Partial coupling and differential regulation of biologically and photo-chemically labile dissolved organic carbon across boreal aquatic networks

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Abstract

Despite the rapidly increasing volume of research on the biological and photochemical degradation of DOC in aquatic environments, little is known on the large-scale patterns in biologically and photo-chemically degradable DOC (Bd-DOC and Pd-DOC, respectively) in continental watersheds, and on the links that exist between these two key properties that greatly influence the flow of carbon from continents to oceans. Here we explore the patterns in the concentrations and proportions of Bd- and Pd-DOC across hundreds of boreal lakes, rivers and wetlands spanning a large range of system trophy and terrestrial influence, and compared the drivers of these two reactive pools of DOC at the landscape level. Using standardized incubations of natural waters, we found that the concentrations of Bd- and Pd-DOC co-varied across all systems studied but were nevertheless related to different pools of dissolved organic matter (DOM, identified by fluorescence analyses) in ambient waters. Concentrations of nutrients and protein-like fluorescent DOM (FDOM) explained nearly half of the variation in Bd-DOC, whereas Pd-DOC was exclusively predicted by DOM optical properties, consistent with the photochemical degradability of specific FDOM pools that we experimentally determined. The concentrations of colored DOM (CDOM), which we use here as a proxy of terrestrial influence, almost entirely accounted for the observed relationship between FDOM and the concentrations of both Bd- and Pd-DOC. The concentrations of CDOM and of the putative bio-labile fluorescence component shifted from complete decoupling in clear-water environments to strong coupling in darker streams and wetlands. This suggests a baseline autochthonous Bd-DOC pool fuelled by internal production that is gradually overwhelmed by land-derived Bd-DOC as terrestrial influence increases across landscape gradients. The importance of land as a major source of both biologically and photo-chemically degradable DOC for continental watersheds resulted in a partial coupling of those carbon pools in natural freshwaters, despite fundamental contrasts in terms of their composition and regulation.

35 **1. Introduction**

36 The movement of terrestrial dissolved organic carbon (DOC) from the land-water interface to
37 the oceans is mediated by its transit through complex and highly heterogeneous continental freshwater
38 networks, where DOC from different sources and origins is simultaneously produced and removed via
39 biotic and abiotic processes (Massicotte and Frenette, 2011;Cole et al., 2007;Battin et al., 2008). The
40 overall role that DOC plays on aquatic ecosystems is well recognized (Findlay and Sinsabaugh, 2002), but
41 there is still debate regarding the direct role of terrestrially derived organic carbon as a substrate for
42 ecological and biogeochemical processes in freshwater ecosystems. More specifically, it is generally
43 accepted that terrestrial DOC may support foodwebs at various trophic levels (Berggren et al.,
44 2010b;Karlsson et al., 2003;Jansson et al., 2007), as well as fuel CO_2 evasion from these systems
45 (Algesten et al., 2004;Lapierre et al., 2013;Berggren et al., 2012), but the relative importance for those
46 processes compared to that of autochthonous sources of organic C (Brett et al., 2009;Wenzel et al.,
47 2012), or terrestrially derived CO_2 (Wallin et al., 2013;Butman and Raymond, 2011), respectively, is still
48 questioned. This questioning largely emerges from unresolved issues concerning terrestrial organic
49 carbon degradability in aquatic ecosystems, which then determines the ability of this carbon to enter
50 aquatic foodwebs and biogeochemical cycles.

51 Microbial and photochemical degradation are the two main pathways by which terrestrial DOC
52 may influence aquatic metabolism (del Giorgio et al., 1999;Obernosterer and Benner, 2004;Bertilsson
53 and Tranvik, 1998) and gas dynamics (Molot and Dillon, 1997;Jonsson et al., 2001;Lapierre et al., 2013),
54 and both processes operate simultaneously in ambient waters. Their magnitude and relative
55 contribution in natural systems depend on environmental factors, such as light availability, water
56 residence time and dissolved ions (Soumis et al., 2007), as well as on factors that are intrinsic to DOC
57 (Guillemette and del Giorgio, 2011). Microbial degradation is thought to preferentially target freshly
58 produced, low-molecular weight molecules with low aromaticity (Amon and Benner, 1996;Wickland et

59 al., 2007), whereas photochemical degradation mainly acts on colored, photo-reactive molecules
60 generally associated to high molecular weight and aromaticity (Benner and Kaiser, 2011;Bertilsson and
61 Tranvik, 1998;Stubbins et al., 2010). These broad chemical properties have thus been associated to
62 distinct pools of DOC with distinct sources (i.-e. the process that imported DOC in the environment, e.g.
63 leaching, exudation) and origins (i.-e. the environment where these processes take place, e.g. terrestrial,
64 riverine, marine).

65 Transposing the geochemical evidence described above to natural landscapes would suggest a
66 shift in the relative importance of these DOC degradation pathways, from a dominance of biological
67 degradation in systems dominated by autochthonous carbon sources, to a dominance of photo-chemical
68 degradation in environments with high terrestrial influence. This scenario, which is based on the
69 simplistic assumption that biological degradability is mostly linked to autochthonous DOC, and that
70 photochemical degradability is mostly associated to terrestrially derived DOC, would lead to a
71 compensatory dynamic wherein the overall (biological + photochemical) degradability of DOC would be
72 to some extent buffered across different environments and along a gradient of terrestrial influence.

73 Although the above assumption may hold for specific aquatic environments, it is unlikely that it
74 applies at the landscape level, in part because there is increasing evidence that land exports to
75 continental waters not only photo-chemically degradable DOC (Molot and Dillon, 1997;Jonsson et al.,
76 2001;Weyhenmeyer et al., 2012), but also significant amounts of biologically degradable DOC (Berggren
77 et al., 2010a;Fellman et al., 2008;Guillemette et al., 2013). For example, significant concentrations of
78 protein-like DOC and small organic acids, typically attributed to autochthonous and bio-labile material,
79 have been measured in soils and headwater streams (Berggren et al., 2010a;Fellman et al., 2009), and
80 carbon pools that are considered recalcitrant from a geochemical perspective (based on their molecular
81 properties and degree of prior processing) may actually be biologically degradable under the right
82 environmental conditions, in soils (Schmidt et al., 2011) or in the water (Marín-Spiotta et al., 2014;Ward

et al., 2013). This implies that there may be faster turnover of terrestrially derived DOC in inland waters than what was previously thought, yet there is a large volume of literature documenting the recalcitrance of this carbon in marine or riverine environments with high residence time (see synthesis by Marín-Spiotta et al., 2014). This would suggest that the degradability of terrestrial DOC may be very different in contrasting aquatic environments, and in particular, that it becomes increasingly stable with time as it circulates through continental watersheds, where the labile portions of the DOC pool imported from upstream are gradually processed and removed from the bulk.

It thus appears that land delivers to inland waters a DOC pool that, depending on the local environmental context, may be both biologically and photo-chemically degradable. If indeed biologically and photo-chemically degradable DOC share, to a certain degree, similar sources and origins, one could expect both functional pools of DOC to co-vary across aquatic environments. This would lead to an additive rather than compensatory dynamic, wherein the overall degradability of DOC would increase as a function of increasing terrestrial export, with major implications for the aquatic carbon cycle. Previous evidence has shown that both Bd-DOC and Pd-DOC tend to increase in boreal freshwaters with increasing terrestrial influence (Lapierre et al., 2013), but the respective drivers of those pools and the degree to which they are coupled across a large diversity of freshwater environments, remain unclear; few if any studies have simultaneously assessed the magnitude and regulation of biological and photochemical degradability across gradients representative of aquatic ecosystems at a landscape level. Here we explore the patterns in the concentrations and proportions of biologically and photo-chemically degradable DOC across boreal lakes, rivers and wetlands, and the degree to which those distinct pools of DOC co-vary in natural waters. We targeted this diversity of aquatic ecosystems because they represent the existing gradient in terms of connectivity with land and therefore in the extent of terrestrial influence on aquatic DOC dynamics. We then use a combination of optical and chemical properties in order to explore how intrinsic DOC composition and extrinsic environmental properties respectively

drive the concentrations of Bd- and Pd-DOC in boreal natural waters. Finally, we explore how a continuous gradient of terrestrial influence (using CDOM as a proxy, see Lapierre et al., 2013) may underlie the patterns in the concentrations of degradable DOC across diverse and complex freshwater networks.

