the lake names is to present the data in a

353   meaningful manner, but it is important to recognize that the actual water samples originated from

354   groundwater samples adjacent to each lake.

355

356   **2.1 *Photodegradation and biodegradation responses in each lake***

357   Photodegradation altered DOC quantity and CDOM significantly more than

358   biodegradation for terrestrial DOC from the watersheds of all four lakes (Table 2, Fig. 1). For the

15

359 photodegradation only treatments, exposure to sunlight resulted in significant production of DIC

360 and increases in S_r, as well as significant decreases in DO, DOC, and SUVA$_{320}$ relative to the

361 biodegradation treatments. The only significant effect of biodegradation on terrestrial DOC was

362 a reduction in DO concentrations compared to the dark control (Fig. 1c). In all other cases, the

363 biodegradation treatments were not significantly different than the control, and the average

364 percent change was close to 0.

365   The terrestrial DOC from the brown-water lakes (Lacawac and Annie) typically followed

366 similar patterns to each other, while the terrestrial DOC from the oligotrophic and eutrophic

367 lakes (Giles and Waynewood) responded more similarly to each other. In the brown-water lakes,

368 we observed a stronger response in DOC quantity (i.e. DOC, DIC, and DO), while the changes in

369 DOC quantity were much more muted in the oligotrophic and eutrophic lakes. The responses of

370 S_r changes in each lake due to sunlight did not differ significantly. All four lakes showed a strong

371 response to changes in terrestrial CDOM (i.e. SUVA$_{320}$ and S_r).

372

Table 2. A summary of the mean (± SD) final concentration of DOC, DIC, DO, SUVA$_{320}$ and S$_r$ in photodegradation (Photo), biodegradation (Bio), and control experimental treatments in groundwater samples from the watersheds of lakes Lacawac, Annie, Giles, and Waynewood. The mean (± SD) initial concentration for each variable is also depicted. The P/B column list the results of a t-test to determine whether photodegradation samples were significantly different from the biodegradation samples (n = 12 for each treatment for the four months). Bolded values indicate the Photo treatments that were statistically different from the Bio treatments (p < 0.05).

Analysis	Treatment	Lacawac (Mean ± SD)	P/B p-value	Annie (Mean ± SD)	P/B p-value	Giles (Mean ± SD)	P/B p-value	Waynewood (Mean ± SD)	P/B p-value
DOC (μmoles L^{-1})	Photo	3600 ± 330	**p < 0.001**	1270 ± 211	**p < 0.001**	692 ± 123	p = 0.08	883 ± 73.3	**p =0.002**
	Bio	4910 ± 674		1810 ± 45.7		608 ± 99.0		765 ± 93.8	
	Control	5110 ± 628		1820 ± 76.9		630 ± 102		783 ± 73.8	
DIC (μmoles L^{-1})	Photo	54 ± 8.2	**p < 0.001**	41.9 ± 11.4	**p < 0.001**	20.4 ± 1.9	**p = 0.02**	32.2 ± 7.3	**p = 0.04**
	Bio	16.1 ± 5.0		25.3 ± 7.2		17.7 ± 3.0		27.1 ± 8.0	
	Control	13.8 ± 4.6		30.4 ± 18.2		15.3 ± 2.1		27.8 ± 3.5	
DO (μmoles L^{-1})	Photo	278 ± 62.4	**p < 0.001**	419 ± 25.9	**p < 0.001**	536 ± 35.6	p = 0.16	522 ± 49.0	**p = 0.05**
	Bio	556 ± 46.4		533 ± 42.2		556 ± 34.3		577 ± 76.9	
	Control	660 ± 29.4		656 ± 32.1		688 ± 60.9		702 ± 57.3	
SUVA$_{320}$ (m^{-1} /mg L^{-1})	Photo	4.3 ± 0.4	**p < 0.001**	2.4 ± 0.4	**p < 0.001**	2.4 ± 0.2	**p < 0.001**	1.8 ± 0.2	**p < 0.001**
	Bio	5.3 ± 0.2		3.8 ± 0.1		4.8 ± 0.3		3.2 ± 0.2	
	Control	5.1 ± 0.2		3.8 ± 0.1		4.7 ± 0.2		3.2 ±0.1	
S$_r$	Photo	1.1 ± 0.0	**p < 0.001**	1.3 ± 0.1	**p < 0.001**	1.4 ± 0.1	**p < 0.001**	1.2 ± 0.1	**p < 0.001**
	Bio	0.7 ± 0.1		0.8 ± 0.0		0.9 ± 0.1		0.8 ± 0.1	
	Control	0.7 ± 0.1		0.8 ± 0.0		0.9 ± 0.1		0.9 ± 0.1	

