Biogeosciences Discuss., 12, 9307–9339, 2015
www.biogeosciences-discuss.net/12/9307/2015/
doi:10.5194/bgd-12-9307-2015


Biogeosciences Discussions
Open Access



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

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Received: 29 May 2015 – Accepted: 01 June 2015 – Published: 23 June 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.







## 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 $\sim 15\,mg\,C\,L^{-1}$ compared to $12.5\,mg\,C\,L^{-1}$ in the unperturbed lakes. In contrast, absorbance and fluorescence measurements showed that all metrics remained within narrow ranges compared to the range observed in natural waters, indicating that forest harvesting did not affect the nature of DOM characterised with spectroscopic techniques. Multivariate statistical analysis showed lakes to be significantly different one year after the perturbation. These results confirm an impact of forestry activities one year after the perturbation. However, this effect seems to be mitigated two years after, indicating that the system shows high resilience and may be able to return to its original condition.

## 1 Introduction

Boreal forests are an ecological, economic and cultural source of wealth in Canada, which contain large areas of wetlands and over 1.5 million of lakes (NRCan, 2005; Kreutzweiser et al., 2008). These lakes receive allochthonous inputs of dissolved and particulate matter from natural sources and anthropic activities (Schindler et al., 1992). Forestry activities in the Canadian Boreal region have increased in the last decades, raising concerns about their potential impact on natural biogeochemical processes in





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soils and the export pathways that deliver dissolved nutrients and organic matter to aquatic ecosystems. After logging, the export of dissolved nutrients to aquatic ecosystems increases, which is primarily related to a higher microbial activity in upper soil layers and the forest floor (Kreutzweiser et al., 2008). This microbial activity converts nutrients from non-mobile to mobile forms, which are exported to receiving waters (Buttle et al., 2005), affecting loads of nutrients and organic compounds in lakes and rivers. Because forestry is the most important industry in much of the boreal region, the potential influence of logging on carbon reservoirs and water quality could be substantial. Therefore, there is a need to understand the long-term effects of forest harvesting on water quality, as well as its short transient repercussions.

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, soils conditions, moisture and temperature regimes, 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 (Fellman et al., 2010) and its functions 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; Anesio et al., 2004; Judd et al., 2006; 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





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that were not logged (i.e. unperturbed lakes), thereby changes due to logging cannot be separated from natural variability. However, a recent study by Winkler et al. (2009) showed increases in nutrients and DOC from before and after logging in eastern Canadian Boreal Shield lakes. These impacts were observed within the first year after the perturbation.

Quantitative and qualitative information about the source, composition and reactivity of the DOC present in a system 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, fluorescence intensity ratios provide data 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 in lakes (Rask et al., 1998; Carignan et al., 2000; Kreutweiser et al., 2008), and therefore, of allochthonous material, fluorescence measurements may be an interesting and a supplementary technique 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.

The objective of this study was to analyse the impact of forestry activities on water quality, and on UV-VIS and fluorescence characteristics of DOC in eastern Canadian





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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) and compared with four undisturbed references lakes (unperturbed lakes). More specifically, we tested the hypotheses that (1) nutrients and DOC would be greater in perturbed lakes than unperturbed lakes one and two years after the perturbation, (2) the UV-VIS and fluorescence signatures of DOM in perturbed lakes would indicate an increase in terrestrially-derived (allochthonous) DOM after logging.

## 2 Materials and methods

### 2.1 Study area

This study was conducted in the province of Québec on the Mistassibi River drainage basin (50°07′30′ N, 71°35′59′ W) located on the Boreal Shield (Fig. 1). The boreal forest of this study area is mainly dominated by virgin mature black spruces (*Picea mariana*) landscapes exploited by the forest industry. The soil layer over the rock is thin, lakes in this region are oligotrophic and all area is forest land (Winkler et al., 2009).

### 2.2 Sampling

Eight lakes with similar morphometric characteristics were selected for this study (Table 1). These eight lakes have been unperturbed in 2008 at the beginning of this survey. In 2009 and 2010, four of these lakes were kept undisturbed (unperturbed lakes) and four other lakes (perturbed lakes) where harvested about 70 % of lake catchment during autumn 2008 (Fig. 1, Table 1). All lakes were sampled once in July in 2008, 2009 and 2010. The experimental unit in this study was the lake. The forest was cut using the careful logging around advanced growth (CLAAG) strategy. CLAAG is a method of preserving advanced growth on the site after harvesting. The advanced growth contributes to site stocking as well as a seed source (larger trees) to regenerate open





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areas. Under this treatment, all trees equal to or greater than 10 cm diameter at breast height (d.b.h.) are harvested (Groot et al., 2005). A 20 m strip of standing forest was intentionally kept along lakes after harvesting activities. All lakes have a drainage ratio higher than 4, and perturbed lakes had a catchment area cut by 69–77 % (Table 1).

Residence time (RT) was calculated for each lake using the following equation:

$$RT = Z_{MD} \times A_{lake}/A_{catchment} \times P \quad (1)$$

where $Z_{MD}$ is the mean depth, $A_{lake}$ is the lake area, $A_{catchment}$ is the catchment area and $P$ is the mean annual precipitation in this region (rainfall and snow). Eq. (1) is an approximation to calculate the residence time for each lake because for lakes, in absence of data, we assumed only precipitation and no infiltration or water uptake by tree roots, no loss of water by evaporation and evapotranspiration to the atmosphere or by groundwater recharge.

