Assessing carbon dynamics in natural and perturbed boreal aquatic systems

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Abstract

Most natural freshwater lakes are net greenhouse gases (GHG) emitters. Compared to natural systems, human perturbations such as watershed wood harvesting and long term reservoir impoundment lead to profound alterations of biogeochemical processes involved in the aquatic cycle of carbon (C). We exploited these anthropogenic alterations to describe the C dynamics in five lakes and two reservoirs from the boreal forest through the analysis of dissolved carbon dioxide (CO_2), methane (CH_4), oxygen (O_2), and organic carbon (DOC), as well as total nitrogen (TN) and phosphorus (TP). Dissolved and particulate organic matter, forest soil/litter and leachates, as well as dissolved inorganic carbon (DIC) were analyzed for elemental and stable isotopic compositions (atomic C:N ratios, $\delta^{13}C_{org}$, $\delta^{13}C_{inorg}$ and $\delta^{15}N_{tot}$). We found links between the export of terrestrial OM to these systems and the dissolved CO_2 and O_2 concentrations in the water column, as well as CO_2 fluxes to the atmosphere. All systems were GHG emitters, with greater emissions measured for systems with larger inputs of terrestrial OM. The differences in CO_2 concentrations and fluxes appear controlled by bacterial activity in the water column and the sediment. Although we clearly observed differences in the aquatic C cycle between natural and perturbed systems, more work on a larger number of water bodies, and encompassing all four seasons should be undertaken to better understand the controls, rates, as well as spatial and temporal variability of GHG emissions, and to make quantitatively meaningful comparisons of GHG emissions (and other key variables) from natural and perturbed systems.

1. Introduction

Surface waters of most lakes worldwide are supersaturated in carbon dioxide (CO_2), with partial pressures (pCO_2) that can be several times higher than the equilibrium concentration [*Kling et al.,* 1991; *Cole et al.,* 1994]. Dissolved CO_2 supersaturation is fueled by several potential sources, such as terrestrial dissolved inorganic carbon (DIC) inputs from groundwaters, or surface runoffs and remineralization of dissolved and particulate organic carbon (DOC and POC) [*McCallister and del Giorgio,* 2008; *Dubois et al.,* 2009, and references therein]. Growing evidence suggests that remineralization of terrigenous organic matter (OM) through photo-oxidation and/or bacterial respiration is the major driver of pCO_2 supersaturation in most freshwater systems [*del Giorgio et al.,* 1997; *Sobek et al.,* 2003; *McCallister and del Giorgio,* 2008]. Terrigenous OM is mainly funneled into lakes by rivers and surface runoffs [*Schindler et al.,* 1997], and helps sustain the aquatic food web through incorporation of DOC into bacterial biomass and/or through its respiration by heterotrophic bacteria [*Pace et al.,* 2004; *Berggren et al.,* 2007; *McCallister and del Giorgio,* 2008]. Indeed, lakes with DOC concentrations higher than 0.42 – 0.50 mmol L^{-1} generally behave as net heterotrophic systems, leading to high pCO_2 and low oxygen supersaturation levels [*Prairie et al.,* 2002]. Increases in the inputs of terrigenous OM into aquatic systems through flooding (e.g., reservoirs impoundment, erection of beaver dams) or wood harvesting on the watershed thus profoundly affect C cycling in aquatic systems [*Duchemin et al.,* 1995, 1999; *Tremblay et al.,* 2005].

Reservoirs are typically created for water flow regulation or for hydro power production; they are thus hydrodynamically very different from natural systems, with large variations in depth, generally shallower water columns and, for shallow reservoirs, the absence of water column stratification in the summer. Like natural lakes, reservoirs are net sources of greenhouse gases (GHG) to the atmosphere [*Duchemin et al.,* 1995; *St-Louis et al.,* 2000; *Tremblay et al.,* 2005]. Emissions of GHG from new reservoirs can reach almost 8 g CO_2/m^2 per day during the first 3 years following impoundment and decline to constant values (approximately 2 g CO_2/m^2 per day) within 10 years [*Tremblay et al.*, 2005; *Roland et al.*, 2010]. However, because of the very high spatial and temporal variability in GHG fluxes for lakes and reservoirs, it is still unclear whether GHG emissions from mature reservoirs (i.e., 10-15 years after impoundment) stabilize at levels higher than those measured for nearby natural water bodies [*Duchemin et al.,* 1995, 1999; *Tremblay et al.,* 2005].

Wood harvesting in the boreal forest leads to higher exports of DOC, total nitrogen and phosphorus (TN and TP, respectively) from land to lakes [*Carignan et al.*, 2000a; *Lamontagne et al.,* 2000], as well as to increased benthic algal and bacterial biomass [*Planas et al.,* 2000]. High inputs of terrigenous DOC (containing colored components such as tannins and lignin) in water bodies can attenuate light penetration and decrease the activity and biomass of primary producers [*Schindler et al.,* 1997; *Planas et al.,* 2000; *Karlsson et al.,* 2009], which could also lead to enhanced bacterial respiration (BR) of terrestrially derived DOC. Increases in exports of TN and TP from land to aquatic systems can increase net primary production (NPP) and BR simultaneously [*Schindler et al.,* 1997; *Carignan and Steedman,* 2000; *Prepas et al.*, 2001; *Karsson et al.,* 2009]. However, to the best of our knowledge, no study has assessed the effect of wood harvesting (increased DOC and nutrient inputs) on both the aquatic cycle of C in boreal lakes and reservoirs, and on the concentrations and atmospheric fluxes of dissolved CO_2 and methane.

Carbon cycling in boreal freshwater aquatic systems is subject to extensive temporal and spatial variability in the inputs and concentrations of dissolved and particulate species, which makes the understanding of the processes that control C dynamics and GHG fluxes extremely difficult. Human perturbations such as reservoir operation and wood harvesting extend the range of aquatic biogeochemical parameters (e.g. pH, [DIC] and [Fe]) observed in natural systems. Our working hypothesis is that such extended scale of biogeochemical measurements allows for more powerful statistical analyses and a better understanding of what controls GHG emissions by unraveling the relationships between GHG emissions and carbon and nutrients loading in aquatic systems.

In this work, we thus used a broad array of bulk water chemical proxies measured on samples collected in the spring and summer of 2007 to assess C cycling in freshwater systems with a natural or perturbed watershed (lakes and reservoirs with a natural or wood harvested watershed). In particular, we explored the following issues (*i*) What are the main biogeochemical characteristics of surface water in the different systems, and what are the sources of surface GHG (CH_4 and CO_2)? (*ii*) What are the relative contributions of allochthonous and autochthonous sources to the DOM and FPOM pools? (*iii*) How do allochthonous DOC inputs affect photosynthesis? (*iv*) How do seasonal and depth variations between systems influence heterotrophic and autotrophic processes? To minimize the complexity of our data set, our samples were collected in water bodies with similar characteristics and during a season when in-lake physical and chemical conditions are fairly stable (summer).

2. Materials and methods

2.1. Study sites

Two hydroelectric reservoirs and five natural lakes situated in the boreal forest of the Province of Quebec (Canada; 46°10′ to 47°46′ N; 76°12′ to 78°24′ W) were sampled for short periods (3 to 7 days at each site, with frequent daily CO_2 and CH_4 measurements) in May (for water DIC and total POC samples only) and July of 2007. Our sampling strategy, directed by logistic and financial considerations, only captures a snapshot picture of highly variable systems at a time when they are in their most stable state. This sampling is however suitable since our main goal is not to systematically compare natural and perturbed systems but to elucidate factors that influence carbon dynamics in these systems. The watershed of one reservoir (Decelles) and two lakes (Clair and Bouleau) were wood harvested less than 2 years before sampling, whereas the watersheds of the remaining water bodies were not exploited. While wood harvesting activities represented only about 1 to 5% of the total watershed drainage area, they were located in the direct vicinity of the water bodies, with non-harvested protection bands about 20 m wide along brooks and water bodies. We estimate from satellite pictures that the percentage of the lake/reservoir shoreline (within 2 km from shore) that was harvested is approximately 10-25% for lakes Clair and Bouleau, and about 5% for the Decelles Reservoir.

The Cabonga and Decelles reservoirs were impounded in 1928 and 1938, respectively. Both are thus representative cases of mature hydroelectric reservoirs. All lakes and reservoirs had watersheds with 42-74% tree coverage (conifers – mostly spruce, and broad-leaves deciduous species such as maple and birch), and 5 to 32% peatland coverage (never situated in the direct vicinity of the water bodies), with the rest mainly being moist soils with less than 1%

of uncovered, mostly granitic, bedrock; additional details on these water bodies are listed in Table 1.

To normalize spatial and depth variability, DOM, POM, nutrients as well as dissolved CO_2 and CH_4 were sampled at four stations within each lake, while nine and eleven stations were sampled in the Cabonga and Decelles reservoirs, respectively. Each sampling station was selected randomly at different pelagic and littoral locations that were most representative of the lake/reservoir morphologies based on the water column depth measurement (random stratified sampling).They were visited on three to eight different occasions.

2.2. Field sampling

Carbon dioxide and methane concentrations and fluxes were obtained using the method and equations of *Soumis et al.* [2008], based on the work of *Cole and Caraco* [1998]. Briefly, four 30-mL samples of surface water (0-30 cm) were collected with 60-mL syringes. Upon return to the laboratory, 30-mL of ultrapure nitrogen (N) gas were added to each syringe to create an inert gas headspace. The syringes were hand-shaken for exactly one minute and seated horizontally for two minutes for phase equilibration. The water sample was then slowly expelled from the syringes and its temperature recorded for equilibrium calculations. The concentration of the gas samples was measured with a Varian-Star 3400 gas chromatograph (GC) fitted with flame ionization and thermal conductivity detectors for CH_4 and CO_2 analysis, respectively. All GC analyses were performed within four hours of sampling. Water temperature and wind speed one meter above water surface were recorded on site; wind speed was extrapolated to 10 meters using the method described in *Soumis et al.* [2008]. Quantification was done using a certified external gas standard of CO_2 and CH_4, each at a concentration of 1.01 % (Scotty 48, Mix 218, Supelco).

Water for nutrient analyses was sampled within the surface layer (0-30 cm) in all water bodies. Water was collected in acid rinsed 60-mL HDPE bottles and kept frozen until analysis. Two 4-mL samples were collected for DOC analysis at each site, doped using mercury dichloride ($HgCl_2$) and kept at 4°C until analysis. Water column CO_2, CH_4, DOC and nutrient profiles were also performed at 0.5 to 5-m intervals using a 12-V submersible pump. A comparison of profiles acquired using the pump and a Kemmerer sampler showed that more reproducible results were obtained for CO_2 and CH_4 using the pump while obtaining the same level of accuracy. Water temperature, pH and dissolved oxygen profiles were recorded using a YSI 6600 multiprobe system.

