

1 **Impact of forest harvesting on water quality and fluorescence**  
2 **characteristics of dissolved organic matter in Eastern Canadian Boreal**  
3 **Shield lakes in summer**

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13

14 **Abstract**

15 Forestry activities in the Canadian Boreal region have increased in the last decades, raising  
16 concerns about their potential impact on aquatic ecosystems. Water quality and fluorescence  
17 characteristics of dissolved organic matter (DOM) were measured over a three-year period in  
18 eight Eastern Boreal Shield lakes: four lakes were studied before, one and two years after  
19 forest harvesting (perturbed lakes) and compared with four undisturbed reference lakes  
20 (unperturbed lakes) sampled at the same time. ANOVAs showed a significant increase in total  
21 phosphorus (TP) in perturbed lakes when the three sampling dates were considered and in  
22 DOC concentrations when considering one year before and one year after the perturbation  
23 only. At one year post-clear cutting DOC concentrations were about 15% greater in the  
24 perturbed lakes at  $\sim 15 \text{ mgC L}^{-1}$  compared to  $12.5 \text{ mgC L}^{-1}$  in the unperturbed lakes. In  
25 contrast, absorbance and fluorescence measurements showed that all metrics remained within

26 narrow ranges compared to the range observed in natural waters, indicating that forest  
27 harvesting did not affect the nature of DOM characterised with spectroscopic techniques.  
28 These results confirm an impact of forestry activities one year after the perturbation. However,  
29 this effect seems to be mitigated two years after, indicating that the system shows high  
30 resilience and may be able to return to its original condition in terms of water quality  
31 parameters assessed in this study.

32

### 33 **1. Introduction**

34 Boreal forests, which contain large areas of wetlands and over 1.5 million of lakes, are an  
35 ecological, economic and cultural source of wealth in Canada (NRCan 2005; Kreutzweiser et  
36 al., 2008). These lakes receive allochthonous inputs of dissolved and particulate matter from  
37 natural sources and anthropic activities (Schindler et al., 1992). Forestry activities in the  
38 Canadian Boreal region have increased in the last decades, raising concerns about their  
39 potential impact on natural biogeochemical processes in soils and the export pathways that  
40 deliver dissolved nutrients and organic matter to aquatic ecosystems. After logging, the export  
41 of dissolved nutrients to aquatic ecosystems increases, which is primarily related to a higher  
42 microbial activity in upper soil layers and the forest floor (Bormann and Likens, 1994;  
43 Kreutzweiser et al., 2008). This microbial activity converts nutrients from non-mobile to  
44 mobile forms, which are exported to receiving waters (Buttle et al., 2005), affecting loads of  
45 nutrients and organic compounds in lakes and rivers. Because forestry is the most extensive  
46 industry in much of the boreal region, the potential influence of logging on carbon reservoirs  
47 and water quality could be substantial. Therefore, there is a need to understand the long-term  
48 effects of forest harvesting on water quality, as well as its short transient repercussions.

49

50 Studies on the effects of logging activities on aquatic ecosystems in the boreal region have  
51 mostly been oriented to lotic systems (e.g. Smith et al., 2003; Laudon et al., 2009; Löfgren et  
52 al., 2009). In contrast, responses of lentic systems to logging activities in the boreal region  
53 have not been as extensively studied. Logging activities such as clear-cutting may produce  
54 significant disturbances to forest watersheds altering biogeochemical processes in soils by  
55 modifying forest vegetation cover and plant community, soils conditions, moisture and  
56 temperature regimes (Schelker et al., 2013b), soil microbial activity, water mobility and losses  
57 of leaching matter to receiving waters (Kreutzweiser et al., 2008). Increases in the watershed  
58 export of suspended solids, nutrients and dissolved organic carbon (DOC) were observed after  
59 one to three years following trees harvesting (Rask et al., 1998; Carignan et al., 2000; Winkler  
60 et al., 2009). DOC is one of the most central biogeochemical features of boreal surface waters  
61 because it affects the food web structure of surface waters in lakes (Findlay and Sinsabaugh,  
62 2003) and it acts as a microbial substrate (Berggren et al., 2007). DOC has been intensively  
63 investigated in environmental research because of its significant role in various  
64 biogeochemical and ecological processes (Findlay and Sinsabaugh, 2003; Birdwell and Engel  
65 2010). However, most of the short-term impact studies of catchment harvesting on lakes, with  
66 the exception of Winkler et al. (2009), did not measure the system before and after the  
67 perturbation in lakes that were not logged (i.e. unperturbed lakes), thereby changes due to  
68 logging cannot be separated from natural variability.

69  
70 Quantitative and qualitative information about the source, composition and reactivity of the  
71 DOC present in an ecosystem at natural abundance concentration can be obtained by  
72 spectroscopic techniques (Coble, 1996; 2007; Deflandre and Gagné, 2001; Weishaar et al.,  
73 2003; Hudson et al., 2007; Fellman et al., 2010). UV-VIS spectroscopy allows  
74 characterization of chromophoric dissolved organic matter (CDOM) while the fluorescence

75 spectra of natural waters show characteristic maxima of few fluorophores that may vary  
76 between environments (Coble, 1996; 2007; Stedmon et al., 2003). Variations in the maximum  
77 excitation or emission wavelength can also provide information relating to structure,  
78 conformation and heterogeneity of DOM as observed by Mobeb et al. (1996) for humic  
79 substances, an important class of molecules found in natural water (Tremblay and Gagné,  
80 2009). Moreover, fluorophores intensities can be used to calculate ratios to track  
81 biogeochemical processes. For instance, differences in the chemical make-up of the DOM  
82 pool can be linked to changes in DOM reactivity and may be used to infer DOM sources  
83 (Jaffé et al., 2008; McKnight et al., 2001). Thus, fluorescence spectra provide data that can be  
84 used to infer the relative contributions of autochthonous and allochthonous organic matter in  
85 natural waters (Parlanti et al., 2000; McKnight et al., 2001; Huguet et al., 2009; Fellman et al.,  
86 2010). As forestry activities can increase the export of nutrients, suspended solids and DOC  
87 into lakes (Rask et al., 1998; Carignan et al., 2000; Kreutweiser et al., 2008), and therefore, of  
88 allochthonous material, fluorescence measurements may be an appropriate tool to assess  
89 logging impact on water quality in watersheds. In a recent study, Kelton et al. (2007) used  
90 fluorescence measurements to compare characteristics of DOM from boreal, agricultural and  
91 urban sites. They observed that DOM from different landscapes could be distinguished by  
92 fluorescence spectroscopy.

93

94 The objective of this study was to analyse the short term impact of forestry activities on water  
95 quality, and on UV-VIS and fluorescence characteristics of DOC in eastern Canadian Boreal  
96 Shield lakes one year before and up to two years after the perturbation. Water quality and  
97 spectroscopic characteristics of four lakes were studied on one occasion before, and on two  
98 occasions after forestry operations (perturbed lakes, P) and compared with four undisturbed  
99 references lakes (unperturbed lakes, UP). More specifically, we tested the hypotheses that 1)

100 nutrients and DOC would be greater in perturbed lakes than unperturbed lakes one and two  
101 years after the perturbation; 2) the UV-VIS and fluorescence signatures of DOM in perturbed  
102 lakes would indicate an increase in terrestrially-derived (allochthonous) DOM after logging.