At each lake, five littoral stations were selected randomly. Dissolved $O_2$, pH, conductivity, and water temperature were measured in situ at each sampling station using a YSI 556 MPS probe. Water transparency was estimated at the deepest zone of the lake using a secchi disc. Water samples were collected with an Alpha$^{TM}$ water sample bottle at 0.5 m below the surface at each sampling station and filtered through 300 µm to remove large zooplankton prior to the determination of physicochemical and biological variables. Samples for total phosphorus (TP), dissolved inorganic phosphorus and nitrogen (DIP and DIN, respectively) and suspended matter filtered for chlorophyll *a* (chl *a*) measurements were kept frozen at −20 °C whereas samples for DOC, CDOM absorption and DOC fluorescence measurements were maintained at 4 °C until analysis after appropriate filtration treatments for each parameter (see later).

### 2.3 Water quality measurements

TP was measured using the molybdenum blue method (Staiton et al., 1977) after autoclaving 50 mL samples with 0.5 g of potassium persulfate for 1 h at 120 °C. TP was afterwards assessed by using an AutoAnalyzer (AA3, Bran +Luebbe, German). DIP





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and DIN were determined using an AutoAnalyzer (AA3, Bran +Luebbe, German) after filtering water samples through a glass-fiber filter (0.22 µm Sartorius). For the determination of chl *a*, water samples were filtered (200 mL or more) onto Whatman GF/F filters. Samples were extracted for 24 h in 90 % acetone at 5 °C in the dark without grinding. Chl *a* was determined using the method of Welschmeyer et al. (1994). For DOC measurements, water samples were filtered through precombusted (500 °C, 5 h) Whatman GF/F filters. For the determination of DOC concentrations, the filtrates were collected in clean amber glass vials with Teflon-lined caps, and samples were acidified with ten µL of 25 % *v*/*v* $H_3PO_4$. The determination of DOC levels were made with a TOC-5000A analyzer (Shimadzu, Kyoto, Japan), following the protocol of Whitehead et al. (2000). DOC reference standards available from the Hansell's Certified Reference Materials (CRM) program were used to test the method. Samples for DOM fluorescence and CDOM absorption measurements were filtered through 0.2 µm filters to remove bacteria and prevent decomposition of the DOC during storage. Samples were stored in dark bottles to prevent photodegradation and photosynthesis.

### 2.4 Absorption and fluorescence measurements

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

$$a_{cDOM}(\lambda) = 2.303 \times A(\lambda)/1 \quad (2)$$

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





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Specific UV absorbance (SUVA) was calculated at 254 nm. $SUVA_{254}$ is defined as the UV absorbance of a water sample at 254 nm divided by the DOC concentration measured in mg C per liter (Weishaar et al., 2003). SUVA is a measure of the absorbance by mg of carbon present in the sample. SUVA also allows an estimation of the aromaticity of the organic carbon present in the samples. Weishaar et al. (2003) assessed the aromaticity of the organic carbon using the following equation:

$$\%\text{aromaticity} = \text{SUVA} \times 6.5 + 3.6 \quad (3)$$

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

Fluorescence measurements were made for the same three stations in each lake using a Fluoromax-4 HORIBA Jobin Yvon fluorometer. Samples were filtered through 0.2 µm polyethersulfone membrane to remove particulate matter. Fluorescence data were processed with the FluorEssence v2.1 software (Horiba Jobin Yvon). Three-dimensional excitation-emission fluorescence matrix (EEM) was used to identify fluorophores present in DOC. The fluorescence EEM spectroscopy involved scanning and recording samples at sequential 5 nm increments of excitation wavelengths between 250 and 500 nm. Emission wavelength increment was 2 nm between 250 and 600 nm. The spectra were obtained by subtracting nanopure water blank spectra to eliminate water Raman scatter peaks. Each sample scan was then used to generate three-dimensional contour plots of fluorescence intensity as a function of excitation and emission wavelengths.

Our samples were characterized by two important fluorescent peaks. The first peak had an excitation maximum near 250–260 nm with an emission maximum near 380–480 nm. The second peak had an excitation maximum near 330–350 nm and an emission maximum near 420–480 nm. These fluorescence signals, called peaks A and C, where assigned to humic-like substances by Coble (1996). No other salient peaks where observed in the fluorescence signal. From the intensity of peaks and other fluorescence signals, we calculated indices to quantify fluorescence properties of DOM.





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The ratio of fluorescence intensity of the two humic-like peaks (A/C) (Coble, 1996) was calculated for each sample. Fluorescence index (FI) was also calculated for each sample as the emission intensity at 470 nm divided by the emission intensity at 520 nm when the excitation energy was set at 370 nm (McKnight et al., 2001; Cory and McKnight, 2005). Another index called the biological/autochthonous index (BIX) (Vacher, 2004; Huguet et al., 2009) was calculated from the ratio of emission intensities at 380 and 430 nm wavelengths when the excitation energy was set at 310 nm, to assess the relative contribution of autochthonous DOM in samples.

### 2.5 Data analysis

Water characteristic variables (TP, DIP, DIN, chl *a*, DOC) and DOM spectroscopic parameters ($a_{\text{cDOM (355)}}$, fluorescence ratio A/C, FI, BIX, $\text{SUVA}_{254}$ and spectral slope) were compared using three-way partly nested analyses of variance (ANOVAs). Factors in the model were: treatment (fixed with two levels, unperturbed and perturbed), lake nested in treatment (random with four lakes per treatment), year (fixed with three years of sampling) and their interactions. Data were transformed when necessary to achieve normality and homogeneity of variance. The principal source of variation of interest for impact assessment was the interaction between the treatment (perturbed/unperturbed) and the year. When this factor was significant, a posteriori comparisons were made using Tukey's test.