Sunlight caused average (± SD) DOC losses relative to the control treatments of 30.5 ± 11.5% and 28.9 ± 8.3% in Lacawac and Annie, respectively (Fig. 1a). In Giles and Waynewood, we observed an average of 9.6 ± 6.5% and 13.4 ± 6.2% increase in DOC concentration, respectively following exposure to sunlight. When we compared lakes within each treatment, there were no significant differences in DOC concentration due to sunlight in Giles vs. Waynewood, whereas Annie and Lacawac were significantly different from the prior two lakes and from each other (ANOVA: $F_{1,3}$ = 70.9, p < 0.001).

Decreases in DOC concentration due to photodegradation could lead to mineralization (i.e. DIC production; Fig. 1b) and therefore oxidation (i.e. DO consumption; Fig. 1c). We

390   observed the production of DIC due to sunlight in all of our lakes (Fig. 1b). In Lacawac and

391   Annie, the average (± SD) percent increases in DIC relative to the control treatments were 350 ±

392   160% and 96.0 ± 79.0%, respectively. The average percent increases relative to controls in Giles

393   and Waynewood were 40.7 ± 19.4% and 23.2 ± 12.7% respectively. The DIC percent change

394   was similar between Giles and Waynewood, and both were statistically different from Annie and

395   Lacawac. The percent DIC change in Lacawac was significantly higher than Annie (ANOVA:

396    $F_{1,3} = 36.4$, $p < 0.001$).

397   In all lakes, both photodegradation and biodegradation led to decreases in DO

398   concentrations (Fig. 1c). Average DO losses due to biodegradation for all four lakes ranged from

399   15 to 18%. DO losses due to photodegradation were more variable. The average DO loss from

400   sunlight in Lacawac and Annie was 58.2 ± 7.8% and 35.9 ± 5.4%, respectively. In Giles and

401   Waynewood, we observed average DO losses of 21.6 ± 7.9% and 25.6 ± 4.7% respectively.

402   While the largest losses of DO due to sunlight were observed in Annie and Lacawac, there was

403   no significant difference between Annie and Waynewood. Giles and Lacawac were significantly

404   different from the other two lakes and from each other (ANOVA: $F_{1,3} = 73.9$, $p < 0.001$).

405   Changes in CDOM due to biodegradation were minimal in all of the lakes (Fig. 1d & 1e).

406   In contrast, photodegradation caused significant changes in all of the lakes, but the magnitude of

407   the change varied by lake. $SUVA_{320}$ decreased in all lakes due to sunlight, but the largest changes

408   were observed in the oligotrophic and eutrophic lakes (Fig. 1d). Average $SUVA_{320}$ values

409   decreased between 16.8% in Lacawac and 48.9% in Giles. The response in Annie and

410   Waynewood were similar, whereas Lacawac and Giles were significantly different from the prior

411   two lakes and each other (ANOVA: $F_{1,3} = 39.7$, $p < 0.001$). In all lakes, S_r increased due to

412   sunlight (Fig. 1e). Average percent increases for the lakes ranged from 46.4% in Waynewood to

413   65.1% in Lacawac. For S_r, the response between Lacawac and Waynewood were significantly

414   different, but those lakes were no different compared to the remaining lakes (ANOVA: $F_{1,3} = 3.1$,

415   p = 0.04).