Large volumes (200-250 L) of water (integrating the entire water column down to a maximum depth of 10 meters) were collected at each sampling site in 50-L pre-rinsed Nalgene containers. The water was passed through a 70-μm nylon mesh filter upon collection. Dissolved organic matter (DOM; < 0.45 μm) and fine particulate organic matter (FPOM; 0.45 – 70 μm) were separated using a tangential flow filtration (TFF) system fitted with a 0.45-μm polyvinylidene difluoride cartridge filter. The TFF system was coupled to a RealSoft PROS/2S reverse osmosis (RO) system which was used to remove all salts, including most inorganic nitrogen species, and to concentrate DOM as described by *Ouellet et al.* [2008]. Briefly, upon feeding the TFF with bulk water using a peristaltic pump, the retentate (containing fine particulate organic carbon, FPOM, >0.45 μm) was returned to the original container while the permeate was fed to the RO system for concentrating DOM. Dilute NaOH rinses of the RO membranes were done between each sample to limit carry-over between samples. Carbon mass balance calculations showed that the mean DOC recoveries of the system were 86.9 ± 2.4 %, while the mean total OC recoveries (fine particulate organic carbon, or FPOC, + DOC) were of

90.4 ± 3.5 % [*Ouellet et al.*, 2008]. The POM and DOM samples were doped with $HgCl_2$ (~0.3 mM final concentration) and freeze-dried in preparation for elemental (C, N and Fe) and isotopic analysis ($\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$).

Water for DIC and POC analyses was sampled every 1 to 5 meters over the entire water column to a maximum of 20 meters in each water body in the spring and summer of 2007. Water samples for DIC analysis were stored in air-tight 500-mL amber glass bottles (no head space), preserved with $HgCl_2$ and kept at 4°C until analysis. The corresponding POC samples were collected on combusted GF/F filters (0.7-µm nominal pore size) and freeze-dried.

2.3. Soil leaching experiment

Humus-free soil litter and sliced soil push-cores (1-cm resolution) representative of the watershed area within 5 to 20 meters of the water systems (in a forested area for Jean, Mary and Cabonga, and between the harvested zone and the shore for Decelles) were collected in May and July 2007. They were then freeze-dried and homogenized in preparation for elemental and isotopic analysis. Additionally, three non-freeze-dried representative boreal forest soil litters (O horizon) as well as the organic, sub-organic and inorganic soil layers (A, B and C horizons) of each core were mixed in a 35-mL Teflon tube with milli-Q water (1:1 v/v) and extracted three times. Aliquots of the extracts were filtered using 0.7-µm GF/F filters and freeze-dried for elemental and isotopic analysis while the remaining aliquots were analyzed for inorganic N content using a TRAACS 800 AutoAnalyser system.

2.4. DOC, total nitrogen and total phosphate measurements

DOC analysis (natural water and concentrated sample) was done in duplicate or triplicate using a Shimadzu 5000A Total Carbon Analyzer, with a reproducibility of ± 5%. TN (dissolved organic nitrogen plus nitrate and nitrite) and TP (organic phosphorus plus phosphate) were analyzed using standard NaOH/$K_2S_2O_8$-based methods (818-47 and 812-86T respectively) from Bran Luebbe Analyzing Technologies on a TRAACS 800 AutoAnalyser.

2.5. Elemental and isotopic measurements

The C and N concentrations as well as δ^{13}C and δ^{15}N compositions were acquired on all DOM and FPOM as well as on the soils and soil leachates using an elemental analyzer EuroVector 3028-HT coupled to an Isoprime GV Instruments isotope ratio mass spectrometer (EA-IRMS). Elemental and isotopic calibration curves were built with IAEA-C6 sucrose (δ^{13}C = -10.45 ± 0.03‰; C = 42.11% [*Coplen et al.*, 2006]), IAEA-N1 ammonium sulfate (δ^{15}N = 0.43 ± 0.07‰; N = 10.60%, [*Böhlke and Coplen,* 1995]) and β-alanine, a pre-calibrated in-lab standard (δ^{13}C = -25.98 ± 0.23‰; C = 40.45% and δ^{15}N = -2.21 ± 0.24‰; N = 15.72%). The samples were decarbonated using HCl fumigation prior to C analysis [*Hedges and Stern,* 1984]; OC (with acidification) and TN (no acidification) concentrations and stable isotope compositions are thus reported here. Reproducibility for the elemental and isotopic analyses was < 1% and < 0.3 ‰, respectively.

DIC concentrations and isotopic ratios were acquired with an Isoprime Multiflow instrument and using two pre-calibrated in-house $CaCO_3$ powders (δ^{13}C = -3.91 ± 0.08 ‰ and 9.58 ± 0.08 ‰, respectively). Standards were accurately weighed to obtain final C concentrations ranging between 1 and 10 mg L^{-1}. Degassed deionized water was added to the powder and quickly transferred to air-tight vials for quantitative analysis. Between 0.5 and 1.5 mL of standards or samples was transferred through the septum of an air-tight and helium-purged 4-mL vial containing 50 µL of phosphoric acid. The vials were mixed and digested for 60 minutes at 60 °C to transform all carbonate species into CO_2 prior to analysis. Standard water blanks and vial blanks were also analyzed to correct for water and air contamination. Reproducibility for DIC concentrations and stable isotope measurements were < 5% and < 0.1‰, respectively.

2.6. DOM-complexed iron

The iron content of the concentrated DOM samples collected with the reverse osmosis system were analyzed for iron by direct injection using an Agilent 7500 series ICP-MS following acidification with nitric acid and internal standard addition (scandium). Quantification was done through external calibration with a Certipur ferric nitrate standard. Five replicate measurements were acquired for each sample, with a precision and accuracy better than 3%.

2.7. Statistical analyses

CO_2 and CH_4, DOC and nutrient measurements were first averaged for each sampling station independently of the number of samples analyzed. Average values for entire water bodies were then calculated using the values obtained from each sampling stations, and standard deviations were propagated using the pooled standard deviations [*Harris,* 2007]. This method prevented the over-representation of the stations with higher sampling frequencies; our results thus integrate spatial and temporal (i.e. daily) variations over the short period spent at each site. Where applicable, the significance of the observed trends was tested using the Welch’s t-test, which allows the evaluation of parameters having unequal data variance and replicates.

3. Results

3.1. Greenhouse gases

Averaged CO_2 and CH_4 concentrations in surface waters for the aquatic systems studied in this work are presented in Table 2. The wood harvested Lake Bouleau, which was recently flooded following the erection of a beaver dam, had very high dissolved CO_2 concentrations (80.4 ± 13.0 $\mu mol\ L^{-1}$). The natural lakes had lower averaged dissolved CO_2 concentrations (24.1 ± 7.4 $\mu mol\ L^{-1}$) compared to all other perturbed water bodies (37.1 ± 7.6 $\mu mol\ L^{-1}$; with $p < 0.15$, Lake Bouleau excluded). Surface water CH_4 concentrations (10.7 to 219 $nmol\ L^{-1}$) were about three orders of magnitudes lower than those of CO_2 (10.7 to 106 $\mu mol\ L^{-1}$) and varied widely, with no clear relationship with reservoir operation, wood harvesting, water column depth and oxygen level (see below). In our study, the two natural lakes monitored for CO_2 and CH_4 had significantly lower CO_2 fluxes (8.5 ± 10.4 mmol $CO_2\ m^{-2}\ d^{-1}$) than all the perturbed systems (31.3 ± 16.3 mmol $CO_2\ m^{-2}\ d^{-1}$; $p < 0.005$). The CH_4 concentrations and fluxes measured in Lake Brock were obtained in periods of low wind, which explains the high water concentration levels and low fluxes recorded for this lake.

We also tested whether the differences in CO_2 concentrations measured in the studied aquatic systems could be explained by variations in OM inputs resulting from differences in watershed size. Plotting the watershed size versus the cumulated CO_2 concentrations of lakes and reservoir with a natural watershed reveals that both parameters were entirely decoupled (slope of -0.06 and $r^2 = 0.08$), thus suggesting that the size of the watershed alone was not the main driver of CO_2 concentrations in the surface waters of these aquatic systems. When plotting natural lakes with non-harvested watersheds and systems with wood-harvested watershed, a strong positive linear correlation was found ($r^2 = 0.90$, $p < 0.05$; not shown) suggestive of a strong effect of wood harvesting on water CO_2 concentrations.

3.2. Water chemistry

The concentration of DOC, TN and TP, as well as pH in the surface waters of the natural and perturbed aquatic systems are presented in Table 3. Averaged water pH and DOC concentrations co-varied (Table 3 and Fig. 2A; $r^2 = 0.94$, $p < 0.005$) with more acidic, DOC-rich waters observed in the perturbed systems.

Average DOC concentrations in the different systems varied widely (0.217 ± 0.010 mmol L^{-1} to 0.699 ± 0.096 mmol L^{-1}), with significantly lower values found in water bodies with a non-harvested watershed (0.217 to 0.415 mmol L^{-1}) compared to systems with a harvested watershed (0.505 to 0.699 mmol L^{-1}, $p < 0.005$). The same trend was observed for TN (9.3-17.5 μmol L^{-1} *vs.* 13.1-30.6 μmol L^{-1}, $p < 0.005$). Including all systems, there was a strong positive linear relationship between DOC and TN concentrations ($r^2 = 0.98$, $p < 0.0005$; Fig. 2B). Strong correlations between DOC and TP ($r^2 = 0.90$, $p < 0.05$; Fig. 2D) as well as CO_2 and TP ($r^2 = 0.78$, $p < 0.12$, not shown; in agreement with *Sobek et al.*, 2003) were found when considering perturbed systems only; TP concentrations in natural lakes did not follow this trend and were higher than in the non-harvested Cabonga Reservoir.

To gain information on the balance and extent of net heterotrophy (CO_2 producing, O_2 consuming bioprocesses) and net autotrophy (CO_2 consuming, O_2 producing bioprocesses) in our systems, all the average CO_2 concentrations and oxygen percentage saturation levels (% O_2) measured in this study were grouped by zones of contrasting physico-chemical characteristics within lakes and reservoirs (epi/hypolimnion, photic, and aphotic; Figure 3). In lakes with wood harvested watersheds, the thermocline was always positioned at a depth corresponding to the bottom of the photic zone (Table 1). A strong negative correlation ($r^2 = 0.90$, $p < 0.0001$) between CO_2 concentrations and % O_2 of hypolimnetic lake water was observed (Figure 3A), reflecting heterotrophic OM consumption. Generally higher % O_2 were found in the photic epilimnion compared to the aphotic hypolimnion in lakes (Figure 3A and B). Reservoirs generally had more uniform dissolved O_2 concentrations over the entire water column owing to hydrodynamic mixing of the water column, which prevents the formation of a thermocline at practically all sampling sites (*Marty et al.*, 2005). As shown in Figures 3C and 3D, CO_2 concentrations were negatively correlated to % O_2 in the wood harvested Decelles Reservoir, ($r^2 = 0.73$, $p < 0.0001$) whereas there was no significant correlation between CO_2 and O_2 for the non-harvested Cabonga Reservoir.

