Sources and fate of terrestrial dissolved organic carbon in lakes of a Boreal Plains region recently affected by wildfire

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Abstract

Downstream mineralization and sedimentation of terrestrial dissolved organic carbon (DOC) render lakes important for landscape carbon cycling in the boreal region, with regulating processes potentially sensitive to perturbations associated with climate change including increased occurrence of wildfire. In this study we assessed chemical composition and reactivity (during both dark and UV incubations) of DOC from lakes and terrestrial sources within a peatland-rich western boreal plains region partially affected by a recent wildfire. While wildfire was found to increase aromaticity of DOC in peat pore-water above the water table, it had no effect on concentrations or composition of DOC from peatland wells and neither affected mineral well or lake DOC characteristics. Lake DOC composition reflected a mixing of peatland and mineral groundwater, with a greater influence of mineral sources to lakes in coarse- than fine-textured settings. Peatland DOC was less biodegradable than mineral DOC, but both mineralization and sedimentation of peatland DOC increased substantially during UV incubations through selective removal of aromatic humic and fulvic acids. DOC composition in lakes with longer residence times had characteristics consistent with increased UV-mediated processing. We estimate that about half of terrestrial DOC inputs had been lost within lakes, mostly due to UV-mediated processes. The importance of within-lake losses of aromatic DOC from peatland sources through UV-mediated processes indicate that terrestrial-aquatic C linkages in the study region are largely disconnected from recent terrestrial primary productivity. Together, our results suggest that characteristics of the study region (climate, surface geology and lake morphometry) render linkages between terrestrial and aquatic C cycling insensitive to the effects of wildfire by determining dominant terrestrial sources and within-lake processes of DOC removal.
1 Introduction

Lakes act as reactors where dissolved organic carbon (DOC) leached from terrestrial ecosystems is mineralized, transformed and sedimented (Tranvik et al., 2009). As a result, lakes accumulate carbon (C) in sediments while simultaneously being net sources of CO$_2$ to the atmosphere (Sobek et al., 2005; Wachenfeldt et al., 2008). Lakes are believed to play a particularly significant role for the C balances in the boreal region, since they cover a large fraction of the landscape and are the recipients of ~5–10% of terrestrial net primary productivity as DOC (Prairie, 2008; Olefeldt et al., 2012). It is now accepted that a large fraction of terrestrially exported DOC is removed through within-lake processes before reaching the ocean (Algesten et al., 2004; Weyhenmeyer et al., 2012). Both microbial and ultraviolet (UV) processes contribute to this removal, but act selectively on different DOC fractions (von Wachenfeldt et al., 2008; Benner and Kaiser, 2011). An improved understanding of the overall and relative contribution of these processes for within-lake removal of terrestrial DOC as a function of catchment and lake characteristics is necessary in order to anticipate implications for linkages between terrestrial and aquatic C cycling associated with climate change, including pulse perturbations such as wildfire.

The chemical composition of DOC differs among terrestrial sources, both within and between ecosystems. Leachates from live vegetation and fresh litter have a high contribution of low molecular weight (LMW) carbohydrates, while leachates from humified organic soils, including peat, often are dominated by highly aromatic high molecular weight (HMW) humic and fulvic acids (Kalbitz et al., 2003a; Wickland et al., 2007). Downward cycling of DOC through mineral soils leads to decreased DOC concentrations and aromaticity and increased contribution of microbial metabolites through selective absorption, microbial processing and desorption (Kaiser and Kalbitz, 2012; Kothawala et al., 2012a). Hydrological connectivity of terrestrial sources determines magnitude, timing and composition of DOC reaching downstream aquatic ecosystems (Ågren et al., 2008; Olefeldt et al., 2012). Peatlands are generally important catchment
sources of DOC as they lack mineral soils that impede and reduce export (Mattson et al., 2005; Creed et al., 2008).

Both microbial and UV-mediated rates of mineralization are linked to DOC composition (Kalbitz et al., 2003a; Obernosterer and Benner, 2004). Aromatic DOC is poorly available for microbes but is readily mineralized or transformed into bioavailable compounds by UV light (Bertilsson and Tranvik, 2000). UV light also enhances rates of sedimentation through flocculation of aromatic DOC (von Wachenfeldt et al., 2008). In the absence of attenuation from aromatic DOC, damaging UV light slows down microbial activity (Tranvik and Bertilsson, 2001; Olefeldt et al., 2013). Both microbial and UV-mediated removal of DOC alters the composition of the remaining pool as a result of selective removal or transformation, often along diverging trajectories (Moran et al., 2000; Kalbitz et al., 2003b; Benner and Kaiser, 2011).

Wildfire annually burns ~1% of the circumboreal forest, and burn area is expected to double by the end of this century as a result of climate change (Flannigan et al., 2009). Wildfire alters the quality of soil organic matter in shallow soil layers both through the loss of polysaccharide aliphatic C associated with fresh litter and through the enrichment and formation of condensed aromatic carbon compounds associated with incomplete combustion (Neff et al., 2005; Certini, 2005). Olefeldt et al. (2013) showed that wildfire had corresponding effects on soil DOC composition in both boreal peatlands and uplands forests, causing increased aromaticity and decreased biodegradability of surface soil leachates. Few studies have assessed the implications of wildfire on aquatic C cycling (cf. Marchand et al., 2009), and studies of catchment DOC exports and lake DOC concentrations have yielded variable responses to fire in different regions (Schindler et al., 1996; Carignan et al., 2000; McEachern et al., 2000; Allen et al., 2003; Betts and Jones, 2009; Marchand et al., 2009). Given the likelihood of increased fire frequencies and severities in boreal regions, particularly continental regions such as wester Canada (Flannigan et al., 2009), a framework for understanding downstream implications of wildfire on lake C cycling and the degradation of terrestrial DOC is needed.
The purpose of this study was to evaluate the potential for wildfire to alter the linkages between terrestrial and aquatic C cycling in a boreal setting. Water samples from lakes and wells collected within and outside a recent wildfire were characterized with regards to water chemistry and DOC composition and reactivity. Several different approaches were used to determine the relative importance of processes responsible for within-lake losses of terrestrial DOC and their dependencies on the mixing of terrestrial DOC sources. In addition to incubation experiments and lake mixing models we particularly rely on optical properties of DOC, including absorbance and fluorescence. Optical properties has been used to characterize bulk properties of different sources, e.g. aromaticity (Weishaar et al., 2003), relative measures of humic/fulvic acids and amino acid abundances (Fellman et al., 2010) as well as used to understand compositional changes associated with microbial and UV-mediated processes (Kalbitz et al., 2003b; Wickland et al., 2007; Benner and Kaiser 2011).

2 Study area

The study area is located in the Boreal Plains ecozone in north-central Alberta, within the Utikuma Region Study Area (URSA) (Devito et al., 2005; EcoRegions Working Group, 1989). The region was partially affected by a wildfire that broke out on 15 May 2011 and eventually burned an area of ∼880 km² (Fire ID: SWF057), including the surroundings of many lakes within URSA (Fig. 1). The landscape in the region is characterized by low relief and a land-cover of peatlands dominated by black spruce (Picea mariana) and uplands dominated by trembling aspen (Populus tremuloides), white spruce (Picea glauca) or pine (Pinus banksiana) depending on glacial landforms and local drainage. Thick glacial deposits dominate the surface geology, including coarse-textured glacio-fluvial sand deposits in the north-west part of the study area transitioning into fine-textured settings with glacio-lacustrine and moraine deposits of clay and silt in the south-eastern parts (Fenton et al., 2003; Devito et al., 2005). The region has a sub-humid climate, with average annual temperature of 1.7 °C and monthly
temperature range of −14.6 to 15.8 °C (EcoRegions Working Group, 1989). The mean annual precipitation is slightly lower than potential evapotranspiration, 481 and 518 mm respectively (Marshall et al., 1999).

