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

P. Glaz[1], J.-P. Gagné[2], P. Archambault[2], P. Sirois[3] and C. Nozais[1]

[1] Département de biologie, chimie et géographie, Université du Québec à Rimouski, Rimouski (QC), Canada

[2] Institut des sciences de la mer de Rimouski, Université du Québec à Rimouski, Rimouski (QC), Canada

[3] Chaire de recherche sur les espèces aquatiques exploitées, Laboratoire des sciences aquatiques, Département des sciences fondamentales, Université du Québec à Chicoutimi, Chicoutimi (QC), Canada

Correspondence to: P. Glaz (patricia_glaz@uqar.ca)

Abstract

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

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

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

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

While the temporal variability and long-term lake response is of interest, our study was designed to analyse the short term impact of forestry activities on water quality, and on UV-VIS and fluorescence characteristics of DOC in eastern Canadian Boreal Shield lakes one year before and up to two years after the perturbation. Water quality and spectroscopic characteristics of four lakes were studied on one occasion before, and on two occasions after forestry operations (perturbed lakes, P) and compared with four undisturbed references lakes

100 (unperturbed lakes, UP). More specifically, we tested the hypotheses that 1) nutrients and

101 DOC would be greater in perturbed lakes than unperturbed lakes one and two years after the

102 perturbation; 2) the UV-VIS and fluorescence signatures of DOM in perturbed lakes would

103 indicate an increase in terrestrially-derived (allochthonous) DOM after logging.

104

105 **2. Materials and methods**

106 **2.1. Study area**

107 This study was conducted in the province of Québec on the forested Mistassibi River drainage

108 basin (50° 07'30' N, 71° 35'59' W) located on the Boreal Shield (Fig. 1). The study area is

109 characterized by old growth forest mainly dominated by mature black spruces (*Picea mariana*)

110 exploited by the forest industry. The soil layer over the rock is thin.

111

112 **2.2. Sampling**

113 Eight lakes, which are oligotrophic in this region (Winkler et al., 2009), with similar

114 geomorphologic characteristics were selected for this study (Table 1). To evaluate the most

115 direct impact of harvesting, headwater lakes were selected, except for UP1, UP3 and P3.

116 Upstream lakes of UP1 and UP3 were unperturbed and for P3, the upstream lake was also

117 unperturbed and very small in comparison of the nominal lake. These eight lakes have been

118 unperturbed in 2008 at the beginning of this survey. In 2009 and 2010, four of these lakes

119 were kept undisturbed (unperturbed lakes) and four other lakes (perturbed lakes) where

120 harvested about 70% of lake catchment during autumn 2008 (Fig. 1, Table 1). All lakes were

121 sampled once in July in 2008, 2009 and 2010. The experimental unit in this study was the

122 lake. The forest was cut using the careful logging around advanced growth (CLAAG) strategy.

123 Under this treatment, all trees equal to or greater than 10 cm diameter at breast height (d.b.h.)

124 are harvested and smaller individuals are protected as future crop trees (Groot et al., 2005). A

125   20 m strip of standing forest was intentionally kept along lakes after harvesting activities. All

126   lakes have a drainage ratio higher than 4, and perturbed lakes had a catchment area cut by 69-

127   77% (Table 1).

128

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

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

131

132   where Z_{MD} is the mean depth $_,$ A_{lake} is the lake area , $A_{catchment}$ is the catchment area , P is the

133   mean annual precipitation in this region (rainfall and snow) and runoff is the runoff

134   coefficient. This coefficient assumes that the percentage of precipitation that becomes runoff

135   is 0.5 for undisturbed lakes and 0.8 for harvested lakes in boreal forests (Bosch and Hewlett,

136   1982; Schelker et al., 2013a). Equation 1 is an approximation to calculate the mean annual

137   lake residence time for each lake because for lakes, in absence of data, we assumed only

138   precipitation and no infiltration or water uptake by tree roots, no loss of water by evaporation

139   and evapotranspiration to the atmosphere or by groundwater recharge.

140

141   At each lake, five littoral stations were selected randomly and sampled from a vessel.

142   Dissolved O_2, pH, conductivity, and water temperature were measured *in situ* at each

143   sampling station using an YSI 556 MPS probe. Water transparency was estimated at the

144   deepest zone of the lake using a Secchi disc. Water samples were collected with a bottle at 0.5

145   m below the surface at each sampling station and filtered through 300 μm to remove large

146   zooplankton prior to the determination of physicochemical and biological variables. Samples

147   for total phosphorus (TP), dissolved inorganic phosphorus and nitrogen (DIP and DIN,

148   respectively) and suspended matter filtered for chlorophyll *a* (chl *a*) measurements were kept

149   frozen at -20°C until analysis. Freezing TP samples can change the concentration observed in

6

150   some cases (Fellman et al., 2008). However, in this study it is assumed that freezing has no

151   effect because SUVA measured for samples are low (see later). Samples for DOC, CDOM

152   absorption and DOC fluorescence measurements were maintained at 4°C until analysis after

153   appropriate filtration treatments for each parameter.

154

155   **2.3. Water quality measurements**

156   TP was measured using the molybdenum blue method (Staiton et al. 1977) after autoclaving

157   50 ml samples with 0.5 g of potassium persulfate for 1 h at 120°C. TP was afterwards

158   assessed by using an AutoAnalyzer (AA3, Bran+Luebbe, German). DIP and DIN were

159   determined using an AutoAnalyzer (AA3, Bran+Luebbe, German) after filtering water

160   samples through a membrane filter (0.2μm Sartorius). For the determination of chl a, water

161   samples were filtered (200 ml or more) onto Whatman GF/F filters. Samples were extracted

162   for 24 h in 90% acetone at 5°C in the dark without grinding. Chl a was determined using the

163   method of Welschmeyer et al. (1994). For DOC measurements, water samples were filtered

164   through precombusted (500°C, 5 h) Whatman GF/F filters. For the determination of DOC

165   concentrations, the filtrates were collected in clean amber glass vials with Teflon-lined caps,

166   and samples were acidified with ten μL of 25% v/v H_3PO_4. The determination of DOC levels

167   were made in NPOC mode with a TOC-5000A or a TOC-V$_{CPN}$ analyzer (Shimadzu, Kyoto,

168   Japan), following a protocol similar to Whitehead et al. (2000). A calibration curve was used,

169   with five concentrations of potassium hydrogen phthalate between 0 and 10 mgC/L to

170   determine the DOC content of samples. DOC reference standards available from the Hansell's

171   Consensus Reference Materials (CRM) program were used to test the instruments. For boreal

172   lakes with high DOC content, lowering the pH below 2, as done in the method, could change

173   the solubility of DOM by driving precipitation or sorption of organic matter to the wall and

174   cap of glass vials. However, the spectroscopic results obtained (see later) support the presence

175 of fulvic instead of humic acids in lake waters. Since fulvic acids are soluble at any pH, the

176 acidification of the samples does not change the concentration of fulvic acids. We expect then

177 that the acidification of the method did not change significantly the concentration of DOC in

178 our samples. Samples for DOM fluorescence and CDOM absorption measurements were

179 filtered through 0.2 μm filters to remove bacteria and prevent decomposition of the DOC

180 during storage. Samples were stored in dark to prevent photodegradation and photosynthesis.

181

182 **2.4. Absorption and fluorescence measurements**

183 CDOM absorption was determined for three stations in each lake with a Perkin Elmer

184 Lambda 12 UV/VIS spectrophotometer, using a 5 cm pathlength quartz cuvette. Absorption

185 measurements were done over the range 200-600 nm with a spectral resolution of 1 nm.

186 Nanopure water was used as the blank to subtract the absorption due to pure water.

187 Absorbance values were converted to absorption coefficient a_{CDOM} (λ) (m^{-1}) using the

188 following equation (Kirk, 1994):

189 $a_{cDOM}(\lambda) = 2.303 \times A(\lambda) \div L$ (2)

190 where $A(\lambda)$ is the absorbance at wavelength λ and L is the pathlength of the cell used in the

191 absorbance measurement in meters. In this study, a_{cDOM} at $\lambda=355$ nm ($a_{cDOM (355)}$) is used for

192 data analysis.