3.3. Bulk organic matter analyses

To estimate the importance of terrestrial litter and soil as OM sources in the aquatic cycle of C, a DOM leaching experiment was carried out on samples collected in the vicinity of the water systems. The litter samples had $\delta^{13}C_{org}$, $\delta^{15}N_{tot}$ and atomic C:N compositions of -27.2 ± 1.1 ‰, -1.0 ± 0.9 ‰, and 35.1 ± 2.0, respectively, while soil OM from deeper horizons was generally more enriched in $\delta^{13}C_{org}$, $\delta^{15}N_{tot}$ and had higher C:N atomic ratios (Table 4). Litter and soil leached large quantities of water soluble OC and organic N (> 99 % of leached TN was organic N; results not shown). In most cases, the $\delta^{13}C$ signatures of the soil leachates were enriched by 1 to 2 ‰ compared to those of the initial bulk material (Table 4), while the enrichment was even greater for $\delta^{15}N$ (1 to 5 ‰). Soil leachates atomic C:N ratios were also much lower than those of bulk OM (decrease ranging between 40 and 70%).

The bulk results obtained from the water column DOM and FPOM samples averaged over the entire water column are shown in Table 5. Only modest variations in $\delta^{13}C$ compositions were observed in DOM ($\delta^{13}C$ from -26.3 to -28 ‰) between water bodies whereas greater differences were observed in FPOM samples ($\delta^{13}C$ from -27.7 to -30.4 ‰). Significantly higher $C:N_{FPOM}$ values were found in perturbed water bodies (as high as 31.2 in the Decelles reservoir; single factor ANOVA, $p < 0.01$). In all the systems studied, Fe and DOC concentrations were strongly correlated ($r^2 = 0.86$, $p < 0.0005$; Figure 4).

3.4. Dissolved inorganic carbon (DIC) and POC isotopic variations

The spring and summer $\delta^{13}C_{DIC}$ data points from all the depth profiles measured in this study were compiled and plotted in Figure 5. Higher DIC concentrations were found at depth (hypo- and epilimnetic aphotic) compared to the surface (epilimnetic photic) waters in all systems; moreover, the variations in DIC concentrations and isotopic signatures between the spring and summer were very similar in all lakes. In Figure 6, the same $\delta^{13}C_{DIC}$ results was plotted against $\delta^{13}C_{POC}$ for samples collected at different depths in each water body. Both parameters were correlated in the spring for harvested systems (Figures 6C [$r^2 = 0.44$, $p < 0.05$] and 6D [$r^2 = 0.60$, $p < 0.0005$]). In summer, only the wood harvested Reservoir Decelles exhibited a covariation between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$, (Figure 6D; $r^2 = 0.43$, $p < 0.0001$).

4. Discussion

In this discussion, we explore the relationships between the high DOC, TN and CO_2 concentrations measured in the perturbed systems and the major GHG producing pathways, namely, bacterial degradation and photo-oxidation. We also discuss the influence of terrestrially derived DOM and FPOM inputs, derived from natural (beaver dam) or human (reservoir impoundment and wood harvesting) perturbations, on primary productivity. Finally, we investigate the effect of seasonal variations on the photosynthetic and bacterial activity, and the links between the inputs of terrestrial organic material and bacterial activity in the different systems.

4.1. Using water chemistry and bulk analyses to study carbon cycling

4.1.1. Carbon/nutrients inputs and GHG concentrations and fluxes

The magnitude of allochthonous OM inputs into a water body is often related to the size of the drainage area [e.g., *Carignan and Steedman*, 2000; *Larson et al.*, 2007], with higher DOC concentrations measured for aquatic system with high watershed area to lake area ratio. In this study, significant correlations between DOC concentrations and this ratio were obtained only when the natural lakes were plotted with the wood harvested systems (Lake Bouleau excluded), suggesting that DOC concentrations are more closely linked to the additional inputs of allochthonous OM caused by increased erosion and OM leaching in the wood harvested systems rather than to natural OM inputs from a large watershed [*Sobek et al.*, 2003].

Increased DOC and dissolved organic acid inputs are also the most probable cause for the increased acidity in systems with high DOC concentrations, such as wood harvested systems

(Figure 2A). Because the water bodies in this study were all located within the same geological region, variations in dissolved bicarbonate concentrations are not likely to have caused important pH changes [*Soumis et al.*, 2004].The terrestrial nature of a large fraction of DOC in these systems is corroborated by a strong covariation between DOC and iron concentrations (Figure 4) as iron originates mostly from land. The same processes that affect the influx of DOC and Fe into aquatic systems also seem to affect the leaching of other biologically important elements such as nitrogen and phosphorous (TN and TP), which are also strongly correlated to DOC (Figure 2B and D).

Allochthonous DOC and nutrient exports to water bodies are followed by enhanced biological and/or photochemical degradation. This pathway, which likely is the primary driver of CO_2 supersaturation in these boreal aquatic systems (*del Giorgio et al.*, 1997; *Osburn et al.*, 2001; *McCallister and del Giorgio,* 2008), is accentuated in systems that have been perturbed by wood harvesting and by flooding and therefore receive the highest inputs of terrestrial OM. In our sample set, Lake Bouleau represents the most heavily affected water body with wood harvesting activities on its watershed and the presence of a recently erected beaver dam that led to local flooding of the surrounding vegetation. Much higher surface dissolved CO_2 and CH_4 concentrations were measured in this system compared to other lakes and reservoirs (Table 2). Very low dissolved O_2 concentrations were also recorded in the water column of this lake (saturation level of only ~3% near the sediment-water interface) suggesting that important OM degradation or CH_4 oxidation to CO_2 occurs [Steinmann et al., 2008]. The physical characteristics of Lake Bouleau (shallow water column, dendritic lake) and its much higher CO_2 and CH_4 concentrations are analogous to a recently flooded system rather than a natural lake, a wood harvested lake or a stabilized reservoir.

Systems with the highest DOC concentrations (flooded systems such as Lake Bouleau and both reservoirs) also emit more methane (Table 2), which suggests higher anaerobic OM degradation in the sediment [*Striegl and Michmerhuizen,* 1998; *Steinmann et al.*, 2008; *Sobek et al.*, 2012]. Methane emitted from sampling stations with a well-defined thermocline likely diffused unrestrained across the entire water column as very little hypolimnetic accumulation was observed (equivalent to less than 0.2% of the daily CH_4 atmospheric emissions).

4.1.2. Sources of OM

Allochtonous OM is mainly introduced into water bodies through the leaching of soils and litters. These soils and litters were sampled in the early spring and leached OM with low atomic C:N ratios and enriched ^{13}C signatures (atomic C:N ratios of 8.4 to 77.0 and δ^{13}C of -26.5 to -23.8 ‰; Table 4). Noteworthy, the OM leachates were compositionally different from the bulk soil and litter OM. As suggested by its isotopic and elemental composition as well as its hydrophilic character, leached OM likely contains labile and readily available N in the form of peptides and amino sugars as well as less reactive heterocyclic polymers. More extensively leached litter, surface soils and leachates obtained later on in the season usually become depleted in N and are thus characterized by higher C:N ratios [*Stepanauskas et al.*, 2000; *Galimov,* 2006; *Berg and McClaugherty*, 2008; *Tremblay et al.* 2009]. The DOM in the lakes and reservoirs is also compositionally different from that of the leachates (C:N of 21.3 to 41.6 and δ^{13}C of -28.0 to -26.3 ‰; Table 5), likely consisting of a mixture of water-soluble materials either leached from the surficial soil layers, derived from in-lake OM production or obtained through reutilization/bacterial reworking [*Schiff et al*, 1997; *Stepanauskas et al.*, 2000; *McCallister and* *del Giorgio,* 2008]. Small bacteria with an effective diameter smaller than the porosity of the filters (0.45 μm) may also have contributed to the DOM pool.

As for DOM, FPOM is a useful tracer for carbon source and cycling and can be supplied to water bodies through two major sources, namely soils/litters and particulate OM derived from autochthonous production (phytoplankton, bacteria and debris). In contrast to DOM however, FPOM end-members have well defined stable isotopic signatures. Terrestrial C_3 plants have traditionally been assigned δ^{13}C compositions of about -27‰ [*Meyers*, 1997], values that are similar to the δ^{13}C values found in this work for boreal forest soil litter and top soil layer (-27.2 ± 1.1 and -26.1 ± 0.9 ‰ for the O and A horizons, respectively; Table 4). Additionally, the δ^{13}C signature of phytoplankton measured in the summer by *Marty and Planas* [2008] in different boreal lakes and reservoirs of Quebec averaged -32.7 ± 1.7 ‰. The carbon isotopic signatures ($\delta^{13}C_{FPOC}$, 0.45 to 70 μm) measured for FPOM in this study ranged between -30.4 and -27.7 ‰. Mass balance calculations using the above end-member signatures reveal a contribution of 22 to 87% for the terrestrial matter (litter and soil), with the rest derived from algal OM (Table 5). This result is supported by the measured atomic $C:N_{FPOM}$ ratios, which fell between the values obtained for the two end-members analyzed in this study (terrestrial litter: 35.1 ± 2.0, Table 4; and cultivated algae: 9.7 ± 0.1, data not shown). The terrestrial contribution calculated using these ratios accounted for 27 to 84% of the total FPOM pool.

To identify the relationship between FPOM sources and their relationship to DIC [*Cole et al.*, 2002; *Lehmann et al.*, 2004], $\delta^{13}C_{DIC}$ was plotted against the $\delta^{13}C_{POC}$ of the FPOM fraction ($\delta^{13}C_{POC}$; Figure 6). The spring $\delta^{13}C_{POC}$ results presented in Figures 6A and B show that water bodies with a non-harvested watershed were dominated by algal OM. The correlations depicted for the harvested lakes and reservoirs (Figures 6C and D, respectively) suggest that high primary production (enriched $\delta^{13}C_{DIC}$) followed the melting of the ice cover in spring and high heterotrophic activities (depleted $\delta^{13}C_{DIC}$) were taking place in summer. Wood harvested lakes and reservoirs were characterized by a higher relative proportion of terrestrial FPOM in the spring, with their $\delta^{13}C$ signature and C:N ratios (11.3 to 23.5, Table 4) closest to those of litter than to algae-derived FPOM (C:N ranging between 9.2 and 11.8, this study). Moreover, the $\delta^{13}C_{POC}$ depletions in lakes during summer generally coincided with lower $C:N_{FPOM}$ ratios (results not shown), which can be explained by a higher relative abundance of phytoplankton, zooplankton and/or bacteria (with atomic C:N ratios varying from 8 to 12, 5 to 6, and 4 to 7, respectively [*del Giorgio and France,* 1996; *Kaiser and Benner,* 2008; *Homblette et al.,* 2009]). Such $\delta^{13}C_{POC}$ patterns were not found in reservoirs, a result that could reflect lower variability in the relative contributions from main FPOM sources and/or more dynamic mixing of the water column.