The region has numerous shallow (∼1 m) lakes of variable size that cover 5–10% of the landscape area. The lakes are naturally meso- to eutrophic and occasionally experience algal blooms (Bayley et al., 2007). Mineral groundwater inputs to lakes are quantitatively more important for lakes in coarse-textured settings due to high hydrological conductivity in quartz sand deposits, but have lower ion and nutrient concentrations for the same reason (Smerdon et al., 2008). In fine-textured settings water movement is restricted to near-surface flow-paths, and mineral groundwater inputs are small. Near-surface flow-paths are dominated by water movement through organic soils in peatlands, and peatlands adjacent to lakes represent important sources of water to the lakes although they can also act as water sinks during dry years (Ferone and Devito, 2004). In contrast, forested upland areas seldom generate hillslope runoff since individual precipitation events rarely exceed soil storage capacity (Redding and Devito, 2008). Rather, the water table often slope against topography, causing water to move from lake into hillslopes to recharge groundwater or be transpired. Inter-annual variability in precipitation causes the lakes to go through multiyear oscillations of drying or wetting that can reduce or increase lake water volumes significantly (Sass and Creed, 2008). Low water levels following dry periods were recorded from 1999 to 2002 and from 2009 to 2010. Water levels rose in early 2011, followed by a stable period that extended through to our sampling in the summer of 2012.

3 Methods and materials

3.1 Peatland pore-water profiles

We used rhizone pore-water samplers (Rhizosphere research products) to establish depth profiles in one peatland that burned in the previous year and in one nearby
unburned peatland. Both peatlands were typical bogs for the region; with peat depths > 100 cm, open canopies of black spruce and a surface layer with *Sphagnum* mosses and Bog Labrador Tea (*Rhododendron groenlandicum*). Wildfire caused preferential burning of *Sphagnum* moss in hollows with an average depth of burn of ∼0.1 m and left a ∼5 mm char layer, while wildfire singed the *Sphagnum* moss in hummocks but left it largely uncombusted. In each peatland, three profiles were located in hummocks and three in hollows, consisting each of rhizon inserted 5, 15 and 30 cm below the peat surface. Rhizons consist of a microporous tube (Ø = 5 mm, length = 100 mm, pore width = 0.1 µm) that is connected to PVC tubing that ends above the surface with a male Luer lock that can be attached to a syringe. Rhizons are capable of collecting pore-water samples both above and below the water table. Next to each profile we inserted stilling wells where the position of the water table was measured. Five sampling occasions were performed between late May and August. Sampling was done by attaching 60 mL syringes to each rhizon, applying vacuum and allowing 10 h to collect pore water. Occasionally the rhizons were unable to collect pore-water samples, yielding 57 and 69 samples from the burned and unburned peatlands respectively, out of 90 possible samples at each site. Pore-water samples were transferred to 25 mL acid washed and pre-rinsed scintillation vials and kept cool until analyzed for DOC concentration and absorbance within two weeks of collection, see below.

### 3.2 Lake and well water sampling

A synoptic sampling of lakes and wells was conducted in late July 2012, one year after the fire. A total of 32 lakes were sampled, using a 3 m rod from the shore of the lake to ensure a representative lake sample taken from ∼30 cm below the water surface. Half of the lakes were located within and half were located outside the perimeter of the recent fire. 21 of the lakes were located in fine-textured settings and 11 in coarse-textured settings (Fig. 1). Seven wells that extend completely into mineral soils were sampled (4–16 meters deep), of which 4 were located in a burned area (Fig. 1). Seven wells in peatlands (∼1 m deep, with no mineral contact) were also sampled, 4 of which were
located in burned peatlands. All wells had been previously developed and were flushed prior to our sampling. In addition, we sampled surface water from small peatland pools (< 50 cm diameter) nearby each peatland well. Peatland well and surface water were indistinct from each other in all regards and are henceforth all referred to as peatland well samples.

Two samples were collected at each lake and well. The first sample was filtered directly in the field through 0.45 µm glass fibre filters (Machery Nagel) into 1 L acid-washed glass bottles. The second sample was also filtered in the field, but stored in 60 mL glass bottles and acidified in the field by adding 100 µL 2 N hydrochloric acid. Both samples were kept on ice in the field, and subsequently stored cool (8°C) until analysis and start of incubation, see below.

A synoptic lake sampling survey was also carried out in July 2003, and included 23 of the 32 lakes that were sampled in 2012. Of the lakes sampled twice (2003 and 2012), 13 of 23 were located within the recent fire-perimeter and 10 outside. In 2003 the region was in a stable hydrological phase following a post-drought recovery of lake levels, similar to conditions in 2012.

### 3.3 Sample analysis

DOC concentrations of samples collected from rhizons, lakes and wells were measured 10–14 days after sampling on a Shimadzu TOC-V. Four point calibration curves over the range 0–100 mg L\(^{-1}\) were established for DOC using standards and MilliQ-water, and each run included one DOC standard (100 mg L\(^{-1}\)) along with at least four MilliQ-water samples to ensure that no analytical drift occurred. Aliquots of 25 mL were taken from each sample and were acidified by 100 µL 2 N hydrochloric acid prior to analysis, unless the sample had already been acidified in the field. Samples were sparged for 2 min to remove dissolved inorganic carbon (DIC). Four injections of each sample were used to calculate average concentrations, yielding an average standard error of 0.2 mg CL\(^{-1}\).

Electrical conductivity (Ec), pH, δ\(^{18}\)O and δD were measured on all well and lake samples. Surface and well water Ec and temperatures were measured on site with
a calibrated Temperature/Level/Conductivity Meter (Solinst Canada). pH was determined from samples analyzed in Biogeochemical Analytical Service Laboratory, University of Alberta, within 48 h of sampling. δ^{18}O and δD were determined by H_2O_{(liquid)} → H_2O_{(vapour)} equilibration laser spectroscopy (Wassenaar et al., 2008) using Los Gatos Liquid Water Isotope Analyzer at the Biogeochemical Analytical Service Laboratory, University of Alberta. Results were expressed as per mil difference (‰), relative to Vienna Standard Mean Oceanic Water.

3.4 Incubation experiments

Lake and well samples that had not been acidified in the field were prepared for incubations under dark and UV-light conditions. Samples were diluted with 0.001 N NaHCO_3 to DOC concentrations of 19.7 ± 1.1 mg CL^{-1} prior to incubation start. Three lake and one mineral well sample had initial DOC concentrations between 14 and 20 mg CL^{-1} and were incubated without dilution, while one mineral well sample with a concentration at 5 mg CL^{-1} and was not incubated. 150 mL of sample was incubated in 250 mL glass jars. An inoculum was prepared from a mix of peat leachates, lake water and Milli-Q water that was filtered through a 1.2 μm glass fibre filter. The inoculum had a DOC concentration of 5 mg CL^{-1}, and 2 mL were added to each incubation jar (representing ~0.2% of total incubated DOC). Incubation jars were flushed with ambient air and sealed with silicone septa screw-on tops at the start of the incubation. Jars were then placed up-side down in a growth chamber set to 17.5 °C air temperature. The growth chamber was equipped with 4 UV lamps (Sylvania R48T12/350BL/VHO/180). Samples incubated under dark conditions were placed under a dark screen, while samples incubated under UV conditions were exposed to light intensities of 20 ± 0.5 Wm^{-2} UV-A (320–400 nm) and 0.07 ± 0.01 Wm^{-2} UV-B (280–320 nm). Light intensities were measured on the inside of 10 empty jars using Solar Light PMA2110 UV-A and PMA 2106 UV-B sensors attached to a PMA2100 unit.

Aliquots of 25 mL were drawn from incubation jars at the start (before being sealed) and after 11 days. Aliquots were filtered through 0.45 μm glass fibre filters and analyzed...
for DOC concentration, absorbance and fluorescence on the same day, see below. By filtering the sample before analysis, DOC losses represent total losses due to mineralization, flocculation and incorporation into microbial biomass. The contribution of mineralization to total losses were measured through headspace analysis. Headspace CO$_2$ concentrations were measured at the start of the incubation and after 1, 3, 6 and 11 days. Each time a 10 mL air sample was drawn for analysis and was subsequently replaced by pure N$_2$. Analyses of headspace samples were done on an infrared gas analyzer (PP Systems, EGM-1) that was calibrated several times daily using a 1000 ppm CO$_2$ standard gas. Headspace CO$_2$ concentration, water temperature and sample pH (assumed constant throughout incubations) were used to calculate concentrations of DIC (Plummer and Busenberg, 1982). Changes in headspace CO$_2$ concentration and DIC concentration were summed for estimates of mineralization rates during the incubations, with DIC production always representing <15% of total mineralization. Assuming that DOC is a mixture of components with different degradation rates, we fitted a double exponential model to the CO$_2$ time-series which yielded estimates of the contribution of a labile and a stable fraction to the total DOC pool, along with degradation half-lives of each fraction (Kalbitz et al., 2003a).