193

194 Specific UV absorbance (SUVA) was calculated at 254 nm. $SUVA_{254}$ is defined as the UV

195 absorbance of a water sample at 254 nm divided by the DOC concentration measured in mg C

196 per liter (Weishaar et al., 2003). SUVA is a measure of the absorbance by mg of carbon

197 present in the sample. SUVA also allows an estimation of the aromaticity of the organic

198 carbon present in the samples.

199   Finally, the spectral slope (S) was calculated fitting an exponential equation between 305 and

200   265 nm (Galgani et al., 2011). Spectral slope is used to provide information on change in the

201   composition/quality of CDOM, including the ratio of humic to fulvic acids (Galgani et al.,

202   2011; Fichot and Benner, 2012).

203

204   Fluorescence measurements were made for the same three stations in each lake using a

205   Fluoromax-4 HORIBA Jobin Yvon fluorometer with a 1 cm quartz cuvette, at 0.1 sec

206   integration time and with the standard R928P photomultiplier tube operating at 950 Volts.

207   Prior to fluorescence analysis, the absorbance of each sample was measured with a UV-VIS

208   spectrophotometer (PerkinElmer Lambda 35). If the absorbance of the sample was higher

209   than 0.05 AUFS, the sample was diluted to obtain absorbance in the range 0.02-0.03 AUFS.

210   At this absorbance, the first and secondary inner filter effects are negligible (Lakowicz, 2006)

211   and no correction has been done for the inner filter effects. Under these conditions, the

212   fluorometer was never saturated. To obtain the three-dimensional excitation-emission

213   fluorescence matrix (EEM), the instrument was operated in ratio mode to correct lamp

214   fluctuation. Emission and excitation spectra were corrected for instrument bias as suggested

215   by the manufacturer. The fluorescence EEM spectroscopy involved scanning and recording

216   samples at sequential 5 nm increments of excitation wavelengths between 250 and 500 nm.

217   Emission wavelength increment was 2 nm between 250 and 600 nm. The spectra were

218   obtained by subtracting nanopure water blank spectra to eliminate water Raman scatter peaks.

219   Each sample scan was then used to generate three-dimensional contour plots of fluorescence

220   intensity as a function of excitation and emission wavelengths.

221

222   Our samples were characterized by two important fluorescent peaks. The first peak had an

223   excitation maximum near 250-260 nm with an emission maximum near 380-480 nm. The

224   second peak had an excitation maximum near 330-350 nm and an emission maximum near

225   420-480 nm. These fluorescence signals, called peaks A and C, where assigned to humic-like

226   substances by Coble (1996). No other salient peaks where observed in the fluorescence signal.

227   From the intensity of peaks and other fluorescence signals, we calculated indices to quantify

228   fluorescence properties of DOM. The ratio of fluorescence intensity of the two humic-like

229   peaks (A/C) (Coble 1996) was calculated for each sample. A change in the ratio of the

230   intensity of these fluorophores reflects a change in the proportions of these fluorophores. A

231   constant ratio A/C suggests a constant composition, a stable input or a stable environment.

232   Fluorescence index (FI) was also calculated for each sample as the emission intensity at 470

233   nm divided by the emission intensity at 520 nm when the excitation energy was set at 370 nm

234   (McKnight et al., 2001; Cory and McKnight, 2005). Two other indexes called the

235   biological/autochthonous index (BIX) (Vacher, 2004; Huguet et al., 2009) and the

236   humification index (HIX) (Zsolnay et al., 1999; Huguet et al., 2009) were calculated to assess

237   the relative contribution of autochthonous DOM in samples. BIX was calculated from the

238   ratio of emission intensities at 380 nm and 430 nm wavelengths when the excitation energy

239   was set at 310 nm. HIX was measured using the excitation wavelength 254 nm and calculated

240   as the ratio of the area under emission spectra at 435-480 nm divided by the area under the

241   300-445 nm region.

242

243   **2.5. Data analyses**

244   Water characteristic variables (TP, DIP, DIN, chl *a*, DOC) and DOM spectroscopic

245   parameters ($a_{cDOM\ (355)}$, fluorescence ratio A/C, FI, BIX, HIX, $SUVA_{254}$ and S) were compared

246   using three-way partly nested analyses of variance (ANOVAs). Factors in the model were:

247   treatment (fixed with two levels, unperturbed and perturbed), lake nested in treatment

248   (random with four lakes per treatment), year (fixed with three years of sampling) and their

10

249 interactions. Data were transformed when necessary to achieve normality and homogeneity of

250 variance. The impact of forest harvesting was measured as an interaction between the

251 treatment (perturbed/unperturbed) and the year (Green, 1979). When this factor was

252 significant, a posteriori comparisons were made using Tukey's test. A BACI design

253 (Underwood, 1991; 1992) was not used in this study since we had a limited number of

254 sampling dates before the perturbation occurred. However, we studied the temporal variation

255 of the system using the time as factor (Archambault et al., 2001) and we did sample one year

256 before the perturbation.

257

258 **3. Results**

259 Monthly, seasonally and annual climatic variables were similar throughout the three sampling

260 years of this study (Table 2). TP concentrations ranged from 4.80 (perturbed, 2008) to 5.75 µg

261 l^{-1} (perturbed, 2009) (Fig. 2). A statistically significant interaction between treatment and year

262 was observed for TP concentrations (Table 3). A posteriori Tukey's test confirmed that

263 unperturbed and perturbed lakes were not significantly different in 2008 (before forest

264 harvesting) nor in 2010 but they were significantly different in 2009 (first year after forest

265 harvesting). TP concentrations increased in the perturbed lakes in 2009 while it slightly

266 decreased in unperturbed lakes. In 2010 TP concentrations were practically the same in

267 unperturbed and perturbed lakes, as a result of increased TP in reference lakes (Fig. 2).

268

269 DIP values ranged from 1.39 (unperturbed, 2010) to 1.96 µg l^{-1} (perturbed, 2009) (Fig. 2) and

270 DIN values ranged from 0.42 (unperturbed, 2008) to 3.02 µg l^{-1} (perturbed, 2009) (Fig. 2).

271 Neither DIP nor DIN values showed significant differences for the interaction between

272 treatment and year (Table 3), although DIN values were higher in perturbed than unperturbed

273 lakes in 2009 and 2010.

274

275 Chl *a* values ranged from 0.41 (unperturbed, 2008) to 1.00 μg l^{-1} (perturbed, 2009) (Fig. 2).

276 Chl *a* values did not show significant differences between treatment and year (Table 3).

277 Although there was an increase in chl *a* concentration in 2009, this increase occurred for both

278 unperturbed and perturbed lakes (Fig. 2).

279

280 DOC concentrations ranged from 11.34 (perturbed, 2008) to 15.27 mg C l^{-1} (perturbed, 2009)

281 (Fig. 2). No significant difference was detected between treatment and year for DOC values

282 (Table 3). However, DOC was substantially higher in 2009 in perturbed lakes than in

283 unperturbed lakes, then decreased in 2010 in perturbed lakes (Fig. 2). In 2009, DOC

284 concentrations ranged from 9.57 to 14.96 mg C l^{-1} in unperturbed lakes and from 13.60 to

285 17.48 mg C l^{-1} in perturbed lakes. Moreover, we performed a three-way ANOVA with the

286 same factors as above but comparing only 2008 and 2009. In this case, the interactions

287 between treatment and year for all the variables were significant for DOC concentrations

288 (df=2/12, MS=32.3253, F=6.2160, p=0.0466) and TP (df=2/12, MS=0.2561, F=20.9793,

289 p=0.0036).