103

## 104 **2. Materials and methods**

### 105 **2.1. Study area**

106 This study was conducted in the province of Québec on the forested Mistassibi River drainage  
107 basin (50° 07'30' N, 71° 35'59' W) located on the Boreal Shield (Fig. 1). The study area is  
108 characterized by old growth forest mainly dominated by mature black spruces (*Picea mariana*)  
109 exploited by the forest industry. The soil layer over the rock is thin.

110

### 111 **2.2. Sampling**

112 Eight lakes, which are oligotrophic in this region (Winkler et al., 2009), with similar  
113 geomorphologic characteristics were selected for this study (Table 1). To evaluate the most  
114 direct impact of harvesting, headwater lakes were selected, except for UP1, UP3 and P3.  
115 Upstream lakes of UP1 and UP3 were unperturbed and for P3, the upstream lake was also  
116 unperturbed and very small in comparison of the nominal lake. These eight lakes have been  
117 unperturbed in 2008 at the beginning of this survey. In 2009 and 2010, four of these lakes  
118 were kept undisturbed (unperturbed lakes) and four other lakes (perturbed lakes) where  
119 harvested about 70% of lake catchment during autumn 2008 (Fig. 1, Table 1). All lakes were  
120 sampled once in July in 2008, 2009 and 2010. The experimental unit in this study was the  
121 lake. The forest was cut using the careful logging around advanced growth (CLAAG) strategy.  
122 Under this treatment, all trees equal to or greater than 10 cm diameter at breast height (d.b.h.)  
123 are harvested and smaller individuals are protected as future crop trees (Groot et al., 2005). A  
124 20 m strip of standing forest was intentionally kept along lakes after harvesting activities. All

125 lakes have a drainage ratio higher than 4, and perturbed lakes had a catchment area cut by 69-  
126 77% (Table 1).

127

128 Mean annual lake residence time was calculated for each lake using the following equation:

$$129 \text{ Mean annual lake residence time} = Z_{\text{MD}} \times A_{\text{lake}} \div A_{\text{catchment}} \times P \times \text{runoff} \quad (1)$$

130

131 where  $Z_{\text{MD}}$  is the mean depth,  $A_{\text{lake}}$  is the lake area,  $A_{\text{catchment}}$  is the catchment area,  $P$  is the  
132 mean annual precipitation in this region (rainfall and snow) and runoff is the runoff  
133 coefficient. This coefficient assumes that the percentage of precipitation that becomes runoff  
134 is 0.5 for undisturbed lakes and 0.8 for harvested lakes in boreal forests (Bosch and Hewlett,  
135 1982; Schelker et al., 2013a). Equation 1 is an approximation to calculate the mean annual  
136 lake residence time for each lake because for lakes, in absence of data, we assumed only  
137 precipitation and no infiltration or water uptake by tree roots, no loss of water by evaporation  
138 and evapotranspiration to the atmosphere or by groundwater recharge.

139

140 At each lake, five littoral stations were selected randomly and sampled from a vessel.  
141 Dissolved  $\text{O}_2$ , pH, conductivity, and water temperature were measured *in situ* at each  
142 sampling station using an YSI 556 MPS probe. Water transparency was estimated at the  
143 deepest zone of the lake using a Secchi disc. Water samples were collected with a bottle at 0.5  
144 m below the surface at each sampling station and filtered through 300  $\mu\text{m}$  to remove large  
145 zooplankton prior to the determination of physicochemical and biological variables. Samples  
146 for total phosphorus (TP), dissolved inorganic phosphorus and nitrogen (DIP and DIN,  
147 respectively) and suspended matter filtered for chlorophyll *a* (chl *a*) measurements were kept  
148 frozen at  $-20^\circ\text{C}$  whereas samples for DOC, CDOM absorption and DOC fluorescence

149 measurements were maintained at 4°C until analysis after appropriate filtration treatments for  
150 each parameter (see later).

151

### 152 **2.3. Water quality measurements**

153 TP was measured using the molybdenum blue method (Staiton et al. 1977) after autoclaving  
154 50 ml samples with 0.5 g of potassium persulfate for 1 h at 120°C. TP was afterwards  
155 assessed by using an AutoAnalyzer (AA3, Bran+Luebbe, German). DIP and DIN were  
156 determined using an AutoAnalyzer (AA3, Bran+Luebbe, German) after filtering water  
157 samples through a membrane filter (0.2µm Sartorius). For the determination of chl *a*, water  
158 samples were filtered (200 ml or more) onto Whatman GF/F filters. Samples were extracted  
159 for 24 h in 90% acetone at 5°C in the dark without grinding. Chl *a* was determined using the  
160 method of Welschmeyer et al. (1994). For DOC measurements, water samples were filtered  
161 through precombusted (500°C, 5 h) Whatman GF/F filters. For the determination of DOC  
162 concentrations, the filtrates were collected in clean amber glass vials with Teflon-lined caps,  
163 and samples were acidified with ten µL of 25% v/v H<sub>3</sub>PO<sub>4</sub>. The determination of DOC levels  
164 were made in NPOC mode with a TOC-5000A or a TOC-V<sub>CPN</sub> analyzer (Shimadzu, Kyoto,  
165 Japan), following a protocol similar to Whitehead et al. (2000). A calibration curve was used,  
166 with five concentrations of potassium hydrogen phthalate between 0 and 10 mgC/L to  
167 determine the DOC content of samples. DOC reference standards available from the Hansell's  
168 Consensus Reference Materials (CRM) program were used to test the instruments. Samples  
169 for DOM fluorescence and CDOM absorption measurements were filtered through 0.2 µm  
170 filters to remove bacteria and prevent decomposition of the DOC during storage. Samples  
171 were stored in dark to prevent photodegradation and photosynthesis.

172

### 173 **2.4. Absorption and fluorescence measurements**

174 CDOM absorption was determined for three stations in each lake with a Perkin Elmer  
175 Lambda 12 UV/VIS spectrophotometer, using a 5 cm pathlength quartz cuvette. Absorption  
176 measurements were done over the range 200-600 nm with a spectral resolution of 1 nm.  
177 Nanopure water was used as the blank to subtract the absorption due to pure water.  
178 Absorbance values were converted to absorption coefficient  $a_{\text{CDOM}}(\lambda)$  ( $\text{m}^{-1}$ ) using the  
179 following equation (Kirk, 1994):

$$180 \quad a_{\text{CDOM}}(\lambda) = 2.303 \times A(\lambda) \div L \quad (2)$$

181 where  $A(\lambda)$  is the absorbance at wavelength  $\lambda$  and  $L$  is the pathlength of the cell used in the  
182 absorbance measurement in meters. In this study,  $a_{\text{CDOM}}$  at  $\lambda=355$  nm ( $a_{\text{CDOM}(355)}$ ) is used for  
183 data analysis.

184

185 Specific UV absorbance (SUVA) was calculated at 254 nm.  $\text{SUVA}_{254}$  is defined as the UV  
186 absorbance of a water sample at 254 nm divided by the DOC concentration measured in mg C  
187 per liter (Weishaar et al., 2003). SUVA is a measure of the absorbance by mg of carbon  
188 present in the sample. SUVA also allows an estimation of the aromaticity of the organic  
189 carbon present in the samples.

190 Finally, the spectral slope ( $S$ ) was calculated fitting an exponential equation between 305 and  
191 265 nm (Galgani et al., 2011).