3.5 Absorbance, fluorescence and PARAFAC analysis

UV-Vis absorption from 200 to 600 nm (1 nm steps) was measured on all samples on a Varian Cary 100 in a 10 mm quartz cuvette, with MilliQ-water used as blank. Absorbance at 254 nm ($A_{254}$) divided by the sample DOC concentration yields specific UV absorbance (SUVA), which has a robust positive relationship with DOC aromaticity (Weishaar et al., 2003).

Fluorescence was measured on a Varian Cary Eclipse, and all data was multiplied by the instrument specific excitation and emission correction factors as well as corrected for primary and secondary inner filter effects using corresponding absorbance spectra (Ohno, 2002). Analytical drift of the instrument was checked daily by locating and calculating the area of the Raman peak at 350 nm excitation with 0.25 nm steps. Raman
peak location was found at 396.7 ± 0.5 σ nm and the σ for peak area was < 5 % of the average area – indicating that there was no significant drift during the experiment. Daily tests of cuvette contamination and blank recordings were also made. Samples were if needed diluted with MilliQ water so that $A_{254}$ was 0.2 ± 0.005 cm$^{-1}$ prior to fluorescence analysis.

Excitation/emission matrices (EEMs) were collected from aliquots drawn at the start and end of incubations. In the EEMs, fluorescence was collected over an excitation range from 240 to 400 nm (5 nm increments) and an emission range from 300 to 550 nm (2 nm increments), using 0.25 s averaging times. Fluorescence intensities were normalized to both the area of the Raman peak and to the sample DOC concentration, thus EEM fluorescence intensities were expressed in Raman Units (R.U.) per unit DOC concentration (i.e. R.U. mgC$^{-1}$L). The collected 171 EEMs were used in a parallel factor (PARAFAC) analysis using DOMFluor Toolbox v.1.7, whereby fluorescing components are identified and their contribution to individual EEMs is quantified (Stedmon and Bro, 2008). The PARAFAC analysis validated a five component model using a split-half approach. Residuals between measured and modeled EEMs by the PARAFAC analysis showed no discernible patterns and had intensities ~2 orders of magnitude lower than in the measured EEMs, indicating that no significant fluorophores were unaccounted for by the model. The components had smooth single peaks in their emission loadings and single or double peaks in their excitation loadings (Fig. 2 and Table 1). Peak regions of each component corresponded well with previously identified fluorophores and components $C_C$ and $C_X$ were accordingly interpreted as being associated with HMW fulvic/humic acids, $C_A$ with HMW fulvic acids, $C_M$ with LMW fulvic/humic acids and $C_T$ with the amino acids tryptophan and tyrosine, free or bound in proteins (Coble, 1996; Fellman et al., 2010).
3.6 Using a hydrological mixing model to assess DOC sources to lakes and within-lake DOC losses

For each lake we solved a mixing model for the fractional contribution from mineral groundwater ($f_M$) and peatland water ($f_P$), using Ec as a conservative tracer:

$$E_{\text{Lake}} = f_M \cdot E_{\text{CM}} + f_P \cdot E_{\text{CP}} \quad (1)$$

where $f_M$ and $f_P$ sum to 1, $E_{\text{Lake}}$ is the measured lake Ec and $E_{\text{CM}}$ and $E_{\text{CP}}$ are representative estimates of mineral groundwater and peatland Ec respectively. For $E_{\text{CP}}$ we used the average Ec measured in peatland well and surface water samples, 55 $\mu$S cm$^{-1}$, see results. Ec of mineral groundwater sources are known to vary between wells in fine (clay) and coarse (quartz sand) textured substrates in the region, and values used as $E_{\text{CM}}$ for lakes in fine and coarse textured sections were 1000 $\mu$S cm$^{-1}$ and 200 $\mu$S cm$^{-1}$ respectively, based on previous measurements of a larger set of wells in the region (Ferone, 2001; Gibbons, 2003).

By assuming conservative behavior of $A_{254}$ and DOC we estimated what lake $A_{254}$ and DOC concentrations would be in the absence of within-lake losses:

$$\text{DOC}_{\text{Est}} = f_M \cdot \text{DOC}_M + f_P \cdot \text{DOC}_P \quad (2)$$

where $\text{DOC}_{\text{Est}}$ is the estimated lake DOC concentration in the absence of within-lake losses and $\text{DOC}_M$ and $\text{DOC}_P$ are mineral groundwater and peatland source DOC concentrations at 19 and 82 mg CL$^{-1}$, see results. $A_{254\text{Est}}$ was estimated analogously. Consequently, the difference between estimated and observed lake $A_{254}$ and DOC concentrations ($A_{254\Delta}$, $\text{DOC}_\Delta$) were assumed to represent within-lake losses of terrestrial DOC inputs. We can further use the observation that ratios of DOC to $A_{254}$ loss differed between incubations under dark and UV conditions, see Appendix, to partition within-lake DOC losses between microbial or UV-mediated losses by rearranging the
following relationships:

\[ \text{DOC}_\Delta = \text{DOC}_{\Delta \text{DARK}} + \text{DOC}_{\Delta \text{UV}} \]  
\[ A_{254\Delta} = A_{254\Delta \text{DARK}} + A_{254\Delta \text{UV}} \]  
\[ \text{DOC}_\Delta = A_{254\Delta \text{UV}} \cdot R_{\text{UV}} + A_{254\Delta \text{DARK}} \cdot R_{\text{DARK}} \]

where subscripts \( \Delta \text{DARK} \) and \( \Delta \text{UV} \) denotes within-lake \( A_{254} \) and DOC losses attributed to biodegradation and UV mediated losses respectively, and \( R_{\text{UV}} \) (63 mg CL\(^{-1}\) cm) and \( R_{\text{DARK}} \) (16 mg CL\(^{-1}\) cm) were the observed ratios of DOC to \( A_{254} \) losses during incubations under UV and dark conditions respectively. A discussion of the assumptions and sensitivities of the mixing model results are found in Appendix A.

### 3.7 Statistical analysis

All statistical analysis was performed in MatLab R2011b. Individual and multiple regressions of with lake DOC composition (SUVA along with the five PARAFAC components) as dependent variables and \( f_P \) and \( \delta^{18}O \) as independent variables were run, reporting \( F \), \( R^2 \), adjusted \( R^2 \) and \( p \) values. Both the \( p \) value for the overall model and for the individual independent variables are reported for multiple regressions. Analysis of covariance (ANCOVA) was used to assess whether lake characteristics (burned/unburned areas or fine/coarse textures settings) influenced the slope of the relationship between lake SUVA and Ec or \( \delta^{18}O \). ANCOVA was also used to assess if the relationship between DOC concentrations in 2003 and 2012 were affected by whether the lake was within or outside the recent fire perimeter. The curve fitting toolbox was used to fit least-square regressions (Levenberg-Marquandt) to CO\(_2\) production time-series, and all reported regressions had \( R^2 > 0.99 \).
4 Results

4.1 Terrestrial DOC sources

Water samples from peatland wells had lower Ec and pH and higher DOC concentrations, $A_{254}$ and SUVA than mineral wells, while $\delta D$ and $\delta^{18}O$ did not differ between peatland and mineral wells (Table 2). Peatland wells also had higher contributions of the $C_C$ and $C_X$ PARAFAC components than mineral wells, while $C_T$ was nearly absent in peatland wells (Fig. 3a). Components $C_A$ and $C_M$ did not differ between peatland and mineral wells. Whether peatland or mineral wells were located within or outside the fire perimeter did not affect water chemistry or DOC composition, including PARAFAC components.

The rhizon depth profiles showed that burned and unburned peatlands had similar patterns of decreasing DOC concentrations above the water table but that unburned peatlands had lower SUVA near or above the water table (Fig. 4). Using rhizon location in relation to the water table rather than to the peat surface led to depth profiles for DOC concentration and SUVA that were similar across hollow and hummock profiles. The water table was located on average $8.5 \pm 7.0$ ($\pm 1 \sigma$) cm below the peat surface adjacent to rhizon profiles in hollows and $31.5 \pm 10.5$ cm below the surface for hummock profiles, with no differences among sampling occasions or between the burned and unburned peatlands (Two-way ANOVA, all $p > 0.05$).