290

291 Two maxima humic-like peaks were observed in all EEM in all samples: peak A and peak C.

292 These peaks are commonly reported in the literature (Coble, 1996; Parlanti et al., 2000) as

293 indicators of the presence of humic substances. The spectroscopic metrics $a_{cDOM\ (355)}$,

294 fluorescence ratio A/C, FI, BIX, HIX, SUVA$_{254}$ and S values showed similar patterns in

295 unperturbed and perturbed lakes over time (Fig. 3). $a_{cDOM\ (355)}$ values ranged from 30.44

296 (unperturbed, 2010) to 40.68 m^{-1} (perturbed, 2009) and showed the same pattern for

297 unperturbed and perturbed lakes, increasing in 2009 and decreasing in 2010 (Fig. 3).

298 Fluorescence ratio A/C values ranged from 1.46 (unperturbed, 2009) to 1.50 (perturbed, 2010)

299   (Fig. 3) and FI values ranged from 1.64 (unperturbed, 2010) to 1.71 (unperturbed, 2009). FI

300   values decreased in 2010 both for unperturbed and perturbed lakes (Fig. 3). BIX values

301   ranged from 0.36 (unperturbed, 2009) to 0.40 (perturbed, 2010). HIX values ranged from

302   20.31 (perturbed, 2010) to 25.37 (unpertubed, 2009). $SUVA_{254}$ values ranged from 1.91

303   (perturbed, 2009) to 2.09 L mg m^{-1} (unperturbed, 2009) and S values ranged from 0.010

304   (unperturbed, 2008) to 0.012 nm^{-1} (perturbed, 2010) (Fig. 3). No significant differences for

305   the interaction between treatment and year were found for any of these variables (Table 4).

306   Chl a significantly correlated with DOC ($r^2 = 0.1202$, F = 14.0689, $p = 0.001$) and TP ($r^2 = $

307   0.0693, F = 7.5166, $p = 0.007$) and DOC significantly correlated with TP ($r^2 = 0.2780$, F =

308   8.2109, $p = 0.005$). The absorption coefficient (a(355)) significantly correlated with DOC

309   concentration in unperturbed and perturbed lakes ($r^2=0.7674$, F=428.8325, p<0.001).

310

311   **4. Discussion**

312   Concentrations of TP measured in unperturbed and perturbed lakes were typical values

313   reported for Boreal Shield lakes (Carignan et al., 2000; Winkler et al., 2009). However,

314   logging disturbance increased the TP content of lakes one year after harvesting as also

315   reported by other authors (Lamontagne et al., 2000; Winkler et al., 2009). Ground disturbance

316   may increase weathering and leaching of phosphorus from exposed mineral soils (Evans et al.,

317   2000). Adsorption of phosphorus to particles and their subsequent transportation by

318   hydrological events can increase the loading of rivers and lakes (Whitson et al., 2005).

319   Phosphorus losses from soils can be promoted by co-leaching with organic solutes such as

320   DOC (Qualls et al., 1991). The presence of DOC can enhance the solubility, mobility and

321   export of phosphorus by limiting the complexation of its dissolved form with cations that

322   would otherwise react to precipitate phosphorus and retain it in soils. This would explain the

323   significant correlation between DOC and TP found in this study. The parallel increase in TP

13

324 and DOC in lakes, one year after harvesting, can suggest a rise in allochthonous import of

325 DOC from watershed to lakes. DOC concentrations measured were typical of conifer boreal

326 forest systems with a mean annual temperature of 2.5^{o}C (Sobek et al., 2007). DOC

327 concentrations significantly increased after harvesting in perturbed lakes, similar to Winkler

328 et al. (2009), suggesting that the system responded immediately after the perturbation.

329

330 In lentic systems, DOC concentrations in surface waters are regulated by processes internal to

331 lakes and external processes occurring in the watersheds where DOC are exported to lakes. In

332 lakes, metabolic compounds released by healthy autotroph and heterotroph organisms,

333 exudation from altered cells resulting from zooplankton grazing and microbial decay of soft

334 tissues of dead organisms may produce or deliver DOC in lakes. DOC can also be removed

335 from water by bacterial degradation, photolytic alteration, heterotrophic respiration (i.e. CO_2

336 evasion) and sorption or aggregation between organic matter and clays that cause

337 sedimentation of particles. As mentioned earlier, the increase in DOC could result from the

338 extracellular release of DOC from phytoplankton (Baines and Pace, 1991). However, the

339 increase observed in DOC one year after harvesting is not parallel with a rise in chl *a* content,

340 suggesting a minor role of phytoplankton exudates on the regulation of DOC level. This is

341 also supported by the absence of characteristic protein-like peaks associated to planktonic

342 production (excitation maxima at 275 and 305-340 nm (Coble, 2007) in our EEM

343 fluorescence spectra (data not shown). Furthermore, the lakes are shallow and hot in summer

344 (15-18 ^{o}C in July). Under these conditions, bacterial mineralization of labile organic matter

345 can be efficient and net production of DOC in lakes should be low. If processes occurring in

346 lakes act as an important sink (destruction or sedimentation) for organic matter, it is the

347 production and transport of DOC from the catchment areas to lakes that control the quantity

348 and quality of organic matter in lakes. The mean annual lake residence times of water in the

lakes studied are short, less than 0.16 years (Table 1). Then, a rapid turnover of water and a quick replacement of DOC occur in these lakes. Under these conditions, variations in quantity and quality of DOC suggest that processes occurring in the drainage basins are of paramount importance to explain changes in the amounts and the chemical composition of DOC in lakes.

The transport of DOM from terrestrial ecosystems to lakes is complex. Thus, several potential processes could give rise to an increase in DOC content in lakes. Many studies suggested that the most important processes to explain increases in DOC after forest harvesting was the rise in organic matter leaching from logging slash; the increase decomposition of organic logging residues and organic matter in the surface soils due to increased forest floor temperature and moisture; and a reduction in evapotranspiration causing an increase in runoff quantity leading to a higher water table favorable to the exportation of DOM from the surface and riparian soils (Qualls et al., 2000; Bishop et al., 2004; Kreutzweiser et al., 2008; Schelker et al., 2013b). However, the largest C-efflux from a forest floor is soil respiration, which has been shown to change as a result of forest disturbance (Grant et al., 2007). Leaching from logging slash or foliage and woody debris mixed to surface soils after forest harvesting could enrich water soil surface in organic components (Qualls et al., 2000). However, studies show that amounts of DOC leached vary with temperature, the nature of woody debris and the lability of organic matter. Coarse residues (stumps, coarse roots, branches) decompose slowly while fine residues (leaves, needles, fine roots, twigs) as well as boreal forest moss and feather mosses can be very quickly metabolized to CO_2 (Wickland et al., 2007; Hanson et al., 2010). During the degradation processes, nitrogen, and low molecular weight organic acids are first removed while lignin and humic substances could persist. Qualls et al. (2000) suggested that higher concentrations of dissolved organic nutrients in solution draining from the forest floor of the cut plots can largely be accounted for by the slash above the leaf litter of the forest floor.

374

375   The input of DOM to lakes from surrounding landscape could produce changes in the amount

376   and the chemical composition or quality of organic matter. However, although total DOC

377   concentrations increased one year after logging, the composition of DOC did not measurably

378   change. This result has also been reported in streams (Burrows et al. 2014). Three-

379   dimensional excitation-emission fluorescence spectra of lake samples studied over three years

380   shown only two major fluorophores associated with allochthonous humic-like components.

381   This constancy in composition suggests that DOC composition was similar for the three years

382   in unperturbed and perturbed lakes, since there was no significant difference between year

383   and treatment for the ratio of fluorescence intensity of the two humic-like peaks (A/C) and

384   since no differences were observed on the UV-VIS spectra between the three years (data not

385   shown). Moreover, FI, BIX and HIX indices showed no significant differences either,

386   indicating there was no change in fluorescence spectra due to logging. FI is an index of the

387   origin of fulvic acids. In this study, FI values were around 1.65 in all lakes and years. Cory et

388   al. (2010) suggested values near 1.2 for DOM of terrestrial origin in a large river of USA and

389   1.55 for microbially derived DOM. However, Korak et al. (2014) have recently shown that FI

390   values can vary by 0.2 units if concentration changes, the highest FI value measured at low

391   DOC concentration. In this study, our measurements were obtained at natural pH, about 5.5 in

392   the lakes studied. Measurements of FI at samples pH other than 6-7.5 as suggested by

393   McKnight et al. (2001) or Cory et al. (2010) could change the range of values used to

394   distinguish sources of DOM because protonation, molecular conformation and fluorescence

395   signal of DOM change with pH. Thus, the relative contribution of autochthonous and

396   allochthonous material cannot be discerned from FI values. BIX values were, however,

397   between 0.35 and 0.42. These results are below 0.7, suggesting that DOM contains very little

398   autochthonous organic matter, and it may be mainly composed of allochthonous matter

16

399   (Vacher, 2004; Birdwell and Engel, 2010). Finally, HIX values were between 20.31 and 25.37,

400   in the range of values reported for soil derived humics (Birdwell and Engel, 2010). This is in

401   agreement with Vacher (2004), who suggested that HIX values larger than 16 indicate a

402   strong humic character and an important terrigeneous contribution.