192

193 Fluorescence measurements were made for the same three stations in each lake using a  
194 Fluoromax-4 HORIBA Jobin Yvon fluorometer with a 1 cm quartz cuvette, at 0.1 sec  
195 integration time and with the standard R928P photomultiplier tube operating at 950 Volts.  
196 Prior to fluorescence analysis, the absorbance of each sample was measured with a UV-VIS  
197 spectrophotometer (PerkinElmer Lambda 35). If the absorbance of the sample was higher  
198 than 0.05 AUFS, the sample was diluted to obtain absorbance in the range 0.02-0.03 AUFS.



199 At this absorbance, the first and secondary inner filter effects are negligible (Lakowicz, 2006)  
200 and no correction has been done for the inner filter effects. Under these conditions, the  
201 fluorometer was never saturated. To obtain the three-dimensional excitation-emission  
202 fluorescence matrix (EEM), the instrument was operated in ratio mode to correct lamp  
203 fluctuation. Emission and excitation spectra were corrected for instrument bias as suggested  
204 by the manufacturer. The fluorescence EEM spectroscopy involved scanning and recording  
205 samples at sequential 5 nm increments of excitation wavelengths between 250 and 500 nm.  
206 Emission wavelength increment was 2 nm between 250 and 600 nm. The spectra were  
207 obtained by subtracting nanopure water blank spectra to eliminate water Raman scatter peaks.  
208 Each sample scan was then used to generate three-dimensional contour plots of fluorescence  
209 intensity as a function of excitation and emission wavelengths.

210

211 Our samples were characterized by two important fluorescent peaks. The first peak had an  
212 excitation maximum near 250-260 nm with an emission maximum near 380-480 nm. The  
213 second peak had an excitation maximum near 330-350 nm and an emission maximum near  
214 420-480 nm. These fluorescence signals, called peaks A and C, were assigned to humic-like  
215 substances by Coble (1996). No other salient peaks were observed in the fluorescence signal.  
216 From the intensity of peaks and other fluorescence signals, we calculated indices to quantify  
217 fluorescence properties of DOM. The ratio of fluorescence intensity of the two humic-like  
218 peaks (A/C) (Coble 1996) was calculated for each sample. Fluorescence index (FI) was also  
219 calculated for each sample as the emission intensity at 470 nm divided by the emission  
220 intensity at 520 nm when the excitation energy was set at 370 nm (McKnight et al., 2001;  
221 Cory and McKnight, 2005). Another index called the biological/autochthonous index (BIX)  
222 (Vacher, 2004; Huguet et al., 2009) was calculated from the ratio of emission intensities at

223 380 nm and 430 nm wavelengths when the excitation energy was set at 310 nm, to assess the  
224 relative contribution of autochthonous DOM in samples.

225

## 226 **2.5. Data analyses**

227 Water characteristic variables (TP, DIP, DIN, chl *a*, DOC) and DOM spectroscopic  
228 parameters ( $a_{cDOM(355)}$ , fluorescence ratio A/C, FI, BIX, SUVA<sub>254</sub> and S) were compared  
229 using three-way partly nested analyses of variance (ANOVAs). Factors in the model were:  
230 treatment (fixed with two levels, unperturbed and perturbed), lake nested in treatment  
231 (random with four lakes per treatment), year (fixed with three years of sampling) and their  
232 interactions. Data were transformed when necessary to achieve normality and homogeneity of  
233 variance. The impact of forest harvesting was measured as an interaction between the  
234 treatment (perturbed/unperturbed) and the year (Green 1979). When this factor was  
235 significant, a posteriori comparisons were made using Tukey's test.

236

## 237 **3. Results**

238 Monthly, seasonally and annual climatic variables were similar throughout the three sampling  
239 years of this study (Table 2). TP concentrations ranged from 4.80 (perturbed, 2008) to 5.75  $\mu\text{g}$   
240  $\text{l}^{-1}$  (perturbed, 2009) (Fig. 2). A statistically significant interaction between treatment and year  
241 was observed for TP concentrations (Table 3). A posteriori Tukey's test confirmed that  
242 unperturbed and perturbed lakes were not significantly different in 2008 (before forest  
243 harvesting) nor in 2010 but they were significantly different in 2009 (first year after forest  
244 harvesting). TP concentrations increased in the perturbed lakes in 2009 while it slightly  
245 decreased in unperturbed lakes. In 2010 TP concentrations were practically the same in  
246 unperturbed and perturbed lakes, as a result of increased TP in reference lakes (Fig. 2).

247

248 DIP values ranged from 1.39 (unperturbed, 2010) to 1.96  $\mu\text{g l}^{-1}$  (perturbed, 2009) (Fig. 2) and  
249 DIN values ranged from 0.42 (unperturbed, 2008) to 3.02  $\mu\text{g l}^{-1}$  (perturbed, 2009) (Fig. 2).  
250 Neither DIP nor DIN values showed significant differences for the interaction between  
251 treatment and year (Table 3), although DIN values were higher in perturbed than unperturbed  
252 lakes in 2009 and 2010.

253

254 Chl *a* values ranged from 0.41 (unperturbed, 2008) to 1.00  $\mu\text{g l}^{-1}$  (perturbed, 2009) (Fig. 2).  
255 Chl *a* values did not show significant differences between treatment and year (Table 3).  
256 Although there was an increase in chl *a* concentration in 2009, this increase occurred for both  
257 unperturbed and perturbed lakes (Fig. 2).

258

259 DOC concentrations ranged from 11.34 (perturbed, 2008) to 15.27  $\text{mg C l}^{-1}$  (perturbed, 2009)  
260 (Fig. 2). No significant difference was detected between treatment and year for DOC values  
261 (Table 3). However, DOC was substantially higher in 2009 in perturbed lakes than in  
262 unperturbed lakes, then decreased in 2010 in perturbed lakes (Fig. 2). In 2009, DOC  
263 concentrations ranged from 9.57 to 14.96  $\text{mg C l}^{-1}$  in unperturbed lakes and from 13.60 to  
264 17.48  $\text{mg C l}^{-1}$  in perturbed lakes. Moreover, we performed a three-way ANOVA with the  
265 same factors as above but comparing only 2008 and 2009. In this case, the interactions  
266 between treatment and year for all the variables were significant for DOC concentrations  
267 ( $df=2/12$ ,  $MS=32.3253$ ,  $F=6.2160$ ,  $p=0.0466$ ) and TP ( $df=2/12$ ,  $MS=0.2561$ ,  $F=20.9793$ ,  
268  $p=0.0036$ ).