Differences between treatment and year for the water characteristics and DOM variables were also evaluated by multivariate statistical analysis. Permutational multivariate analysis of variance (PERMANOVA ver. 1.6, Anderson, 2005) was performed using the Euclidean distance similarity measure as recommended for environmental variables (Clarke and Gorley, 2001). Data were standardized and normalized before analysis. This analysis had the same structure as the univariate ANOVA model described above, but it uses permutations to determine distributions of test-statistics. The number of permutations used was 4999.





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## 3 Results

TP concentrations ranged from 4.80(±0.12) (perturbed, 2008) to 5.75(±0.16) $\mu g\,L^{-1}$ (perturbed, 2009) (Fig. 2). A statistical significant interaction between treatment and year was observed for TP concentrations (Table 2). A posteriori Tukey's test confirmed that unperturbed and perturbed lakes were not significantly different in 2008 (before forest harvesting) nor in 2010 but they were significantly different in 2009 (after forest harvesting). TP concentrations increased in the perturbed lakes in 2009 while they slightly decreased in unperturbed lakes. In 2010 TP concentrations were practically the same in unperturbed and perturbed lakes, as a result of increased TP in reference lakes (Fig. 2).

DIP values ranged from 1.39(±0.16) (unperturbed, 2010) to 1.96(±0.16) $\mu g\,L^{-1}$ (perturbed, 2009) (Fig. 2) and DIN values ranged from 0.42(±0.09) (unperturbed, 2008) to 3.02(±0.24) $\mu g\,L^{-1}$ (perturbed, 2009) (Fig. 2). Neither DIP nor DIN values showed significant differences for the interaction between treatment and year (Table 2), although DIN values were higher in perturbed than unperturbed lakes in 2009 and 2010.

Chl *a* values ranged from 0.41(±0.03) (unperturbed, 2008) to 1.00(±0.08) $\mu g\,L^{-1}$ (perturbed, 2009) (Fig. 2). Chl *a* values did not show significant differences between treatment and year (Table 2). Although there was an increase in chl *a* concentration in 2009, this increase occurred for both unperturbed and perturbed lakes (Fig. 2).

DOC concentrations ranged from 11.34(±0.46) (perturbed, 2008) to 15.27(±0.32) $mg\,C\,L^{-1}$ (perturbed, 2009) (Fig. 2). No significant difference was detected between treatment and year for DOC values (Table 2). However, DOC was substantially higher in 2009 in perturbed lakes than in unperturbed lakes, then decreased in 2010 in perturbed lakes (Fig. 2). In 2009, DOC concentrations ranged from 9.57 to 14.96 $mg\,C\,L^{-1}$ in unperturbed lakes and from 13.60 to 17.48 $mg\,C\,L^{-1}$ in perturbed lakes. Moreover, we performed a three-way ANOVA with the same factors as above but comparing only 2008 and 2009. In this case, the interaction between





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treatment and year was significant for DOC concentrations (d$f$ = 2/12, MS = 32.3253, $F$ = 6.2160, $p$ = 0.0466) and TP (d$f$ = 2/12, MS = 0.2561, $F$ = 20.9793, $p$ = 0.0036).

Two maxima humic-like peaks were observed in all EEM in all samples: peak A at excitation maximum 250–260 nm and emission maximum 380–480 nm and peak C at excitation maximum 330–350 nm and emission maximum 420–480 nm. These peaks are commonly reported in the literature (Coble, 1996; Parlanti et al., 2000) as indicators of the presence of humic substances. The spectroscopic metrics $a_{\mathrm{cDOM}\,(355)}$, fluorescence ratio A/C, FI, BIX, $\mathrm{SUVA}_{254}$ and spectral slope values showed similar patterns in unperturbed and perturbed lakes over time (Fig. 3). $a_{\mathrm{cDOM}\,(355)}$ values ranged from 30.44(±1.09) (unperturbed, 2010) to 40.68(±1.25) $\mathrm{m}^{-1}$ (perturbed, 2009) and showed the same pattern for unperturbed and perturbed lakes, increasing in 2009 and decreasing in 2010 (Fig. 3). Fluorescence ratio A/C values ranged from 1.46(±0.02) (unperturbed, 2009) to 1.50(±0.01) (perturbed, 2010) (Fig. 3) and FI values ranged from 1.64(±0.10) (unperturbed, 2010) to 1.71(±0.10) (unperturbed, 2009). FI values decreased in 2010 both for unperturbed and perturbed lakes (Fig. 3). BIX values ranged from 0.36(±0.01) (unperturbed, 2009) to 0.40(±0.01) (perturbed, 2010). $\mathrm{SUVA}_{254}$ values ranged from 1.91(±0.03) (perturbed, 2009) to 2.09(±0.07) L mg $\mathrm{m}^{-1}$ (unperturbed, 2009) and spectral slope values ranged from 0.010(±0.003) (unperturbed, 2008) to 0.012(±0.003) $\mathrm{nm}^{-1}$ (perturbed, 2010) (Fig. 3). Aromaticity ranged from 14.7 (perturbed, 2009) to 18.5 % (unperturbed, 2009).

No significant differences for the interaction between treatment and year were found for any of these variables (Table 3). Moreover, PERMANOVA analysis revealed no significant interaction between treatment and year (d$f$ = 2/12, MS = 21.03, Pseudo-$F$ = 1.6245, $p$ = 0.1324) for the water characteristics and DOM variables. The absorption coefficient (a(355)) significantly correlated with DOC concentration in unperturbed and perturbed lakes ($r^2$ = 0.7674, $F$ = 428.8325, $p < 0.001$) (Fig. 4).