2.Methods

2.1 Study regions and sampling

Over the summer period from 2009 to 2013 we sampled a wide range of lakes (236), streams (204), rivers and wetlands (83; mostly beaver ponds). Those systems span over a very large geographic range (Fig. 1), which translates into very diverse climate, landscape and limnological properties. In particular, mean annual temperature and precipitation ranged from -5.7 to 4.8 °C and from 334 to 1289 mm, respectively, and catchment vegetation ranged from mixed conifer and deciduous in the south to black spruce moss forest in the north; tundra-type vegetation covered the northern-most, highest altitude sites. Aquatic environmental properties spanned over most of the freshwater gradients reported in the literature, with DOC, CDOM (a440 nm, naperian units), TN, TP and Chl *a* concentrations ranging from 0.4 - 123.9 mg L^{-1}, 0.05 - 30.0 m^{-1}, 0.03 - 1.90 mg L^{-1}, 2.24-248.2 µg L^{-1} and 2.2 - 248.2 µg L^{-1}, respectively, across the sampling sites (Lapierre et al. 2013). Hydrology and morphometry were also very different across the systems studied, with rivers ranging from Strahler order 1 to 6, and lakes and wetlands ranging from 0.01 to 2300 km^2 (Lapierre et al., 2013), as well as mean depth and discharge ranging over several orders of magnitude (Lapierre and del Giorgio, 2012;Campeau et al., 2014). The different sites were seldom part of the same catchment except for the largest lakes and rivers that drained vast territories.

Water was sampled at 0.5 m from the surface from the deepest measured point of lakes. It was sampled near the shore of streams, rivers and wetlands and in all cases, it was immediately filtered (0.45 µm) and stored in acid-washed glass vials for DOC, optical analyses and inorganic N. Samples for total nitrogen (TN) and phosphorus (TP) were also stored in acid-washed glass vials but were not filtered. All samples were immediately stored in cold and dark conditions. Analyses were typically performed within a month; optical measurements and inorganic N were typically performed within two weeks.

2.2 Biological and chemical analyses

136 DOC concentration was measured on an OI 1010 TIC-TOC (TX, USA) analyzer following sodium
137 persulfate digestion. We analyzed TP spectrophotometrically after persulfate digestion and TN was
138 analyzed as nitrate following alkaline persulfate digestion and measured on an Alpkem FlowSolution IV
139 autoanalyzer; ambient nitrites and nitrates were measured individually prior to persulfate digestion
140 (APHA, 1998). Ammonium was measured by fluorescence following Holmes et al. (1999). Chl *a* samples
141 were analyzed spectrophotometrically after filtration on Whatman (GF/F) filters and hot ethanol (90 %)
142 extraction (Marker and Nusch, 1980). Filters were sonicated prior to extraction. Each of those variables
143 has been collected in duplicates in the field; we present the mean here.

144 *2.3 Optical analyses*

145 The absorbance of colored dissolved organic matter (CDOM) was measured on nanopure-
146 corrected samples of filtered ambient water from 230 to 700 nm, using a UV-visible Ultrospec 2100
147 spectrometer (Biochrom, Cambridge, UK) and a 2-cm quartz cuvette. We report CDOM as the absorption
148 coefficient at 440 nm (in m^{-1}, naperian units), calculated by dividing the optical absorbance at 440 nm by
149 the path length in meters and multiplying by 2.303 (Cuthbert and del Giorgio, 1992). We also calculated
150 proxies of DOC aromaticity and molecular weight by estimating the DOC specific absorbance at 254 nm
151 ($SUVA_{254}$) and the ratio of absorbance at 250 nm to 365 nm (Spencer et al., 2009a), respectively. The
152 former was calculated by dividing absorption coefficients at 254 nm by DOC concentration and the latter
153 was directly obtained from the ratio of absorption coefficients at these specified wavelengths.
154 Fluorescence intensity was measured on a Shimadzu RF5301 PC (Shimadzu, Kyoto, Japan),
155 across excitation wavelengths of 275– 450nm (5 nm increments) and emission wavelengths of 280–600
156 nm (2nm increments) in order to build excitation-emission matrices (EEMs). A parallel factor (PARAFAC)
157 model (Stedmon et al., 2003) was developed to identify and quantify groups of DOM that shared similar
158 optical properties and distribution across the sampled sites. Fluorescence data were corrected for inner-

159 filter effect and standardized to Raman units using the FDOMcorr 1.6 toolbox (Murphy et al., 2010) in
160 MATLAB (MathWorks, Natick, MA, USA). The model was based on 1349 samples from ambient waters
161 and from photochemical degradation experiments, and was performed on corrected data using the
162 DOMfluor 1.7 toolbox (Stedmon and Bro, 2008); only part of the data are reported here. The initial
163 dataset comprised 1577 samples; samples for which absorbance within the 1 cm cuvette was higher
164 than 0.6 at 254 nm were excluded due to potential for ineffective inner filter effect correction (Miller et
165 al., 2010), which could bias the final model. We express the "concentrations" of fluorescence
166 components as the maximum fluorescence intensity at the peak. These represent relative
167 concentrations that may be used to explore the cross-sample patterns for a given component, but this
168 does not necessarily mean that one unit of a given component represents an equal amount of DOM
169 compared to one unit of any other component.

170 *2.4 Biological and photochemical DOC degradation*

171 We carried out standardized biological and photochemical degradation experiments in order to
172 derive a concentration of degradable DOC that did not depend on varying incubation conditions and
173 would thus be fully comparable across ecosystems and in time (Lapierre et al., 2013). The experiments
174 were started on the same day that the samples were collected. Biological degradation experiments were
175 carried out in water that was filtered through 2.8 µm nominal pore size GF/D filters (Whatman) in order
176 to maintain the *in situ* bacterial community and thus to avoid re-inoculation. Water samples were
177 incubated in the dark at a fixed incubation time (14 days) and temperature (20°C). The results presented
178 in Figs. 2 and 3 correspond to the concentrations in biologically degradable DOC (Bd-DOC), expressed as
179 the absolute amount of DOC removed over a period of 14 days, calculated as the difference in
180 concentration before and after degradation. Percent degradable DOC was calculated as the fraction
181 represented by the difference between DOC concentration at the start of the experiment and Bd-DOC,
182 multiplied by 100.

183 A subset of the filtered (2.8 µm) water was used for photochemical degradation experiments,
184 which were carried out in a solar simulator (Qsun XE1-BC, Qlab, FL, USA) under a standard light dose
185 (0.68 W m^{-2} at 340 nm, spectrum representative of natural sunlight) in 24 mm diameter glass tubes
186 disposed horizontally. Given the strong light dose and the small cross-section of the tubes, there was a
187 negligible effect of the CDOM concentrations on the effective light dose inside the tubes, even for the
188 most colored samples (See Appendix A for details). The amount of light energy available in the vial for
189 wavelengths comprised between 300 and 450 nm, responsible for most photochemical processing of
190 DOC (Vähätalo et al., 2000), averaged 130.8 W m^{-2} and did not vary substantially across samples due to
191 self-shading (std.dev. = 9.2 W m^{-2}; 10th and 90th percentiles = 118.4 and 140.4 W m^{-2}, respectively)
192 compared to the range of variation measured in the concentrations of photo-chemically degradable
193 DOC (Pd-DOC), which spanned several orders of magnitude. Consequently, standardizing the
194 concentrations in Pd-DOC for the corrected light dose in the corresponding tubes could in no way alter
195 the patterns and conclusions of the current study (see Figure A2). We therefore report the uncorrected
196 values (in mg C L^{-1} of photo-chemically degradable DOC). We assume that most bacteria could not
197 survive the very strong UV dose and thus significantly contribute to the DOC loss in irradiation
198 experiments; even if that were not the case, the DOC loss rates (expressed per day) were always at least
199 one order of magnitude higher in photochemical degradation experiments compared to biological
200 degradation experiments conducted in the dark (Lapierre et al., 2013).

201 Photo-exposure time (24 hours) and temperature (24 °C) were the same for all experiments
202 (Lapierre et al., 2013). The data presented in Figs. 2 and 3 correspond to the amount of DOC removed in
203 1 day under those conditions; considering diel light cycles and the natural light intensity at the studied
204 latitudes, this would roughly correspond to six days of natural light exposure in the sampled regions.
205 Irradiated samples were stored in 40 ml glass tubes and directly analyzed for DOC concentration. We

206 also measured DOM optical properties before and after irradiation for a subset (n = 187) of the samples.
207 The fluorescence data were included in the PARAFAC model.

208 *2.5 Statistical analyses*

209 Analyses of variance, simple and multiple linear regressions and principal components analyses
210 (PCA) were performed on log-transformed data in JMP 7.0.1 software. Data were centered and
211 standardized before performing the PCA. The best multiple linear regression (MLR) models were
212 identified using forward step-wise selection based on change in Akaike information criterion (AIC.)
213 Moving window regressions (MWR) of fluorescence component C6 against CDOM concentrations were
214 performed successively on subsets of 250 samples (about half of the sample size) sorted by increasing
215 CDOM.
216

217 **3. Results**

218 *3.1 Patterns in the amounts and proportions of degradable DOC*

219 The amounts of DOC removed in these standardized incubations ranged from 0.05 to 15.2 mg L^{-1}
220 and from almost 0 to 26.0 mg L^{-1}, for biological and photochemical degradation, respectively (Fig. 2).
221 This represented 0.13% to 54.3%, and from 0.04 to 72.6% of the ambient DOC pool where those
222 samples were collected, respectively (Fig. 2). These numbers represent potential degradation under
223 standardized conditions and depending on environmental conditions may not be expressed in situ; they
224 should not be considered as representative of ambient rates. They do allow, however, to isolate DOC
225 degradability while minimizing the influence of site-specific conditions, such as temperature or
226 irradiation, and thus to explore the patterns and drivers of this degradability over a large range of DOC
227 properties.