403

404     $SUVA_{254}$ values (1.91 to 2.09) were slightly lower than values reported in other studies in

405   boreal forests (Wickland et al., 2007; Balcarczyk et al., 2009), indicating a relatively low

406   aromaticity for DOC. Wickland et al. (2007) reported low SUVA values (between 1.9 and 2.3)

407   for well or moderately well-drained soils. They associate the low value of SUVA to the

408   presence of hydrophilic organic matter (HPIOM). Guggenberger et al. (1994) found that

409   HPIOM appeared to be partly microbially synthesized and partly plant-derived with a high

410   degree of oxidative biodegradation suggesting that HPIOM are relatively small molecule with

411   many oxidized side-chains. S values were similar to values found in other studies in boreal

412   forest systems (Galgani et al., 2011). Our results showed no significant difference of $SUVA_{254}$

413   or S values (taking into account the interaction between the treatment and the year of

414   sampling). This suggests that forest harvesting resulted in an increase in the quantity of DOC

415   available (as DOC concentrations were significantly higher in 2009) without changes in terms

416   of quality. DOC quality varies to a large extent depending on its terrestrial origin in terms of

417   bioavailability (Berggren et al., 2007; Ågren et al., 2008). As the fluorescence can help to

418   differentiate between plant and microbially-synthesized DOC (McKnight et al., 2001),

419   increased runoff after harvesting would have resulted in DOC increases but DOC had a very

420   close composition before and after harvesting. Similar findings were reported in twenty-three

421   forested lakes in central Quebec, where DOC concentrations increased in logged lakes, but no

422   changes in aromaticity of DOC were observed (O'Driscoll et al., 2006).

423

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

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

449 contribute to a selective washing of humic substances. Boyer et al. (1996) suggested that

450 DOC in upper soil might accumulate during periods of low flow and be exported during

451 periods of high flows. However, DOC in deep soils horizons could be immobilized through

452 sorption onto mineral phases or by precipitation with polyvalent cations (Qualls et al., 2000;

453 Hansson et al., 2010; Kaiser and Kalbitz, 2012). The sorption could be more effective to

454 retain humic than fulvic acids (Weng et al., 2006). Moreover, washing of logging slash can

455 decrease the pH by 0.9 units for leachate of fresh needle litter (Hansson et al., 2010). Such

456 reduction in pH could decrease the solubility of humic substances by more than 50% (Tipping

457 and Woof, 1990) and cause a stronger sorption of humic acids compared to fulvic acids

458 (Weng et al., 2006). However, because fulvic acids are soluble at any pH, by definition, it is

459 the apparent solubility of humic acids that decrease during leaching of logging slash and

460 through transport of DOC from watershed to lakes. The resulting effect will be a possible

461 enrichment of water soil surface in fulvic acids exported to lakes. The spectroscopic

462 parameters measured are in agreement with our hypothesis that DOC is mainly composed of

463 fulvic acids.

464

465 Although there appears to be a recovery of water chemistry (TP and DOC) by year 2, there

466 are confounding factors that can obscure real recovery or delayed effects. For example,

467 Schelker et al. (2012) have seen a long lasting forestry effect on both hydrology and DOC on

468 aquatic systems in the boreal region. Biogeochemical processes in watersheds do not all

469 respond immediately to logging effects, i.e., tree removal and ground disturbance. Some

470 processes may take a few years, such as changes in organic matter composition and

471 processing on the forest floor, changes in vegetation composition from which the DOC is

472 derived, before those changes affect export of nutrients and subsequent changes to lake water

473 chemistry. Also, hydrological conditions (especially runoff) greatly affect solute movement to

474   surface waters (Fawcett et al., 1994), and it is possible that year 2 was different hydrologically

475   than the preceding and may have masked delayed effects. Inter-annual variability could also

476   have affected the export of nutrients and DOC to the lakes. However, since monthly,

477   seasonally and annual climatic variables were similar throughout the three years of sampling

478   (Table 2), we can then assume that in this study, forest harvesting is a major factor

479   influencing the system comparing to a natural factor such as annual precipitation. Lastly,

480   carbon and nutrients can be transformed (i.e. immobilized, mineralized, evaded as CO_2)

481   before being input into lakes (Ledesma et al. 2015). There is thus the potential for substantial

482   changes in many of the lake water parameters measured before they enter each lake.

483

484   In conclusion, this study indicated that logging activities appeared to increase significantly TP

485   and DOC export to oligotrophic lakes of the Eastern Canadian Boreal Shield one year after

486   the perturbation. This impact on water chemistry due to logging activity appeared to have

487   been short-term with recovery to pre-logging conditions two years after harvest. Nevertheless,

488   it has to be kept in mind that the number of perturbed and unperturbed lakes in this study was

489   only four, respectively and that they were sampled one month each year due to logistic

490   constraints. Sampling multiple times per year at each lake would have permitted to estimate

491   the influence that seasonal and natural events (i.e. snow melt and storms) have upon the

492   response parameters. Furthermore, the study did not address the potential for delayed or

493   longer-term changes in water chemistry that could result from biogeochemical processes in

494   the lake catchments adjust to forest recovery after harvest. However, this three-year period

495   study shows interesting results. It suggests changes in DOC and TP keeping the quality of the

496   CDOM almost unaffected. Moreover, the spectroscopic data converge to suggest that fulvic

497   acids are the mobile form of CDOM carried to lakes and that fulvic acids respond rapidly to

498 forest harvesting contrary to humic acids. Fulvic and humic acids are the most important

499 components of DOC and CDOM.

500

501 **Acknowledgements**

516

517

518

519 **References**

520 Ågren, A., Berggren, M., Laudon, H., and Jansson, M.: Terrestrial export of highly

521 bioavailable carbon from small boreal catchments in spring floods. Freshwater Biol., 53, 964–

522 972, 2008.

523

524 Archambault, P., Banwell, K., and Underwood, A. J.: Temporal variation in the structure of

525 intertidal assemblages following the removal of sewage. Mar. Ecol. Prog. Ser., 222, 51–62,

526 2001.

527

528 Baines, S. B, and Pace, M. L.: The production of dissolved organic matter by phytoplankton

529 and its importance to bacteria: Patters across marine and freshwater systems. Limnol.

530 Oceanogr., 36, 1078–1090, 1991.

531

532 Balcarczyk, K. L., Jones, J. B., Jaffe, R., and Maie, N.: Stream dissolved organic matter

533 bioavailability and composition in watersheds underlain with discontinuous permafrost.

534 Biogeochemistry, 94, 255–270, 2009.

535

536 Berggren, M., Laudon, H., and Jansson, M.: Landscape regulation of bacterial growth

537 efficiency in boreal freshwaters. Global Biogeochem. Cycles, 21, GB4002, 2007.

538

539 Birdwell, J. E., and Engel, A. S.: Characterization of dissolved organic matter in cave and

540 spring waters using UV–Vis absorbance and fluorescence spectroscopy. Org. Geochem., 41,

541 270–280, 2010.

542

543 Bishop, K., Seibert, J., Köhler, S., and Laudon, J.: Resolving the double paradox of rapidly

544 mobilized old water with highly variable responses on runoff chemistry. Hydrol. Proc., 18,

545 185–189, 2004.