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## 4 Discussion

Concentrations of TP measured in unperturbed and perturbed lakes were typical values reported for Boreal Shield lakes (Carignan et al., 2000; Winkler et al., 2009). However, logging disturbance increased the TP content of lakes one year after harvesting as also reported by other authors (Lamontagne et al., 2000; Winkler et al., 2009). The origin of this increase can result from many factors. Forest harvesting affects availability and movement of nutrients because of changes in soil moisture and soil saturation, temperature, microbial activity, plant uptake and mineralization (Kreutzweiser et al., 2008). Other processes more specific to phosphorus may influence its fate. Ground disturbance may increase weathering and leaching of phosphorus from exposed mineral soils (Evans et al., 2000). Adsorption of phosphorus to particles and their subsequent transportation by hydrological events can increase the loading of rivers and lakes (Whitson et al., 2005). Phosphorus losses from soils can be promoted by co-leaching with organic solutes such as DOC (Qualls et al., 1991). The presence of DOC can enhance the solubility, mobility and export of phosphorus by limiting the complexation of its dissolved form with cations that would otherwise react to precipitate phosphorus and retain it in soils. The parallel increase in total phosphorus and DOC in lakes, one year after harvesting, can suggest a rise in allochthonous import of DOC from watershed to lakes. DOC concentrations measured were typical of conifer boreal forest systems with a mean annual temperature of 2.5 °C (Sobek et al., 2007) and did not significantly increase analysing the interaction between treatment and year of sampling, taking into account the three years, one before and two after the perturbation. However, when we compared one year before and one year after the perturbation, DOC concentrations significantly increased after harvesting in perturbed lakes, similar to Winkler et al. (2009), suggesting that the system responded immediately after the perturbation but quickly recovered when the concentration of organic matter is the metric studied.

In lentic systems, DOC concentrations in surface waters are regulated by processes internal to lakes and external processes occurring in the watersheds where DOC are





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exported to lakes. In lakes, metabolic compounds released by healthy autotroph and heterotroph organisms, exudation from altered cells resulting from zooplankton grazing and microbial decay of soft tissues of dead organisms may produce or deliver DOC in lakes. DOC can also be removed from water by bacterial degradation, photolytic alteration, and sorption or aggregation between organic matter and clays that cause sedimentation of particles. As mentioned earlier, the increase in DOC could result from the extracellular release of DOC from phytoplankton (Baines and Pace, 1991). However, the increase observed in DOC one year after harvesting is not parallel with a rise in chl *a* content, suggesting a minor role of phytoplankton exudates on the regulation of DOC level. This is also supported by the absence of characteristic protein-like peaks associated to planktonic production (excitation maxima at 275 and 305–340 nm (Coble, 2007) in our EEM fluorescence spectra (data not shown)). Furthermore, the lakes are shallow and hot in summer (15–18 °C in July). Under these conditions, bacterial mineralization of labile organic matter can be efficient and net production of DOC in lakes should be low. Also, in sunny season, the photodegradation could be efficient to transform autochthonous organic matter to $CO_2$ (Genning et al., 2001; Winter et al., 2007). If processes occurring in lakes act as an important sink (destruction or sedimentation) for organic matter, it is the production and transport of DOC from the catchment areas to lakes that control the quantity and quality of organic matter in lakes. The mean residence times of water in the lakes studied are short, less than 0.2 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. It is suggested that sorption, desorption, precipitation, dissolution, exoenzyme hydrolysis, cell uptake, microbial decomposition of soils, microbial death/lysis, abiotic condensation to form humic substances, photochemical degradation, hydrologic transport, alteration and leaching of logging residues can affect DOM production and cycling within water-





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sheds during the transit of land-derived DOM to lakes (Qualls et al., 2000; Wickland et al., 2007; Jaffé et al., 2008; Kaiser and Kalbitz, 2012; Singh et al., 2014). Thus, several potential processes could give rise to an increase in DOC content in lakes. However 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., 2013).

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 $CO_2$ (Webster and Benfield, 1986; 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. However the impact of leaching logging slash on DOC could be on short term, as observed in this study, because the fast degradation of labile organic matter and also because forest removal prevents the introduction of new leaf litter production for few years after clearing forest vegetation.

The input of DOM to lakes from surrounding landscape could produce changes in the amount and the chemical composition or quality of organic matter. However, CDOM absorption, a metric of DOC quality, did not appear to be affected by forest harvesting since no significant differences were found for the interaction between year and treat-





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ment for $a_{cDOM}$ (355). This observation suggests that the quality of organic matter in lakes is not somewhat different between before and after logging operations. Thus, although total DOC concentrations increased one year after logging, the composition of DOC did not measurably change, which is also supported by fluorescence measurements. Three-dimensional excitation-emission fluorescence spectra of lake samples studied over three years showed only two major fluorophores associated with allochthonous humic-like components. This amazing constancy in composition suggests that DOC composition was similar for the three years in unperturbed and perturbed lakes, since there was no significant difference between year and treatment for the ratio of fluorescence intensity of the two humic-like peaks (A/C). Moreover, FI and BIX indices showed no significant differences either, indicating there was no change in fluorescence spectra due to logging. FI is an index of the origin of fulvic acids. In this study, FI values were around 1.65 in all lakes and years. McKnight et al. (2001) suggested values near 1.4–1.5 for DOM of terrestrial origin in a large river of USA and > 1.6 for microbially derived DOM. However, these typical values are obtained at pH 2. In this study, our measurements are obtained at natural pH, about pH 5.5 in the lakes studied. Measurements of FI at samples pH other than 2 could change the range of values used to distinguish sources of DOM because protonation, molecular conformation and fluorescence signal of DOM change with pH. Thus, the relative contribution of autochthonous and allochthonous material cannot be discerned from FI values. BIX values were, however, between 0.35 and 0.42. These results are below 0.7, suggesting that DOM contains very little autochthonous organic matter, and it may be mainly composed of allochthonous matter (Vacher, 2004; Birdwell and Engel, 2010).