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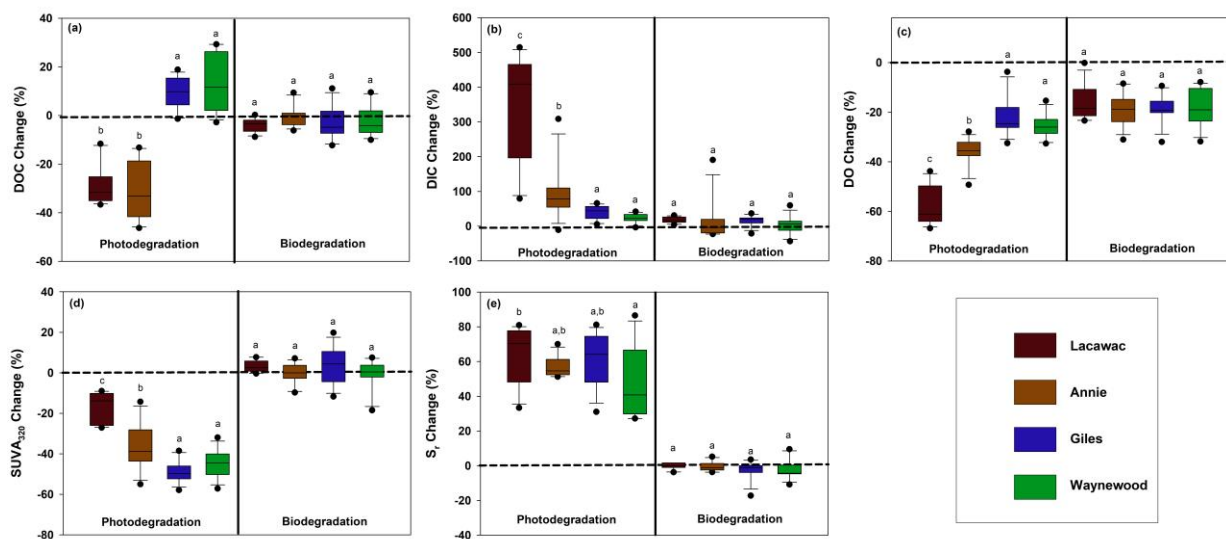
Figure 1. The monthly average percent change from the dark and killed control treatments
(dashed line) in each lake for photodegradation (left) and biodegradation (right) for (a) DOC, (b)
DIC, (c) DO, (d) $SUVA_{320}$, and (e) S_r. Statistical differences (p < 0.05) between lakes are
indicated by different letters above each boxplot. For each boxplot n =12 replicates.

2.2 *Fate of DOC*

424   Of the four pools of carbon we identified in the groundwater samples entering our study

425   lakes, we found the average amount of carbon processed by sunlight ranged from 0.6% to ~30%

426   (Fig. 2). Carbon in Giles and Waynewood (< 1%) showed little response to sunlight, whereas the

427   response in Annie and Lacawac (~30%) was much higher over the 7-day experiments. The

428   dominant pathway through which sunlight interacted with DOC was through partial

429   photodegradation in these latter two lakes. About 1% of the carbon pool was photomineralized in

430   the brown water lakes. The amount of carbon processed via biodegradation was minimal in all

431 lakes (ranging from 0.2–4%). The fraction of the unprocessed carbon pool ranged from a low of

432 66% for Lacawac to a high of 97% for Waynewood. An average of 2.6 to 33% of the carbon

433 pool was processed in one week. The photomineralization data represents a minima value for