269

270 Two maxima humic-like peaks were observed in all EEM in all samples: peak A and peak C.  
271 These peaks are commonly reported in the literature (Coble, 1996; Parlanti et al., 2000) as  
272 indicators of the presence of humic substances. The spectroscopic metrics  $a_{cDOM}$  (355),

273 fluorescence ratio A/C, FI, BIX, SUVA<sub>254</sub> and S values showed similar patterns in  
274 unperturbed and perturbed lakes over time (Fig. 3).  $a_{\text{cDOM}}(355)$  values ranged from 30.44  
275 (unperturbed, 2010) to 40.68  $\text{m}^{-1}$  (perturbed, 2009) and showed the same pattern for  
276 unperturbed and perturbed lakes, increasing in 2009 and decreasing in 2010 (Fig. 3).  
277 Fluorescence ratio A/C values ranged from 1.46 (unperturbed, 2009) to 1.50 (perturbed, 2010)  
278 (Fig. 3) and FI values ranged from 1.64 (unperturbed, 2010) to 1.71 (unperturbed, 2009). FI  
279 values decreased in 2010 both for unperturbed and perturbed lakes (Fig. 3). BIX values  
280 ranged from 0.36 (unperturbed, 2009) to 0.40 (perturbed, 2010). SUVA<sub>254</sub> values ranged from  
281 1.91 (perturbed, 2009) to 2.09  $\text{L mg m}^{-1}$  (unperturbed, 2009) and S values ranged from 0.010  
282 (unperturbed, 2008) to 0.012  $\text{nm}^{-1}$  (perturbed, 2010) (Fig. 3). No significant differences for  
283 the interaction between treatment and year were found for any of these variables (Table 4).  
284 Chl *a* significantly correlated with DOC ( $r^2 = 0.1202$ ,  $F = 14.0689$ ,  $p = 0.001$ ) and TP ( $r^2 =$   
285  $0.0693$ ,  $F = 7.5166$ ,  $p = 0.007$ ) and DOC significantly correlated with TP ( $r^2 = 0.2780$ ,  $F =$   
286  $8.2109$ ,  $p = 0.005$ ). The absorption coefficient ( $a(355)$ ) significantly correlated with DOC  
287 concentration in unperturbed and perturbed lakes ( $r^2=0.7674$ ,  $F=428.8325$ ,  $p<0.001$ ).

288

#### 289 **4. Discussion**

290 Concentrations of TP measured in unperturbed and perturbed lakes were typical values  
291 reported for Boreal Shield lakes (Carignan et al., 2000; Winkler et al., 2009). However,  
292 logging disturbance increased the TP content of lakes one year after harvesting as also  
293 reported by other authors (Lamontagne et al., 2000; Winkler et al., 2009). Ground disturbance  
294 may increase weathering and leaching of phosphorus from exposed mineral soils (Evans et al.,  
295 2000). Adsorption of phosphorus to particles and their subsequent transportation by  
296 hydrological events can increase the loading of rivers and lakes (Whitson et al., 2005).  
297 Phosphorus losses from soils can be promoted by co-leaching with organic solutes such as

298 DOC (Qualls et al., 1991). The presence of DOC can enhance the solubility, mobility and  
299 export of phosphorus by limiting the complexation of its dissolved form with cations that  
300 would otherwise react to precipitate phosphorus and retain it in soils. This would explain the  
301 significant correlation between DOC and TP found in this study. The parallel increase in TP  
302 and DOC in lakes, one year after harvesting, can suggest a rise in allochthonous import of  
303 DOC from watershed to lakes. DOC concentrations measured were typical of conifer boreal  
304 forest systems with a mean annual temperature of 2.5°C (Sobek et al., 2007). DOC  
305 concentrations significantly increased after harvesting in perturbed lakes, similar to Winkler  
306 et al. (2009), suggesting that the system responded immediately after the perturbation.

307

308 In lentic systems, DOC concentrations in surface waters are regulated by processes internal to  
309 lakes and external processes occurring in the watersheds where DOC are exported to lakes. In  
310 lakes, metabolic compounds released by healthy autotroph and heterotroph organisms,  
311 exudation from altered cells resulting from zooplankton grazing and microbial decay of soft  
312 tissues of dead organisms may produce or deliver DOC in lakes. DOC can also be removed  
313 from water by bacterial degradation, photolytic alteration, heterotrophic respiration (i.e. CO<sub>2</sub>  
314 evasion) and sorption or aggregation between organic matter and clays that cause  
315 sedimentation of particles. As mentioned earlier, the increase in DOC could result from the  
316 extracellular release of DOC from phytoplankton (Baines and Pace, 1991). However, the  
317 increase observed in DOC one year after harvesting is not parallel with a rise in chl *a* content,  
318 suggesting a minor role of phytoplankton exudates on the regulation of DOC level. This is  
319 also supported by the absence of characteristic protein-like peaks associated to planktonic  
320 production (excitation maxima at 275 and 305-340 nm (Coble, 2007) in our EEM  
321 fluorescence spectra (data not shown). Furthermore, the lakes are shallow and hot in summer  
322 (15-18 °C in July). Under these conditions, bacterial mineralization of labile organic matter

323 can be efficient and net production of DOC in lakes should be low. If processes occurring in  
324 lakes act as an important sink (destruction or sedimentation) for organic matter, it is the  
325 production and transport of DOC from the catchment areas to lakes that control the quantity  
326 and quality of organic matter in lakes. The mean annual lake residence times of water in the  
327 lakes studied are short, less than 0.16 years (Table 1). Then, a rapid turnover of water and a  
328 quick replacement of DOC occur in these lakes. Under these conditions, variations in quantity  
329 and quality of DOC suggest that processes occurring in the drainage basins are of paramount  
330 importance to explain changes in the amounts and the chemical composition of DOC in lakes.

331

332 The transport of DOM from terrestrial ecosystems to lakes is complex. Thus, several potential  
333 processes could give rise to an increase in DOC content in lakes. Many studies suggested that  
334 the most important processes to explain increases in DOC after forest harvesting was the rise  
335 in organic matter leaching from logging slash; the increase decomposition of organic logging  
336 residues and organic matter in the surface soils due to increased forest floor temperature and  
337 moisture; and a reduction in evapotranspiration causing an increase in runoff quantity leading  
338 to a higher water table favorable to the exportation of DOM from the surface and riparian  
339 soils (Qualls et al., 2000; Bishop et al., 2004; Kreutzweiser et al., 2008; Schelker et al.,  
340 2013b). However, the largest C-efflux from a forest floor is soil respiration, which has been  
341 shown to change as a result of forest disturbance (Grant et al., 2007). Leaching from logging  
342 slash or foliage and woody debris mixed to surface soils after forest harvesting could enrich  
343 water soil surface in organic components (Qualls et al., 2000). However, studies show that  
344 amounts of DOC leached vary with temperature, the nature of woody debris and the lability of  
345 organic matter. Coarse residues (stumps, coarse roots, branches) decompose slowly while fine  
346 residues (leaves, needles, fine roots, twigs) as well as boreal forest moss and feather mosses  
347 can be very quickly metabolized to CO<sub>2</sub> (Wickland et al., 2007; Hanson et al., 2010). During

348 the degradation processes, nitrogen, and low molecular weight organic acids are first removed  
349 while lignin and humic substances could persist. Qualls et al. (2000) suggested that higher  
350 concentrations of dissolved organic nutrients in solution draining from the forest floor of the  
351 cut plots can largely be accounted for by the slash above the leaf litter of the forest floor.