4.2 Lake water chemistry and DOC characteristics

Sampled lakes exhibited a large variability in water chemistry, with averages of Ec: $133 \pm 70 \mu \text{Scm}^{-1}$, pH: $7.99 \pm 0.95$, DOC: $35.7 \pm 13.3 \text{mg C L}^{-1}$, $\delta D$: $-100.8 \pm 6.7$‰ and $\delta^{18}O$: $-9.00 \pm 1.38$‰ (all data represents averages $\pm 1 \sigma$). Concentrations of DOC measured in 2003 were similar to DOC concentrations in 2012, suggesting no effect of the 2011 fire (Fig. 5). Lakes in fine-textured settings had significantly higher DOC concentrations than lakes in coarse-textured settings (averages of 42.5 and 24.1 mg CL$^{-1}$,
t test: p < 0.001), but lake setting did not significantly influence lake Ec, pH, δD or δ18O. With regards to a mixing of terrestrial sources, lakes generally had Ec and DOC concentrations intermediate to observations in mineral and peatland wells, while lake pH, δD and δ18O were higher than values observed in wells. Enriched lake δD and δ18O relative to water sources along with deviation from the local meteoric water line suggest evaporative isotopic enrichment (Fig. 6).

Lakes also exhibited a large variability in DOC composition, with systematic differences between lakes in fine and coarse-textured settings. Average lake SUVA among all lakes was 2.00 ± 0.48 LmgC⁻¹m⁻¹, with higher estimates for lakes in fine-textured than coarse-textured settings (averages at 2.19 and 1.64 LmgC⁻¹m⁻¹, respectively, t test: p < 0.001). Lakes in fine-textured settings also had higher C_C, C_A, C_X and C_M than lakes in coarse-textured settings, while C_T was lower (Fig. 3a). Variation in lake SUVA was significantly related to both lake Ec and δ18O, where lake hydrogeological setting altered the relationship between lake SUVA and Ec (Fig. 7). Lake f_P (see below), which takes into account the difference in mineral groundwater Ec between fine and coarse-textured settings to estimate the relative contribution of peatland water, had significant relationships with all DOC composition indices (Table 3). Multiple regressions showed that lake DOC composition, particularly SUVA, C_C and C_X, were best described by models that included both f_P and δ18O. Whether lakes were located within or outside the recent fire-perimeter did not affect any of the lake DOC composition indices, neither on its own nor in combination with f_P and δ18O (not shown).

4.3 Well and lake DOC incubations

There was no difference in DOC concentration between lake and well samples that were acidified/filtered at the time of sampling versus those that had been filtered only (pair-wise t test, p = 0.35), suggesting that there was no significant DOC degradation in the filtered samples prior to the start of the incubation experiment.
Changes in DOC concentrations during dark incubations found that mineral well DOC was more readily lost than DOC from peatland wells (4.8 ± 4.2 % loss versus −0.5 ± 2.5 % loss, respectively: t test, p = 0.015) (Fig. 8). Loss of DOC from lake samples was also low at 0.10 ± 2.7 %. Neither hydrogeological setting nor fire history influenced loss of DOC during dark incubations from lake samples. There was a weak but significant relationship between sample SUVA and DOC loss during dark incubations across all incubations ($R^2 = 0.06$, $n = 51$, $p = 0.04$), but the relationship was not consistent with results from a similar incubation of soil leachates (Olefeldt et al., 2013) (Fig. 9a). Losses of DOC during UV incubations were lower than during dark incubations for mineral well samples, −2.0 ± 2.7 % (i.e. UV − dark incubation losses), while UV incubation significantly enhanced losses for peatland DOC, +13.9 ± 3.5 %. The difference between DOC losses during UV and dark incubations was strongly related to sample initial SUVA among all samples (Fig. 9b). Again, neither lake setting nor fire history affected the difference between UV and dark incubation DOC losses.

Production of CO$_2$ from lake samples was similar in magnitude to DOC losses during both dark and UV incubations (pair-wise t test, $n = 76$, $p = 0.23$), though DOC losses were more variable likely due to larger measurement error of DOC concentrations than CO$_2$ production (Fig. 8). For mineral wells the production of precipitate, likely calcium carbonate, yielded CO$_2$ uptake rather than release, and their CO$_2$ production was therefore not considered further. For peatland well samples, CO$_2$ production was lower than DOC losses during UV incubations (7.0 ± 1.1 % loss versus 14.3 ± 2.5 % loss respectively; pairwise t test, $n = 12$, $p < 0.001$), suggesting substantial production of particulate organic carbon (Fig. 8). The double exponential fit to CO$_2$ production time-series estimated that 1.1 % of the DOC pool in lake and peatland well samples was labile during dark incubations and had a half-life of 3.3 days, while the stable pool had a half-life of 5500 days. During UV incubations lakes and peatland samples had labile fractions at 3.0 and 6.6 %, respectively, with common half-lives of 4.8 days and 460 days, respectively, for the labile and stable DOC pools.
Lake and well samples exhibited decreasing SUVA during UV incubations (pair-wise $t$ test, $p < 0.001$), while SUVA remained stable during dark incubations ($p = 0.31$). Decreased SUVA during UV incubations was a result of consistently more rapid $A_{254}$ loss than DOC loss (16.4% versus 5.3% losses on average, respectively, across all samples). Only minor changes were found for PARAFAC components during dark incubations, while $C_C$, $C_X$ and $C_M$ decreased and $C_T$ increased during UV incubations (Fig. 3b).

### 4.4 Mixing model results

Mixing model results suggested that peatland water was the dominant input to lakes in fine-textured settings (average $f_P = 0.93$), while mineral waters made a substantial contribution to lakes in coarse-textured settings (average $f_P = 0.58$) (Table 4). Peatlands were thus estimated to account for 98% of terrestrial DOC inputs to lakes in fine-textured settings on average and 79% of inputs to lakes in coarse-textured settings. Assuming conservative behaviour of DOC, the mixing model estimated lake DOC concentrations that were on average 33 mg CL$^{-1}$ higher than those observed, i.e. suggesting that on average 46% of terrestrial DOC inputs to lakes had been removed through within-lake processes (Table 4). Analogously the mixing model estimated that $A_{254}$ had been reduced by 68% on average.

Partitioning of the total within-lake DOC losses using $R_{DARK}$ and $R_{UV}$ suggested that biodegradation was responsible for 12% of within-lake losses of total terrestrial DOC inputs (8.6 mg CL$^{-1}$), while UV mediated degradation was responsible for 35% (25.0 mg CL$^{-1}$). Hence, three quarters of within-lake losses were attributed to UV-mediated processes. Partitioning of estimated within-lake DOC losses were not affected by lakes being located within or outside the recent fire perimeter. Losses attributed to UV-mediated processes increased with higher lake $\delta^{18}$O ($R^2 = 0.29$, $n = 30$, $p < 0.001$), while both total losses and dark losses were unaffected by $\delta^{18}$O.
5 Discussion

5.1 Links between mixing of terrestrial DOC sources and lake DOC composition and biodegradability.

Much of the variability in DOC composition among lakes could be attributed to the mixing of DOC from shallow peatland groundwater and from deeper mineral sources. In other regions it has been shown that DOC aromaticity in rivers increases with increased peatland catchment cover (Ågren et al., 2008; Olefeldt et al., 2012). However, in our study region it is difficult to assess lake water sources using ecosystem configuration within topographically delineated catchments due to deep and heterogenous glacial deposits and complex groundwater hydrology (Devito et al., 2005). For example, we observed large variability in lake DOC aromaticity even for lakes completely surrounded by peatlands (SUVA ranging between 1.3 and 2.9 L mg C$^{-1}$ m$^{-1}$). Instead, we used Ec as a conservative tracer to assess the relative contribution from different water sources, with lake water constituting a mix of mineral groundwater with high Ec and peatland runoff with low Ec. The mixing model took into account that mineral groundwater in fine textured mineral soils have higher Ec than in coarse textured soils. Peatland contribution to lake water, $f_P$, was most strongly related to DOC composition as indicated by SUVA and by PARAFAC components $C_C$ and $C_X$ ($R^2$ between 0.59 and 0.55). These DOC composition indices also had the largest differences between peatland and mineral sources, further emphasizing that a mixing of terrestrial sources is a primary control on lake DOC composition.

The two primary sources of terrestrial DOC to lakes in the study region, shallow peatland groundwater and deep mineral groundwater, differed both in terms of DOC composition and biodegradability. Peatland well DOC had lower biodegradability than mineral well DOC, possibly due to higher aromaticity (as indicated by SUVA), higher humic/fulvic acid contributions (PARAFAC components $C_C$ and $C_X$) and lower protein contribution to the DOC pool (PARAFAC component $C_T$) (cf. Kalbitz et al., 2003a). Similar differences between DOC biodegradability and composition has been observed in
sub-arctic Alaska where peatland thermokarst DOC had lower biodegradability along with lower protein-type fluorescence and higher SUVA than DOC samples from groundwater springs (Balcarczyk et al., 2009).