434 each lake due to some of the DIC partitioning into the headspace of each vial.
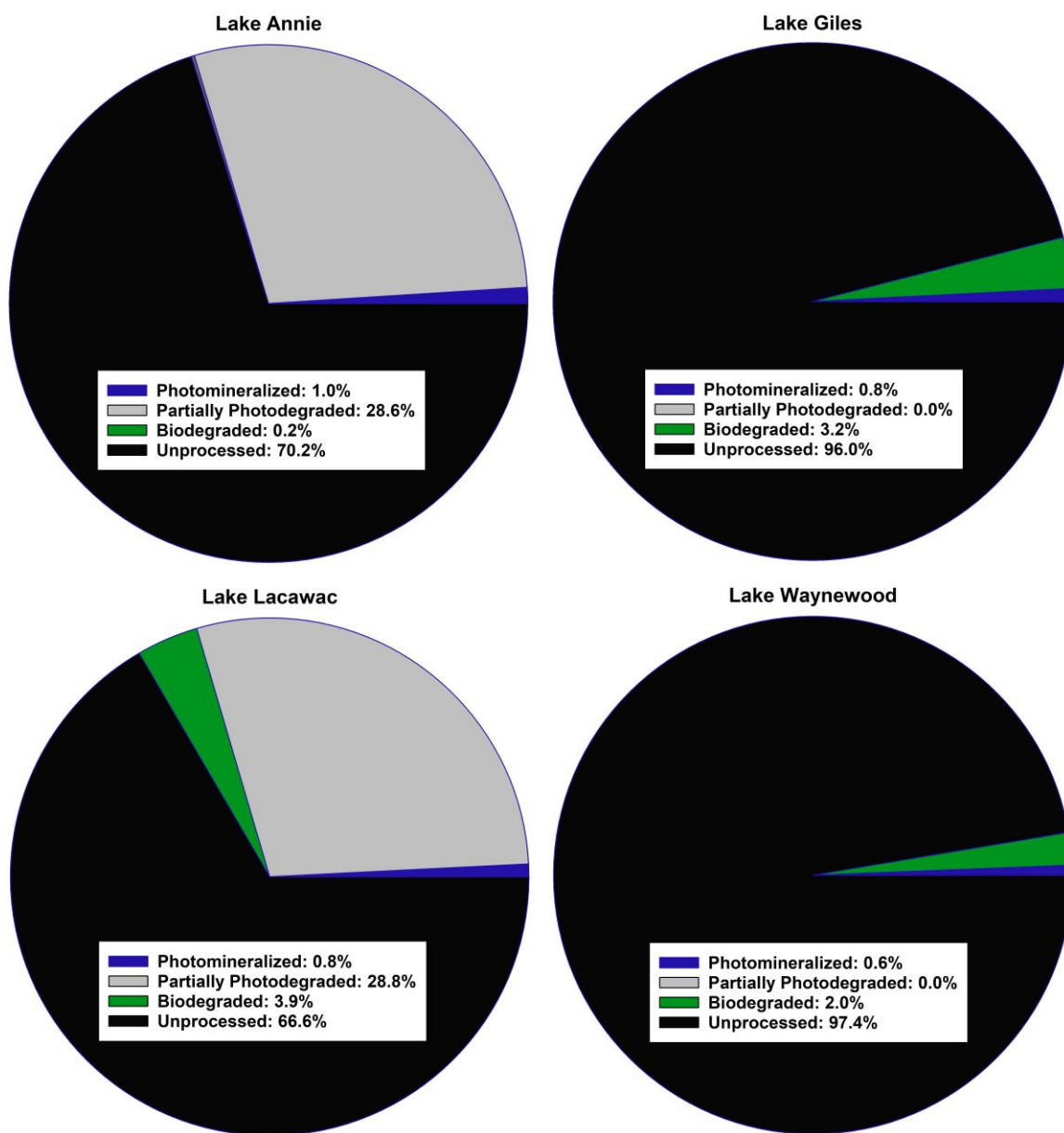
Figure 2. A summary of the average fate of carbon in the groundwater samples from our study
lakes (see methods section for explanation of calculations). All terms were converted to a carbon
basis. Photomineralized describes the amount of carbon completely mineralized to CO_2 by

20

439 sunlight. Partially photodegraded describes the amount of carbon processed by sunlight minus
440 the amount photomineralized. Biodegraded describes the amount of carbon lost through
441 biodegradation. Unprocessed carbon describes the remaining carbon that was not processed by
442 photodegradation or biodegradation.
443

444 **2.3 *DOC response by lake trophic status***

445   For the descriptive discriminant analysis (DDA) to classify the lakes, we found that the

446 five metrics were strongly correlated with one another (Table 3). In general, the changes in DOC,

447 DIC, and DO were more strongly correlated with one another than with $SUVA_{320}$ and S_r and vice

448 versa (Table 3). We will refer to the changes in DOC, DIC, and DO as "DOC quantity" and the

449 changes in $SUVA_{320}$ and S_r as "CDOM" for brevity.

450

451 **Table 3**. Pearson correlations between the measured changes in the five metrics: DOC, DIC, DO,
452 $SUVA_{320}$, and S_r.

	DOC	DIC	DO	$SUVA_{320}$
DIC	-0.934			
DO	0.869	-0.837		
$SUVA_{320}$	-0.705	-0.671	-0.666	
S_r	-0.027	0.021	0.163	-0.319

453
454   DDA produced three functions (axes) with canonical correlations of 0.961, 0.753, and

455 0.181 (Fig. 3). Collectively, the entire model was significant (Wilks' $\lambda = 0.032$; $F_{15, 108} = 17.79$; p

456 < 0.001). Effect size was calculated following Sherry and Henson (2010) as $1 – $ Wilks' λ, and

457 therefore the overall model explains 96.8% of the variation among lakes. Functions 1 through 3

458 and 2 through 3 were significant ($p < 0.001$ for both). Function 3 was not significant ($p = 0.710$)

459 and therefore is not discussed further. Functions 1 through 3 collectively explain 92.4% of the

460 shared variance while functions 2 through 3 collectively explain 56.7% of the shared variance.