$SUVA_{254}$ values (1.91 to 2.09) were slightly lower than values reported in other studies in boreal forests (Wickland et al., 2007; Balcarczyk et al., 2009), showing a relatively low aromaticity for DOC. Wickland et al. (2007) reported low SUVA values (between 1.9 and 2.3) for well or moderately well-drained soils. They associate the low value of SUVA to the presence of hydrophilic organic matter (HPIOM). Guggenberger et al. (1994) found that HPIOM appeared to be partly microbially synthesized and partly





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plant-derived with a high degree of oxidative biodegradation, suggesting that HPIOM are relatively small molecule with many oxidized side-chains. Spectral slope values were similar to values found in other studies in boreal forest systems (Galgani et al., 2011). Our results showed no significant difference of $SUVA_{254}$ or spectral slope values (taking into account the interaction between the treatment and the year of sampling). This suggests that forest harvesting resulted in an increase in the quantity of DOC available (as DOC concentrations were significantly higher in 2009) without changes in terms of quality. DOC quality varies to a large extent depending on its terrestrial origin in terms of bioavailability (Berggren et al., 2007; Ågren et al., 2008). As the fluorescence can help to differentiate between plant and microbially-synthesized DOC (McKnight et al., 2001), increased runoff after harvesting would have resulted in DOC increases but DOC had a very close composition before and after harvesting. Similar findings were reported in twenty-three forested lakes in central Quebec, where DOC concentrations increased in logged lakes, but no changes in aromaticity of DOC were observed (O'Driscoll et al., 2006).

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, $SUVA_{254}$ and spectral slope. 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





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





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Although there appears to be a recovery of water chemistry (TP and DOC) by year 2, there are confounding factors that can obscure real recovery or delayed effects. For example, Schelker et al. (2012) have seen a long lasting forestry effect on both hydrology and DOC on aquatic systems in the boreal region. Biogeochemical processes in watersheds do not all respond immediately to logging effects, i.e., tree removal and ground disturbance. Some processes may take a few years, such as changes in organic matter composition and processing on the forest floor, changes in vegetation composition from which the DOC is derived, before those changes affect export of nutrients and subsequent changes to lake water chemistry. Also, hydrological conditions (especially runoff) greatly affect solute movement to surface waters (Fawcett et al., 1994), and it is possible that year 2 was different hydrologically than the preceding and may have masked delayed effects. Inter-annual variability could also have affected the export of nutrients and DOC to the lakes. However, we calculated annual precipitations for the three sampling years, and the values did not differ. Annual precipitation one year after harvesting (2009) was 627 mm whereas two years after harvesting (2010) it was 573 mm. We can then assume that in this study, forest harvesting is a major factor influencing the system comparing to a natural factor such as annual precipitation.

In conclusion, this study indicated that logging activities appeared to increase significantly TP and DOC export to oligotrophic lakes of the Eastern Canadian Boreal Shield one year after the perturbation. This impact on water chemistry due to logging activity appeared to have been short-term with recovery to pre-logging conditions two years after harvest. Nevertheless, it has to be kept in mind that the number of perturbed and unperturbed lakes in this study was only four, respectively. The study did not address the potential for delayed or longer-term changes in water chemistry that could result from biogeochemical processes in the lake catchments adjust to forest recovery after harvest. As pointed out by Palviainen et al. (2014), most of the impact studies are short-term and thus improved knowledge about the long-term impacts of current forest management methods on water quality is needed. Fluorescence measurements





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showed that forest harvesting did not affect the nature of DOC under this three years study, indicating no effect of harvesting on DOC-origin exported to lakes.

*Acknowledgements.* This research project was supported by a public grant from the Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT) to C. Nozais and P. Sirois and by grants from the Natural Sciences and Engineering Research Council of Canada to C. Nozais and J.-P. Gagné. P. Glaz was supported by a PhD fellowship from FQRNT. We are grateful to people who contributed to the sampling in the field: Myriam Bergeron, Yan Bhérer, Gabriel Diab, Dominic Gauthier, Philippe Beaulieu, Vanessa Paradis, Tommy Larouche, Hubert Philippon, Katrine Chalut and Geneviève Brouillet-Gauthier. We also thank AbitibiBowater Inc. for providing land use information and field facilities, R. Carignan for his contribution on determination of TP and T. Buffin-Bélanger for providing help with hydrological analysis. This manuscript was improved by M. González, M. Vanni and their laboratories affiliates. This is a contribution to the research programs of Centre d'études nordiques, Centre de la science de la biodiversité du Québec, Centre de recherche sur la Boréalie and to the Chaire de recherche sur les espèces aquatiques exploitées.