4.1.3. In-lake bioprocesses affected by DOC cycling

The increase in allochthonous DOC inputs associated with wood harvesting (observed here and also reported by *Carignan et al.* [2000b]) resulted in a decrease in light penetration depth (Table 1) which, in turn, likely inhibited hypolimnetic photosynthesis [*Karlsson et al.,* 2009]). In our study, hypolimnetic photosynthesis occurred only in natural lakes owing to the greater light penetration depths resulting from the lower DOC concentrations (Figure 3A, empty circles, Table 1). Dissolved O_2 production from autotrophic activity sometimes even surpassed bacterial O_2 utilization in the studied systems, resulting in O_2 supersaturation. Epilimnetic CO_2 concentrations were for the most part decoupled from O_2 saturation levels; this phenomenon was mostly observed in the photic/epilimnetic zones of the non-harvested systems and suggests that a process other than heterotrophy, likely CO_2 efflux to the atmosphere, was a significant pathway for CO_2 loss (Figure 3). The thermocline, which was in place in all lakes during the stratified period, therefore acts as a semi-permeable barrier to dissolved gases. The transfer of GHG and O_2 to the epilimnion likely is controlled by the cumulated partial pressure of each gas and the storage capacity of both water layers [*Kim et al.*, 2006].

The $\delta^{13}C$ signatures of DIC ($\delta^{13}C_{DIC}$, which includes all form of dissolved carbonate species: dissolved $CO_2 + H_2CO_3$, HCO_3^- and CO_3^{2-}) help constrain the sources and sinks of C in aquatic systems. Plots of $\delta^{13}C_{DIC}$ *vs.* $[DIC]^{-1}$ are used to gain insight on the mixing behaviour (heterotrophic *vs.* autotrophic activity) of the DIC pool through seasonal variations in $\delta^{13}C_{DIC}$ signatures [*Karlsson et al.*, 2008]. It is important to note that in our work, the $\delta^{13}C_{DIC}$ signatures can only be used qualitatively as the relative abundances of the different carbonate species are pH dependent and average pH values for the aquatic systems studied here varied between about 6.2 and 8.2. Despite the fact that the bulk stable isotope signatures measured in our samples integrate all forms of dissolved inorganic carbon, such pH driven variations in the relative abundances of the different carbonate species could affect the $\delta^{13}C_{DIC}$ data through exchange of dissolved CO_2 between the water column and the atmosphere. However, this potential bias mostly affects samples collected in the epilimnion or in non-stratified water columns. Furthermore, all the surface water samples were supersaturated in dissolved CO_2 with respect to equilibrium concentration, which alleviates the importance of this potential bias.

Hypolimnetic lake waters are usually heterotrophic as shown by a strong negative correlation between CO_2 and O_2 ($r^2 = 0.90$, $p < 0.0001$; Figure 3A) which suggests that dissolved O_2 is mainly consumed via bacterial OC degradation, methanotrophic CH_4 oxidation and photooxidation resulting in the production of CO_2 (*Striegl and Michmerhuizen,* 1998; *McCallister and del Giorgio,* 2008; *Osburn et al.* 2001). Interestingly, hypolimnetic $\delta^{13}C_{DIC}$

signatures are often ^{13}C-depleted (as low as -41 ‰, Figures 5A and C) compared to reservoirs (Figures 5B and D), which indicates that a significant fraction of highly depleted CH_4 originating from methanotrophic activity is oxidized and is in fact a major contributor to the total DIC pool. Because sedimentary methane δ^{13}C compositions fluctuate by as much as 16 ‰ within periods as short as 24 hours [*Jedrysek,* 1995], its exact contribution to total $\delta^{13}C_{DIC}$ cannot be calculated with accuracy. Isotopic evidence of methane contribution to the DIC pool was observed only for high DIC concentration samples within or just below the thermocline of lakes (which were all stratified during both the spring and summer sampling). Both natural and wood-harvested lakes showed substantial seasonal variability in $\delta^{13}C_{DIC}$ with more enriched $\delta^{13}C_{DIC}$ signatures in spring (-3.9 to -24.8 ‰) compared to the summer (-13.9 to -41.3 ‰; Figure 5A and 5C). These broad seasonal differences suggest that, in addition to methane oxidation, photo- and bacterial oxidation of the reactive and δ^{13}C depleted DOC pool was probably also responsible for the summer depletion of $\delta^{13}C_{DIC}$ [*Osburn et al.,* 2001; *McCallister and del Giorgio,* 2008]. This conclusion, supported by recent findings [*Brothers et al.*, 2012], shows that most of the water column CO_2 accumulation during stratified periods in lakes and young reservoirs of the boreal forest is due to pelagic rather than benthic respiration.

Our surface CH_4 concentrations and diffusive atmospheric flux measurements (Table 2) were in general two to three orders of magnitude lower than those for CO_2. Methane originating from these systems is most likely generated by the fermentation of OM followed by the splitting of acetate into CO_2 and CH_4 in the sediment resulting in ^{13}C-enriched CO_2 and ^{13}C-depleted CH_4 [*Steinmann et al.,* 2008; *Dubois et al.,* 2009]. While this is an important CH_4 production pathway, the samples collected in the hypolimnetic zone of the lakes were too δ^{13}C-depleted for acetate splitting to be the main process by which DIC was generated (Figures 5A and C).

Alternatively, these results suggest that the processes leading to depleted $\delta^{13}C_{DIC}$ signatures in the hypolimnion were predominantly microbial degradation of DOC (producing $\delta^{13}C_{CO2}$ from -28.0 to -26.3 ‰, Table 5) and/or CH_4 oxidation (producing $\delta^{13}C_{CO2}$ from -63.0 to -47.5 ‰; *Jedrysek*, 1995). The relationships between $[DIC]^{-1}$ and $\delta^{13}C_{DIC}$ shown for the wood harvested lakes in Figure 5C (spring [$r^2 = 0.34$, $p < 0.05$]) and for the wood harvested reservoir in Figure 5D (spring and summer [$r^2 = 0.81$, $p < 0.0001$ and $r^2 = 0.50$, $p < 0.0001$], respectively) suggest that the concentration and stable isotope composition of the DIC pool were mostly controlled by the combined influence of DOC degradation (causing low $[DIC]^{-1}$ and $\delta^{13}C_{DIC}$ depletion), photosynthesis and photo-oxidation (causing high $[DIC]^{-1}$ and $\delta^{13}C_{DIC}$ enrichment) in these systems [*Lehmann et al.,* 2004; *McCallister and del Giorgio,* 2008; *Vähätalo and Wetzel,* 2008].

4.2. Summary and implications

Only a limited number of studies have focused on the modifications in the aquatic C cycle caused by reservoir impoundment and wood harvesting. Perturbed systems receive large quantities of terrestrial materials through flooding or increased erosion, which profoundly affect the biogeochemistry of these systems compared to natural lakes. Wood harvesting more strongly affects C cycling than mature reservoir operation because it leads to a higher export of nitrogen-rich, and potentially more reactive terrestrial OM to aquatic systems. Its effects should however diminish rapidly with forest re-growth. Export of terrestrial OM caused by recent forest cutting favors heterotrophy over autotrophy, which results in the depletion of O_2 and the potential loss of animal and fish populations. The recovery period needed for aquatic systems to return to their pre-harvesting condition should thus be evaluated carefully through long-term biogeochemical monitoring. Our findings also show that wood harvesting history should be documented when selecting water bodies for large scale CO_2 and CH_4 emission studies, particularly in cases where the emissions from mature reservoirs and natural lakes are compared. Much higher variability and important biases may be introduced if significant portions of the watersheds are exploited for wood harvesting. Our results further suggest that the current Canadian regulations prescribing non-harvested buffer strips of 20 m between water bodies/streams and harvested areas are not sufficient as they could not prevent large quantities of DOM and nutrients to leach into the water bodies and alter the biogeochemical processes controlling C cycling in these systems.

It remains a matter of debate whether or not differences in yearly GHG emissions between lakes and reservoirs are significant, especially when non-linear events, such as ice breakup, lake overturn and gradual hypolimnion-epilimnion CO_2 and CH_4 transfers are considered. We however maintain that the biogeochemistry of these lakes and reservoirs contrast significantly, even when lakes are compared to reservoirs that are over 80 years old. The cause and significance of these differences are still not fully measured or understood. Further work should target the role of the contrasting redox conditions prevailing in the water column and surface sediments of reservoirs (oxic) and lakes (hypolimnion of stratified lakes becoming increasingly O_2-depleted during the summer), and how they affect OM degradation rates in sediments.

While including perturbed and natural systems in a study such as this one helps highlight trends and relationships controlling C and N cycling in boreal aquatic systems, a better understanding of all biogeochemical variables is a key prerequisite for predicting the impact of anthropogenic forcing on small (wood harvesting, reservoir impoundment) and large (climate change) temporal and spatial scales. Perturbed water bodies receive higher inputs of terrestrial materials, which alters the delicate balance between heterotrophy, autotrophy and photochemistry that exists in natural systems. In this work, we clearly observed that these perturbed systems are more prominent CO_2 emitters in the spring and summer months compared to natural systems, although more work on a much larger number of water bodies, and encompassing all four seasons should be undertaken to better understand the controls, rates, as well as spatial and temporal variability of GHG emissions, and to make quantitatively meaningful and accurate comparisons of GHG emissions (and other key variables) from natural and perturbed systems.

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References

Berg, B. and C. McClaugherty (2008) *Plant Litter,* 2nd ed. Springer-Verlag Berlin Heidelberg, Berlin Heidelberg.

Berggren, M., H. Laudon and M. Jansson (2007) Landscape regulation of bacterial growth efficiency in boreal freshwaters, *Global Biogeochem. Cycles 21*, GB4002, doi:10.1029/2006GB002844.

Böhlke, J. K., and T. B. Coplen (1995) Interlaboratory comparison of reference materials for nitrogen-isotope-ratio measurements, in Reference and intercomparison materials for stable isotopes of light elements: Vienna, International Atomic Energy Agency, IAEA-TECDOC-825, 51-66.

Brothers, S. M., Y. T. Prairie and P. A. del Giorgio (2012) Benthic and pelagic sources of carbon dioxide in boreal lakes and a young reservoir (Eastmain-1) in eastern Canada, *Global Biogeochem. Cycles 26*, GB1002, doi:10.1029/2011GB004074

Carignan, R., P. D'Arcy and S. Lamontagne (2000a) Comparative impacts of fire and forest harvesting on water quality in Boreal Shield lakes, *Can. J. Fish. Aquat. Sci.* 57, 105-117.

Carignan, R., D. Planas and C. Vis (2000b) Planktonic production and respiration in oligotrophic Shield lakes, *Limnol. Oceanogr.* 45, 189-199.