461   Function 1 represents a new variate that is a linear combination of the changes in the five

462 variables that best discriminates the lakes from one another. This new variate is composed

463 mainly of DOC, with a function coefficient of 0.465 and a structure coefficient of 0.821 (Table

464 4). Of note are also DIC, DO, and SUVA$_{320}$ that had smaller function coefficients (< 0.45), but

465 had large structure coefficients (> 0.45). This result suggests that Function 1 is mainly related to

466 DOC quantity. Function 2, also a new variate that is a linear combination of the five measured

467 changes, is composed mainly of SUVA$_{320}$ (function coefficient = 0.985 and structure coefficient

468 = 0.719; Table 4). Function 2 is orthogonal to Function 1 and together they discriminate the four

469 lakes (Fig. 3).

470
471 **Table 4**. The solution for changes in measured independent variables that predict the dependent
472 variable, lake. Structure coefficients (r_s) and communality coefficients greater than $|0.45|$ are in
473 bold. Coeff = standardized canonical function coefficient; r_s = structure coefficient; r_s^2 = squared
474 structure coefficient.
475

	Function 1			Function 2		
Variable	Coeff.	r_s	$r_s^2(\%)$	Coeff.	r_s	$r_s^2(\%)$
DOC	0.465	**0.821**	67.40	0.639	0.278	40.83
DIC	-0.337	**-0.703**	11.36	-0.059	-0.216	0.35
DO	0.440	**0.679**	19.36	-0.124	0.009	1.54
SUVA$_{320}$	-0.139	**-0.473**	1.93	0.985	**0.719**	97.02
S$_r$	0.244	0.068	5.95	-0.238	-0.434	5.66

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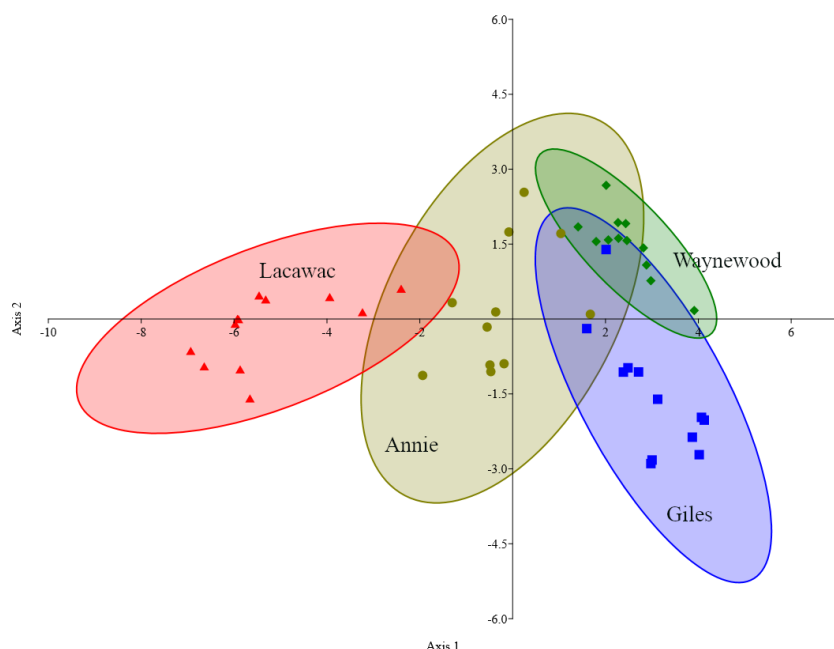
Figure 3. Canonical plot scores and 95% confidence ellipses from descriptive discriminant analysis of the measured changes (i.e. treatment minus control) in the five variables (DOC, DIC, DO, $SUVA_{320}$, and S_r) and four lakes: Annie (olive circles), Giles (blue squares), Lacawac (red triangles), and Waynewood (green diamonds). Only photodegradation samples were included in this analysis.

DDA correctly classified 89.4% of the samples to their collection site (Fig. 3). One

sample from Annie was incorrectly assigned to Waynewood, two samples from Giles were

incorrectly assigned to Waynewood, and two samples from Lacawac were incorrectly assigned

to Annie. All of the Waynewood samples were correctly classified.