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

| | UP1 | UP2 | UP3 | UP4 | P1 | P2 | P3 | P4 |
|---|---|---|---|---|---|---|---|---|
| Latitude N<br>Longitude W | 50°25′44″<br>71°57′28″ | 50°29′22″<br>71°57′32″ | 50°23′13″<br>72°1′24″ | 50°28′34″<br>71°57′15″ | 50°30′9″<br>71°47′1″ | 50°31′25″<br>71°56′26″ | 50°30′40″<br>71°56′5″ | 50°28′11″<br>71°46′51″ |
| Lake area ($km^2$) | 0.170 | 0.169 | 0.063 | 0.031 | 0.288 | 0.090 | 0.277 | 0.043 |
| Catchment area ($km^2$) | 0.916 | 2.799 | 0.586 | 0.202 | 2.895 | 1.761 | 2.416 | 0.339 |
| Drainage area ($km^2$) | 0.746 | 2.630 | 0.523 | 0.171 | 2.606 | 1.671 | 2.138 | 0.296 |
| Drainage ratio | 4.388 | 15.562 | 8.301 | 5.516 | 9.024 | 18.567 | 7.706 | 6.883 |
| Harvested area (% of catchment area) | – | – | – | – | 72.9 | 69.1 | 71.6 | 77.0 |
| Residence time (year) | 0.21 | 0.03 | 0.01 | 0.07 | 0.20 | 0.05 | 0.19 | 0.06 |
| 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 ($\mu S\,cm^{-1}$) | 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 ($\mu g\,L^{-1}$) | 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 ($\mu g\,L^{-1}$) | 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* ($\mu g\,L^{-1}$) | 0.427 (0.065) | 0.390 (0.061) | 0.617 (0.200) | 0.363 (0.050) | 0.982 (0.212) | 0.546 (0.060) | 0.681 (0.161) | 0.486 (0.072) |
| TP ($\mu g\,L^{-1}$) | 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) |





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**Table 2.** Results of the three-way ANOVA testing the effect of treatment (tr: perturbed, unperturbed), lake, year and their interactions on TP, DIP, DIN, chl *a* and DOC. Variables were transformed to achieve normality and homogeneity of variance. The principal source of variation of interest is the interaction between the treatment and the year of sampling. * $p < 0.05$.

| Variable | | tr | lake (tr) | year | tr × year | lake (tr) × year | Residual |
|---|---|---|---|---|---|---|---|
| | d*f* | 1 | 6 | 2 | 2 | 12 | 96 |
| Log TP | SS | 0.0724 | 0.0136 | 0.1848 | 0.1473 | 0.0218 | 0.0204 |
| | *F* | 5.3016 | 0.6261 | 8.4664 | 6.7476 | 1.0720 | |
| | *p* | 0.0608 | 0.7072 | 0.0051* | 0.0108* | 0.3923 | |
| Log DIP | SS | 0.2812 | 0.9655 | 2.5920 | 1.3356 | 1.5446 | 0.2692 |
| | *F* | 0.2914 | 0.6254 | 1.6794 | 0.8654 | 5.7367 | |
| | *p* | 0.6088 | 0.7077 | 0.2275 | 0.4456 | < 0.0001* | |
| Log DIN | SS | 10.5133 | 0.3878 | 20.8774 | 0.5012 | 1.3449 | 0.3145 |
| | *F* | 27.1961 | 0.2995 | 15.8572 | 0.3807 | 4.2766 | |
| | *p* | 0.0018* | 0.9257 | 0.0004* | 0.6913 | < 0.0001* | |
| Log chl *a* | SS | 3.0749 | 0.6966 | 3.2958 | 0.2903 | 0.2325 | 0.1329 |
| | *F* | 4.4156 | 2.9975 | 14.1832 | 1.2495 | 1.2495 | |
| | *p* | 0.0803 | 0.0501 | 0.0007* | 0.3214 | 0.0685 | |
| Log DOC | SS | 0.0087 | 0.1365 | 0.3794 | 0.1277 | 0.0711 | 0.0050 |
| | *F* | 0.0636 | 1.9192 | 5.3368 | 1.7959 | 14.0117 | |
| | *p* | 0.8093 | 0.1585 | 0.0220* | 0.2078 | < 0.0001* | |





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**Table 3.** Results of the three-way ANOVA testing the effect of treatment (tr: perturbed, unperturbed), lake, year and their interactions on absorbance coefficients of CDOM ($a_{cDOM}$) at 355 nm, A : C peak ratios, fluorescence index (FI), biological/autochthonous index (BIX), specific UV absorbance at 254 nm ($SUVA_{254}$) and spectral slope. The principal source of variation of interest is the interaction between the treatment and the year of sampling. * $p < 0.05$.

| Variable | | tr | lake (tr) | year | tr × year | lake (tr) × year | Residual |
|---|---|---|---|---|---|---|---|
| | d*f* | 1 | 6 | 2 | 2 | 12 | 48 |
| $a_{cDOM}$ ($\lambda$ = 355) | SS | 6.8107 | 316.257 | 137.191 | 133.382 | 110.28 | 14.9540 |
| | *F* | 0.0244 | 3.2195 | 1.3500 | 1.3125 | 7.3746 | |
| | *p* | 0.8808 | 0.0384* | 0.2950 | 0.3043 | < 0.0001* | |
| A : C | SS | 0.0171 | 0.0138 | 0.0023 | 0.0017 | 0.0033 | 0.0015 |
| | *F* | 0.8500 | 4.5067 | 1.1267 | 0.8261 | 2.1633 | |
| | *p* | 0.3899 | 0.0192* | 0.2952 | 0.3962 | 0.0357* | |
| FI | SS | 0.0090 | 0.0031 | 0.0227 | 0.0009 | 0.0019 | 0.0008 |
| | *F* | 1.0200 | 1.8899 | 21.9200 | 0.8836 | 2.6229 | |
| | *p* | 0.3510 | 0.1627 | < 0.0001* | 0.3532 | 0.0101* | |
| BIX | SS | 0.0082 | 0.0017 | 0.0025 | 0.0001 | 0.0015 | 0.0003 |
| | *F* | 4.6487 | 1.4229 | 3.9774 | 0.2433 | 4.1159 | |
| | *p* | 0.0802 | 0.2815 | 0.0552 | 0.6254 | 0.0003* | |
| $SUVA_{254}$ | SS | 0.0861 | 0.2174 | 0.7176 | 0.3519 | 0.3650 | 0.0006 |
| | *F* | 4.1442 | 0.6293 | 2.0661 | 1.0132 | 5.5623 | |
| Spectral slope | SS | $1.65 \times 10^{-6}$ | $8.6 \times 10^{-6}$ | $3.32 \times 10^{-5}$ | $7.43 \times 10^{-6}$ | $5.59 \times 10^{-6}$ | $1.39 \times 10^{-6}$ |
| | *F* | 0.2034 | 1.5891 | 6.2488 | 1.3995 | 4.2403 | |
| | *p* | 0.6675 | 0.2313 | 0.0133* | 0.2831 | < 0.0001* | |