546

547 Bosch, J. M., and Hewlett, J. D.: A review of catchment experiments to determine the effect

548 of vegetation changes on water yield and evaporation, J. Hydrol., 55, 3-23, 1982.

549

550 Bormann, F. H., and Likens, G.: Pattern and process in a forested ecosystem: disturbance,

551 development and the steady state based on the Hubbard Brook ecosystem study. Springer-

552 Verlag, New York, 1994.

553
554 Boyer, E. W., Hornberger, G. M., Bencala, K. E., and McKnight, D.: Overview of a simple

555 model describing variation of dissolved organic carbon in an upland catchment. Environ. Ecol.

556 Mod. Simul. Managem., 86, 183–188, 1996.

557
558 Burrows, R. M., Magierowski, R. H., Fellman, J. B., Clapcott, J. E., Munks, S. A, Roberts, S.,

559 Davies, P. E. and Barmuta, L. A: Variation in stream organic matter processing among years

560 and benthic habitats in response to forest clearfelling, For. Ecol. Manag., 327, 136-147, 2014.

561

562 Buttle, J. M., Creed, I. F., and Moore, R. D.: Advances in Canadian forest hydrology, 1999-

563 2003. Hydrol. Proc., 19, 169–200, 2005.

564

565 Carignan, R., D'Arcy, P., and Lamontagne, S.: Comparative impacts of fire and forest

566 harvesting on water quality in Boreal Shield lakes. Can. J. Fish. Aq. Sci., 57, 105–117, 2000.

567

568   Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation–

569   emission matrix spectroscopy. Mar. Chem., 51, 325–346, 1996.

570

571   Coble, P. G.: Marine optical biogeochemistry: The chemistry of ocean color. Chem. Rev., 107,

572   402–418, 2007.

573

574   Cory, R. M., and McKnight, D. M.: Fluorescence spectroscopy reveals ubiquitous presence of

575   oxidized and reduced quinones in dissolved organic matter. Environ. Sci. Technol., 39, 8142–

576   8149, 2005.

577

578   Cory, R. M., McNeill, K., Cotner, J. P., Amado, A., Purcell, J. M., and Marshall A. G.:

579   Singlet oxygen in the coupled photochemical and biochemical oxidation of dissolved organic

580   matter. Environ. Sci. Technol. 44, 3683-3689, 2010.

581

582   Deflandre, B., and Gagné, J.-P.: Estimation of dissolved organic carbon (DOC)

583   concentrations in nanoliter samples using UV spectroscopy. Water Res., 35, 3057–3062, 2001.

584

585   Evans, J. E., Prepas, E. E., Devito, K. J., and Kotak, B.G.: Phosphorus dynamics in shallow

586   subsurface waters in an uncut and cut subcatchment of a lake on the Boreal Plain. Can. J.

587   Fish. Aq. Sci., 57, 60–72, 2000.

588

589   Fawcett, R. S., Christensen, R. B., and Tierney, D. P.: The impact of conservation tillage on

590   pesticide runoff into surface water: A review and analysis. J Soil Water Conserv, 49, 126–135,

591   1994.

592

593 Fellman, J. B., D'Amore, D. V., and Hood, E.: An evaluation of freezing as a preservation

594 technique for analyzing dissolved organic C, N and P in surface water samples. Sci. Total

595 Environ., 392, 305–312, 2008.

596

597 Fellman, J. B., Hood, E., and Spencer, R. G. M.: Fluorescence spectroscopy opens new

598 windows into dissolved organic matter dynamics in freshwater ecosystems: A review. Limnol.

599 Oceanogr., 55, 2452–2462, 2010.

600

601 Fichot, C., and Benner, R.: The spectral slope coefficient of chromophoric dissolved organic

602 matter ($S_{275-295}$) as a tracer of terrigenous dissolved organic carbon in river-influenced ocean

603 margins. Limnol. Oceanogr., 57, 1453-1466, 2012.

604

605 Findlay, S. E. G., and Sinsabaugh, R. L.: Aquatic Ecosystems: Interactivity of dissolved

606 organic matter. Academic Press, California, 2003.

607

608 Galgani, L., Tognazzi, A., Rossi, C., Ricci, M., Galvez, J. A., Dattilo, A. M., Cozar, A.,

609 Bracchini, L., and Loiselle, S. A.: Assessing the optical changes in dissolved organic matter in

610 humic lakes by spectral slope distributions. J. Photochem. Photobiol., 102, 132–139, 2011.

611

612 Grant, R. F., Barr, A. G., Black, T. A., Gaumont-Guay, D., Iwashita, H., Kidson, J.,

613 McCaughey, H., Morgenstern, K., Murayama, S., Nesic, Z., Saigusa, N., Shashkov, A., and

614 Zha, T.: Net ecosystem productivity of boreal jack pine stands regenerating from clearcutting

615 under current and future climates, Glob. Change Biol., 13, 1423-1440, 2007.

616

617 Green, R. H.: Sampling design and statistical methods for environmental biologists. Wiley,
618 Chichester, 1979.

619

620 Groot, A., Lussier, J.-M., Mitchell, A. K., and MacIsaac, D. A.:A silvicultural systems
621 perspective on changing forestry practices. Forest Chron, 81, 50–55, 2005.

622

623 Guggenberger, G., Zech, W., and Schulten, H. R.: Formation and mobilization pathways of
624 dissolved organic matter: evidence from chemical structural studies of organic matter
625 fractions in acid forest floor solutions. Org. Geochem., 21, 51–66, 1994.

626

627 Hanson, K., Kleja, D. B., Kalbitz, K., and Larsson, H.: Amounts of carbon mineralised and
628 leached as DOC during decomposition of Norway spruce and roots. Soil Biol. Biochem. 42,
629 178–185, 2010.

630

631 Hudson, N., Baker, A., and Reynolds, D.: Fluorescence analysis of dissolved organic matter
632 in natural, waste and polluted waters – a review. River Res. Appl. 23, 631–649, 2007.

633

634 Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., and Parlanti, E.:
635 Properties of fluorescent dissolved organic matter in the Gironde Estuary. Org. Geochem. 40,
636 706–719, 2009.

637

638 Jaffé, R., McNight, D., Maie, N., Cory, R., McDowell, W. H., and Campbell, J. L.: Spatial
639 and temporal variations in DOM composition in ecosystems: The importance of long-term
640 monitoring of optical properties. J. Geophys. Res., 113, G04032, 2008.

641

642   Kaiser, K., and Kalbitz, K.: Cycling downard-dissolved organic matter in soils. Soil Biol.

643   Biochem., 52, 29–32, 2012.

644

645   Kelton, N., Molot, L. A., and Dillon, P. J.: Spectrofluorometric properties of dissolved

646   organic matter from Central and Southern Ontario streams and the influence of iron and

647   irradiation. Water Res., 41, 638–646, 2007.

648

649   Kirk, J. T. O.: Light and Photosynthesis in Aquatic Ecosystems, Second Edition, Cambridge

650   Univ. Press, 1994.

651

652   Korak, J. A., Dotson, A. D., Summers, R. S., and Rosario-Ortiz, F. L.: Critical analysis of

653   commonly used fluorescence metrics to characterize dissolved organic matter. Water Res. 49,

654   327-338, 2014.

655

656   Kreutzweiser, D. P., Hazlett, P. W., and Gunn, J. M.: Logging impacts on the

657   biogeochemistry of boreal forest soils and nutrient export to aquatic systems: A review.

658   Environ. Rev., 16, 157−159, 2008.

659

660   Kögel-Knabner, I.: The macromolecular organic composition of plant and microbial residues

661   as inputs to soil organic matter. Soil Biol. Biochem., 34, 139–162, 2002.

662

663   Lakowicz, J. R.: Principles of fluorescence spectroscopy. 3rd edition, Springer, 2006.

664

665   Lamontagne, S., Carignan, R., D'Arcy, P., Prairie, Y. T., and Paré, D.: Element export in

666   runoff from eastern Canadian Boreal Shield drainage basins following forest harvesting and

667   wildfires. Can. J. Fish. Aq. Sci., 57, 118–128, 2000.