Carignan, R. and R. J. Steedman (2000) Impacts of major watershed perturbations on aquatic ecosystems, *Can. J. Fish. Aquat. Sci. 57*, 1-4.

Cole, J. J. and N. F. Caraco (1998) Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF_6, *Limnol. Oceanogr. 43*, 647–656.

Cole, J. J., N. F. Caraco, G.W. Kling and T.K. Kratz (1994) Carbon dioxide supersaturation in the surface waters of lakes, *Science 265*, 1568-1570.

Cole, J. J., S. R. Carpenter, J. F. Kitchell and M.L. Pace (2002) Pathways of organic carbon utilization in small lakes: Results from a whole-lake ^{13}C addition and coupled model, *Limnol. Oceanogr. 47*, 1664-1675.

Coplen, T.B., W. A. Brand, M. Gehre, M. Groening, H. A. J. Meijer, B. Toman and R.M. Verkoutren (2006) New guidelines for ^{13}C measurements, *Anal., Chem., 78*, 2439-2441.

del Giorgio, P.A. and J. J. Cole (1998) Bacterial growth efficiency in natural aquatic systems, *Ann. Rev. Ecol. Syst. 29*, 503-541.

del Giorgio, P. A. and R.L. France (1996) Ecosystem-specific patterns in the relationship between zooplankton and POM or microplankton $\delta^{13}C$, *Limnol. Oceanogr. 41*, 359-365.

del Giorgio, P. A., J. J. Cole, and A. Cimbleris (1997) Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems, *Nature 385*, 148-151.

Dubois, K., R. Carignan and J. Veizer (2009) Can pelagic net heterotrophy account for carbon fluxes from eastern Canadian lakes?, *Appl. Geochem.* doi :10.1016/j.apgeochem.2009.03.001.

Duchemin, E., M. Lucotte, R. Canuel and A. Chamberland (1995) Production of the greenhouse gases CH_4 and CO_2 by hydroelectric reservoirs of the boreal region, *Global Biogeochem. Cycles 9*, 529-540.

Duchemin, E., M. Lucotte and R. Canuel (1999) Comparison of static chamber and thin boundary layer equation methods for measuring greenhouse gas emissions from large water bodies, *Environ. Sci. Technol. 33*, 350-357.

Galimov, E.M. (2006) Isotope organic geochemistry, *Org. Geochem. 37*, 1200-1262.

Harris, D.C. (2007) *Quantitative Chemical Analysis*, 7th ed. W. H. Freeman, New York.

Hedges, J.I. and J.H. Stern (1984) Carbon and nitrogen determinations of carbonate containing solids, *Limnol. Oceanogr. 29*, 657-663.

Homblette, N., F. Darchambeau, M. Heldal, S. Norland, P. Servais and J.-P. Descy (2009) Stoichiometry of bacteria and algae in Lake Kivu, Aquatic Science Meeting, ASLO, Nice, France.

Jedrysek, M. O. (1995) Carbon isotope evidence for diurnal variations in methanogenesis in freshwater lake sediments, *Geochim. Cosmochim. Acta. 59*, 557-561.

Kaiser, K. and R. Benner (2008) Major bacterial contribution to the ocean reservoir of detrital organic carbon and nitrogen, *Limnol. Oceanogr. 53*, 99-112.

Karlsson, J., J. Ask and M. Jansson (2008) Winter respiration of allochthonous and autochthonous organic carbon in a subarctic clear-water lake, *Limnol. Oceanogr. 53*, 948-954.

Karlsson, J., M. P. Byström, J. Ask, P. Ask, L. Persson and M. Jansson (2009) Light limitation of nutrient-poor lake ecosystems, *Nature 460*, 506-509.

Kim, C., Y. Nishimura and T. Nagata (2006) Role of dissolved organic matter in hypolimnetic mineralization of carbon and nitrogen in a large, monomictic lake, *Limnol. Oceanogr. 51*, 70–78.

Kling, G. W., G. W. Kipphut and M.C. Miller (1991) Arctic lakes streams as gas conduits to the atmosphere: Implications for tundra carbon budgets, *Science 251*, 298-301.

Lamontagne, S., R. Carignan, P. D'Arcy, Y. T. Prairie and D. Paré (2000) Element export in runoff from eastern Canadian Boreal Shield drainage basins following forest harvesting and wildfires, *Can. J. Fish. Aquat. Sci. 57*: 118-128.

Larson, J. H., P. C. Frost, Z. Zheng, C. A. Johnston, S. D. Bridgham, D. M. Lodge and G. A. Lamberti (2007) Effects of upstream lakes on dissolved organic matter in streams, *Limnol. Oceanogr. 52*, 60-69.

Lehmann, M. F., S. M. Bernasconi and J. A. McKenzie (2004) Seasonal variation of the δ^{13}C and δ^{15}N of particulate and dissolved carbon and nitrogen in Lake Lugano: Constraints on biogeochemical cycling in a eutrophic lake, *Limnol. Oceanogr. 49*, 415-429.

McCallister, S. L. and P. del Giorgio (2008) Direct measurement of the δ^{13}C signature of carbon respired by bacteria in lakes: Linkages to potential carbon sources, ecosystem baseline metabolism, and CO_2 fluxes, *Limnol. Oceanogr. 53*, 1204-1216.

Marty, J. and D. Planas (2008) Comparison of methods to determine algal δ^{13}C in freshwater, *Limnol. Oceanogr.: Methods 6*, 51-63.

Marty, J., D. Planas, B. Pinel-Alloul and G. Méthot (2005) Planktonic community dynamics over time in a large reservoir and heir influence on carbon budgets, in *Greenhouse gas emissions – Fluxes and processes*, edited by A. Tremblay, L. Varfalvy, C. Rohem and M. Garneau, pp. 421-440, Springer, New York.

Meyers, P. A. (1997) Organic geochemical proxies of paleooceanographic, paleolimnologic, and paleoclimatic processes, *Org. Geochem. 27*, 213-250.

Osburn, C. L., D. P. Morris, K. A. Thorn and R. E. Moeller (2001) Chemical and optical changes in freshwater dissolved organic matter exposed to solar radiation, *Biogeochem. 54*, 251-278.

Ouellet, A., D. Catana, J.-B. Plouhinec, M. Lucotte and Y. Gélinas (2008) Elemental, isotopic and spectroscopic assessment of chemical fractionation of dissolved organic matter sampled with a portable reverse osmosis system, *Environ. Sci. Technol. 42*, 2490-2495.

Pace, M. L., J .J. Cole, S .R. Carpenter, J. F. Kitchell, J. R. Hodgson, M. C. Van de Bogert, D. L. Bade, E. S. Kritzberg and D. Bastviken (2004) Whole-lake carbon-13 additions reveal terrestrial support of aquatic food webs, *Nature 427*, 240-243.

Planas, D., M. Desrosiers, S.-R. Groulx, S. Paquet and R. Carignan (2000) Pelagic and benthic algal responses in eastern Canadian Boreal Shield lakes following harvesting and wildfires, *Can. J. Fish. Aquat. Sci. 57*, 136-145.

Prairie, Y. T., D. F. Bird and J. J. Cole (2002) The summer metabolic balance in the epilimnion of southeastern Quebec lakes, *Limnol. Oceanogr. 47*, 316-321.

Prepas, E. E., B. Pinel-Alloul, D. Planas, G. Méthot, S. Paquet and S. Reedyk (2001) Forest harvest impacts on water quality and aquatic biota on the Boreal Plain: introduction to the TROLS lake program, *Can. J. Fish. Aquat. Sci. 58*, 421-436.

Roland, F, L. O. Vidal, F. S. Pacheco, *et al.* (2010) Variability of carbon dioxide flux from tropical (Cerrado) hydroelectric reservoirs, *Aquat. Sci. 72*, 283-293.

Schindler, D. W., P. Jefferson Curtis, S. E. Bayley, B. R. Parker, K. G. Beaty and M. P. Stainton (1997) Climate-induced changes in the dissolved organic carbon budgets of boreal lakes, *Biogeochem. 36*, 9-28.

Schiff, S. L., R. Aravena, S. E. Trumbore, M. J. Hinton, R. Elgood and P. J. Dillon (1997) Export of DOC from forested catchments on the precambian shield of central Ontario: clues from ^{13}C and ^{14}C, *Biogeochem. 36*, 43-65.

Sobek, S., G. Algesten, A.-K. Bergström, M. Jansson and L. J. Tranvik (2003) The catchment and climate regulation of pCO_2 in boreal lakes, *Global Change Biol. 9*, 630-641.

Sobek, S., T. DelSontro, N. Wongfun, B. Wehrli (2012) Extreme organic carbon burial fuels intense methane bubbling in a temperate reservoir, *Geophys. Res. Lett. 39, L01401, doi:10.1029/2011GL050144.*

Soumis, N., E. Duchemin, R. Canuel and M. Lucotte (2004) Greenhouse gas emissions from reservoirs of the western United States, *Global Biogeochem. Cycles 18*, GB3022, doi:10.1029/2003GB002197.

Soumis, N., R. Canuel and M. Lucotte (2008) Evaluation of two current approaches for the measurement of carbon dioxide diffusive fluxes from lentic ecosystems, *Environ. Sci. Technol. 42*, 2964-2969.

Steinmann, P., B. Eilrich, M. Leuenberger and S. J. Burns (2008) Stable carbon isotope composition and concentrations of CO_2 and CH_4 in the deep catotelm of a peat bog, *Geochim. Cosmochim. Acta. 72*, 6015-6026.

Striegl, R. G., and C. M. Michmerhuizen (1998) Hydrologic influence on methane and carbon dioxide dynamics at two north-central Minnesota lakes, *Limnol. Oceanogr. 43*, 1519-1529.

St-Louis, V. L., C. A. Kelly, E. Duchemin, J. W. M. Rudd and D. M. Rosenberg (2000) Reservoir surfaces as sources of greenhouse gases to the atmosphere: a global estimate, *Bioscience 50*, 766-775.

Tremblay, A., J. Therrien, B. Hamlin, E. Wichmann and L. J. LeDrew (2005) GHG emissions from boreal reservoirs and natural aquatic ecosystems, in *Greenhouse gas emissions – Fluxes and processes*, edited by A. Tremblay, L. Varfalvy, C. Rohem and M. Garneau, pp. 209-232, Springer, New York.

Vähätalo, A. V. and R. G. Wetzel (2008) Long-term photochemical and microbial decomposition of wetland-derived dissolved organic matter with alteration of 13C:12C mass ratio. *Limnol. Oceanogr. 53*, 1387-1392.

Figures Captions

Figure 1. Map of eastern Canada showing the selected sampling sites located in the southern boreal forest ecosystem. Exact coordinates are listed in Table 1.

Figure 2. Relationship between measured surface bulk water parameters and dissolved organic carbon (DOC). In A) pH, B) total nitrogen (TN), C) carbon dioxide (CO_2), and D) total phosphorus (TP); each data point represents the average value for each aquatic system.