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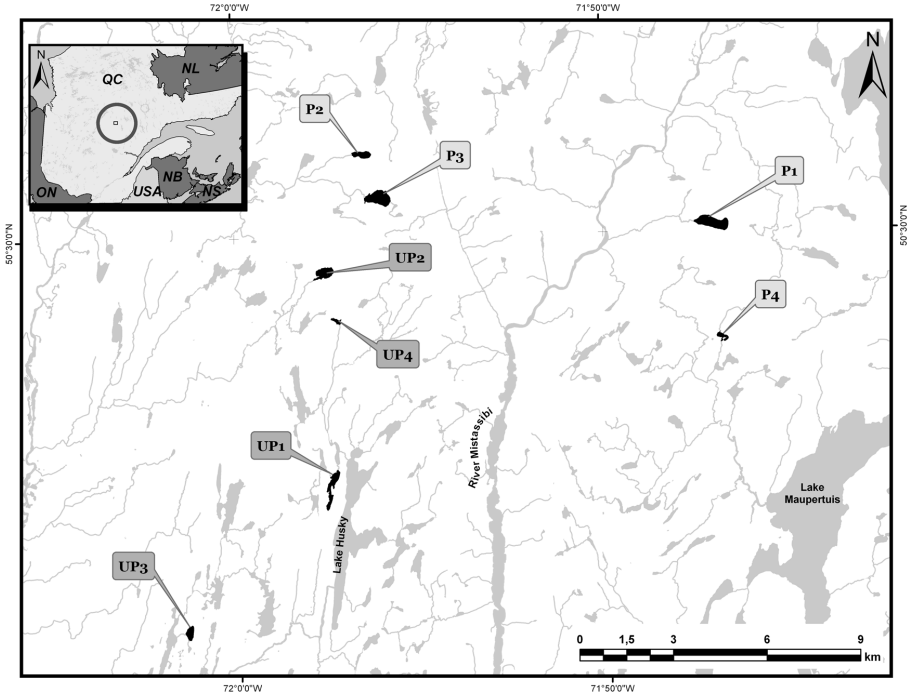


**Figure 1.** Location of the eight study lakes sampled in 2008, 2009 and 2010. UP, unperturbed lakes; P, perturbed lakes (harvested in 2009).





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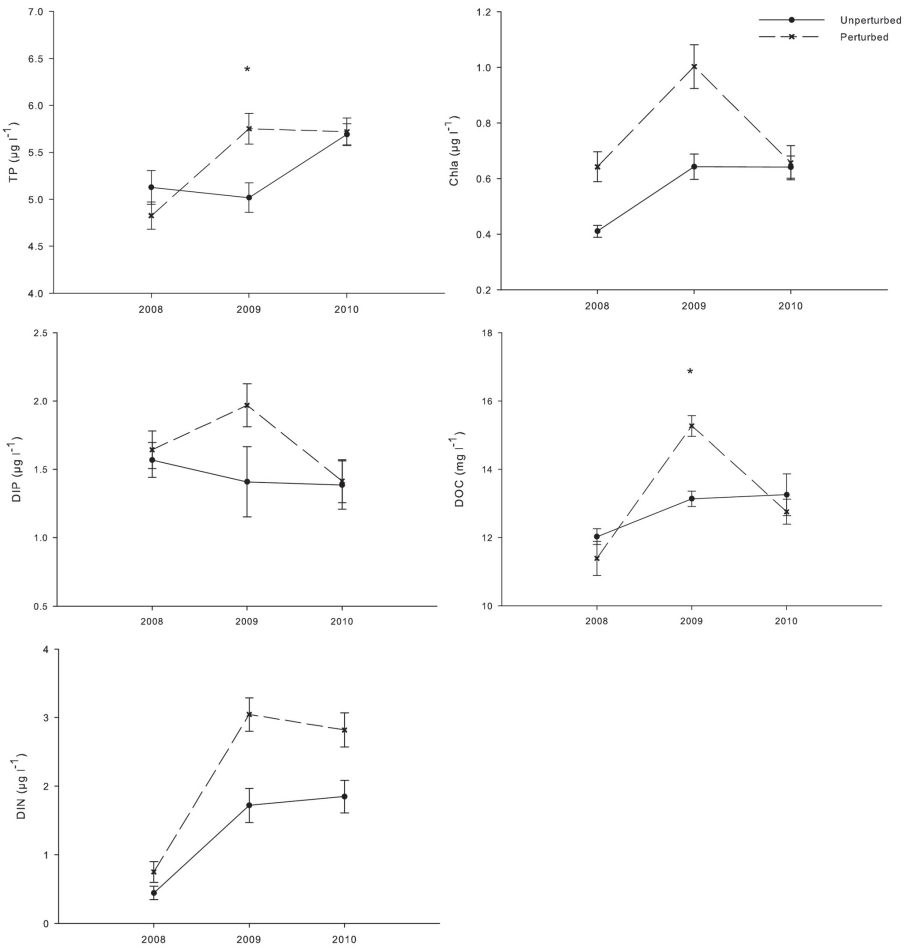