3. Discussion

3.1 *Comparing the relative importance of photodegradation and biodegradation*

Despite a large number of studies examining the effects of either photodegradation or

biodegradation on DOC processing, very few have conducted simultaneous *in-situ* experiments

of the relative importance of both processes for transforming DOC from the watersheds of a

range of different lakes. Our results indicate that sunlight was the primary process in the surface

494   waters responsible for degrading terrestrial DOC from the watershed of all four lakes.

495   Biodegradation played a minimal role in changing the DOC quantity and CDOM. We observed

496   decreases in DOC, DO, and $SUVA_{320}$ due to sunlight and saw increases in DIC and S_r. The loss

497   of DOC, as well as a shift to more photobleached, and lower molecular weight organic material

498   is consistent with prior studies on these lakes that evaluated just the effects of sunlight (Morris

499   and Hargreaves, 1997). Exceptions to DOC loss due to photodegradation occurred in Giles and

500   Waynewood. In these lakes, we observed an increase in average DOC concentrations. In Giles,

501   there was significant production of DOC in June and July. In Waynewood, significant production

502   occurred in May and July. We speculate that this production may be due to the lysing of any

503   microbes remaining in solution. Increases may also be attributed to interactions with iron. We

504   have no measurable evidence, but a number of samples from Giles and Waynewood contained a

505   red precipitate at the conclusion of the one-week experiments. Iron-bound DOC could have been

506   released back into the water. Subsequent photodegradation experiments using water from Giles

507   and Waynewood have also indicated DOC production (Dempsey, unpublished).

508   Dissolved oxygen was the lone variable where biodegradation led to decreases relative to

509   the controls, but the differences between lakes were not significant. We attributed the changes in

510   DO to the "sloppy feeding" of bacteria, where they produce DOC through exudates and then

511   assimilate it (Evans et al., 2017). The above results are similar to observations in Arctic and

512   tropical waters in that photodegradation was more important than biodegradation on short time

513   scales (Cory et al., 2014; Chen and Jaffé, 2014; Amado et al., 2003). Interestingly, we found that

514   terrestrial DOC from the watersheds of lakes of different trophic status was processed

515   differently, resulting in DIC production and DOC degradation for the brown-water lakes

516   (Lacawac and Annie), but greater changes in $SUVA_{320}$ for the oligotrophic and eutrophic lakes

517   (Giles and Waynewood). This highlights the need to account for lake trophic status in predicting

518   DOC processing and CO_2 emissions from lakes.

519

520   **3.2 *Dominant degradation process***

521   Based on our study design we were able to identify four pools of carbon:

522   photomineralized, partially photodegraded, biodegraded, and unprocessed. The dominant

523   degradation pathway across all lakes was partial photodegradation (i.e. loss of DOC, but no

524   mineralization), although the size of each carbon pool varied by lake. In the brown-water lakes,

525   ~28% of the total carbon pool was partially photodegraded and ~1% was photomineralized. In

526   the oligotrophic and eutrophic lakes ~0.7% of the carbon was photomineralized and none of the

527   carbon was partially photodegraded. The values reported here for photomineralization are

528   underestimates. Actual values are likely to be higher since we did not account for DIC that

529   partitioned into the headspace of the exetainer vials. If we assume a 1:1 (O_2: CO_2) respiration

530   quotient (RQ) (Cory et al, 2014) and use our DO data in the Fig 2 calculations,

531   photomineralization in Annie and Lacawac could be as high as 13 and 7.5% of the carbon pool

532   respectively. Use of the oxygen data is less than ideal since several authors have reported RQ

533   values different than 1:1 (Allesson et al, 2016 and Xie et al, 2004).

534   Observations in Toolik Lake showed 70% of the total carbon pool being processed by

535   sunlight during the open water period (~3 months) (Cory et al., 2014). Other estimates have

536   found that photomineralization of DOC accounts for only 8-14% of total water column CO_2

537   production (Granéli et al., 1996; Jonsson et al., 2001; Koehler et al., 2014; Vachon et al., 2016b).