228 The amounts and proportions of degradable DOC were typically lower in lakes than in rivers and
229 wetlands (Fig. 2). Both the amounts and proportions of Bd-DOC were highest in wetlands, whereas
230 rivers contained the highest proportions of Pd-DOC, but similar amounts of Pd-DOC compared to
231 wetlands (Fig. 2). There was no relationship at all between the percent Bd-DOC and Pd-DOC across the
232 ensemble of almost 300 lakes, rivers and wetlands for which those measurements were available (Fig.
233 3a). There was, however, a significant positive relationship between the absolute amounts of Bd-DOC
234 and Pd-DOC in lakes (, rivers and wetlands separately. There was thus a significant coupling between
235 both pools of DOC when all the systems were considered together , and this coupling was typically
236 stronger in rivers and wetlands than in lakes (Fig. 3b). There was a very large scatter around the
237 regression, however, and concentrations of Pd-DOC ranged by more than one order of magnitude for
238 any given amount of Bd-DOC, and *vice-versa*.

239 *3.2 The PARAFAC model*

240 The PARAFAC model identified six fluorescence components (Fig. 4), corresponding to humic-,
241 fulvic- and protein-like material that are widely reported in freshwaters. In particular, quantitative
242 comparison of our components to published components (using OpenFluor database, (Murphy et al.,
243 2014)) revealed that components C1 and C2 reported here matched very well previously reported
244 humic-like, terrestrially derived material identified in a variety of aquatic environments (Stedmon et al.,
245 2003;Shutova et al., 2014). Component C5 and C6 matched widely reported components (Cory and
246 McKnight, 2005;Fellman et al., 2008;Kothawala et al., 2013b, among others), which have been
247 associated to microbially derived humic-like and freshly produced protein-like material, respectively.
248 The whole spectra of components C3 and C4 did not show a strong match with any fluorescence
249 component published in the OpenFluor database, but had fluorescence peaks comparable to other
250 published humic- and fulvic like material (Guillemette and del Giorgio 2012, Lu et al 2013); these
251 components had excitation spectra ranging in the UV-B and UV-A regions (Fig. 4), indicating that they
252 strongly absorb light at those wavelengths.
253 Although the model was not run with samples with the highest absorbance, as described in the
254 Methods section, it was subsequently used to estimate the concentration of fluorescence components
255 in highly colored samples for which the inner-effect correction may not optimal. Hence, for the 43
256 samples with absorbance ranging from 0.6 to up to 1.2 at 254 nm (cm^{-1}), the concentration of
257 tryptophan-like component C6 may have been slightly under-estimated whereas the concentration of
258 the remaining fulvic- and humic-like components may have been over-estimated by up to 20% (Miller et
259 al., 2010). Recent findings, however, suggest that the correction that we have performed adequately
260 corrects for inner-filter effect for absorbance up to 1.5 cm^{-1}, such that the bias, if any, would actually be
261 much smaller (Kothawala et al., 2013a) Similar to the range of variation in Pd-DOC, the concentrations
262 in the different fluorescence components varied by several orders of magnitude across the sampled

263 sites, and thus the small bias that may be present in these 43 highly colored samples is unlikely to
264 influence the patterns reported here.

265 *3.3 Linking patterns in degradable DOC to DOM composition and nutrients*

266 There were significant differences in the amounts and proportions of degradable DOC across
267 different types of systems (Figure 2), and a principal component analysis (PCA) further shows that lakes,
268 rivers and wetlands tend to group not only in terms of concentrations of total and degradable DOC, but
269 also in terms of DOM composition and nutrient concentrations (Fig. 5). The concentrations of DOC,
270 CDOM, the individual fluorescence components identified by the PARAFAC model, and nutrients all
271 tended to co-vary along a "concentration" axis (Component 1 of the PCA plot), which explained 45.4% of
272 the total variability in the measured variables (Fig. 5). Fluorescence components C1, C2 and C3, as well
273 as CDOM had the highest loadings on axis 1, and rivers and wetlands tended to have the highest scores
274 on this axis. The absolute amounts of Bd-DOC and Pd-DOC were also positively associated to this axis,
275 implying that systems with higher amounts of DOM and nutrients tended to have overall more
276 degradable DOC.

277 The links between DOC degradability and composition are captured by the second axis of the
278 PCA, which explained 23.7% of the variability. Concentrations of nutrients, as well as concentrations and
279 proportions of protein-like C5 and C6 are all situated in the top half of the PCA, along with the a250:365
280 absorbance ratio (proxy of low molecular weight) and Bd-DOC, whereas the amounts and proportions of
281 humic- or fulvic-like C1, C2 and C4, as well as $SUVA_{254}$ and Pd-DOC, clustered in the lower half of the PCA
282 (Fig. 5); there was no clear system-specific distinction along this "composition" axis. These results
283 suggest that whereas the absolute amounts of biological and photochemical degradability are both
284 associated to the total amount of DOC, these two aspects of degradability are clearly linked to distinct
285 pools within the bulk DOC.

286 *3.4 The drivers of the concentrations of biologically and photo-chemically degradable DOC*

287 The differential regulation of Bd-DOC and Pd-DOC is more clearly expressed by their direct
288 relationships with nutrients and the various DOM components (Table 1); pH and the concentration of
289 Chl *a* were not significant predictors when the variables presented in Table 1 were included. Likewise,
290 the inclusion of a categorical variable for system type (Lake, River, Wetland), or for the sampling region
291 (see Fig. 1) did not improve the fit in multiple regression models predicting either component of
292 degradability. There was thus no systematic ecosystem- or region-specific differences in the relationship
293 between Bd-DOC and its predictors, suggesting that the amount of biologically degradable DOC in the
294 studied systems is mainly a function of DOM composition and nutrients regardless of the type of aquatic
295 environment and the region where they lie.
296 Bd-DOC was strongly related to both DOM and nutrient concentrations (Fig. 5, Table 1), and TN
297 was the strongest single predictor (Table 1). Among the fluorescence components, the concentration of
298 protein-like component C6 was the strongest predictor of Bd-DOC (Model a, Table 1); no other
299 component had a significant effect on Bd-DOC once C6 was included. In contrast to Bd-DOC, DOM
300 optical properties played a greater role as predictors of Pd-DOC. The best MLR models for Pd-DOC
301 included a positive relationship with both the abundance and the relative proportions of component C3,
302 and negative relationships with the proportions of components C5 and C6 (Table 1). The EEMs analysis
303 allowed to identify specific pools of DOM that are particularly linked to ambient DOC biological or
304 photochemical degradability, but the concentration aspect was mostly captured by CDOM (measured as
305 absorbance at 440 nm, see methods) alone in both cases (Table 1, model c, g). In particular, when
306 concentrations of CDOM were included in MLR, no other variable associated to concentration of DOM
307 was significant in predicting Pd-DOC, but qualitative aspects of DOM, such as the percent contribution
308 of C3 and C6 (the latter negatively related) still significantly improved the model.
309 *3.5 Factors influencing the relationship between the concentrations of biologically and photo-chemically*
310 *degradable DOC*

311 The above patterns in nutrients and DOM concentration and composition were reflected in the
312 residuals of the relationship between Bd-DOC and Pd-DOC. Sites with higher concentrations of CDOM
313 and proportions of the very photo-chemically degradable fluorescence component C3 (see below)
314 tended to contain more Pd-DOC per unit Bd-DOC (Table 1, model h). Conversely, sites with higher
315 proportions of protein-like component C6 and higher nutrient concentrations tended to have a DOC
316 pool that was more biologically degradable per unit Pd-DOC.

317 *3.6 Susceptibility of DOM components to photochemical degradation*

318 We further explored the photochemical degradability of specific pools of DOM in a subset of the
319 irradiation experiments. Component C3, which emerged as one of the main drivers of Pd-DOC, was
320 extremely photosensitive and was often completely removed after 12 to 24 hours of irradiation. In
321 contrast, components C5 and C6, the latter being a major driver of Bd-DOC (Table 1), appeared to be
322 largely un-reactive to irradiation, whereas the concentration of component C4 systematically increased
323 following irradiation, suggesting the photo-chemically mediated production of this component.
324 Components 1 and 2 showed an intermediate photochemical degradability, with an average loss of 24%
325 and 57%, respectively, of their initial fluorescence during incubations (Fig. 6). It is interesting to note
326 that these patterns of selective photochemical degradation of specific DOC components were very
327 consistent among ecosystem types and regions (see error bars in Fig. 6).