Biodegradability of mineral well DOC was, however, much lower than that of leachates from surface soils, despite similar SUVA values and PARAFAC characteristics (Olefeldt et al., 2013). Hence, DOC composition as determined through absorbance/fluorescence techniques cannot be used to indicate DOC biodegradability universally. Although strong relationships have been found between DOC composition and biodegradability for leachates from organic soils, fresh litter and live vegetation (cf. Kalbitz et al., 2003; Olefeldt et al., 2013), several studies including this study suggest that such relationships are altered or lost when DOC composition has been affected by photodegradation or selective adsorption/desorption in mineral soils (Moran et al., 2000; Holmes et al., 2008; Roehm et al., 2009). Non-aromatic DOC compounds have weak absorbing and fluorescing properties and are thus poorly characterized in optical DOC composition indices, yet may have a wide variability in biodegradability. For example, DOC in surface soil leachates has a high contribution of highly biodegradable aliphatic carbohydrates (Kalbitz et al., 2003a), while non-aromatic DOC in mineral soils is more likely related to microbial exudations and resulting from selective absorption/desorption processes (Kothawala et al., 2012a) and non-aromatic DOC following exposure to UV-light is partly derived from lignin compounds (Benner and Kaiser, 2011).

Lake DOC biodegradability was low for all lakes (ranging between 0.3 and 2.1% DOC loss as measured by CO₂ production) and was not related to observed DOC composition or the estimated relative contribution of mineral/peatland waters. Thus there was no indication that lake DOC with a greater contribution from mineral groundwater sources had higher biodegradability. A long term dark incubation study found that initial decay of DOC from clearwater lakes was higher than for brownwater lake DOC, but that this difference disappeared after 5 months and that cumulative losses over 3.5 yr were similar (~35%) across lakes regardless of initial DOC composition (Koehler et al.,...
2012). Since the lakes in our study region have long residence times, it is possible that initial differences in biodegradability between different sources have converged.

We estimated using a mixing-model that 46% of terrestrial DOC inputs into the sampled lakes on average had been lost due to within-lake processes. Although the 11 day biodegradability of lake DOC was low in this study, long term incubations of lake DOC suggest that microbial degradation in lakes with long water residence time could be responsible for the majority of within-lake terrestrial DOC losses (35% losses over 3.5 yr; Koehler et al., 2012). However, both short and long term dark incubations cause only minor changes in DOC composition, including minor increases in aromaticity (Kothawala et al., 2012b; Olefeldt et al., 2013). In contrast, all sampled lakes, including those completely dominated by peatland DOC inputs, had lower aromaticity and lower $C_C$ and $C_X$ fluorescence than observed in peatland DOC. These patterns in lake DOC composition strongly suggest that UV-mediated processes could contribute significantly to within-lake degradation of terrestrial DOC.

### 5.2 Support for significant contribution of UV mediated processes to within-lake loss of terrestrial DOC

Incubations under UV conditions influenced DOC loss in several ways compared to under dark conditions. The difference between DOC losses during UV and dark incubations was strongly related to initial sample SUVA, causing substantially increased losses during UV incubations for peatland well DOC while losses decreased slightly for mineral well DOC. Reduced DOC loss during UV incubations for samples of low aromaticity has previously been observed (Tranvik and Bertilsson, 2001), possibly linked to the damaging effects of UV light on microbes in the absence of UV attenuation. Mineralization dominated lake DOC losses during UV incubations as estimates of CO$_2$ production and change in DOC concentration yielded equal estimates. Contrary, during UV incubations peatland samples had change in DOC concentrations that suggested much greater DOC losses than estimated through CO$_2$ production, indicating
substantial production of particulate organic carbon either through increased microbial biomass or UV-mediated flocculation (von Wachenfeldt et al., 2008).

Photochemical transformations are related to the total amount of absorbed UV radiation (Bertilsson and Tranvik 2000). Because DOC concentrations were standardized at the start of the incubations, sample with higher SUVA in our incubations also had higher $A_{254}$ and therefore absorbed more UV light. Thus DOC concentration and composition may not be related to the rate of UV-mediated DOC removal in lakes but rather regulate the depth over which UV processes occur. In humic freshwater lakes, UV attenuation is strongly linked to DOC concentration with approximate depths for 99% attenuation of UV-B radiation at 4 and 40 cm for lakes with 60 and 10 mg CL$^{-1}$ DOC concentrations, respectively (Arts et al., 2000). Although UV-mediated removal is restricted to shallow surface layers, the substantially increased rates of degradation during UV incubations along with the fact that most of the sampled lakes are shallow ($\sim$ 1–2 m) and remain well mixed throughout summers suggests UV-mediated removal may still contribute significantly to within-lake losses of terrestrial DOC.

Observed changes in DOC composition during UV incubations are consistent with previous studies that have shown that photodegradation acts primarily on aromatic DOC, causing both mineralization, flocculation (von Wachenfeldt et al., 2008) and production of LMW acids that subsequently become available for microbial degradation (Bertilsson and Tranvik 2000; Obernosterer and Benner 2004; Brinkmann 2003). Peatland DOC exhibited substantial decreases in SUVA and PARAFAC components $C_C$ and $C_X$ (associated with HMW humic and fulvic acids) but increases in $C_T$ (associated with amino acids) during UV incubations. As a result of these changes, peatland DOC composition at the end of the UV incubations resembled the initial composition of lake DOC, particularly for profiles of the PARAFAC components.

Long residence times of water in lakes of the study region cause evaporation to be an important part of the water balance of lakes, even in groundwater flow-through systems (Smerdon et al., 2005; Ferone and Devito, 2004). Variability in observed evaporative enrichment of $\delta^{18}$O and $\delta^D$ in lakes relative to sources can therefore be assumed to
serve as a relative measure of lake water residence times. Lake with more highly enriched $\delta^{18}$O, indicating longer residence time, also had DOC composition indices consistent with shifts observed during UV incubations of peatland DOC, including lower SUVA, $C_C$ and $C_X$. Thus, observed lake DOC composition appeared to be a function of both the relative contribution from different terrestrial sources along with a variable degrees of within-lake photodegradation related to residence time. The incubation further showed that such changes in DOC composition were concurrent with significant DOC loss. The mixing model estimated that three quarters of the total within-lake DOC loss was due to UV-mediated processes, with the remainder due to microbial degradation alone. Although the mixing model was based on several assumptions, we consider the finding that UV-mediated degradation play an important role for within-lake losses in the study region to be robust with regards to those assumptions, see Appendix.

Taken together, this study presents several independent results that are consistent with substantial contribution of UV-mediated degradation of aromatic DOC for within-lake losses of terrestrial DOC. Estimates of the contribution of UV light to total lake CO$_2$ emissions in humic Swedish lakes has been estimated to $\sim$ 10 $\%$, but these estimates include the CO$_2$ emissions due to the rapid turnover of autochtonous DOC and may therefore underestimate the importance of UV-mediated degradation of allochtonous DOC (Graneli et al., 1996; Jonsson et al., 2001). Lakes in our study region appear to have characteristics that enhance UV-mediated losses over microbial processes alone. This includes shallow water depths ($<2$ m) that promote mixing and exposure of DOC to UV light, along with a sub-humid climate that in combination with regional hydrogeology result in lakes primarily receiving highly aromatic peatland DOC which is poorly biodegradable but susceptible to photodegradation. Hence, our study region may represent a region where UV-mediated processes are relatively more important for within-lake losses of terrestrial DOC than in other regions.

Whether aquatic turnover of terrestrial DOC is primarily driven by old or modern C sources is not well known. While labile DOC sources linked to recent terrestrial primary production has been modelled to dominate aquatic C cycling in a Swedish lake despite
representing only a small fraction of lake inputs (Berggren et al., 2010), microbially resired CO₂ from lakes in Quebec has been shown to be highly aged (McCallister and del Giorgio, 2012). Our results show that highly aromatic peatland DOC, which likely has an aged component (Garnett et al., 2012), is poorly biodegradable but rapidly mineralized once exposed to UV light. Thus aged organic matter that is stable in terrestrial ecosystems can rapidly become mineralized once entering aquatic ecosystems.