Figure 3. Relationship between carbon dioxide (CO_2) and dissolved oxygen (O_2) saturation levels in A) the hypolimnetic zone (empty circles, natural lakes only), B) the photic epilimnetic zone, and the photic epilimnetic zone of the C) non-harvested and D) harvested reservoirs. Each data point represents an average value for an individual water sample.

Figure 4. Relationships between DOC and dissolved iron collected by tangential flow filtration - reverse osmosis. Each data point represents an individual 250 L sample concentrated to about 8 L and analyzed for DOC and dissolved iron.

Figure 5. Relationship between the $\delta^{13}C$ signature of DIC and the inverse of DIC concentrations (spring = black circles and squares; summer = grey circles and squares) in the water column of (A) natural lakes (Brock and Jean), (B) non-harvested reservoir (Cabonga), (C) harvested lakes (Clair and Bouleau) and (D) harvested reservoir (Decelles). Each data point represents an average value for an individual water sample.

Figure 6. Relationship between the δ^{13}C signatures of DIC and POC (spring = black circles and squares; summer = grey circles and squares); both fractions were sampled at same depths in the water column of (A) natural lakes (Brock and Jean), (B) non-harvested reservoir (Cabonga), (C) harvested and flooded lakes (Clair and Bouleau) and (D) harvested reservoir (Decelles). Each data point represents an average value for an individual water sample.

Figure 1.

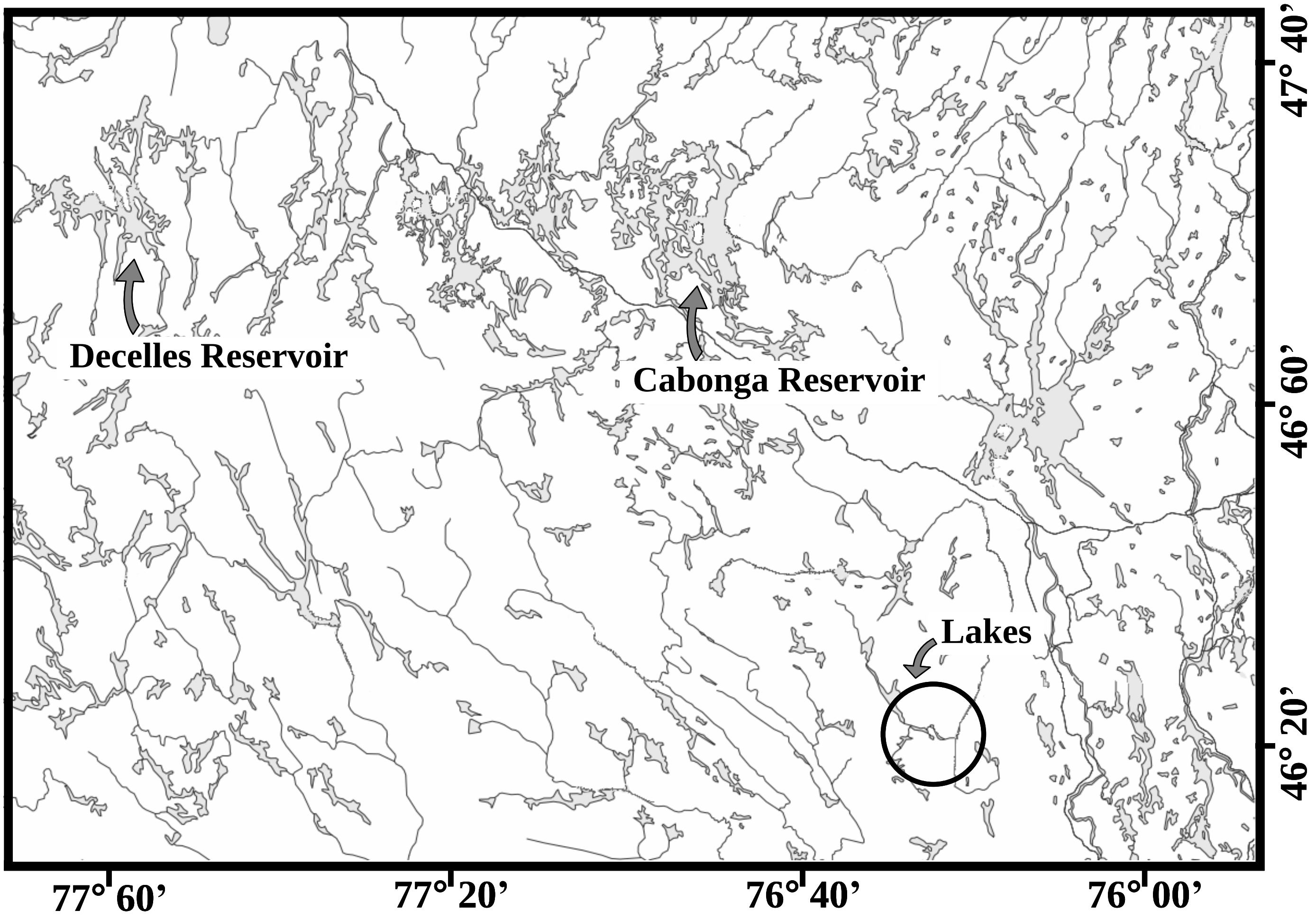

Decelles Reservoir
Cabonga Reservoir
Lakes
47° 40’
46° 60’
46° 20’
77° 60’
77° 20’
76° 40’
76° 00’

Figure 2.

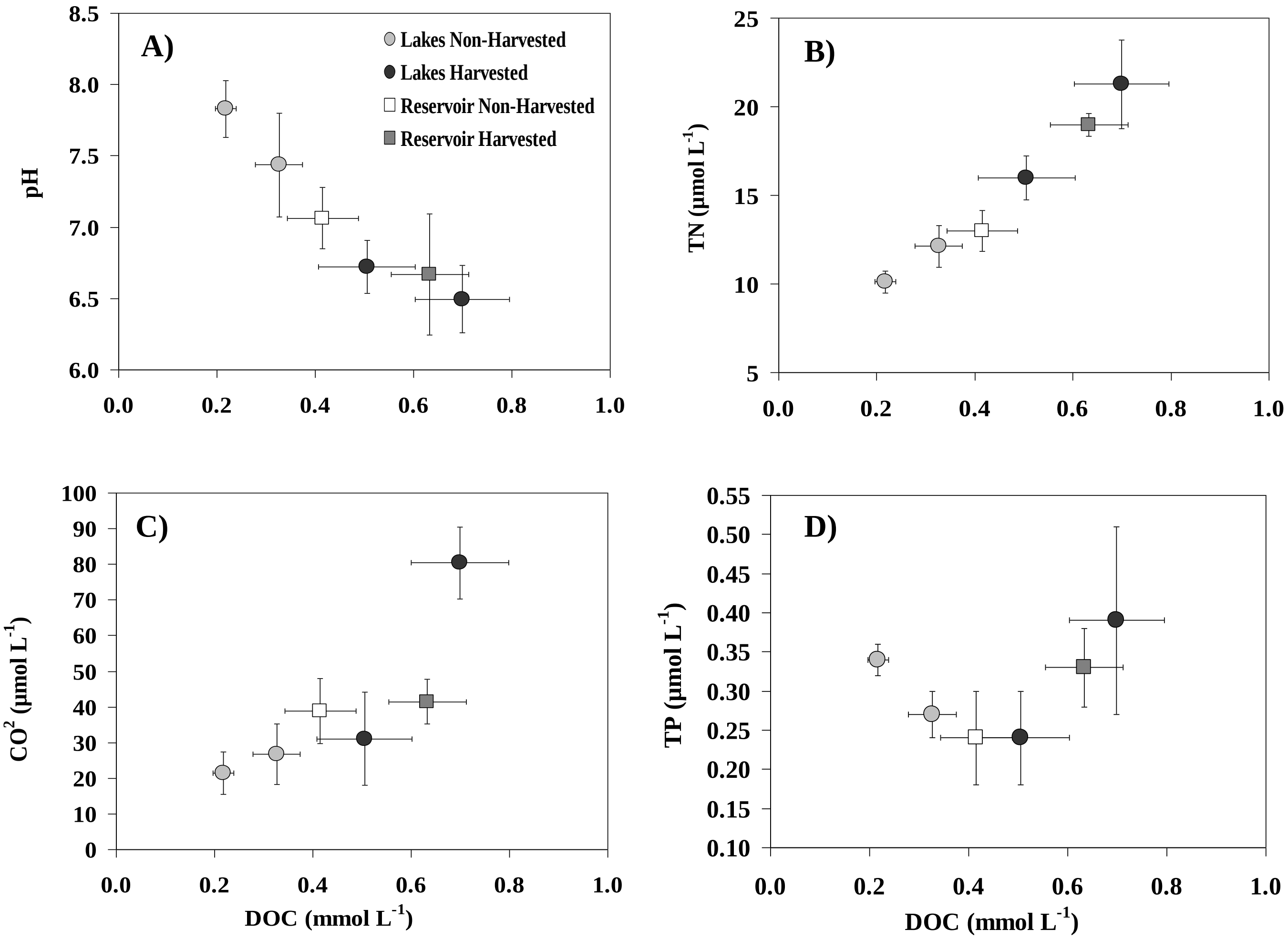

A)
B)
C)
D)
● Lakes Non-Harvested
● Lakes Harvested
□ Reservoir Non-Harvested
■ Reservoir Harvested
pH
8.5
8.0
7.5
7.0
6.5
6.0
TN (µmol L-1)
25
20
15
10
5
CO2 (µmol L-1)
100
90
80
70
60
50
40
30
20
10
0
TP (µmol L-1)
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.0
0.2
0.4
0.6
0.8
1.0
DOC (mmol L-1)
DOC (mmol L-1)

Figure 3.