328 *3.7 Patterns of biologically and photo-chemically degradable DOC across gradients of terrestrial*
329 *influence*

330 Despite the fact that different pools of DOM were linked to the concentrations of Pd-DOC vs Bd-
331 DOC (Table 1), CDOM itself accounted for as much variability in both Pd-DOC and Bd-DOC as any
332 combination of fluorescence components, in terms of concentration. Coherent with the PCA (Fig. 5), this
333 suggests that environments with high terrestrial influence also have higher concentrations and
334 proportions of specific DOC pools associated to both Pd-DOC or Bd-DOC. Figure 5 shows the very strong

relationships that exist between CDOM and the photo-sensitive fluorescence components C2 and C3. The relationship between CDOM and component C6, which was linked to Bd-DOC, was less obvious in the PCA (Fig. 5). In this regard, there was an overall weak positive relationship between CDOM and C6 (Fig. 7a). Interestingly, the shape of this relationship varied greatly over a gradient of terrestrial influence (using CDOM as a proxy, see (Lapierre et al., 2013)). An analysis of discrete portions of this gradient using moving window regression (MWR) showed that the relationship between C6 and CDOM was not significant in low-CDOM environments (Fig. 7b), but became significant at CDOM (a440) concentrations of approximately 3 m^{-1}. Beyond this point, both the r^2 and the slope of the relationship consistently increased with CDOM concentration until the slope stabilized when the lowest CDOM in the MWR was around 4 m^{-1}. There was thus a strong link between CDOM and C6 in systems with elevated CDOM concentrations ranging from 4 to 30 m^{-1}. These results indicate that the amount of bio-labile DOC, as reflected by the C6 component of DOM, is completely uncoupled to CDOM at low levels of water color, but that the two become strongly coupled in systems with stronger terrestrial influence.

4. Discussion

4.1 Origin, age, freshness and degradability of DOC

The core result that we report here is that the concentrations of biologically and photo-chemically degradable DOC are uncoupled within any particular site, but that they nevertheless tend to positively co-vary across large geographical and environmental gradients, and in particular, along a gradient of terrestrial influence (Fig. 3b). These two functional groups of DOC are associated to compositionally distinct pools that are subject to differential regulation across the landscape, and their coupling is only apparent when both aspects of DOC degradability are assessed simultaneously over very broad gradients of terrestrial influence and across a wide range of aquatic ecosystems, as we have done in this study. This pattern likely reflects the expression of the different intrinsic DOC properties as well as environmental conditions (Guillemette and del Giorgio, 2011;Marín-Spiotta et al., 2014) that are encountered across the very diverse natural freshwater environments studied here.

The prevailing view on aquatic DOC biological degradability has been based on the notion that material from autochthonous origin is typically fresh and highly degradable whereas material from terrestrial origin tends to be old and highly altered, and thus does not contribute much to microbial processes (Hedges et al., 1988;Dittmar and Kattner, 2003;Amon and Benner, 1996). Origin and age, however, have different implications and different links to the notion of “freshness” (defined as the time relative to when DOM left its site of production, e.g. soil, aquatic organisms, and was imported into the aquatic environment) in different types of systems. For instance, in the open-ocean, freshly produced is synonymous with autochthonous and young, whereas terrestrially derived implies leftovers of a pool that entered the aquatic network months, years or even centuries before (Anderson and Williams, 1999), and is therefore both old and diagenetically altered. The terrestrially derived DOC pool in such systems is not expected to contain significant amounts of highly labile (consumed within hours to days), or even semi-labile (consumed within months to years, see Carlson (2002)) compounds. In contrast,

373 most continental aquatic environments are directly connected to a terrestrial source that delivers DOC
374 within a time frame of hours or days (Müller et al., 2013), and terrestrial DOC is therefore freshly
375 imported, but may still be either young or old (Mayorga et al., 2005;Raymond et al., 2007;Marín-Spiotta
376 et al., 2014). Recent work suggests that freshly imported terrestrial organic carbon can be readily
377 degraded in lakes and rivers even if it is extremely old (McCallister and del Giorgio, 2012;Kleber et al.,
378 2011), thus suggesting that age and origin may not be the best predictors of DOC biological degradability
379 across continental and marine waters.

380 Freshness thus appears to be a better common driver than age or origin to place apparently
381 differing patterns of DOC biological degradability on a common gradient that is independent of the type
382 of aquatic ecosystem studied. In this regard, studies in arctic rivers have shown that DOC is typically
383 more labile during the spring freshet (Mann et al., 2012;Holmes et al., 2008), when DOC has been
384 freshly imported into the aquatic environment. Likewise, DOC was more labile in temperate streams
385 characterized by low temperatures, presumably because it has been less altered than the DOC found in
386 warmer streams and thus conserved in a "fresher" state (Lu et al., 2013). Our results suggest that the
387 same basic pattern may apply not only seasonally, but also across the whole boreal aquatic network:
388 Close to the land-water interface, most of the biologically labile DOC appears to be of terrestrial origin,
389 as suggested by the increasingly tight coupling between CDOM (measured as absorbance at 440 nm, see
390 methods) and bio-labile component C6 as CDOM increases (Fig. 7). Furthermore, the highest
391 concentrations and proportions of both biologically and photo-chemically labile DOC are found in low
392 order rivers and wetlands (Fig. 2), supporting the notion that these are major hotspots for
393 biogeochemical processes in continental waters (Denfeld et al., 2013;Campeau et al., 2014). Systems
394 with greater CDOM content thus tend to contain higher concentrations of biologically and photo-
395 chemically degradable DOC (Lapierre et al., 2013), because in such environments the DOM pool is
396 fresher and contains high amounts of photo-sensitive DOM (Fig. 6, Table 1), as well as bio-labile,

397 protein-like DOM (Fig. 7, Table 1), which interestingly, closely resembles DOM from autochthonous
398 origin (Stedmon et al., 2007;Lapierre and Frenette, 2009, Fig. 7).

399 *4.2 The underlying basis of patterns in degradable DOC*

400 The patterns in the concentrations of biologically and photo-chemically degradable DOC
401 reported here allow to identify DOM pools and environmental factors that are linked to DOC
402 degradability across boreal freshwater networks. In our study the amounts of Bd-DOC and Pd-DOC were
403 measured separately, but there are known synergistic effects between the biological and photochemical
404 processing of DOC in natural environments (Miller and Moran, 1997), wherein biological and
405 photochemical processes may operate on the same DOM pool (Koehler et al., 2012). The overall
406 degradation potential of DOC could thus be different in ambient waters where these processes actually
407 co-occur, as opposed to our experimental conditions where no such interaction was possible. The
408 objective of this study, however, was not to estimate the total concentration of degradable DOC, or the
409 realized expression of this potential degradability *in situ*, but rather to explore the large-scale patterns in
410 Bd-DOC and Pd-DOC and their respective drivers across a wide variety of aquatic environments in the
411 most comparable manner possible.

412 Both intrinsic DOM properties and environmental conditions appeared to play a role in
413 determining the concentrations and relative proportions of degradable DOC observed in these boreal
414 freshwater environments. Bd-DOC was linked to nutrient concentration, and to DOM concentration and
415 composition (Fig. 5, Table 1). The influence of TN (and TP) on Bd-DOC may be threefold: 1) it may be
416 related to increased primary production and thus to the production of an autochthonous Bd-DOC
417 component (Descy et al., 2002;Demarty and Prairie, 2009); 2) it may be related to the stimulating effect
418 of nutrients on DOC degradation rates (Wickland et al., 2012;Guillemette et al., 2013); 3) it may be
419 related to DOM stoichiometry (Sun et al., 1997;Fellman et al., 2009). Chlorophyll *a* concentration,
420 however, was unrelated to Bd-DOC, and although we did not determine organic N, our measurements

421 show that the sum of ammonium, nitrates and nitrites represented on average 8% of TN, and never
422 more than 50%. These results thus suggest that an important fraction of the N in our systems was in the
423 form of DON and contained within the DOM itself along with DOC. The same is probably true for
424 phosphorus, although we do not have measurements of inorganic P to support this contention. It would
425 seem that the inclusion of N as a predictor of Bd-DOC is mostly (although not exclusively) reflecting
426 intrinsic DOM properties, i.-e. the stoichiometry and therefore quality of the DOM that was originally
427 loaded from land. This potential effect of DOM quality was reflected in absorbance and fluorescence
428 analyses, as protein-like C6 was the only DOM optical property that was related to Bd-DOC, consistent
429 with previous studies (Guillemette and del Giorgio, 2011;Fellman et al., 2008). The percent contribution
430 of C6 to total fluorescence was further strongly and positively related to the a250:a365 ratio, and
431 negatively to $SUVA_{254}$ (Fig. 5), consistent with previously reported relationships of those absorbance
432 properties with microbial processes such as bacterial production and growth efficiency (Berggren et al.,
433 2008).