5.3 Influence of wildfire on terrestrial DOC sources and aquatic DOC cycling

Wildfire has been found to have varying impacts on catchment DOC export and lake DOC concentrations and biodegradability in different regions. While Alaskan catchments had decreased DOC export following wildfire (Betts and Jones, 2009), no change in DOC export was found for catchments on the boreal shield in Quebec (Lamontagne et al., 2000). Comparative studies in the foothills and sub-arctic eco-regions of central and northern Alberta, respectively, found that average DOC concentrations were 40–50 % higher in lakes with recently burned surroundings compared to nearby lakes with unburned surroundings (McEachern et al., 2000; Allen et al., 2003). In our study region there was no influence of wildfire on lake DOC concentrations, but URSA differs significantly from the other studied regions in Alberta with regards to topography, dominant ecosystems and runoff. Lakes on the boreal shield of Quebec were also found to not be influenced by wildfire with regards to DOC concentrations (Carignan et al., 2000). However, Marchand et al. (2009) found that wildfire increased lake DOC biodegradability in Quebec, something we did not observe in this study. It remains an open question whether these contrasting results can be reconciled into a single framework by considering regional characteristics (e.g. climatic controls on hydrology), local characteristics (e.g. surface geology and dominant ecosystems) and fire characteristics (e.g. severity and timing) (cf. Pinoul-Allel et al., 2002; Devito et al., 2005; Turetsky et al., 2010).

The strongest potential for wildfire to alter linkages between terrestrial and aquatic C cycling in the study region is by altering the magnitude or composition of peatland
DOC export, given the importance of peatland DOC sources across all lakes. Upland ecosystems in the study region rarely generate hillslope runoff (Redding and Devito, 2008) and are thus assumed to contribute negligible DOC inputs to lakes. In the absence of DOC export from forested hillslopes, peatlands dominated terrestrial DOC export to lakes in fine-textured settings and was complemented by a minor fraction of DOC from mineral groundwater sources to lakes in coarse-textured settings.

Wildfire did not alter composition or biodegradability of mineral well DOC in this study, likely due to the processes of selective absorption, degradation and desorption that affect DOC composition as it slowly cycles downwards in mineral soils (Kaiser and Kalbitz, 2012). In contrast, a recent study showed that DOC leached from surface peat collected in burned peatlands had higher aromaticity and lower biodegradability than leachates from unburned bogs (Olefeldt et al., 2013). The peatland pore-water profiles in this study did also find that DOC near the peat surface had higher SUVA in burned than unburned peatlands but that this effect was smaller or insignificant at and below the water table. Both the production of highly aromatic char and the removal of live *Sphagnum* moss could explain the change in DOC composition. Live *Sphagnum* moss is a known source of highly biodegradable DOC (Wickland et al., 2007), and near-surface sources are known to contribute to downstream peatland DOC export during snowmelt and following rain events when the water table is high, resulting in reduced aromaticity (Austnes et al., 2010; Olefeldt and Roulet, 2012). However, peatland DOC export is generally dominated by DOC with characteristics similar to those observed in the peatland wells in this study (Ågren et al., 2008), i.e. with high aromaticity and low biodegradability regardless of fire history. While there was large variation among lakes in DOC concentration, composition and biodegradability, none of this variation could be attributed to lakes being located within or outside the recent fire perimeter. Hence, although wildfire created a potential for altered downstream export by altering near-surface peatland DOC sources, the lack of a signal in lake DOC composition suggests that peatland export is dominated by DOC from deeper peat layers below the water table that were not altered by wildfire.
6 Conclusions

Several approaches were used to understand the mixing of terrestrial DOC sources and the relative importance of microbial versus UV-mediated processes for within-lake DOC losses in a boreal region partly affected by a recent wildfire. Peatland well DOC was poorly biodegradable and had high contributions from aromatic humic and fulvic acids that drastically increased losses during UV incubations as a result of both increased mineralization and flocculation. Mineral well DOC had lower aromaticity and higher contribution of amino acids than peatland DOC and accordingly had higher dark incubation losses and lower sensitivity to photodegradation. Lake water chemistry and DOC composition suggested that peatlands completely dominated terrestrial DOC inputs to lakes in fine-textured settings while mineral DOC made a minor contribution to lakes in coarse-textured settings. Lake DOC composition was, however, further influenced by water residence time, showing trends consistent with altered DOC composition of peatland DOC during UV-incubations. We used a simple mixing model to estimate that nearly half of terrestrial DOC inputs to our lakes had been removed from the lake water column, with three quarters of the removal attributed to UV-mediated processes. Wildfire was not found to influence lake DOC concentrations, composition or DOC losses during either dark or UV incubations. We argue that the resistance of terrestrial-aquatic C linkages to change following wildfire in this region is a result of how regional and local characteristics cause lakes to predominately receive and selectively process highly aromatic DOC derived from deeper peat layers just below the water table where wildfire did not alter DOC characteristics. As wildfire did alter DOC composition above the water table, it is possible that wildfire influences terrestrial-aquatic C links to a greater degree in regions where near surface sources are relatively more important for lake C cycling.
Appendix A

Mixing model assumptions and sensitivities

The results from the mixing model is dependent on both the constants used (DOC_P, DOC_M, A_254P, A_254M, EC_P, EC_M, R_DARK and R_UV) as well as a number of implicit assumptions. The mixing model is used in three steps, first to calculate f_P and f_M, next to calculate DOC_Δ and A_254Δ and lastly to partition DOC_Δ into DOC_ΔUV and DOC_ΔDARK – and each step is associated with specific assumptions.

Using the mixing model to calculate f_P and f_M using a two end-member mixing model assumes that Ec mixes conservatively, that end-members are properly characterized and that no other end-members make a significant contribution. Some non-linearity in the mixing of Ec has been shown for samples with high conductivities. Acid-base reactions mean that H^+ in low pH samples are neutralized when mixed with near neutral mineral groundwater, which could further lead to non-linearity when mixed. However, neither effect is large and cannot be considered to significantly affect the results (McClesky et al., 2011). While peatland wells had Ec within a narrow range, 57 ± 14 µScm⁻¹, there was a much broader range for observed mineral well Ec, 1155 ± 833 µScm⁻¹. However, a wider set of mineral wells have been regularly sampled within URSA, and have found that mineral wells in the fine-textured settings have Ec that is significantly higher than for wells in coarse-textured regions (~1000 and ~200 µScm⁻¹, respectively) (Ferone, 2001; Gibbons, 2003). Hence, while local differences in mineral groundwater Ec introduce errors for individual lakes, overall among lakes we assume no bias. Direct input to lakes from precipitation can be an important water source to lakes in the region, regardless of landform (Ferone and Devito, 2004; Smerdon et al., 2005), inputs that cause a dilution on lake Ec. However, precipitation inputs are generally balanced by evaporation losses in the region, although with large inter-annual variability that is reflected in lake levels. Over the year prior to sampling, only minor changes to lake levels were observed and we therefore assume...
that precipitation and evaporation have been equal and precipitation can thus be disre-
garded in the mixing model.

In order to estimate DOC$_\Delta$, it is assumed that peatland and mineral DOC contribu-
tions dominate the DOC pool in lakes. Autochthonous inputs derived from lake primary
production are thus assumed negligible. Although lake primary production primarily re-
results in particulate organic matter, autochthonous DOC production is likely high also. However, rapid turnover of autochthonous DOC mean that its concentrations remain
relatively low. The fraction of lake DOC that is autochtonous increases in lakes with
higher productivity and with lower terrestrial inputs. Using the empirical relationship
between lake Chl a (data from Sass et al., 2008) and $A_{440}$ (data from this study) pre-
presented by Bade et al. (2007), we estimate that autochthonous DOC represents < 10 %
of the total DOC pool in all but three of the sampled lakes. Thus, even though the
lakes are eutrophic, their high $A_{440}$ indicates that terrestrial DOC sources dominate.
The three lakes where autochthonous contribution was estimated to be higher (10–
25 %) were all located in coarse-textured settings. The generally low contribution of
autochthonous DOC means that it will have a low influence on DOC$_\Delta$, but would mean
that our reported DOC$_\Delta$ estimated are slightly underestimated.