**Figure 2.** Comparison between treatments (unperturbed, perturbed) and years (2008, 2009, 2010) of TP, DIP, DIN, chl *a* and DOC. Vertical bars represent standard errors. * $p < 0.05$.





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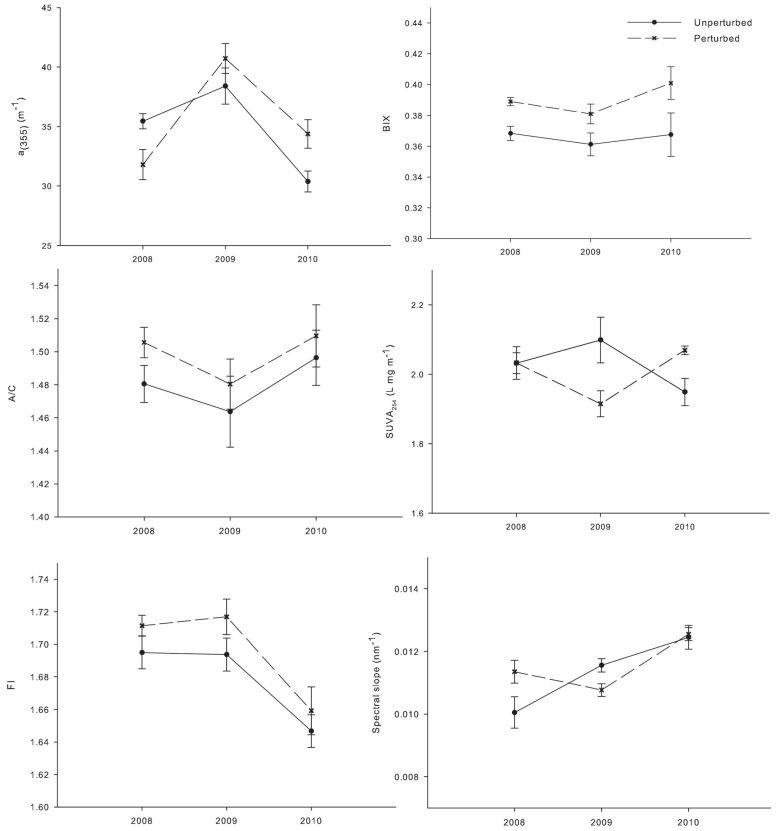


**Figure 3.** Comparison between treatments (unperturbed, perturbed) and years (2008, 2009, 2010) of $a_{cDOM}$ ($\lambda = 355$), A/C, FI, BIX, $SUVA_{254}$ and spectral slope. Vertical bars represent standard errors.





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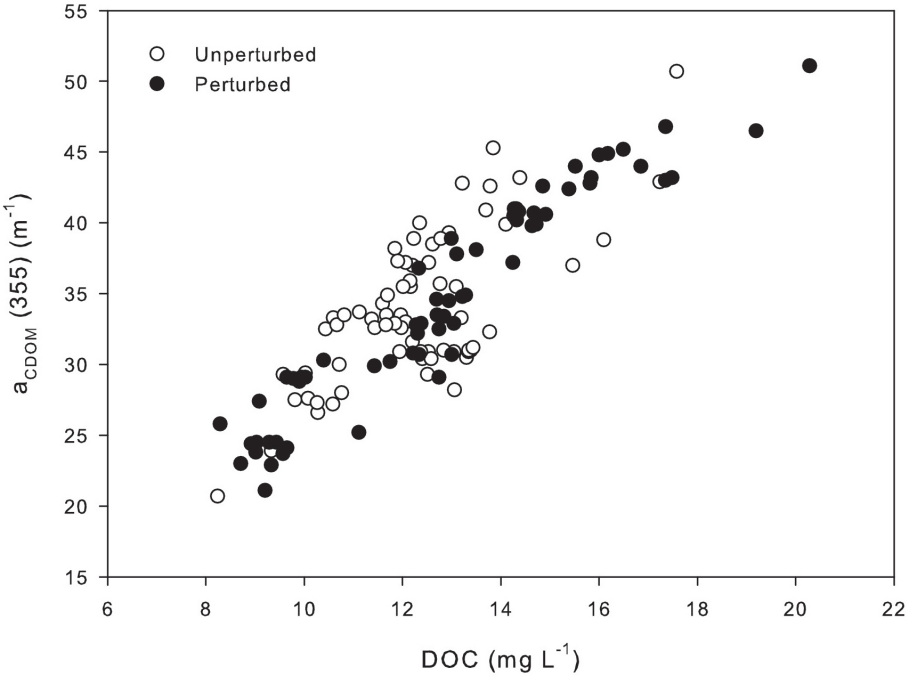


**Figure 4.** Relationship between the absorption coefficient ($a_{cDOM}$ ($\lambda$ = 355)) and DOC concentration in unperturbed and perturbed lakes. All samples from all lakes are represented.





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