434 The patterns in Pd-DOC, on the other hand, were exclusively explained by DOM optical
435 properties (Table 1). Extrinsic chemical factors are known to drive the photochemical degradation of
436 DOC (Porcal et al., 2014), and Pd-DOC was indeed significantly correlated with pH ($r^2 = 0.13$, $p < 0.001$, n
437 = 391) and iron concentration ($r^2 = 0.35$, $p < 0.001$, n = 216). These variables, however, were not
438 significant when included in multiple linear regression models containing DOM concentration or
439 composition, and CDOM entirely accounted for the concentration-effect of FDOM (Table 1), suggesting
440 that water color integrates several key biochemical properties that collectively determine
441 photochemical reactivity. The connection of Pd-DOC with CDOM or terrestrial influence in general is
442 intuitive, as land-derived DOM is typically associated to highly photo-reactive material with high humic
443 and lignin contents (Spencer et al., 2009b;Hernes et al., 2009;Stubbins et al., 2010). The average loss of
444 DOC in our incubations was 13%, whereas on average 41% of CDOM was lost during the same

445 experiments. This supports the widely accepted notion that colored DOM is preferentially removed by
446 photochemical oxidation (Graneli et al., 1996;Weyhenmeyer et al., 2012), and more importantly,
447 suggests that specific DOM pools (as shown by fluorescence components) contribute more than others
448 to the photochemical losses of DOC (Lu et al., 2013): the degradability of the various fluorescence
449 components (Fig. 6) mostly reflects the degree to which they absorb light in the UVA region (Fig. 4).
450 These results thus suggest a strong top-down control of DOM composition by photochemical processes,
451 which is reflected in the large-scale patterns of DOM composition across boreal freshwater ecosystems.
452 Certain fluorescence components were extremely photosensitive (Fig. 6); in particular, component C3
453 was typically completely degraded by light within 24h (Fig. 6). The ambient waters differ from
454 experimental conditions in terms of the light climate, but these results nonetheless suggest that there
455 are substantial losses of these fluorescence components in natural environments, and clearly indicate
456 that the photochemical loss rates of C3 are much faster than those of other components. This implies
457 that there must be a constant replenishment of this very reactive DOM across continental watersheds in
458 order to maintain the observed concentrations, such that the contribution of this highly photosensitive
459 DOM (e.g. C3) to aquatic biogeochemical processes is probably greater than what is suggested by its
460 ambient concentrations alone.

461 *4.3 Linking DOM optical properties to degradability patterns*

462 Previous work has shown that the links between the patterns of DOC consumption and the
463 dynamics of specific DOM pools identified on the basis of fluorescence are much more complex than
464 what is generally recognized, because most of these components appear to be both consumed and
465 produced by biotic and abiotic processes across diverse aquatic environments (Guillemette and del
466 Giorgio, 2012;Romera-Castillo et al., 2011;Kothawala et al., 2013b). In this regard, Fig. 6 shows a
467 consistent behaviour of the various fluorescence components in response to irradiation across lakes,
468 rivers and wetlands with very different environmental properties. It also shows that concentrations of

469 humic/fulvic component C4 systematically increased after exposure to sunlight, yet this component co-
470 varies positively and significantly with Pd-DOC ($r^2 = 0.30$, $p < 0.001$). Photosensitive component C3 (Fig.
471 5) also co-varies positively with Pd-DOC (Table 1), but clearly the mechanism underlying both
472 relationships is completely different.

473 Component C4 has an emission spectrum comparable to that of very photo-reactive C3, but the
474 excitation spectrum shifts towards shorter wavelengths (Fig. 4), suggesting that the former may be a
475 photoproduct of the latter. Given its excitation spectrum (Fig. 4), however, it is unlikely that component
476 C4 is unreactive to irradiation; Figure 6 most likely reflects the net balance of co-occurring
477 photochemical production and degradation processes rather than true reactivity, suggesting that DOC
478 that is potentially photo-reactive may be produced autochthonously in aquatic ecosystems via
479 photochemical processes. Likewise, it has been shown that photo-reactive components such as
480 component C3 reported here are also systematically produced by microbial processes during controlled
481 incubations (Guillemette and del Giorgio, 2012). To add complexity to this framework, not only may
482 biologically labile DOC be produced from the photochemical alteration of terrestrially derived DOC
483 (Bertilsson et al., 1999;Cory et al., 2013), but it can also be rendered more recalcitrant to microbial
484 degradation upon exposure to solar radiation (Tranvik and Bertilsson, 2001). It is difficult to quantify
485 those interactions, in particular the biotic (Guillemette and del Giorgio, 2012) and abiotic (Fig. 6)
486 production of Pd-DOC, but those different results nonetheless highlight the multiple processes, on land
487 and in the water, which fuel the aquatic pools of both Bd-DOC and Pd-DOC. Linking DOC degradability
488 measurements with DOM optical properties allows to uncover some of those interactions between
489 production and removal processes, which may not be detected purely based on the characterization of
490 the DOM found in ambient waters.

491 In the present study we have identified specific fluorescent DOM components associated to
492 either the biological or photochemical degradability of the ambient DOC pool across hundreds of lakes,

493 rivers and wetlands (Table 1, Figs. 3, 5). Our own work in this regard (Stubbins et al., submitted) suggests
494 that these fluorescent components involve not only the molecules responsible for the fluorescence
495 properties, but also that they tend to co-vary with a host of other, non-fluorescent compounds. The
496 molecules responsible for the actual fluorescence of these components may be acting both as
497 substrates, and perhaps more importantly, as tracers of a variety of non-fluorescent pools that share
498 similar sources and sinks, and which may themselves be the main substrates of these microbial
499 reactions.

500 In this regard, the very strong photochemical degradability of component C3 (Fig. 5), combined
501 with published evidence of consistent losses of a comparable component over a gradient of land cover
502 and water retention time in the landscape (Kothawala et al., 2013b;Lu et al., 2013), suggest that it is
503 indeed acting as a substrate for photochemical degradation, and that C3 is a causal driver of Pd-DOC in
504 freshwater environments. Our measurements, however, cannot confirm whether component C6 is
505 mostly driving Bd-DOC as a substrate for microbial processes or acting as a tracer of co-varying bio-labile
506 molecules. Regardless, our results indicate that Bd-DOC and Pd-DOC pools may be adequately tracked
507 by specific DOM properties across a large diversity of freshwater environments, presumably because
508 optical measurements allow to target meaningful DOM pools comprising different molecules which
509 share common production, importation, and removal processes.

510 *4.4 Land as a source of both biologically and photo-chemically degradable DOC*

511 Although it may appear intuitive that both Bd-DOC and Pd-DOC increase with overall DOC, the
512 coupling between the concentrations of Bd-DOC and Pd-DOC implies that they share at least some basic
513 sinks, or more likely, sources, in boreal watersheds. The biological and photochemical processes
514 responsible for the removal of DOC from those boreal freshwaters are driven by different extrinsic
515 variables and target different DOM pools (Table 1, Fig. 6), and the biological and photochemical
516 degradability of DOC, expressed as the fraction of DOC that is biologically or photo-chemically

517 degradable in standardized conditions, are completely decoupled (Fig. 3a). The collective evidence
518 discussed above thus rather suggests that Bd-DOC and Pd-DOC partly share land as a common origin,
519 and the relatively weak coupling between both DOC pools suggest that the relative contribution of land-
520 derived DOC to Bd-DOC differs greatly across systems.

521 In this regard, autochthonous processes such as phytoplankton and macrophyte primary
522 production are known to generate fresh, protein-like DOM in freshwaters (Demarty and Prairie,
523 2009;Lapierre and Frenette, 2009), and more importantly, may supply the Bd-DOC pool independently
524 of terrestrial sources. This appears to be the case in several systems studied here, as the coupling
525 between Pd-DOC and Bd-DOC was weaker in lakes (Fig. 3b), and the amount of bio-labile DOM,
526 expressed in the patterns of component C6, was completely independent from CDOM in the lower
527 portion of the CDOM gradient (Fig. 7) where most lakes and some large rivers were found. A comparable
528 pattern has been reported in Swedish lakes (Kothawala et al., 2013b) where the equivalent protein-like
529 FDOM component appeared to be relatively invariable across gradients of lake DOC and water retention
530 time. Contrary to that study, however, we observed a stronger relationship between C6 and CDOM as
531 CDOM increased (Fig. 7), such that highly colored systems (mostly streams and wetlands) contained
532 much higher concentrations of component C6. The inclusion of rivers ranging from Strahler order 1 to 6,
533 and of a diversity of wetlands, greatly expands the range of terrestrial influence relative to what can be
534 observed based on lakes alone, and may explain the differences between our two studies. This may be a
535 combination of low macrophyte cover and algal biomass in these typically oligotrophic boreal systems,
536 the inhibition of autochthonous processes by CDOM-induced light limitation (Karlsson et al., 2009), and
537 perhaps more importantly, the high rate of supply of terrestrial labile DOC in highly colored systems
538 (Berggren et al., 2010a).