In partitioning DOC$_\Delta$ into dark microbial and UV-mediated losses, the main assump-
tion is that we have properly characterized $R_{DARK}$ and $R_{UV}$ through our relatively short
incubation experiments. In our incubation experiments (using pooled data from this
study and from Olefeldt et al., 2013, which used an identical experimental design)
we observed higher ratios of DOC to $A_{254}$ losses during dark, $63.3 \pm 13.3$ (95% CI
of slope) mgCL$^{-1}$ cm, than during UV incubations, $16.3 \pm 2.6$ mgCL$^{-1}$ cm (Fig. A1).
We used the difference between UV and dark losses to arrive at $R_{UV}$, since this
would represent the additional losses associated with UV-processes. Selective loss of
absorbance during UV exposure is well known (Moran et al., 2000; Benner and
Kaiser, 2011), but no comparative estimates of $R_{UV}$ was found in the literature. For
long term (3.5 yr) dark incubations of lake DOC, Kothawala et al. (2012b) report $R_{DARK}$
of 30 mgCL$^{-1}$ cm, i.e. lower than observed in our incubations but still higher than our
Lower $R_{\text{DARK}}$ for a long term than short term incubations is consistent with selective rapid losses of non-aromatic DOC early during incubations. Depending on the residence time of DOC in lake water, we could have overestimated $R_{\text{DARK}}$ in the mixing model. Changing $R_{\text{DARK}}$ from 63 to 30 mgCL$^{-1}$ cm in the mixing model reduces the importance of UV-mediated processes from 76 to 62% of DOC$_{\Delta}$, i.e. it does not alter the conclusion that UV-mediated processes are likely to be responsible for a majority of within-lake losses of terrestrial DOC.

We also assessed the uncertainties of mixing model results using a boot strap analysis with 95% confidence intervals of constants used in the model: Ec$_{\text{M}}$ (1000 ± 500 for lakes in a fine textured setting and 200 ± 50 for lakes in coarse textured settings), Ec$_{\text{P}}$ (55 ± 24 µScm$^{-1}$), DOC$_{\text{M}}$, DOC$_{\text{P}}$ (19 ± 15 and 82 ± 35 mgCL$^{-1}$ respectively), $A_{254\text{M}}$, $A_{254\text{P}}$ (0.15 ± 0.05 and 3.03 ± 0.25 cm$^{-1}$) and $R_{\text{DARK}}$ and $R_{\text{UV}}$ as noted above. Applying the bootstrap analysis on a hypothetical lake with characteristics defined by the median observations among lakes in fine-textured settings (Ec = 129 µScm$^{-1}$, DOC = 47 mgCL$^{-1}$ and $A_{254} = 1.05$ cm$^{-1}$), we found that 90% of the 3000 configurations yielded results within the ranges 0.05–0.15 for $f_{\text{P}}$, 50–103 mgCL$^{-1}$ for DOC$_{\text{Est}}$, 3–56 mgCL$^{-1}$ for DOC$_{\Delta}$, −14 to 18 mgCL$^{-1}$ for DOC$_{\Delta\text{DARK}}$ and 15–43 mgCL$^{-1}$ for DOC$_{\Delta\text{UV}}$. Similar estimates for a hypothetical lake with medium characteristics of lakes in coarse textured settings (Ec = 115 µScm$^{-1}$, DOC = 27 mgCL$^{-1}$ and $A_{254} = 0.43$ cm$^{-1}$) were 0.41–0.71 for $f_{\text{P}}$, 35–76 mgCL$^{-1}$ for DOC$_{\text{Est}}$, 9–50 mgCL$^{-1}$ for DOC$_{\Delta}$, −4 to 21 mgCL$^{-1}$ for DOC$_{\Delta\text{DARK}}$ and 10–32 mgCL$^{-1}$ for DOC$_{\Delta\text{UV}}$. Hence, although uncertainties of the constants cause large uncertainties of the results, the main conclusions of the mixing model remain robust.

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References


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Table 1. Description of DOC fluorescence components identified by PARAFAC analysis.

<table>
<thead>
<tr>
<th>Component</th>
<th>Ex&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>Em (nm)</th>
<th>Description</th>
<th>Primary Peaks&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Probable sources&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_C$</td>
<td>&lt;240, 330</td>
<td>444</td>
<td>UV-A/C fulvic/humic, HMW</td>
<td>A + C</td>
<td>T</td>
</tr>
<tr>
<td>$C_A$</td>
<td>&lt;240</td>
<td>432</td>
<td>UV-A fulvic, HMW</td>
<td>A</td>
<td>T</td>
</tr>
<tr>
<td>$C_X$</td>
<td>255, 380</td>
<td>522</td>
<td>UV-A/C fulvic/humic HMW</td>
<td>–</td>
<td>T</td>
</tr>
<tr>
<td>$C_M$</td>
<td>&lt;240, 305</td>
<td>396</td>
<td>UV-A/C fulvic/humic LMW</td>
<td>A + M</td>
<td>T, A, M</td>
</tr>
<tr>
<td>$C_T$</td>
<td>&lt;240, 275</td>
<td>336</td>
<td>Amino acids; Tryptophan and Tyrosine, free or bound in protein</td>
<td>T + B</td>
<td>T, A, M</td>
</tr>
</tbody>
</table>

<sup>a</sup>Wavelengths in bold indicate secondary maxima.

<sup>b</sup>See Coble (1996) and Fellman et al. (2010) for further details on primary fluorescing peaks.

<sup>c</sup>T – terrestrial, plant or soil organic matter, A – autochtonous production, M – microbial processing
**Table 2. Water chemistry of terrestrial DOC sources. Averages ± 1 σ.**

<table>
<thead>
<tr>
<th></th>
<th>Mineral wells</th>
<th>Burned area n = 4</th>
<th>Unburned area n = 5</th>
<th>Burned area n = 9</th>
<th>Unburned area n = 4</th>
</tr>
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<tbody>
<tr>
<td><strong>Ec (μS cm⁻¹)</strong></td>
<td>1310 ± 820⁻ᵃ</td>
<td>1042 ± 780⁻ᵃ</td>
<td>594 ± 145</td>
<td>541 ± 110</td>
<td></td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>7.32 ± 0.37</td>
<td>7.46 ± 0.24</td>
<td>4.76 ± 1.22</td>
<td>4.27 ± 0.80</td>
<td></td>
</tr>
<tr>
<td><strong>δ¹⁸O (‰)</strong></td>
<td>-18.7 ± 0.97</td>
<td>-19.0 ± 0.46</td>
<td>-18.1 ± 1.19</td>
<td>-18.1 ± 1.19</td>
<td></td>
</tr>
<tr>
<td><strong>δ¹⁸O (‰)</strong></td>
<td>-19.0 ± 0.46</td>
<td>-18.1 ± 1.19</td>
<td>-18.1 ± 1.19</td>
<td>-18.1 ± 1.19</td>
<td></td>
</tr>
<tr>
<td><strong>δ¹⁸O (‰)</strong></td>
<td>-19.0 ± 0.46</td>
<td>-18.1 ± 1.19</td>
<td>-18.1 ± 1.19</td>
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<tr>
<td><strong>δ¹⁸O (‰)</strong></td>
<td>-19.0 ± 0.46</td>
<td>-18.1 ± 1.19</td>
<td>-18.1 ± 1.19</td>
<td>-18.1 ± 1.19</td>
<td></td>
</tr>
<tr>
<td><strong>DOC (mgCl⁻¹)</strong></td>
<td>16.6 ± 7.3</td>
<td>28.3 ± 11.4</td>
<td>88.6 ± 18.8</td>
<td>88.6 ± 18.8</td>
<td></td>
</tr>
<tr>
<td><strong>A²₅₄ (cm⁻¹)</strong></td>
<td>0.15 ± 0.07</td>
<td>0.19 ± 0.06</td>
<td>0.19 ± 0.06</td>
<td>0.19 ± 0.06</td>
<td></td>
</tr>
<tr>
<td><strong>SUVA (L mg C⁻¹ m⁻¹)</strong></td>
<td>0.89 ± 0.11</td>
<td>0.69 ± 0.11</td>
<td>0.69 ± 0.11</td>
<td>0.69 ± 0.11</td>
<td></td>
</tr>
</tbody>
</table>

⁻ᵃ Mineral well Ec was influenced by soil texture, see text.
Table 3. Regression analysis where lake DOC composition indices (SUVA along with the five PARAFAC components) are dependent variables while \( f_P \) (indicating relative contribution from peatland and mineral DOC sources to lakes) and \( \delta^{18}O \) (a proxy for lake water residence time) are continuous independent variables.