668

669   Laudon, H., Hedtjärn, J., Schelker, J., Bishop, K., Sørensen, R., and Ågren, A.: Response of

670   dissolved organic carbon following forest harvesting in a boreal forest. Ambio, 38, 381–386,

671   2009.

672

673   Ledesma, J. L. J., Grabs, T., Bishop, K. H., Schiff, S. L., and Köhler, S. J. : Potential for long-

674   term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments.

675   Glob. Change Biol. 21, 2963–2979.

676

677   Löfgren, S., Ring, E., von Brömsen, C., Sørensen, R., and Högbom, L.: Short-term effects of

678   forest harvesting on the water chemistry in two boreal streams in northern Sweden: a paired

679   catchment study. Ambio, 38, 347–356, 2009.

680

681   McKnight, D. M., Boyer, E. W., Westerhof, P. K., Doran, P. T., Kulbe, T., and Anderson, D.

682   T.: Spectrofluorometric characterization of dissolved organic matter for indication of

683   precursor organic material and aromaticity. Limnol. Oceanogr. 46, 38–48, 2011.

684

685   Mobed, J. J., Hemmingsen, S. L., Autry, J. L., and McGown, L. B. Fluorescence

686   characterization of IHSS humic substances: total luminescence spectra with absorbance

687   correction. Environ. Sci. Technol. 30, 3061–3065, 1996.

688

689 Moore, T. R., and Dalva, M. Soem control on the release of dissolved organic carbon by plant

690 tissues and soils. Soil Sci. 166, 38–47, 2001.

691

692 NRCan: The state of Canada's forests 2004-2005, the boreal forest. Natural Resources

693 Canada, Canadian Forest Service, Ottawa, Ontario, 2005.

694

695 O'Driscoll, N. J., Siciliano, S. D., Peak, D., Carignan, R., and Lean, D. R. S.: The influence of

696 forestry activity on the structure of dissolved organic matter in lakes: Implications for

697 mercury photoreactions. Sci. Total Environ., 366, 880–893, 2006.

698

699 Parlanti, E., Wörz, K., Geoffroy, L., and Lamotte, M.: Dissolved organic matter fluorescence

700 spectroscopy as a tool to estimate biological activity in a coastal zone submitted to

701 anthropogenic inputs. Org. Geochem, 31, 1765–1781, 2000.

702

703 Qualls, R. G., and Haines, B. L.: Geochemistry of dissolved organic nutrient in water

704 percolating through a forest ecosystem. Soil Sci. Soc. Am. J., 55, 1112–1123, 1991.

705

706 Qualls, R. G., Haines, B. L., and Swank, W. T.: Fluxes of dissolved organic carbon and humic

707 substances in a deciduous forest. Ecology, 72, 254–266, 1991.

708

709 Qualls, R. G., Haines, B. L., Swank, W. T., and Tyler, S. W.: Soluble organic and inorganic

710 nutrient fluxes in clearcut and mature deciduous forests. Soil Sci. Soc. Am. J., 64, 1068–1077,

711 2000.

712

713 Rask, M., Nyberg, K., Markkanen, S. L., and Ojala, A.: Forestry in catchments: Effects on

714 water quality, plankton, zoobenthos and fish in small lakes. Boreal Environ. Res., 3, 75–86,

715 1998.

716

717 Romero-Kutzner, V., Packard, T. T., Berdalet, E., Roy, S. O., Gagné, J.-P., and Gomez, G.:

718 Respiration quotientvariability: bacterial evidence. Mar. Ecol. Prog. Ser., 519, 47–59, 2015.

719

720 Schelker, J., Eklöf, K., Bishop, K., and Laudon, H.: Effects of forestry operations on

721 dissolved organic carbon (DOC) concentrations and export in boreal first-order streams. J.

722 Geophys. Res.: Biogeosciences, 117, G01011, 2012.

723

724 Schelker, J., Kuglerová, L., Eklöf, K., Bishop, K. and Laudon, H. Hydrological effects of

725 clear-cutting in a boreal forest − Snowpack dynamics, snowmelt and streamflow responses.

726 Journal Hydrol 484, 105-114, 2013a.

727

728 Schelker, J., Grabs, T., Bishop, K., and Laudon, H.: Drivers of increased organic carbon

729 concentrations in stream water following forest disturbance: Separating effects of changes in

730 flow pathways and soil warming. Biogeosciences, 118, 1814–1827, 2013b.

731

732 Schindler, D. W., Bayley, S.E., Curtis, P. J., Parker, B. R., Stainton, M. P., and Kelly, C. A.:

733 Natural and man-caused factors affecting the abundance and cycling of dissolved organic

734 substances in precambrian shield lakes. Hydrobiologia, 229, 1–21, 1992.

735

736   Smith, D. W., Prepas, E. E., Putz, G., Burke, J. M., Meyer, W. L., and Whitson, I.: The forest

737   watershed and riparian disturbance study: a multi-discipline initiative to evaluate and manage

738   watershed disturbance on the Boreal Plain of Canada. J. Environ. Eng. Sci., 2, S1–S13, 2003.

739

740   Stainton, M. P., Capel, M. J., and Armstrong, F. A. J.: The chemical analysis of fresh water.

741   2nd ed. Can. Fish. Mar. Serv. Misc. Spec. Publ. No. 25, 1977.

742

743   Stedmon, C. A., Markager, S., and Bro, R.: Tracing dissolved organic matter in aquatic

744   environments using a new approach to fluorescence spectroscopy. Mar. Chem., 82, 239–254,

745   2003.

746

747   Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., and Cole, J. J.: Patterns and

748   regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. Limnol.

749   Oceanogr., 52, 1208–1219, 2007.

750

751   Tipping, E., and Woof, C.: Humic substances in acid organic soils: modelling their release to

752   the soil solution in terms of humic charge. J. Soil Sci., 41, 573−586, 1990.

753

754   Tremblay, L., and Gagné, J.-P.: Organic matter distribution and reactivity in the waters of a

755   large estuarine system. Mar. Chem., 116, 1−12, 2009.

756

757   Underwood, A. J.: Beyond BACI: Experimental designs for detecting human environmental

758   impacts on temporal variations in natural populations. Aust. J. Mar. Freshwater Res., 42, 569–

759   587, 1991.

760

761 Underwood, A. J.: Beyond BACI – the detection of environmental impacts on populations in

762 the real, but variable, world. J. Exp. Mar. Biol. Ecol., 161, 145–178, 1992.

763

764 Vacher, L.: Étude par fluorescence des propriétés de la matière organique dissoute dans les

765 systèmes estuariens. Cas des estuaires de la Gironde et de la Seine, Ph.D. Thesis, Université

766 Bordeaux I, Bordeaux, France, 2004.

767

768 Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., and Mopper, K.:

769 Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and

770 reactivity of dissolved organic carbon. Environ. Sci. Technol., 37, 4702–4708, 2003.

771

772 Welschmeyer, N. A.., Strom, S., Goericke, R., Ditullio, G., Belvin, M., and Petersen, W.:

773 Primary production in the sub-arctic pacific-ocean - project super. Prog. Oceanogr., 32, 101–

774 135, 1994.

775 Weng, L., van Riemsdijk, W. H., Koopal, L. K., and Hiemstra, T.: Adsorption of humic

776 substances on goethite: comparison between humic acids and fulvic acids. Environ. Sci.

777 Technol., 15, 7494–7500, 2006.

778

779 Whitehead, R. F., De Mora, S., Demers, S., Gosselin, M., Monfort, P., and Mostajir, P.:

780 Interactions of ultraviolet-B radiation, mixing, and biological activity on photobleaching of 61

781 natural chromophoric dissolved organic matter: a mesocosm study. Limnol. Oceanogr. 45,

782 278–291, 2000.

783

784 Whitson, I. R., Abboud, S., Prepas, E. E., and Chanasyk, D. S.: Trends in dissolved

785 phosphorous in Gray Luvisol soil profiles after harvest. Can. J. Soil Sci., 85, 89–101, 2005.