538   We observed ~30% of the carbon pool being processed by sunlight within one week in our lakes

539   and this was restricted to the brown-water lakes. Similar to Toolik Lake, the dominant

25

540   degradation process was partial photodegradation. Partial photodegradation can alter CDOM and

541   stimulate subsequent bacterial respiration. Degradation of CDOM can have important effects for

542   downstream ecosystems if it can be further processed and released as CO_2 or instead is buried or

543   exported downstream (Weyhenmeyer et al., 2012; Catalan et al., 2016; Chen and Jaffe, 2014;

544   Biddanda and Cotner, 2003). It is thus important to include all sunlight-driven degradation

545   processes to fully account for its relative importance.

546   Differences between the responses observed in the Arctic and our temperate/subtropical

547   lakes are most likely explained by the initial concentration and quality of terrestrially derived

548   DOC and time. In the Arctic, glacial meltwater can be highly photolabile and dominated by

549   seasonal inputs of DOC from shallow or deep soils (Cory et al., 2014; Spencer et al., 2014; and

550   Kaiser et al., 2017). In temperate regions, DOC tends to contain more humic and fulvic acids

551   derived from soils, which may be less photolabile than Arctic DOC. Additionally, we did not

552   integrate our results over the entire water column because the samples were analyzed on the

553   surface of a single lake. Over the entire water column, photodegradation could have processed

554   additional carbon. In clear-water lakes, DOC may be photodegraded down to the 1% UV-A

555   attenuation depth (Osburn et al., 2001), which ranged from 0.7-4.7 m in our study lakes (Table

556   1).

557

558   **3.3 *Response of lakes to photodegradation***

559   With an increase in extreme precipitation events, terrestrial DOC inputs are likely to

560   increase in many aquatic ecosystems (Rahmstorf and Coumou, 2011; Westra et al., 2014). By

561   using groundwater as a proxy of terrestrial inputs from the watersheds of different types of lakes,

562   we simulated the effects of storm events and compared the sensitivity of different terrestrial

563   DOC sources to photodegradation. Interestingly, we found DOC from the watersheds of

564   oligotrophic and eutrophic lakes showed stronger changes in CDOM, compared to DOC from the

565   watersheds of the brown-water lakes that showed significantly larger changes in DOC quantity.

566   This difference may be due to the more allochthonous nature of the brown-water DOC, which is

567   highly photolabile, resulting in greater changes in DOC quantity due to its ability to absorb UV

568   radiation (Bertilsson and Tranvik, 2000). The less allochthonous and more microbially derived

569   DOC from the watersheds of the eutrophic and oligotrophic lakes may be less photolabile with

570   fewer UV-absorbing chromophores. Results of the DDA may be helpful in predicting changes in

571   other lakes based on their trophic status. $SUVA_{320}$ is the variable most likely to change due to

572   photodegradation in eutrophic and oligotrophic lakes. In contrast, DOC concentration is the

573   variable most likely to change in brown-water lakes due to photodegradation. Both results (DOC

574   and $SUVA_{320}$) highlight how lakes of varying trophic status respond to photodegradation. These

575   results can be used to predict how lakes not included in this study will respond to increased DOC

576   concentrations (i.e. browning).

577   Across our study lakes, changes in DIC production scaled linearly with initial

578   groundwater DOC concentration. Lacawac had the highest initial DOC concentration (59.4 ± 6.1

579   mg L^{-1}) and the highest average DIC production, while Giles had the lowest initial DOC

580   concentration (6.0 ± 0.6 mg L^{-1}) and the lowest average DIC production. This suggests that the

581   initial DOC concentration plays a critical role in determining the fate of DOC (Leech et al.,

582   2014; Lapierre et al., 2013). Lake temperature can also influence photodegradation. In this

583   study, average lake temperature increased from May through July (SI Table 1). Porcal et al.

584   (2015) showed that the largest loss of DOC occurred in warmer (i.e. 25 ºC) waters due to

585   photodegradation. Additionally, DIC production was higher in those waters compared to colder

586   water (9 ºC) (Porcal et al., 2015) Recent research has also reported that residence time controls

587   organic carbon decomposition across a wide range of freshwater ecosystems (Catalan et al.,

588   2016, Evans et al., 2017). However, extreme precipitation events may shorten the residence time

589   of lakes, effectively flushing out fresh DOC and preventing significant in-lake degradation from

590   occurring (de Wit et al., 2018). For the terrestrial DOC from the oligotrophic and eutrophic

591   lakes, a significant fraction was not degraded, which may mean that terrestrial inputs from these

592   watersheds undergoes less immediate in-lake processing and instead is exported downstream.