352

353 The input of DOM to lakes from surrounding landscape could produce changes in the amount  
354 and the chemical composition or quality of organic matter. However, although total DOC  
355 concentrations increased one year after logging, the composition of DOC did not measurably  
356 change. This result has also been reported in streams (Burrows et al. 2014). Three-  
357 dimensional excitation-emission fluorescence spectra of lake samples studied over three years  
358 shown only two major fluorophores associated with allochthonous humic-like components.  
359 This constancy in composition suggests that DOC composition was similar for the three years  
360 in unperturbed and perturbed lakes, since there was no significant difference between year  
361 and treatment for the ratio of fluorescence intensity of the two humic-like peaks (A/C).  
362 Moreover, FI and BIX indices showed no significant differences either, indicating there was  
363 no change in fluorescence spectra due to logging. FI is an index of the origin of fulvic acids.  
364 In this study, FI values were around 1.65 in all lakes and years. Cory et al. (2010) suggested  
365 values near 1.2 for DOM of terrestrial origin in a large river of USA and 1.55 for microbially  
366 derived DOM. However, Korak et al. (2014) have recently shown that FI values can vary by  
367 0.2 units if concentration changes, the highest FI value measured at low DOC concentration.  
368 In this study, our measurements were obtained at natural pH, about 5.5 in the lakes studied.  
369 Measurements of FI at samples pH other than 6-7.5 as suggested by McKnight et al. (2001) or  
370 Cory et al. (2010) could change the range of values used to distinguish sources of DOM  
371 because protonation, molecular conformation and fluorescence signal of DOM change with  
372 pH. Thus, the relative contribution of autochthonous and allochthonous material cannot be

373 discerned from FI values. BIX values were, however, between 0.35 and 0.42. These results  
374 are below 0.7, suggesting that DOM contains very little autochthonous organic matter, and it  
375 may be mainly composed of allochthonous matter (Vacher, 2004; Birdwell and Engel, 2010).  
376  
377 SUVA<sub>254</sub> values (1.91 to 2.09) were slightly lower than values reported in other studies in  
378 boreal forests (Wickland et al., 2007; Balcarczyk et al., 2009), indicating a relatively low  
379 aromaticity for DOC. Wickland et al. (2007) reported low SUVA values (between 1.9 and 2.3)  
380 for well or moderately well-drained soils. They associate the low value of SUVA to the  
381 presence of hydrophilic organic matter (HPIOM). Guggenberger et al. (1994) found that  
382 HPIOM appeared to be partly microbially synthesized and partly plant-derived with a high  
383 degree of oxidative biodegradation suggesting that HPIOM are relatively small molecule with  
384 many oxidized side-chains. S values were similar to values found in other studies in boreal  
385 forest systems (Galvani et al., 2011). Our results showed no significant difference of SUVA<sub>254</sub>  
386 or S values (taking into account the interaction between the treatment and the year of  
387 sampling). This suggests that forest harvesting resulted in an increase in the quantity of DOC  
388 available (as DOC concentrations were significantly higher in 2009) without changes in terms  
389 of quality. DOC quality varies to a large extent depending on its terrestrial origin in terms of  
390 bioavailability (Berggren et al., 2007; Ågren et al., 2008). As the fluorescence can help to  
391 differentiate between plant and microbially-synthesized DOC (McKnight et al., 2001),  
392 increased runoff after harvesting would have resulted in DOC increases but DOC had a very  
393 close composition before and after harvesting. Similar findings were reported in twenty-three  
394 forested lakes in central Quebec, where DOC concentrations increased in logged lakes, but no  
395 changes in aromaticity of DOC were observed (O'Driscoll et al., 2006).

396



397 In this study, we measured DOC and optical properties of organic matter to provide  
398 information on the amount, quality, and origin of organic matter. DOC increases one year  
399 after harvesting, but this rise is not accompanied by variations in spectroscopic parameters  
400  $a_{cDOM(355)}$ , fluorescence ratio A/C, FI, BIX, SUVA<sub>254</sub> and S. What concludes from these  
401 results? At least two points can contribute to our observations. An increase in DOC without  
402 change in spectroscopic metrics means that the DOC introduced in the system does not absorb  
403 or fluoresce following UV-VIS irradiation. If compounds have double bonds or aromatic  
404 moieties, these compounds will absorb light and give alteration in spectroscopic metrics, not  
405 observed in this study. However, if dissolved organic matter contains mostly sigma chemical  
406 bonds, these bonds could be hidden to the metrics used because sigma bonds absorb near 200  
407 nm far from the wavelengths (>254 nm) used in the proxies measured. This suggests that low  
408 molecular weight organic acids, hydrocarbons, lipids, or carbohydrates can contribute to the  
409 rise in DOC without change in spectroscopic properties in the UV-VIS wavelength. Low  
410 molecular weight organic acids are used rapidly by bacteria (Romero-Kutzner et al., 2015).  
411 Their occurrence in DOC is unlikely. However, hydrocarbons, lipids and carbohydrates exist  
412 in plants (Kögel-Knabner, 2002) and simple sugars and nonhumic-bound polysaccharides  
413 could contribute to the increment in DOC at least for deciduous forest ecosystem (Qualls and  
414 Haines, 1991). In a study on the release of DOC from plant tissues, Moore and Dalva (2001)  
415 observed that DOC leaching is more efficient from fresh material than from old material. This  
416 could contribute to the higher level of DOC one year after logging. The composition of the  
417 new DOC could be lipid-like or carbohydrate-like compounds.

418

419 Our fluorescence results suggest that humic substances are the ubiquitous compounds  
420 exported to lakes. The decrease in evapotranspiration following the clearing forest vegetation  
421 (causing a change in the hydrologic regime) and the leaching of logging slash could

422 contribute to a selective washing of humic substances. Boyer et al. (1996) suggested that  
423 DOC in upper soil might accumulate during periods of low flow and be exported during  
424 periods of high flows. However, DOC in deep soils horizons could be immobilized through  
425 sorption onto mineral phases or by precipitation with polyvalent cations (Qualls et al., 2000;  
426 Hansson et al., 2010; Kaiser and Kalbitz, 2012). The sorption could be more effective to  
427 retain humic than fulvic acids (Weng et al., 2006). Moreover, washing of logging slash can  
428 decrease the pH by 0.9 units for leachate of fresh needle litter (Hansson et al., 2010). Such  
429 reduction in pH could decrease the solubility of humic substances by more than 50% (Tipping  
430 and Woof, 1990) and cause a stronger sorption of humic acids compared to fulvic acids  
431 (Weng et al., 2006). However, because fulvic acids are soluble at any pH, by definition, it is  
432 the apparent solubility of humic acids that decrease during leaching of logging slash and  
433 through transport of DOC from watershed to lakes. The resulting effect will be a possible  
434 enrichment of water soil surface in fulvic acids exported to lakes. The spectroscopic  
435 parameters measured are in agreement with our hypothesis that DOC is mainly composed of  
436 fulvic acids.

437

438 Although there appears to be a recovery of water chemistry (TP and DOC) by year 2, there  
439 are confounding factors that can obscure real recovery or delayed effects. For example,  
440 Schelker et al. (2012) have seen a long lasting forestry effect on both hydrology and DOC on  
441 aquatic systems in the boreal region. Biogeochemical processes in watersheds do not all  
442 respond immediately to logging effects, i.e., tree removal and ground disturbance. Some  
443 processes may take a few years, such as changes in organic matter composition and  
444 processing on the forest floor, changes in vegetation composition from which the DOC is  
445 derived, before those changes affect export of nutrients and subsequent changes to lake water  
446 chemistry. Also, hydrological conditions (especially runoff) greatly affect solute movement to

447 surface waters (Fawcett et al., 1994), and it is possible that year 2 was different hydrologically  
448 than the preceding and may have masked delayed effects. Inter-annual variability could also  
449 have affected the export of nutrients and DOC to the lakes. However, since monthly,  
450 seasonally and annual climatic variables were similar throughout the three years of sampling  
451 (Table 2), we can then assume that in this study, forest harvesting is a major factor  
452 influencing the system comparing to a natural factor such as annual precipitation. Lastly,  
453 carbon and nutrients can be transformed (i.e. immobilized, mineralized, evaded as CO<sub>2</sub>)  
454 before being input into lakes (Ledesma et al. 2015). There is thus the potential for substantial  
455 changes in many of the lake water parameters measured before they enter each lake.