786

787 Wickland, K. P., Neff, J. C., and Aiken, G. R.: Dissolved organic carbon in Alaskan Boreal

788 Forest: sources, chemical characteristics, and biodegradability. Ecosystems, 10, 1323–1340,

789 2007.

790

791 Winkler, G., Leclerc, V., Sirois, P., Archambault, P., and Bérubé, P.: Short-term impact of

792 forest harvesting on water quality and zooplankton communities in oligotrophic headwater

793 lakes of the eastern Canadian Boreal Shield. Boreal Environ. Res., 14, 323–337, 2009.

794

795 Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B., Saccomandi, F.: Differentiating with

796 fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying.

797 Chemosphere 38, 45–50, 1999.

798 Table 1. Characteristics of the eight studied Canadian Boreal Shield lakes (UP: unperturbed lakes; P: perturbed lakes). Dissolved oxygen (DO),

799 pH, conductivity, temperature, secchi depth, total phosphorus (TP), dissolved inorganic phosphorous (DIP), dissolved inorganic nitrogen (DIN),

800 chlorophyll a (chl *a*) and dissolved organic carbon (DOC) are reported as means (SD) over the sampling stations on the photic zone before the

801 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^2)	0.17	0.17	0.06	0.03	0.29	0.09	0.28	0.04
Catchment area (km^2)	0.92	2.80	0.59	0.20	2.89	1.76	2.42	0.34
Drainage area (km^2)	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^{-1})	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^{-1})	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^{-1})	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^{-1})	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^{-1})	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 *a* (µg l^{-1})	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^{-1})	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)

802

803   Table 2. Monthly (July), seasonally (May, June, July) and annual average of climatic

804   variables during the three years of the study (2008, 2009 and 2010).

805

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

806   Table 3. Results of the three-way ANOVA testing the effect of treatment (tr : perturbed,

807   unperturbed), lake, year and their interactions on TP, DIP, DIN, chl *a* and DOC. Variables

808   were transformed to achieve normality and homogeneity of variance. The principal source of

809   variation of interest is the interaction between the treatment and the year of sampling.

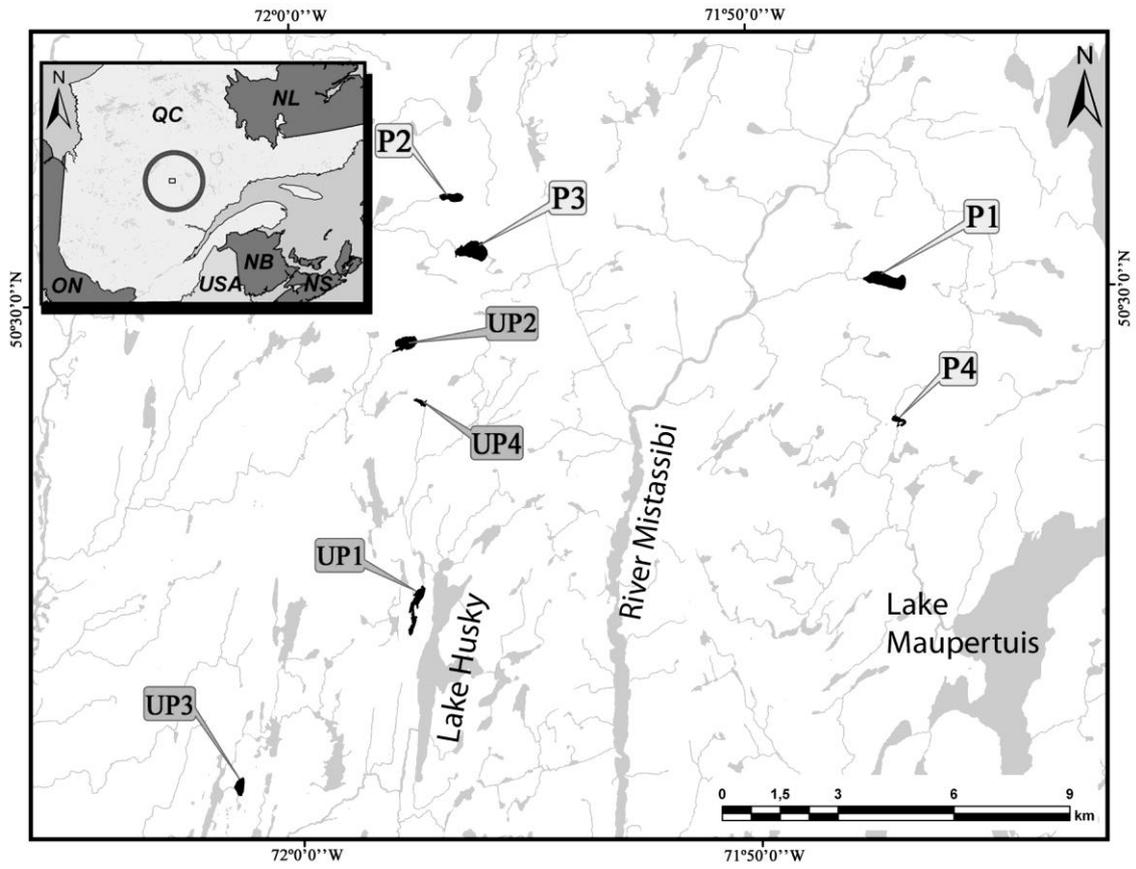810   Significant p values ($p < 0.05$) are in bold.

811

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	**<0.05**	**<0.05**	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	**<0.001**	
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	**<0.05**	0.92	**<0.001**	0.69	**<0.001**	
Log chl *a*	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	**<0.001**	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	**<0.05**	0.21	**<0.001**	

812 Table 4. Results of the three-way ANOVA testing the effect of treatment (tr: perturbed,

813 unperturbed), lake, year and their interactions on absorbance coefficients of CDOM (a_{cDOM}) at

814 355 nm, A:C peak ratios, fluorescence index (FI), biological/autochthonous index (BIX),

815 humification index (HIX), specific UV absorbance at 254 nm ($SUVA_{254}$) and spectral slope

816 (S). The principal source of variation of interest is the interaction between the treatment and

817 the year of sampling. Significant p values ($p < 0.05$) are in bold.

818

| Variable		tr	lake (tr)	year	tr x year	lake (tr) x year	Residual
	df	1	6	2	2	12	48
a_{cDOM} (λ=355)	SS	6.81	316.26	137.19	133.38	110.28	14.95
	F	0.02	3.22	1.35	1.31	7.37	
	p	0.88	**<0.05**	0.29	0.30	**<0.001**	
A:C	SS	0.02	0.01	0.01	0.01	0.01	0.01
	F	0.85	4.51	1.13	0.83	2.16	
	p	0.39	**<0.05**	0.29	0.39	**<0.05**	
FI	SS	0.01	0.01	0.02	0.01	0.01	<0.001
	F	1.02	1.89	21.92	0.88	2.62	
	p	0.35	0.16	**<0.001**	0.35	**<0.05**	
BIX	SS	0.01	0.01	0.01	0.01	0.01	<0.001
	F	4.65	1.42	3.98	0.24	4.12	
	p	0.08	0.28	0.05	0.62	**<0.001**	
HIX	SS	35.97	287.71	140.16	9.47	222.06	<0.001
	F	2.55	9.56	4.97	0.33	3.69	
	p	0.11	**<0.05**	**<0.05**	0.71	**<0.001**	
$SUVA_{254}$	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	$1.65\ 10^{-6}$	$8.6\ 10^{-6}$	$3.32\ 10^{-5}$	$7.43\ 10^{-6}$	$5.59\ 10^{-6}$	$1.39\ 10^{-6}$
	F	0.20	1.59	6.25	1.40	4.24	
	p	0.67	0.23	**<0.05**	0.28	**<0.001**	