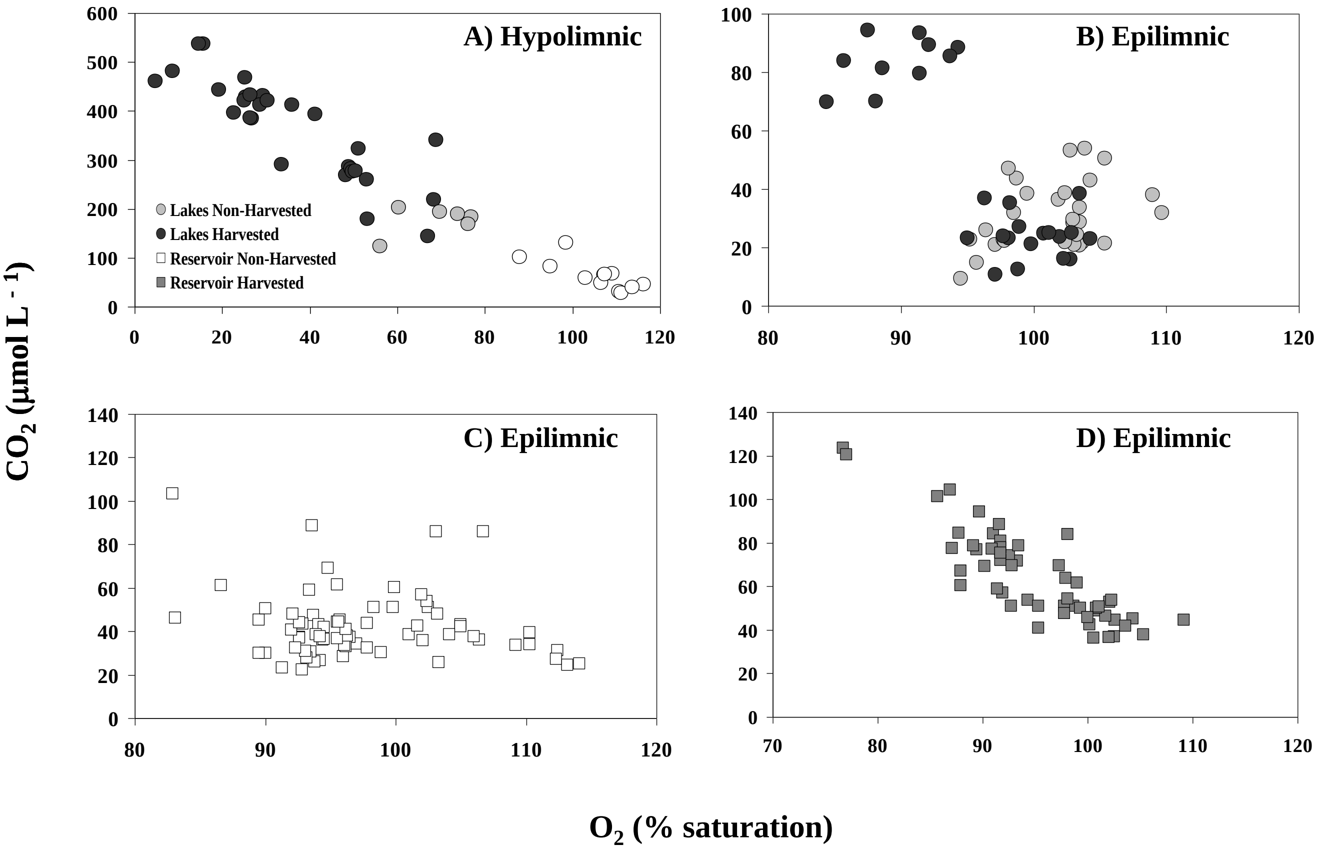

A) Hypolimnic
B) Epilimnic
C) Epilimnic
D) Epilimnic
● Lakes Non-Harvested
● Lakes Harvested
□ Reservoir Non-Harvested
■ Reservoir Harvested
CO_2 (µmol L $^{-1}$)
O_2 (% saturation)
600
500
400
300
200
100
0
0
20
40
60
80
100
120
100
80
60
40
20
0
80
90
100
110
120
140
120
100
80
60
40
20
0
80
90
100
110
120
140
120
100
80
60
40
20
0
70
80
90
100
110
120

Figure 4.

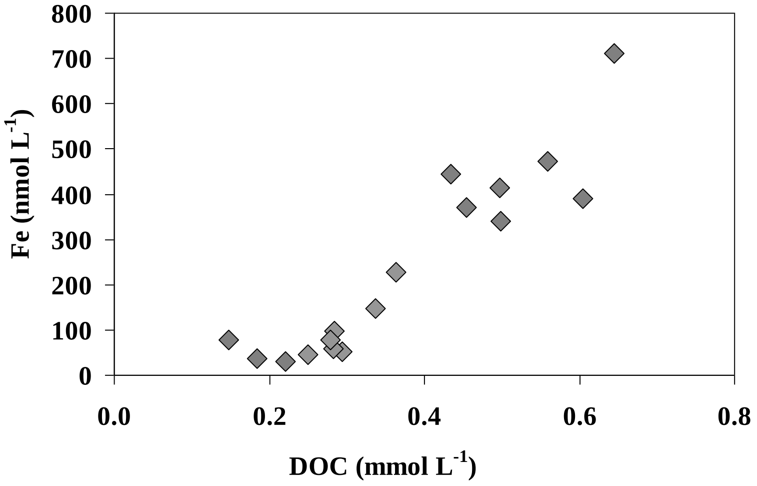
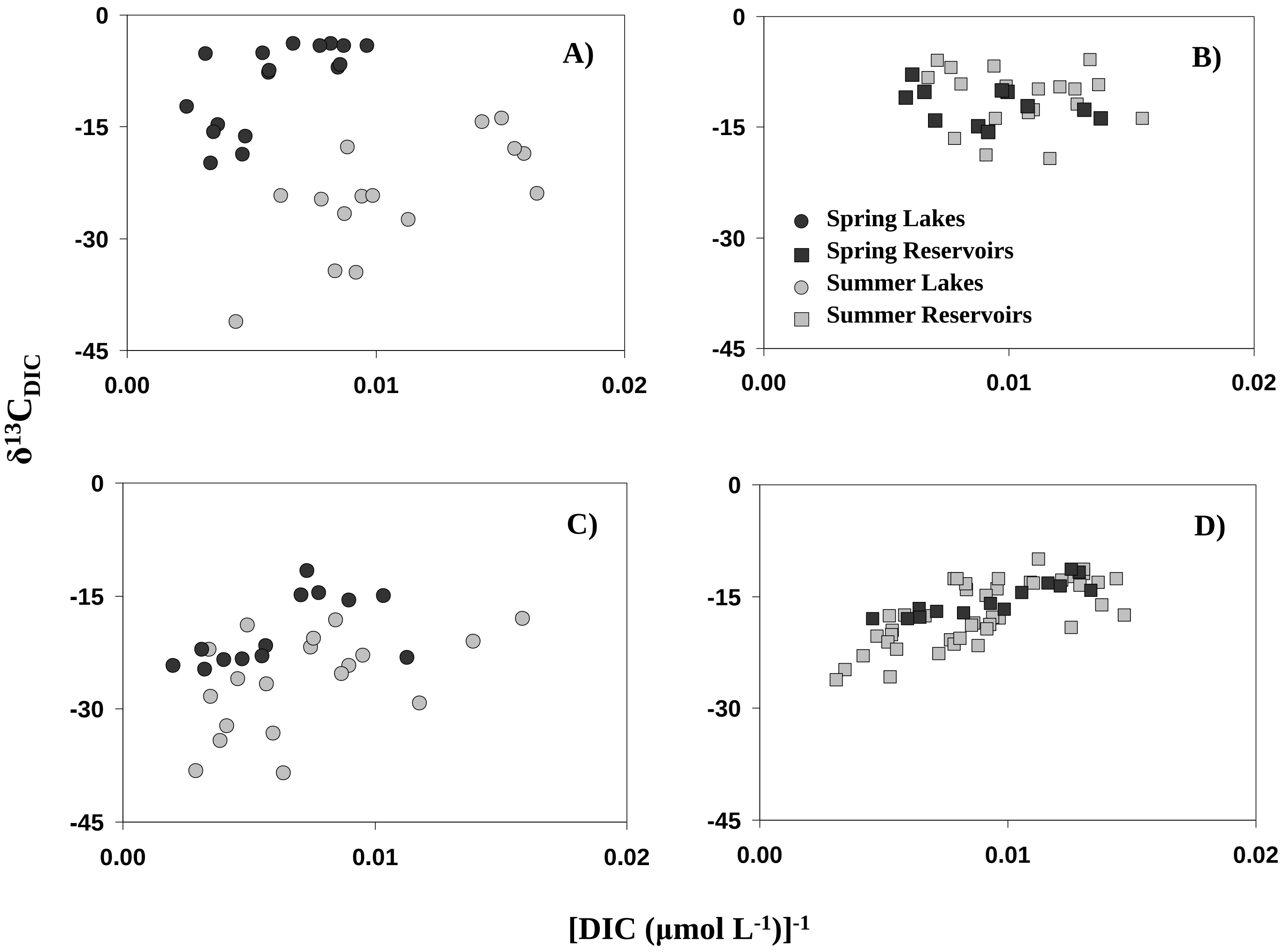
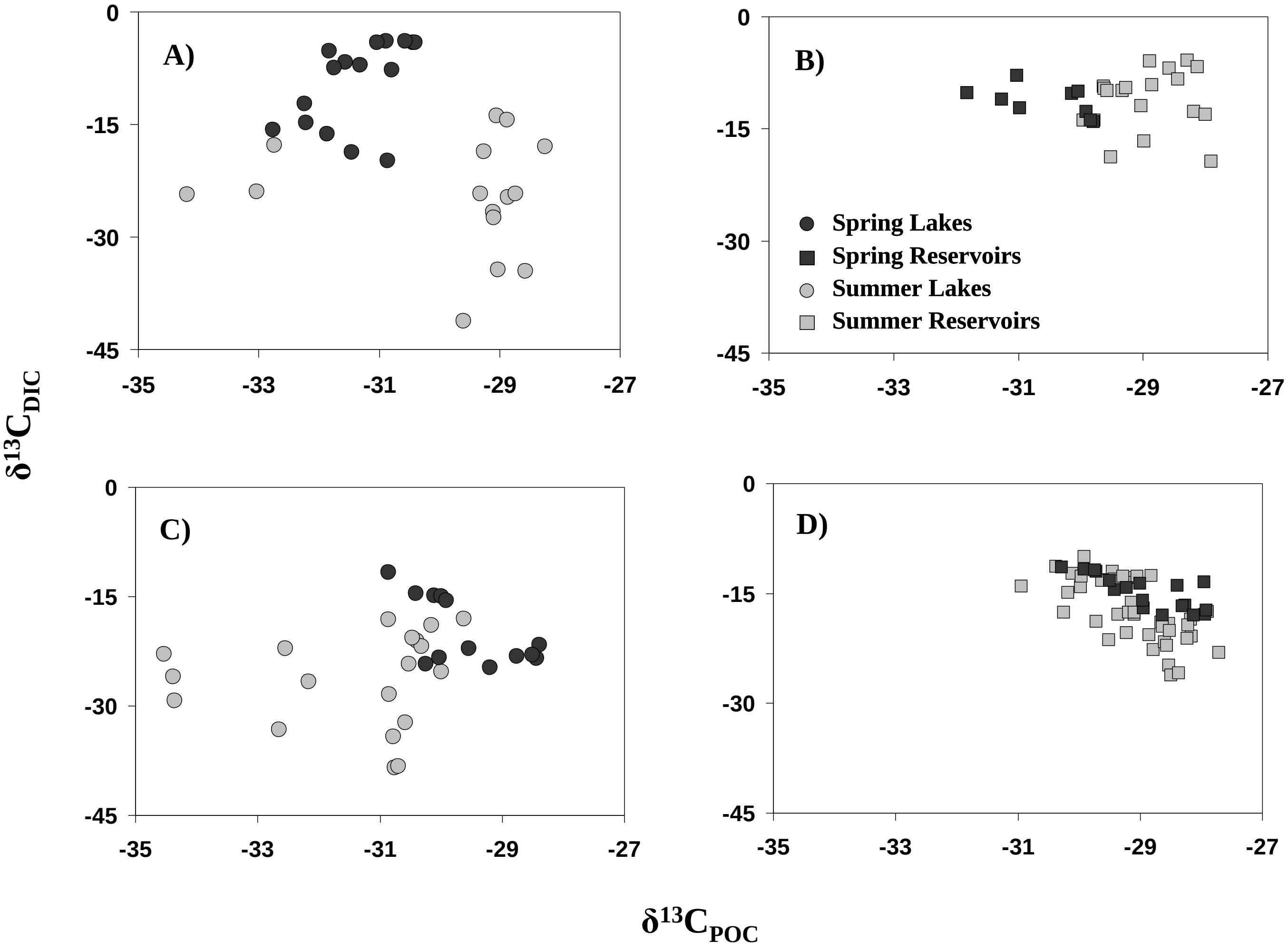

800
700
600
500
400
300
200
100
0
Fe (nmol L^{-1})
0.0
0.2
0.4
0.6
0.8
DOC (mmol L^{-1})

Figure 5.