539 There would thus appear to be a baseline of autochthonous Bd-DOC that is always present in
540 those aquatic environments and varies more or less randomly across gradients of CDOM in response to

541 simultaneously increasing nutrients (Lapierre and del Giorgio, 2012) and light limitation (Karlsson et al.,
542 2009). This baseline may be reflected in the significant intercept of the relationship between Bd-DOC
543 and Pd-DOC (Fig. 3b), which would suggest that in systems with very low terrestrial influence and almost
544 no Pd-DOC, there is still a significant pool of Bd-DOC that is likely from autochthonous origin.
545 Autochthonous sources may indeed be the main driver of Bd-DOC across narrow CDOM gradients, as
546 previously reported (Kritzberg et al., 2004;Guillemette et al., 2013;McCallister and del Giorgio, 2008),
547 but the land-derived Bd-DOC might be the one pool which varies consistently across gradients of
548 terrestrial influence and may thus better explain the patterns in DOC degradability across continental
549 watersheds. These patterns collectively suggest that terrestrially derived Bd-DOC increases
550 proportionately faster than or independently from autochthonous Bd-DOC along a gradient of increasing
551 CDOM, such that land becomes an important, and even the main source of Bd-DOC as terrestrial
552 influence increases. This in turn may explain why bio-labile component C6 (and the molecules it tracks)
553 may actually accumulate and reach high concentrations in wetlands and rivers with very high terrestrial
554 influence, whereas in lakes it is typically decoupled from CDOM (Fig. 7), as well as from DOC
555 concentrations and water retention time (Kothawala et al., 2013b), since in the latter systems
556 production, importation and removal may be closer to steady-state.

557 Our results highlight the apparent links that tie terrestrial influence, water retention time and
558 DOC freshness with DOC composition and degradability across boreal freshwaters. In a previous study
559 we had shown that the concentrations of both Bd-DOC and Pd-DOC tended to increase with CDOM
560 content (Lapierre et al., 2013), resulting in increases in CO_2 flux. This result also suggested an additive
561 dynamic of DOC degradability along a gradient of terrestrial influence, and here we show that the role of
562 land as a major source of both biologically and photo-chemically degradable DOC to continental
563 watersheds results in a pattern of co-variation between these two key pools of carbon across boreal
564 aquatic networks, despite fundamental contrasts in terms of their composition and regulation. The

potential of terrestrially derived organic carbon to contribute to ecological and biogeochemical processes in boreal freshwaters is thus apparently not limited by its degradability, at least in environments with high terrestrial influence where this carbon has been freshly imported.

Appendix A

Standardizing Pd-DOC based on average light dose in the experimental tubes

One of the main objective of this study was to assess the patterns in the concentrations of photo-chemically degradable DOC, in the most standardized way possible. While the photochemical degradation experiments have been conducted in standardized conditions in terms of incoming light dose, exposure time and temperature, the average light dose within the experimental tubes varied depending on CDOM content which attenuated a fraction of the incoming light and resulted in self-shading. We tested the potential significance of this self-shading effect on the reported patterns by comparing the uncorrected Pd-DOC values to light-standardized concentrations, which were obtained by dividing each Pd-DOC concentration by the average light energy available (accounting for self-shading, see below) in the corresponding tube in which the experiment was conducted.

Absorbance scans were obtained for half of an empty glass tube (to account for the energy lost when passing through the glass, see Fig. A1) as well as for the colored dissolved organic matter (CDOM) contained in each sample, as described in the Methods section. The tubes were round, horizontally disposed in the solar simulator and had an inner diameter of 24 mm, so we calculated the proportion of each wavelength that was remaining in ten different 2.4 mm-thick sections of the tube. The solar simulator light had a total light dose of 750 W m^{-2} and a spectrum representative of the sunlight (Fig. A1), which was used to calculate the total amount of light energy (in W m^{-2}) available in each section of the experimental tube by multiplying the incoming light dose by (1 - fraction absorbed (by glass and CDOM)). Only the 300-450 nm range of wavelengths was used. The lamp emitted substantial amounts of longer wavelengths, which were not significantly absorbed by either the glass or CDOM, thus although those wavelengths (450-750 nm) contribute a large fraction of the total energy delivered, they typically do not contribute much to photochemical processes (Vähätalo et al., 2000). Including these wavelengths would thus tend to attenuate the cross-sample differences in average light dose.

We then calculated a weighted average in the amount of light energy contained in the ten layers based on the relative volume that each occupies in the tube. The average light dose varied little in the tubes (see section 2.4 in Methods) but the measured concentrations in Pd-DOC among samples varied by more than three orders of magnitude (Fig. 3b). As a result, although standardizing the raw Pd-DOC values by the average effective light dose within the corresponding experimental tube resulted in a certain bias when comparing the lowest to the highest CDOM samples, when these individual differences are put in perspective of the whole set of Pd-DOC data (which ranges over several orders of magnitude) the little amount of variation that is generated the relationship is barely noticeable. (Fig. A2). There was a small amount of variation for the highest CDOM samples, but this potential variation is arguably smaller than measurement error in other reported variables against which Pd-DOC is correlated. We thus chose to present uncorrected Pd-DOC values, which are more intuitively comparable to the concentrations of Bd-DOC (in mg L^{-1}) that we report in this study.

Appendix A Figure legend

Figure A1. Comparing the lamp spectrum to light absorption from the glass and from CDOM. The same scan was used to correct for absorption of light by glass for all the samples, whereas the corresponding CDOM scan was used for each sample; the illustrated CDOM scan corresponds to a representative river sample.

Figure A2. Comparing uncorrected *vs* light-standardized concentrations of Pd-DOC based on CDOM self-shading for wavelengths ranging 300-450 nm.

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Table 1. Multiple linear regression models predicting the concentrations of photo-chemically and biologically degradable DOC across boreal lakes, rivers and wetlands. Abbreviations are defined in the text. Fluorescence components in square brackets correspond to the absolute concentration of the specified component. The sign in parentheses denotes the sign of the coefficient in the MLR model.

Response variable	Model	Predictors	n	adj. r^2	AIC
Bd-DOC	a	(+)[C6]	323	0.35	-675
	b	(+)TN	319	0.40	-683
	c	(+)TN, (+)CDOM	317	0.45	-696
	d	(+)TN, (+)[C6]	317	0.45	-693
	e	(+)TN, (+)[C6], (+)TP	316	0.46	-699
Pd-DOC	f	(+) [C3], (-) %C5, (-) %C6	392	0.67	-818
	g	(+) CDOM, (+) %C3, (-) %C6	392	0.73	-887
Residuals of Pd-DOC vs Bd-DOC	h	(+)%C3, (+)CDOM, (-)%C6, (-)TP	264	0.27	-406

865 **Figure legends**

866 Figure 1. Distribution of the sampling sites across seven boreal regions (James Bay, Abitibi, Laurentians,
867 Saguenay, Chibougamau, Schefferville) of Quebec, Canada. Grey lines and area represent large rivers
868 and lakes; green lines delimit the main watersheds in Quebec.

869 Figure 2. Amounts and proportions of biologically and photo-chemically degradable DOC across the
870 three main types of systems studied. Lines represent the 25, 50 and 75 percentiles, points, 5 and 95
871 percentiles. Different letters denote statistically different ($p < 0.01$) means across groups, based on
872 ANOVA and Tukey-Kramer post-hoc analyses. Bd-DOC (percent and absolute) : n = 201 for lakes, n = 71
873 for rivers, n = 53 for wetlands. Pd-DOC (percent and absolute): n = 193 for lakes, n = 136 for rivers, n =
874 67 for wetlands.

875 Figure 3. Relationship between the proportions (a) and amounts (b) of biologically and photo-chemically
876 degradable DOC across boreal lakes, rivers and wetlands. a) n = 262, not significant. b) lakes: log(Bd-
877 DOC) = 0.16log(Pd-DOC) - 1.67, $p = 0.0003$, $r^2 = 0.11$, n = 161; rivers: (log(Bd-DOC) = 0.88log(Pd-DOC) -
878 1.59, $p < 0.0001$, $r^2 = 0.33$, n = 58); wetlands (log(Bd-DOC) = 0.78log(Pd-DOC) - 1.34, $p < 0.0001$, $r^2 = 0.23$,
879 n = 50; overall relationship: log(Bd-DOC) = 0.71 log(Pd-DOC) -1.48, $p < 0.001$, n = 268.

880 Figure 4. Fluorescence signatures of the components identified by the PARAFAC model. Fluorescence
881 peaks are observed at the following wavelengths (nm), for excitation and emission,respectively
882 (secondary peak in parentheses): C1: 275, 424; C2: 275(340), 484; C3: 275(345), 436; C4: 334, 446; C5:
883 300, 388; C6: 275, 334

884 Figure 5. Principal component analysis of concentrations of degradable DOM, DOM optical properties
885 and nutrients across boreal lakes, rivers and wetlands. Abbreviations are defined in the text.

Fluorescence components in square brackets correspond to the absolute concentration of the specified component.

Figure 6. Average loss of specific fluorescence components based on the difference in concentration before and after irradiation for samples originating from boreal lakes, rivers and wetlands. Rates have been reported on a per day basis based on the average of the FDOM loss measured after 12 and 24 hours; this allowed to better quantify the photochemical susceptibility of C3 which was commonly completely degraded after 24 hours, hence the average per day loss of over 100 %. n = 121

Figure 7. Concentrations of protein-like C6 as a function of CDOM in lakes, rivers and wetlands. a: r^2 = 0.32, $p < 0.001$, n = 519. b: Parameters of moving window regressions performed on discrete portions of the dataset based on increasing CDOM. Total sample size was 519, but individual regressions were performed on subsets of 250 samples; a total of 270 regressions were thus performed. "x" signs denote non-significant regressions. X axis shows the lowest CDOM concentration included in the regression for which the parameters are reported. The first regression was thus performed on samples for which CDOM ranged from 0.12 to 3.11 m^{-1}, whereas the last regression was performed on samples for which CDOM ranged from 5.55 to 30.0. Note that the slope characterizes the log(C6) vs log(CDOM) relationship.