Figure 1. Location of the eight study lakes sampled in 2008, 2009 and 2010. UP, unperturbed lakes; P, perturbed lakes (harvested in 2009).
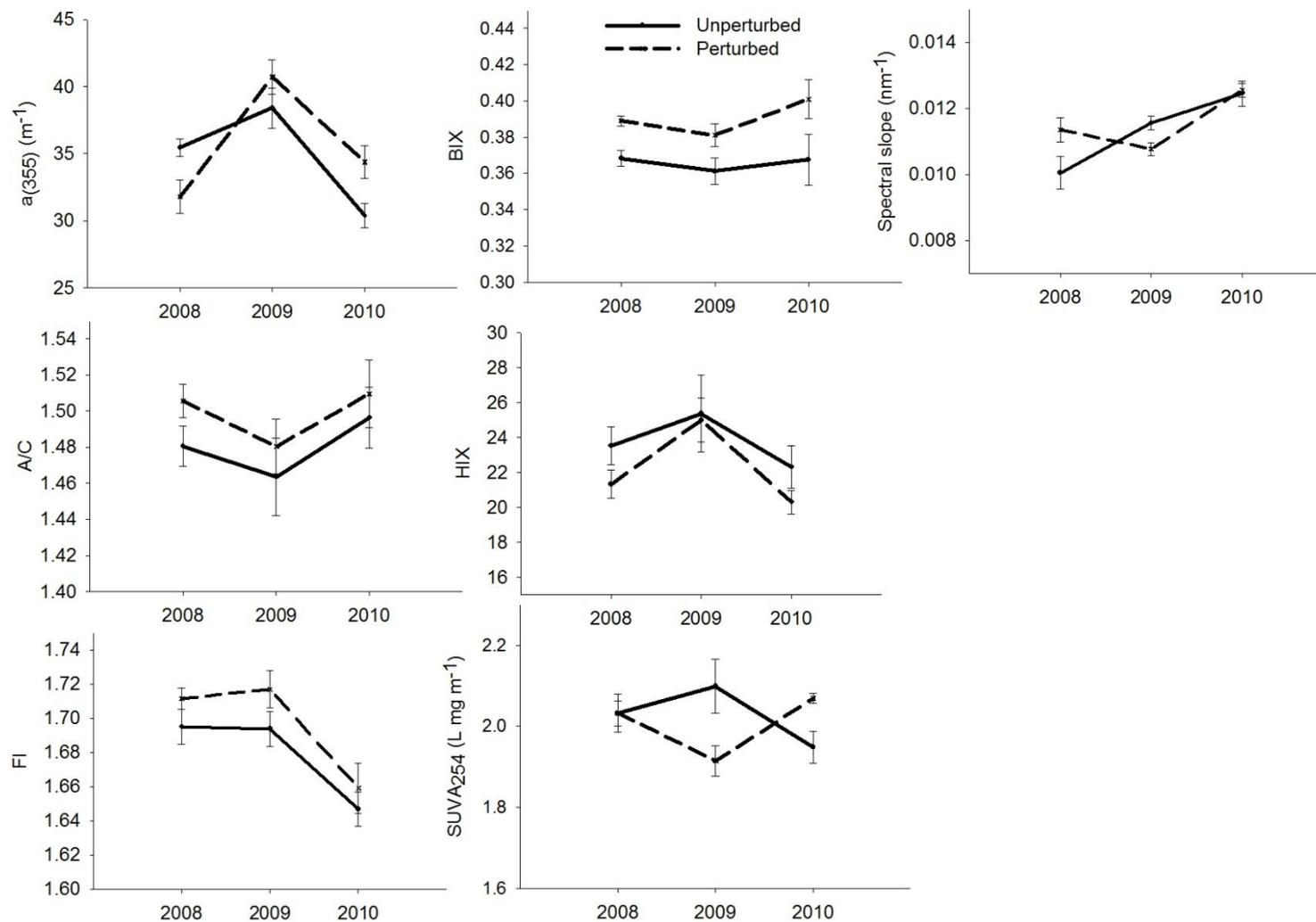
825
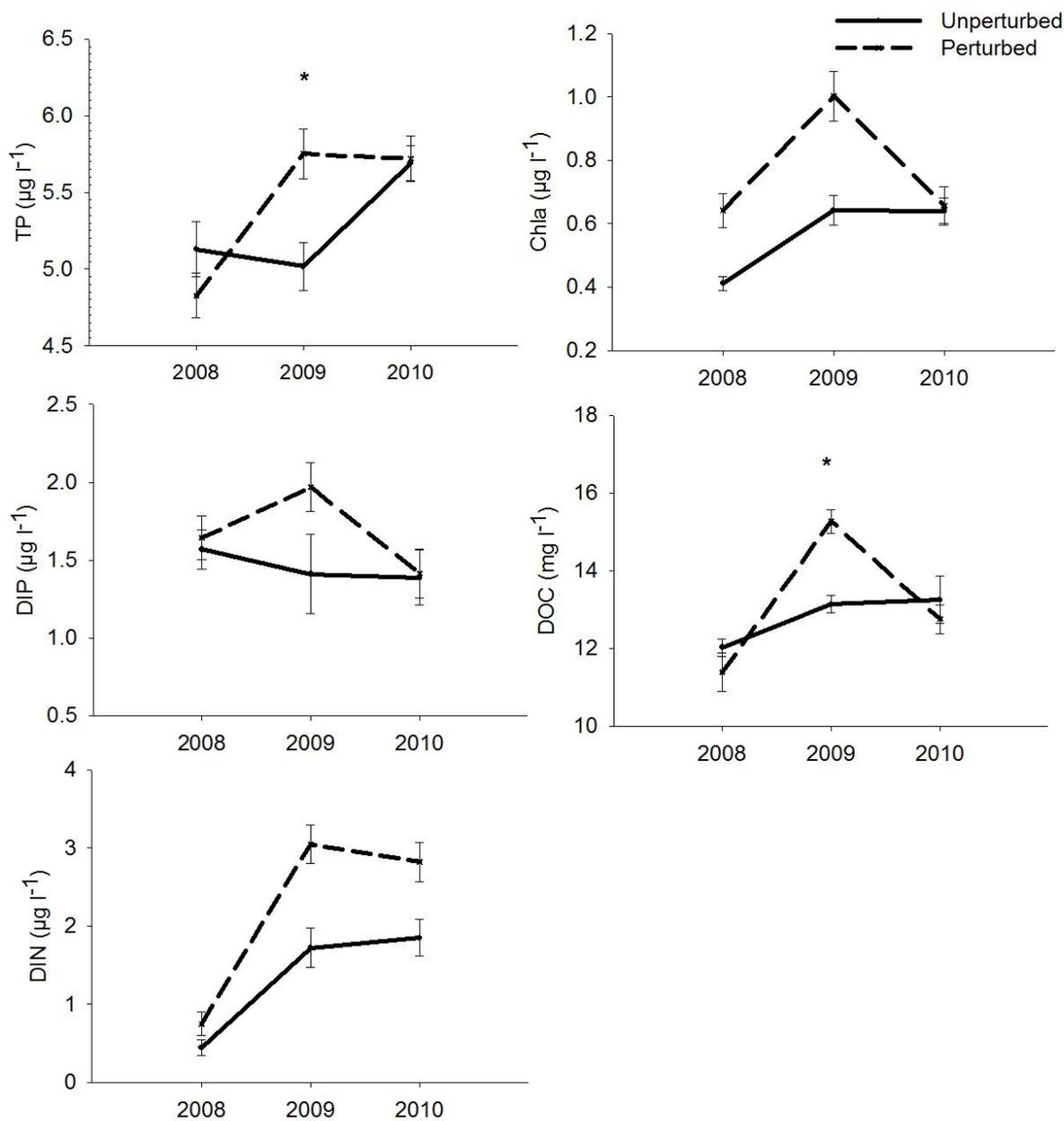
Figure 2. Comparison between treatments (unperturbed, perturbed) and years (2008, 2009, 2010) of TP, DIP, DIN, chl *a* and DOC. Vertical bars represent standard errors. * p<0.05.

828

829

830

831   Figure 3. Comparison between treatments (unperturbed, perturbed) and years (2008, 2009, 2010) of a_{cDOM} (λ=355), A/C, FI, BIX, HIX, SUVA$_{254}$

832   and spectral slope. Vertical bars represent standard errors.