456

457 In conclusion, this study indicated that logging activities appeared to increase significantly TP  
458 and DOC export to oligotrophic lakes of the Eastern Canadian Boreal Shield one year after  
459 the perturbation. This impact on water chemistry due to logging activity appeared to have  
460 been short-term with recovery to pre-logging conditions two years after harvest. Nevertheless,  
461 it has to be kept in mind that the number of perturbed and unperturbed lakes in this study was  
462 only four, respectively and that they were sampled one month each year due to logistic  
463 constraints. Sampling multiple times per year at each lake would have permitted to estimate  
464 the influence that seasonal and natural events (i.e. snow melt and storms) have upon the  
465 response parameters. Furthermore, the study did not address the potential for delayed or  
466 longer-term changes in water chemistry that could result from biogeochemical processes in  
467 the lake catchments adjust to forest recovery after harvest. However, this three-year period  
468 study shows interesting results. It suggests changes in DOC and TP keeping the quality of the  
469 CDOM almost unaffected. Moreover, the spectroscopic data converge to suggest that fulvic  
470 acids are the mobile form of CDOM carried to lakes and that fulvic acids respond rapidly to

471 forest harvesting contrary to humic acids. Fulvic and humic acids are the most important  
472 components of DOC and CDOM.

473

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748 Table 1. Characteristics of the eight studied Canadian Boreal Shield lakes (UP: unperturbed lakes; P: perturbed lakes). Dissolved oxygen (DO),  
 749 pH, conductivity, temperature, secchi depth, total phosphorus (TP), dissolved inorganic phosphorous (DIP), dissolved inorganic nitrogen (DIN),  
 750 chlorophyll a (chl *a*) and dissolved organic carbon (DOC) are reported as means (SD) over the sampling stations on the photic zone before the  
 751 perturbation (2008). Lake UP3 was not deep enough to sample secchi depth.

	UP1	UP2	UP3	UP4	P1	P2	P3	P4
Latitude N	50° 25' 44"	50° 29' 22"	50° 23' 13"	50° 28' 34"	50° 30' 9"	50° 31' 25"	50° 30' 40"	50° 28' 11"
Longitude W	71° 57' 28"	71° 57' 32"	72° 1' 24"	71° 57' 15"	71° 47' 1"	71° 56' 26"	71° 56' 5"	71° 46' 51"
Lake area (km <sup>2</sup> )	0.17	0.17	0.06	0.03	0.29	0.09	0.28	0.04
Catchment area (km <sup>2</sup> )	0.92	2.80	0.59	0.20	2.89	1.76	2.42	0.34
Drainage area (km <sup>2</sup> )	0.75	2.63	0.52	0.17	2.61	1.67	2.14	0.29
Drainage ratio	4.39	15.56	8.30	5.52	9.02	18.57	7.71	6.88
Harvested area (% of catchment area)	-	-	-	-	72.9	69.1	71.6	77.0
Mean annual lake residence time (year)	0.10	0.01	0.005	0.03	0.16	0.04	0.15	0.05
Maximum depth (m)	5.0	2.0	0.5	2	9	4.5	7.5	2
Secchi depth (m)	1.25	1.50	n/a	1.75	1.50	1.65	1.40	1.40
DO (mg l <sup>-1</sup> )	8.61 (0.13)	9.52 (0.68)	7.51 (0.38)	7.22 (0.15)	8.47 (0.20)	8.24 (0.08)	8.21 (0.23)	8.46 (0.57)
pH	5.92 (0.10)	5.75 (0.02)	5.94 (0.05)	5.87 (0.07)	5.92 (0.06)	5.02 (0.05)	5.62 (0.15)	5.38 (0.28)
Conductivity (µS cm <sup>-1</sup> )	11.93 (0.64)	12.50 (0.05)	19.00 (0.54)	9.40 (0.15)	13.40 (0.00)	11.92 (0.12)	12.65 (0.14)	14.67 (0.45)
Temperature (°C)	17.86 (0.80)	17.09 (0.65)	16.71 (0.74)	16.99 (0.24)	17.13 (0.36)	16.71 (0.06)	17.45 (0.24)	15.65 (0.50)
DOC (mg l <sup>-1</sup> )	10.78 (0.57)	12.06 (0.58)	12.56 (1.01)	12.33 (0.48)	11.91 (0.73)	9.82 (0.40)	8.98 (0.43)	13.73 (1.04)
DIP (µg l <sup>-1</sup> )	1.81 (0.31)	2.10 (0.58)	1.29 (0.56)	1.49 (0.41)	1.88 (0.74)	1.54 (0.41)	1.20 (0.14)	2.04 (0.91)
DIN (µg l <sup>-1</sup> )	0.24 (0.12)	0.75 (0.51)	0.31 (0.18)	n/a	0.60 (0.12)	n/a	0.73 (0.10)	0.32 (0.27)
Chl <i>a</i> (µg l <sup>-1</sup> )	0.43 (0.06)	0.39 (0.06)	0.62 (0.20)	0.36 (0.05)	0.98 (0.21)	0.55 (0.06)	0.68 (0.16)	0.49 (0.07)
TP (µg l <sup>-1</sup> )	5.05 (0.26)	4.95 (0.52)	5.77 (0.50)	5.13 (1.01)	5.09 (0.70)	4.69 (0.47)	5.26 (0.70)	4.65 (0.55)

752



753 Table 2. Monthly (July), seasonally (May, June, July) and annual average of climatic  
754 variables during the three years of the study (2008, 2009 and 2010).

755

Variable (Average)	2008	2009	2010
Monthly temperature (°C)	16.1	15.6	17.3
Seasonally temperature (°C)	12.5	11.7	13.2
Annual temperature (°C)	-5.0	-5.1	-2.8
Monthly precipitation (mm)	5.1	2.8	4.1
Seasonally precipitation (mm)	46.1	44.2	44.8
Annual snow depth (mm)	390	320	350