A)
B)
C)
D)
0
-15
-30
-45
0.00
0.01
0.02
● Spring Lakes
■ Spring Reservoirs
○ Summer Lakes
□ Summer Reservoirs
$\delta^{13}C_{DIC}$
[DIC (µmol L^{-1})]$^{-1}$

770 Figure 6.



771

Table 1. Characteristics of the sampled water bodies

Water body	System	Land use	Lake area (km^2)	Drainage area (km^2)	Mean slope[a] (%)	Peatland Area (%)	# of stations	Water depth (m)[b]	T° depth (m)[c]	Photic depth (m)[d]	Coordinates
Brock	Lake	Natural	0.82	6.35	N/A	N/A	4	3 to 27	6	14.2	46° 16' 26.4" N 76° 20' 35.2" W
Mary	Lake	Natural	0.58	1.80	1.26	31.5	1	1.5 to 10	5	N/A	46° 15' 37.2" N 76° 12' 50.8" W
Jean	Lake	Natural	1.88	7.31	5.87	24.2	4	6 to 32	5.5	8.4	46° 21' 43.9" N 76° 20' 42.1" W
Clair	Lake	Wood harvested	1.75	47.0	7.75	8.2	4	5 to 17	4.5	4.0	46° 11' 06.7" N 76° 24' 53.2" W
Bouleau	Lake / flooded	Wood harvested	0.34	8.23	7.1	5.1	4	4 to 20	3.0	3.0	46° 14' 16.5" N 76° 27' 13.9" W
Cabonga	Reservoir	Natural	434	2 616	N/A	N/A	9	3 to 23	none	3.0 to 7.3	47° 20' 07.0" N 76° 34' 51.0" W
Decelles	Reservoir	Wood harvested	237	13 131	N/A	N/A	11	2 to 21	none	2.5 to 3.4	47° 41' 50.9" N 78° 10' 38.9" W

[a] Watershed mean slope calculated from : Slope = 100*tan(angle), where the maximum angle is 45 degrees and tan represents the tangent function. [b] Ranges of sampling sites water depth, which including the deepest location in lakes. [c] T° stands for thermocline. [d] Depth at which light intensity falls below the 1% level. Underlined water bodies indicate wood harvesting.

Table 2. Carbon dioxide and methane concentrations in surface waters and fluxes to the atmosphere

Water body	# of stations	*n* [a]	$[CO_2]$ (µmol L^{-1})		$[CH_4]$ (nmol L^{-1})		Wind speed [b]	CO_2 Fluxes [c] (mmol CO_2 m^{-2} d^{-1})		CH_4 Fluxes [c] (µmol CH_4 m^{-2} d^{-1})	
			Average [d]	Range	Average [d]	Range	Average [d]	Average	Range	Average	Range
L. Brock	4	11	21.4 (6.0)	14.7 - 31.8	99.4 (19.3)	62.9 - 141	2.1 (3.4)	4.0 (2.6)	0.9 - 8.9	31 (54)	0 - 146
L. Jean	4	22	26.7 (8.6)	19.4 - 50.4	73.2 (27.5)	33.6 - 218	7.0 (6.0)	13.0 (14.5)	2.9 - 55.0	214 (286)	0 – 939
L. Clair	4	16	31.1 (10.1)	10.7 - 43.8	41.3 (12.6)	10.7 - 54.9	5.9 (4.3)	17.0 (7.0)	5.8 - 30.2	123 (282)	0 - 519
L. Bouleau	4	20	80.4 (13.0)	62.5 - 106	72.6 (25.7)	40.8 - 156	6.8 (3.7)	60.4 (23.1)	29.1 – 105.1	417 (418)	10 - 1515
R. Cabonga	9	35	38.8 (9.2)	13.1 - 61.9	57.8 (14.9)	22.2 - 129	11.4 (5.3)	28.7 (12.8)	7.7 - 54.1	434 (498)	18 - 2420
R. Decelles	11	62	41.5 (6.3)	27.7 - 59.8	67.3 (20.8)	27.0 - 145	11.2 (6.2)	38.6 (20.3)	10.3 – 104.5	579 (534)	0 – 2875

[a] Total number of measurements evenly distributed within the number of sampling stations. [b] Wind speed at 1 m above water surface. [c] Due to large variations in wind speed, standard deviations of corresponding averages were not calculated. [d] Standard deviations are shown between parentheses (details in materials and methods section). The total sampling and analysis error was 4.1 ± 1.7%. Underlined water bodies indicate wood harvesting.

Table 3. Water chemistry variables measured in this project

Water body	# of stations	[DOC] (mmol L^{-1})		pH		[TN] (μmol L^{-1})		[TP] (μmol L^{-1})
		n [a]	Average [b]	*n* [a]	Average [b]	*n* [a]	Average [b]	Average [b]
L. Brock	4	7	0.217 (0.010)	4	7.83 (0.20)	8	10.1 (0.6)	0.34 (0.02)
L. Mary	1	1	0.394 (N/A)	N/A	N/A	1	15.7 (N/A)	0.40 (N/A)
L. Jean	4	16	0.326 (0.048)	8	7.31 (0.31)	12	12.1 (1.2)	0.27 (0.03)
L. Clair	4	10	0.505 (0.099)	7	6.73 (0.26)	10	16.0 (1.2)	0.24 (0.06)
L. Bouleau	4	18	0.699 (0.096)	8	6.55 (0.36)	19	21.3 (2.5)	0.39 (0.12)
R. Cabonga	9	33	0.415 (0.072)	19	6.98 (0.22)	30	13.0 (1.2)	0.24 (0.06)
R. Decelles	10	37	0.633 (0.079)	13	6.68 (0.37)	7	19.0 (0.6)	0.33 (0.05)

[a] Total number of measurements evenly distributed within the number of sampling stations.

[b] Standard deviations are shown between parentheses (details in materials and methods section).

Underlined water bodies indicate wood harvesting.

Table 4. Bulk organic carbon and nitrogen in soils and their dissolved organic matter leachates

Sample	Soil depth (cm)	Soil				Soil leachate			
		OC (%)^a	δ^{13}C (‰)^b	δ^{15}N (‰)^b	(C:N)$_a$	OC (%)^a	δ^{13}C (‰)^b	δ^{15}N (‰)^b	(C:N)$_a$
Boreal soil litter	surface	41.2	-27.2	-1.0	35.1	38.2	-26.0	0.7	21.6
L. Mary	1-2	37.9	-27.1	0.8	20.7	22.3	-25.2	4.8	9.5
	7-9	30.3	-25.8	6.3	22.9	22.9	-24.2	11.2	8.4
	12-15	5.4	-24.9	5.5	35.9	22.8	-24.5	9.5	9.4
L. Jean	1-2	50.5	-26.7	-0.7	30.7	36.4	-25.0	2.4	16.3
	9-12	22.9	-25.4	3.1	66.8	42.6	-23.8	5.4	21.3
	15-20	2.8	-25.1	N/A	N/A	18.1	-23.9	4.9	20.1
R. Cabonga	1-2	47.4	-26.2	1.6	36.6	46.9	-26.2	4.2	17.6
	7-9	8.5	-26.4	3.0	44.0	34.3	-24.1	4.3	25.7
	12-15	4.0	-25.5	4.4	35.6	25.4	-25.3	7.1	18.4
R. Decelles	1-2	49.2	-27.9	-3.4	53.4	41.8	-26.5	-0.7	28.5
	12-15	21.4	-26.3	0.6	115.7	40.9	-25.7	2.5	38.6
	15-20	4.4	-26.2	-2.0	251.9	37.7	-25.6	-0.4	77.0

^{a,b} Analytical uncertainties of 1%$^{(a)}$ and 0.2‰$^{(b)}$. Underlined water bodies indicate wood harvesting.

Table 5. Bulk organic carbon and nitrogen in dissolved and fine particulate organic matter

Water body	# of stations	DOM						FPOM				
		OC (μmol L^{-1})	OC (%)^{a}	δ^{13}C (‰)^{b}	δ^{15}N (‰)^{b}	(C:N)$_{a}$	Fe (nmol L^{-1})^{c}	OC (μmol L^{-1})	OC (%)^{a}	δ^{13}C (‰)^{b}	δ^{15}N (‰)^{b}	(C:N)$_{a}$
L. Brock	1	148	9.1	-28.0	-0.4	21.3	77.2	12.9	21.6	-28.6	0.2	12.1
L. Mary	1	184	6.3	-26.3	-2.7	21.6	37.0	25.1	25.6	-27.7	0.9	11.8
L. Jean	1	221	10.9	-26.8	-1.7	29.8	30.7	37.1	27.2	-28.6	-0.3	14.0
L. Clair	1	434	16.8	-27.1	-1.1	32.0	443.5	80.8	33.4	-28.6	0.1	18.7
L. Bouleau	1	506	16.9	-27.5	-1.9	33.2	N/A	77.5	27.8	-30.4	0.2	23.7
R. Cabonga	7	299	13.2	-27.0	-1.2	33.4	100.6	44.9	28.2	-28.7	-0.3	19.1
		(39)	(1.4)	(0.2)	(1.0)	(3.9)	(65.9)	(27.6)	(5.7)	(0.4)	(0.6)	(2.4)
R. Decelles	6	543	18.8	-27.1	-1.6	41.6	450.2	43.5	26.0	-28.7	1.6	24.9
		(73)	(2.8)	(0.2)	(1.5)	(8.3)	(135)	(21.6)	(4.7)	(0.5)	(0.3)	(4.5)

^{a,b} Analytical uncertainties of 1%$^{(a)}$ and 0.2‰$^{(b)}$. ^{c} Iron complexed to dissolved organic matter exclusively. Numbers between parentheses are standard deviations, and underline names indicate wood harvesting.