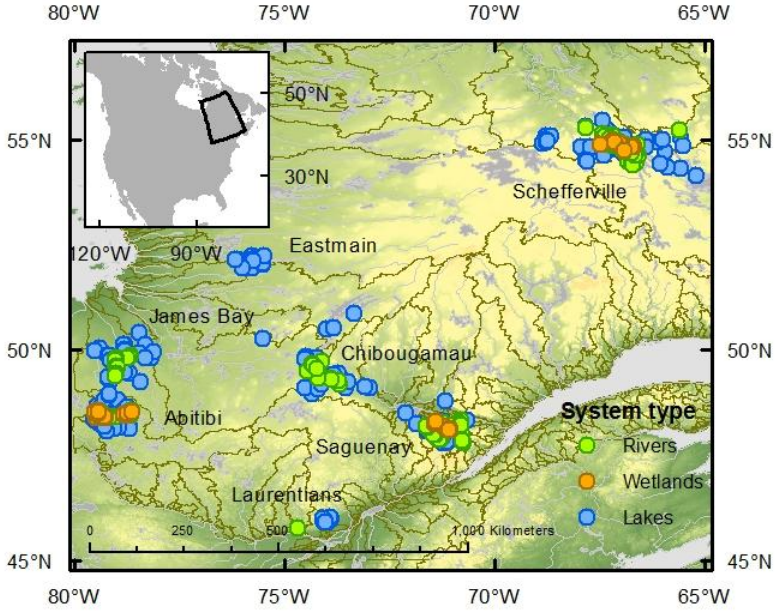
80°W
75°W
70°W
65°W
55°N
50°N
45°N
50°N
30°N
120°W
90°W
Scheffer ville
Eastmain
James Bay
Chibougamau
Abitibi
Saguenay
Laurentians
System type
Rivers
Wetlands
Lakes
0
250
500
1,000 Kilometers

Figure 1.

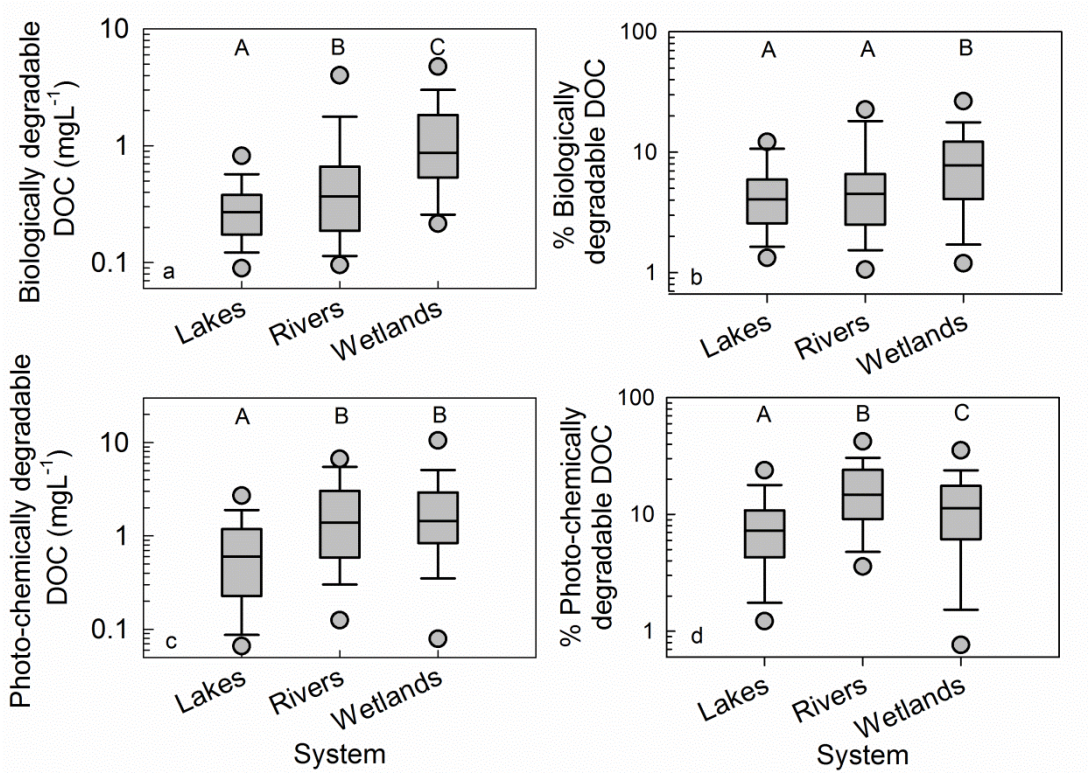
Biologically degradable DOC (mgL-1)
10
1
0.1
a
A
B
C
Lakes
Rivers
Wetlands
% Biologically degradable DOC
100
10
1
b
A
A
B
Lakes
Rivers
Wetlands
Photo-chemically degradable DOC (mgL-1)
10
1
0.1
c
A
B
B
Lakes
Rivers
Wetlands
System
% Photo-chemically degradable DOC
100
10
1
d
A
B
C
Lakes
Rivers
Wetlands
System

Figure 2.

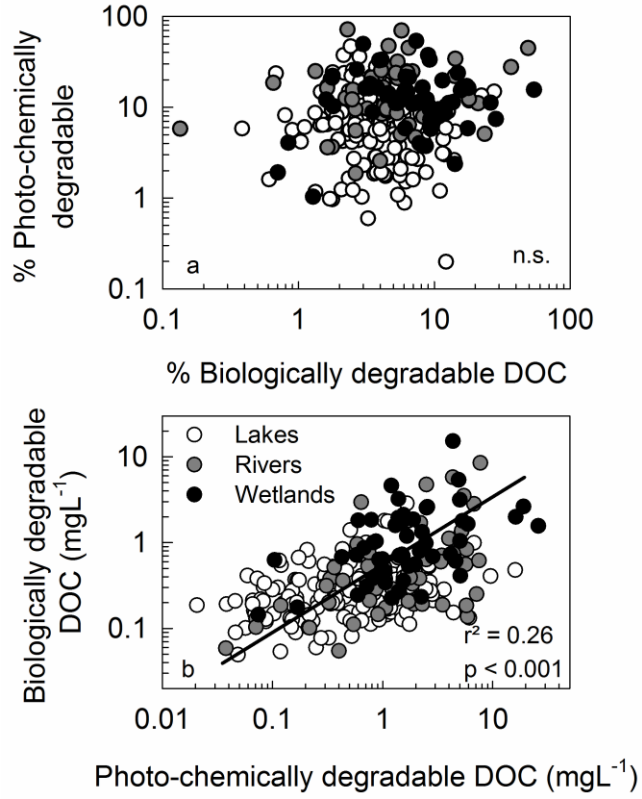
% Photo-chemically degradable
100
10
1
0.1
a
n.s.
0.1
1
10
100
% Biologically degradable DOC
Biologically degradable DOC (mgL-1)
Lakes
Rivers
Wetlands
10
1
0.1
b
r² = 0.26
p < 0.001
0.01
0.1
1
10
Photo-chemically degradable DOC (mgL-1)

Figure 3.

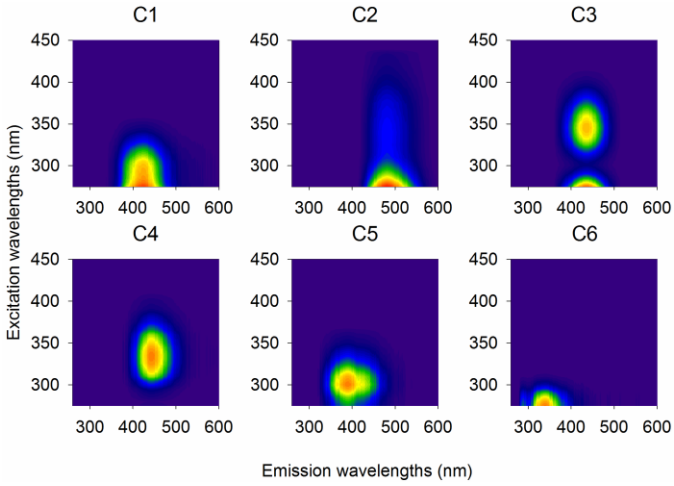
C1
C2
C3
C4
C5
C6
450
400
350
300
300 400 500 600
Excitation wavelengths (nm)
Emission wavelengths (nm)

Figure 4.