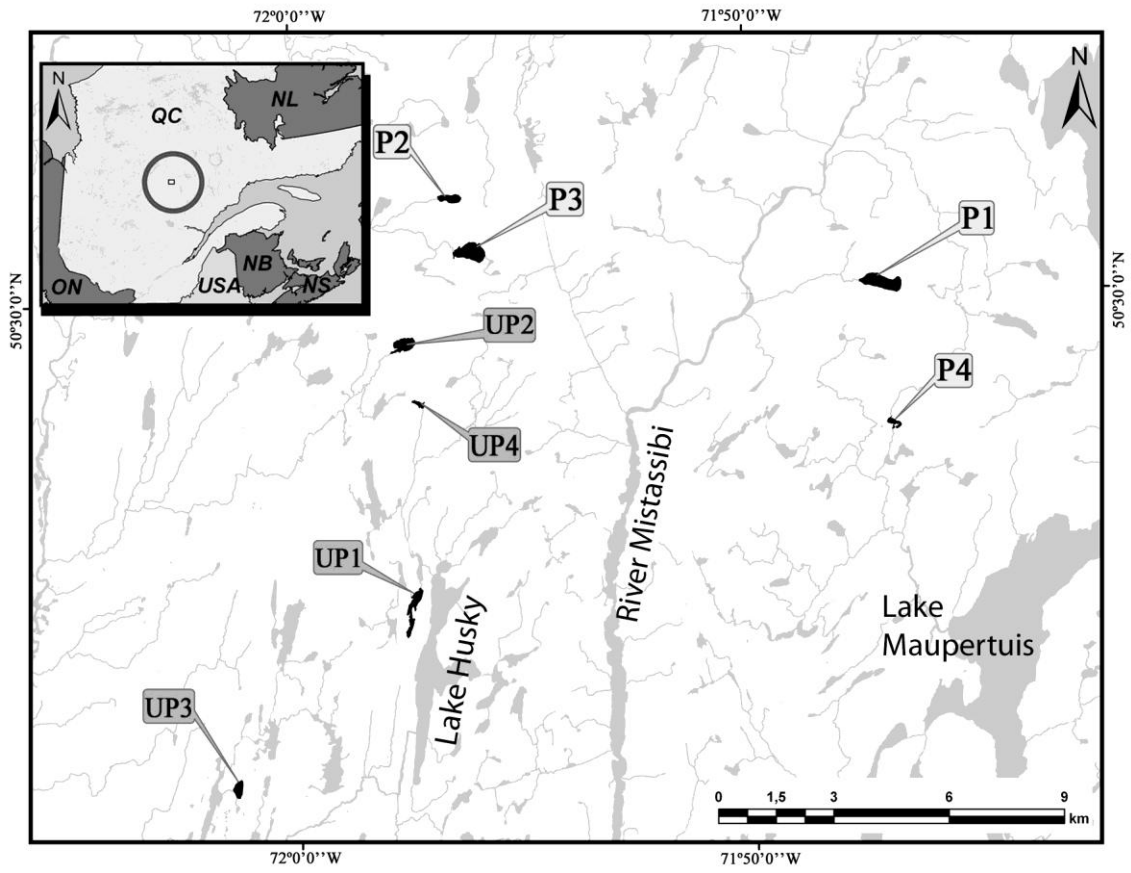
756 Table 3. Results of the three-way ANOVA testing the effect of treatment (tr : perturbed,  
757 unperturbed), lake, year and their interactions on TP, DIP, DIN, chl *a* and DOC. Variables  
758 were transformed to achieve normality and homogeneity of variance. The principal source of  
759 variation of interest is the interaction between the treatment and the year of sampling.  
760 Significant p values ( $p < 0.05$ ) are in bold.  
761

Variable		Tr	lake (tr)	year	tr x year	lake (tr) x year	Residual
	df	1	6	2	2	12	96
Log TP	SS	0.07	0.01	0.18	0.15	0.02	0.02
	F	5.30	0.63	8.46	6.75	1.07	
	p	0.06	0.71	<b>&lt;0.05</b>	<b>&lt;0.05</b>	0.39	
Log DIP	SS	0.28	0.96	2.59	1.33	1.54	0.27
	F	0.29	0.62	1.68	0.86	5.74	
	p	0.61	0.71	0.23	0.44	<b>&lt;0.001</b>	
Log DIN	SS	10.51	0.39	20.88	0.50	1.34	0.31
	F	27.19	0.30	15.86	0.38	4.28	
	p	<b>&lt;0.05</b>	0.92	<b>&lt;0.001</b>	0.69	<b>&lt;0.001</b>	
Log chl <i>a</i>	SS	3.07	0.69	3.29	0.29	0.23	0.13
	F	4.41	2.30	14.18	1.25	1.25	
	p	0.08	0.05	<b>&lt;0.001</b>	0.32	0.07	
Log DOC	SS	0.01	0.13	0.38	0.13	0.07	0.01
	F	0.06	1.92	5.34	1.79	14.01	
	p	0.81	0.16	<b>&lt;0.05</b>	0.21	<b>&lt;0.001</b>	

762 Table 4. Results of the three-way ANOVA testing the effect of treatment (tr: perturbed,  
763 unperturbed), lake, year and their interactions on absorbance coefficients of CDOM ( $a_{cDOM}$ ) at  
764 355 nm, A:C peak ratios, fluorescence index (FI), biological/autochthonous index (BIX),  
765 specific UV absorbance at 254 nm ( $SUVA_{254}$ ) and spectral slope (S). The principal source of  
766 variation of interest is the interaction between the treatment and the year of sampling.  
767 Significant p values ( $p < 0.05$ ) are in bold.

768

Variable		tr	lake (tr)	year	tr x year	lake (tr) x year	Residual
$a_{cDOM}$ ( $\lambda=355$ )	df	1	6	2	2	12	48
	SS	6.81	316.26	137.19	133.38	110.28	14.95
	F	0.02	3.22	1.35	1.31	7.37	
A:C	p	0.88	<b>&lt;0.05</b>	0.29	0.30	<b>&lt;0.001</b>	
	SS	0.02	0.01	0.01	0.01	0.01	0.01
	F	0.85	4.51	1.13	0.83	2.16	
FI	p	0.39	<b>&lt;0.05</b>	0.29	0.39	<b>&lt;0.05</b>	
	SS	0.01	0.01	0.02	0.01	0.01	<0.001
	F	1.02	1.89	21.92	0.88	2.62	
BIX	p	0.35	0.16	<b>&lt;0.001</b>	0.35	<b>&lt;0.05</b>	
	SS	0.01	0.01	0.01	0.01	0.01	<0.001
	F	4.65	1.42	3.98	0.24	4.12	
$SUVA_{254}$	p	0.08	0.28	0.05	0.62	<b>&lt;0.001</b>	
	SS	0.09	0.22	0.72	0.35	0.36	<0.001
	F	4.14	0.63	2.07	1.01	5.56	
S	SS	$1.65 \cdot 10^{-6}$	$8.6 \cdot 10^{-6}$	$3.32 \cdot 10^{-5}$	$7.43 \cdot 10^{-6}$	$5.59 \cdot 10^{-6}$	$1.39 \cdot 10^{-6}$
	F	0.20	1.59	6.25	1.40	4.24	
	p	0.67	0.23	<b>&lt;0.05</b>	0.28	<b>&lt;0.001</b>	