593   Our results indicate that differences in the fate and processing of DOC from the watersheds of a

594   range of lake types have important implications for determining which lakes may release more

595   CO_2 versus export DOC downstream (Weyhenmeyer et al., 2012; Zwart et al., 2015;

596   Weyhenmeyer and Conley, 2017).

597   Even though we observed similar responses to photodegradation in the brown-water lakes

598   (Fig. 1), the magnitude of the response varied and may have been related to the initial DOC

599   concentration. Initial concentrations (mg L^{-1}) of terrestrial DOC from Lacawac (59.4 ± 6.1) were

600   almost 3x higher than Annie (20.7 ± 0.5). Average DOC losses for both lakes due to

601   photodegradation were ~30%. The main difference between Lacawac and Annie was the DIC

602   percent change due to photodegradation (Fig. 1b). Average percent increases in DIC for Lacawac

603   were close to 400%, whereas in Annie it was ~85%. Despite the fact that both Annie and

604   Lacawac are brown-water lakes, their different DIC production rates indicate that certain types of

605   terrestrial DOC may be more photolabile than others and capable of outgassing large amounts of

606   CO_2. The DDA analysis did also pick out the separation between Lacawac and Annie primarily

607   on axis 1 (DOC). The responses in Annie shared similarities with the other 3 lakes while

608   Lacawac only overlapped with Annie. When put in the context of the entire DOC pool for each

609   lake, photomineralization accounted for 1% of the carbon loss. We anticipated that terrestrial

610   DOC from subtropical lakes would undergo additional microbial processing due to the higher

611   temperatures year-round. In a comparison between boreal Swedish and tropical Brazilian lakes,

612   Graneli et al., (1998) also found strong similarities in changes of DOC concentrations and DIC

613   production between lakes from the different latitudes. A weak significant correlation between

614   DOC concentration and DIC production has also been observed in Amazon clear water systems

615   (Amado et al., 2003)

616

617   **Conclusions**

618   Here we showed that photodegradation can be more important than biodegradation in

619   processing watershed inputs of terrestrial DOC on short time scales in the surface waters of a

620   lake. The responses that we observed varied with lake trophic status. Quantitative changes in

621   DOC, DIC, and DO were strongest in the terrestrial DOC from the watersheds of the brown-

622   water lakes, whereas the largest changes in $SUVA_{320}$ were observed in the terrestrial DOC from

623   the watersheds of the eutrophic and oligotrophic lakes. Consistent with prior studies, we found

624   that sunlight can impact not only changes in the concentration, but also CDOM characteristics.

625   We observed a range of 2.6 to 33% of the carbon pool processed in one week. As DOC

626   concentrations increase in some aquatic ecosystems, the potential for increased CO_2 outgassing

627   due to photo-mineralization also increases. On short time scales, sunlight had important impacts

628   on our study lakes. Future studies should focus on additional lakes, longer timescales, and

629   integrating DIC production throughout the water column.

630   Over the next century, DOC concentrations in northern boreal lakes are projected to

631   increase by 65% (Larsen et al., 2011). Thus, understanding the fate of terrestrial sourced organic

632   material will be essential for predicting the ecological consequences for lakes and downstream

633   ecosystems (Solomon et al., 2015; Williamson et al., 2015; Finstad et al., 2016). Improving

634   estimates of organic carbon processing in lakes will be an important component of creating more

635   complete carbon budgets (Hanson et al., 2004; 2014) and global estimates of CO_2 emissions can

636   be more accurately scaled to reflect the ability of lakes to act as CO_2 sinks or sources as

637   browning continues (Lapierre et al., 2013, Evans et al., 2017).

638

648

649   **Data Availability:**

650   Data and metadata will be made available in the Environmental Data Initiative repository. Data

651   archiving will be led by C. Dempsey and J. Brentrup.

652

653

654

655 **Author Contribution Statement**

656 CMD, JAB, and CEW designed the study with help from LBK, EEG, and HMS. CMD, JAB,

657 SM, and HMS collected the water samples and ran the experiments. DPM provided the

658 analytical equipment for measuring DIC and DOC. CMD and JAB analyzed the data, and CMD

659 and MTG conducted the statistical and DDA analyses. CMD and JAB wrote the manuscript with

660 contributions from all of the authors.

661

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