<table>
<thead>
<tr>
<th>Model</th>
<th>( R^2 )</th>
<th>Adj. ( R^2 )</th>
<th>( F )</th>
<th>Overall p</th>
<th>( f_P )</th>
<th>( \delta^{18}O )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUVA ( (\text{L mg C}^{-1} \text{m}^{-1}) ) =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = 0.65 + 1.63 \times f_P )</td>
<td>0.59</td>
<td>0.58</td>
<td>40.69</td>
<td>&lt; 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = 0.57–0.15 \times \delta^{18}O )</td>
<td>0.15</td>
<td>0.12</td>
<td>4.94</td>
<td>0.034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = −0.42 + 1.57 \times f_P – 0.12 \times \delta^{18}O )</td>
<td>0.69</td>
<td>0.67</td>
<td>30.41</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.006</td>
</tr>
<tr>
<td>( C_{C} ) (R.U. mgC(^{-1})L) =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = 0.001 + 0.072 \times f_P )</td>
<td>0.56</td>
<td>0.55</td>
<td>35.93</td>
<td>&lt; 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = 0.012–0.006 \times \delta^{18}O )</td>
<td>0.11</td>
<td>0.08</td>
<td>3.59</td>
<td>0.068</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = −0.032 + 0.069 \times f_P – 0.005 \times \delta^{18}O )</td>
<td>0.63</td>
<td>0.61</td>
<td>23.37</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.029</td>
</tr>
<tr>
<td>( C_{A} ) (R.U. mgC(^{-1})L) =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = 0.021 + 0.036 \times f_P )</td>
<td>0.34</td>
<td>0.31</td>
<td>14.25</td>
<td>&lt; 0.001</td>
<td></td>
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<tr>
<td>( = 0.005–0.005 \times \delta^{18}O )</td>
<td>0.18</td>
<td>0.15</td>
<td>6.17</td>
<td>0.019</td>
<td></td>
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</tr>
<tr>
<td>( = −0.032 + 0.069 \times f_P – 0.005 \times \delta^{18}O )</td>
<td>0.48</td>
<td>0.44</td>
<td>12.26</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.013</td>
</tr>
<tr>
<td>( C_{X} ) (R.U. mgC(^{-1})L) =</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>( = 0.002 + 0.047 \times f_P )</td>
<td>0.55</td>
<td>0.53</td>
<td>33.78</td>
<td>&lt; 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = 0.005–0.004 \times \delta^{18}O )</td>
<td>0.11</td>
<td>0.08</td>
<td>3.43</td>
<td>0.075</td>
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<tr>
<td>( = −0.024 + 0.046 \times f_P – 0.003 \times \delta^{18}O )</td>
<td>0.62</td>
<td>0.59</td>
<td>21.61</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.037</td>
</tr>
<tr>
<td>( C_{M} ) (R.U. mgC(^{-1})L) =</td>
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<td></td>
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</tr>
<tr>
<td>( = 0.018 + 0.029 \times f_P )</td>
<td>0.49</td>
<td>0.47</td>
<td>27.03</td>
<td>&lt; 0.001</td>
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<tr>
<td>( = 0.024–0.002 \times \delta^{18}O )</td>
<td>0.06</td>
<td>0.02</td>
<td>1.74</td>
<td>0.198</td>
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<td></td>
</tr>
<tr>
<td>( = 0.006 + 0.028 \times f_P – 0.001 \times \delta^{18}O )</td>
<td>0.52</td>
<td>0.49</td>
<td>14.78</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.194</td>
</tr>
<tr>
<td>( C_{T} ) (R.U. mgC(^{-1})L) =</td>
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<tr>
<td>( = 0.023–0.006 \times f_P )</td>
<td>0.13</td>
<td>0.10</td>
<td>4.18</td>
<td>0.051</td>
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</tr>
<tr>
<td>( = 0.030 + 0.001 \times \delta^{18}O )</td>
<td>0.14</td>
<td>0.11</td>
<td>4.67</td>
<td>0.039</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( = −0.032 + 0.069 \times f_P – 0.005 \times \delta^{18}O )</td>
<td>0.25</td>
<td>0.19</td>
<td>4.49</td>
<td>0.021</td>
<td>0.061</td>
<td>0.048</td>
</tr>
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</table>
Table 4. Variability of mixing model results among lakes within each hydrogeological setting. Averages ± 1 σ.

<table>
<thead>
<tr>
<th></th>
<th>Lakes fine-textured settings</th>
<th>Lakes coarse-textured setting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n = 16 )</td>
<td>( n = 11 )</td>
</tr>
<tr>
<td>( f_M )</td>
<td>0.07 (± 0.06)*</td>
<td>0.42 (± 0.30)*</td>
</tr>
<tr>
<td>( f_P )</td>
<td>0.93 (± 0.06)*</td>
<td>0.58 (± 0.30)*</td>
</tr>
<tr>
<td>( \text{DOC}_\text{Est} \ (\text{mgCL}^{-1}) )</td>
<td>78 (± 4)*</td>
<td>56 (± 19)*</td>
</tr>
<tr>
<td>( \text{DOC}_\Delta \ (\text{mgCL}^{-1}) )</td>
<td>36 (± 14)</td>
<td>29 (± 15)</td>
</tr>
<tr>
<td>( \text{DOC}_{\Delta \text{DARK}} \ (\text{mgCL}^{-1}) )</td>
<td>7 (± 11)</td>
<td>10 (± 7)</td>
</tr>
<tr>
<td>( \text{DOC}_{\Delta \text{UV}} \ (\text{mgCL}^{-1}) )</td>
<td>29 (± 4)*</td>
<td>20 (± 9)*</td>
</tr>
</tbody>
</table>

* denotes variables where there was a significant difference (\( t \) test, \( p < 0.05 \)) between lakes in fine and coarse-textured settings.
**Fig. 1.** Map of Utikuma Region Study Area (URSA) in north-central Alberta, Canada. Fire polygon retrieved from Canadian Forest Service (2011).
Fig. 2. Outline of peak locations for all five DOC fluorescence PARAFAC components. Outlines were drawn at equal excitation/emission loadings among components.
Fig. 3. Maximum fluorescing intensities ($F_{\text{max}}$) of the five PARAFAC components for terrestrial DOC sources and lake DOC. (A) Start of incubation PARAFAC component $F_{\text{max}}$ for lakes and wells, reporting averages ± 1 σ for 4 mineral wells, 11 peat wells, 19 lakes in fine textured settings and 11 lakes in coarse textured settings. (B) Comparison of average PARAFAC profiles at the start of the incubation versus after dark and UV incubations.
Fig. 4. Depth profiles of (A) SUVA and (B) DOC concentrations in an unburned and a burned bog. Averages ± 1 σ are shown for samples taken within each 10 cm depth segment. Significant differences (t test, p < 0.05) between burned and unburned bogs are indicated (*).
Fig. 5. Comparison of lake DOC concentrations in 2012 and 2003, where a subset of the lakes are located within a 2011 fire perimeter. Individual trendlines for lakes in burned and unburned areas were not different (ANCOVA, $F_{1,19} = 0.51, p = 0.52$) and a single trendline is shown.
Fig. 6. Isotopic signatures of mineral wells, peat wells and lake samples. Shown are also the global meteoric water line (GMWL, dashed), the local meteoric water line (LMWL) and a linear fit for all lake samples ($R^2 = 0.78$, $n = 30$, $p < 0.001$).
Fig. 7. Variability and relationships between water chemistry and SUVA for lakes and terrestrial sources, (A) Ec and (B) $\delta^{18}O$. Only significant ($p < 0.05$) relationships are shown with trend lines. Lakes in fine and coarse-textured settings had differing logarithmic relationships for SUVA/Ec (ANCOVA, $F_{1,26} = 4.45$, $p = 0.01$) while all lakes had a common linear relationship for SUVA/$\delta^{18}O$ ($F_{1,26} = 0.42$, $p = 0.52$).
Fig. 8. Production of CO$_2$ during dark and UV incubations of lake DOM samples, reported as a fraction of the initial DOC pool, compared to measurements of DOC loss, comparing initial and end of incubation DOC concentrations. Error bars indicate ± 1 σ, n = 30. Results from mineral well incubations not included since CO$_2$ production estimates were affected by calcium carbonate precipitation.
Fig. 9. Influence of SUVA on dark incubation losses (A) and the difference between UV and dark incubation losses (B). Data on dark DOC losses from surface peat leachates, to which the trendline is fitted, is from Olefeldt et al. (2013), where a similar incubation method was used.
Fig. A1. Relationships between DOC and $A_{254}$ losses during 11 day incubations. Data shown includes results both from this study and from Olefeldt et al. (in review) which used an identical experimental setup.