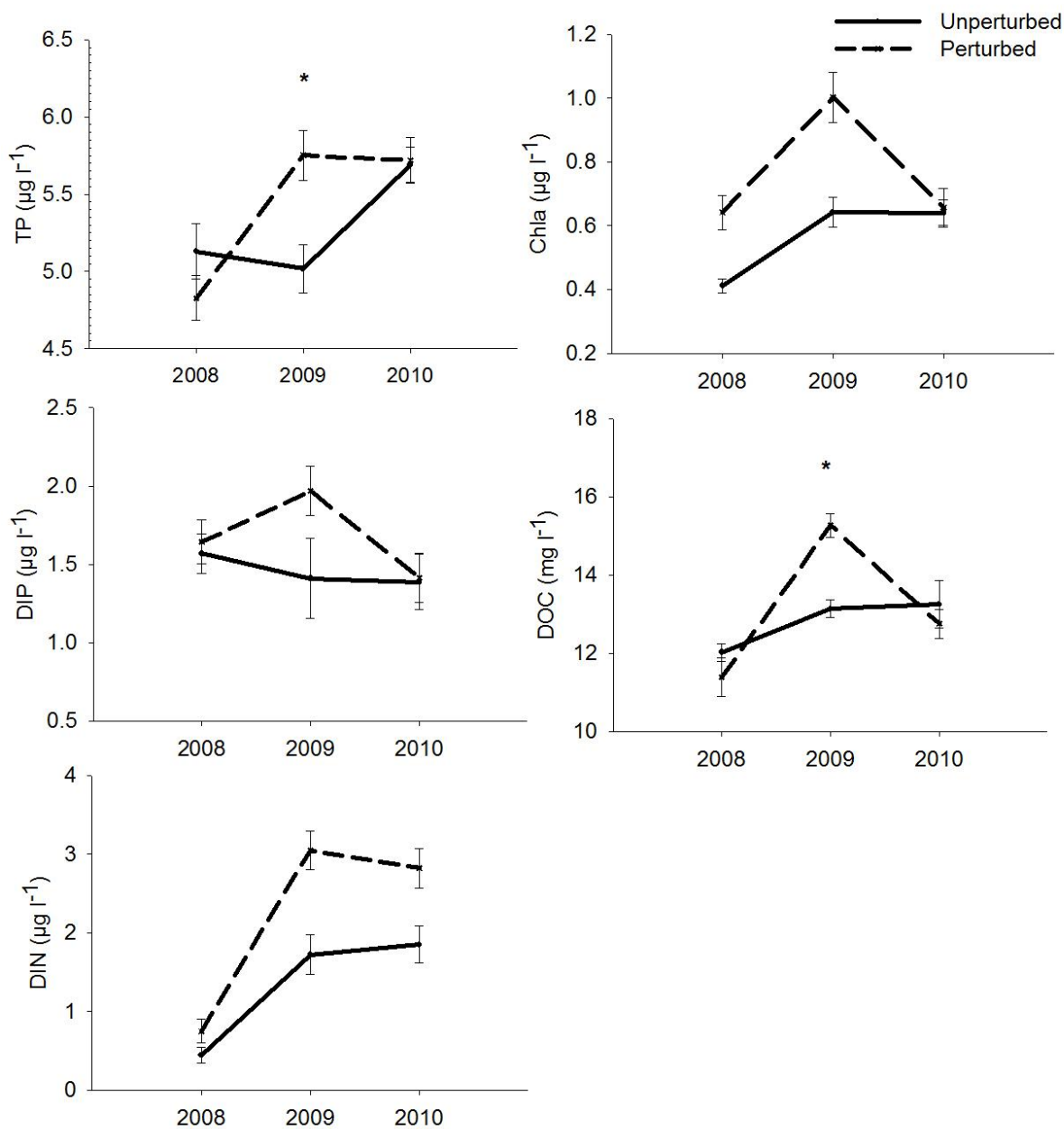


770

771 Figure 1. Location of the eight study lakes sampled in 2008, 2009 and 2010. UP, unperturbed  
772 lakes; P, perturbed lakes (harvested in 2009).

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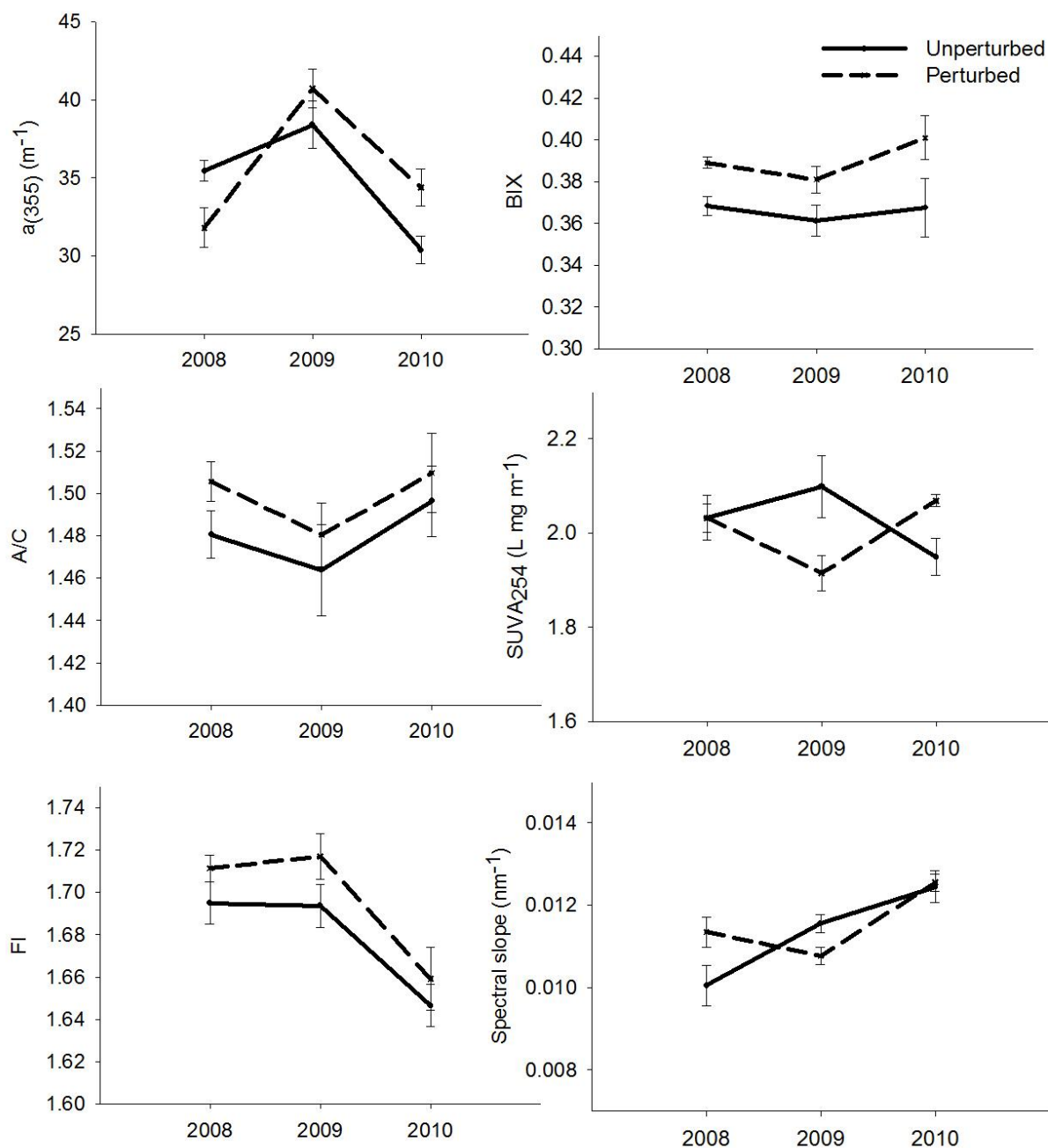


775

776 Figure 2. Comparison between treatments (unperturbed, perturbed) and years (2008, 2009,  
 777 2010) of TP, DIP, DIN, chl *a* and DOC. Vertical bars represent standard errors. \* p<0.05.

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779



780

781 Figure 3. Comparison between treatments (unperturbed, perturbed) and years (2008, 2009,  
 782 2010) of  $a_{cDOM}$  ( $\lambda=355$ ), A/C, FI, BIX, SUVA<sub>254</sub> and spectral slope. Vertical bars represent  
 783 standard errors .