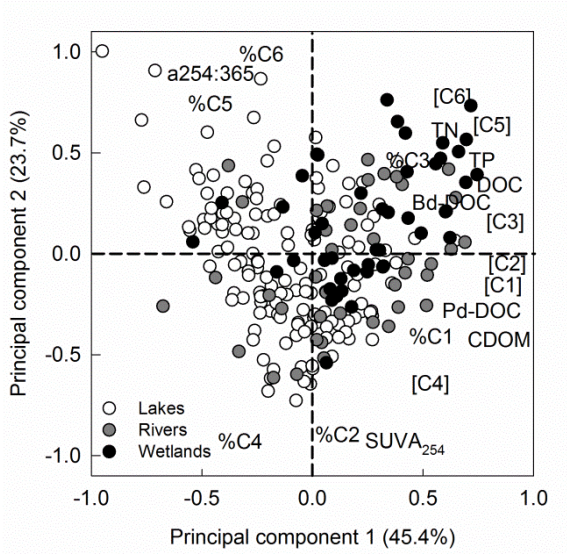
%C6
a254:365
%C5
[C6]
TN
[C5]
%C3
TP
DOC
Bd-DOC
[C3]
[C2]
[C1]
Pd-DOC
%C1
CDOM
[C4]
Lakes
Rivers
Wetlands
%C4
%C2
SUVA254
Principal component 2 (23.7%)
Principal component 1 (45.4%)
1.0
0.5
0.0
-0.5
-1.0
-1.0
-0.5
0.0
0.5
1.0

Figure 5.

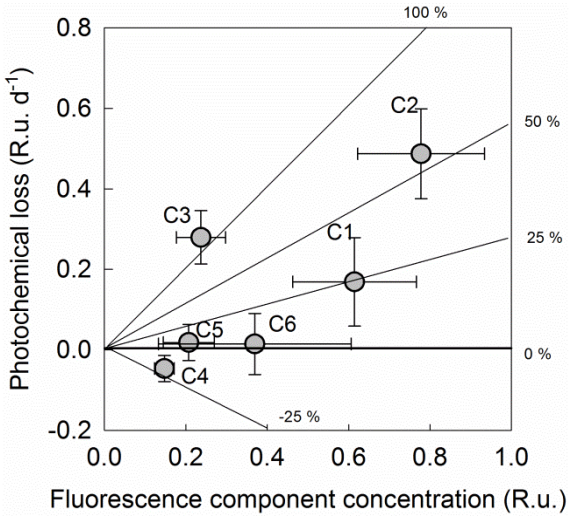
100 %
50 %
25 %
0 %
-25 %
C1
C2
C3
C4
C5
C6
0.8
0.6
0.4
0.2
0.0
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
Photochemical loss (R.u. d-1)
Fluorescence component concentration (R.u.)

Figure 6.

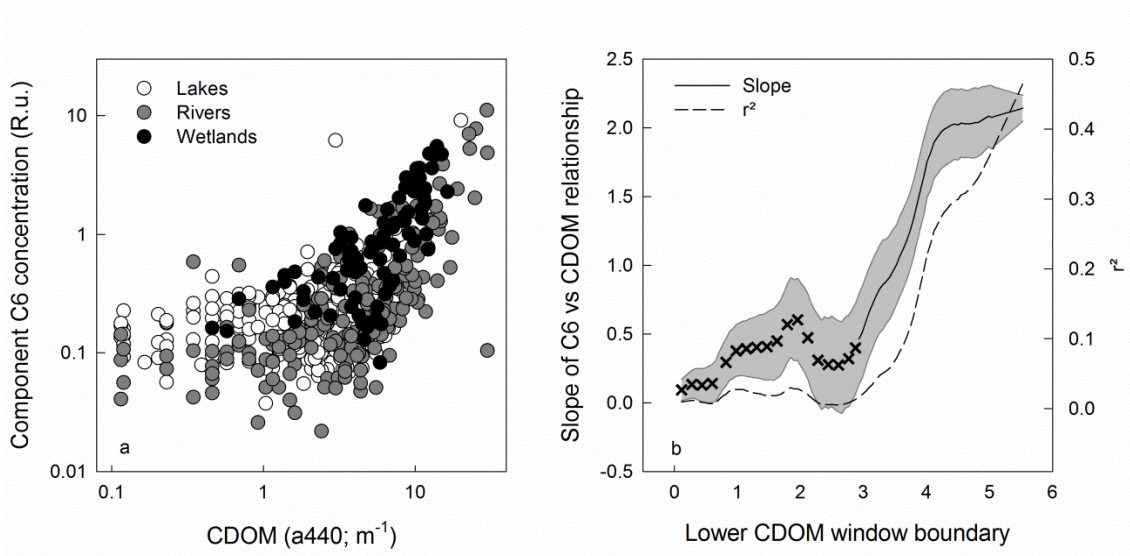
Lakes
Rivers
Wetlands
Component C6 concentration (R.u.)
CDOM (a440; m-1)
a
Slope
r²
Slope of C6 vs CDOM relationship
Lower CDOM window boundary
b

Figure 7.

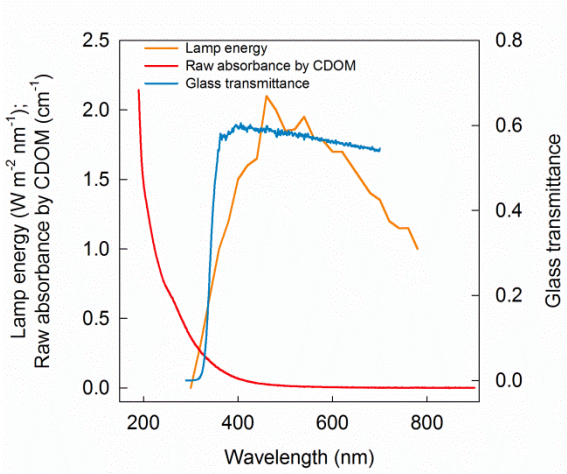
Lamp energy
Raw absorbance by CDOM
Glass transmittance
Lamp energy (W m-2 nm-1);
Raw absorbance by CDOM (cm-1)
Glass transmittance
Wavelength (nm)
2.5
2.0
1.5
1.0
0.5
0.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800

Figure A1.

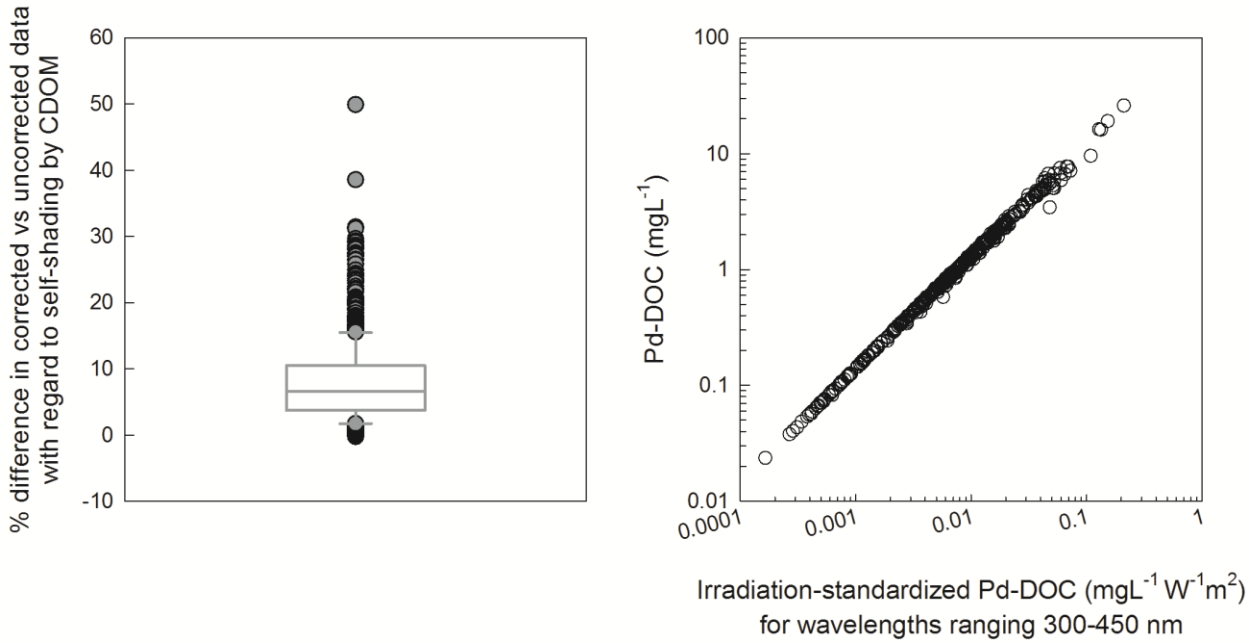
% difference in corrected vs uncorrected data with regard to self-shading by CDOM
60
50
40
30
20
10
0
-10
Pd-DOC (mgL-1)
100
10
1
0.1
0.01
0.0001
0.001
0.01
0.1
1
Irradiation-standardized Pd-DOC (mgL-1 W-1m2) for wavelengths ranging 300-450 nm

Figure A2.