Influence of the permafrost boundary on dissolved organic matter characteristics in rivers within the Boreal and Taiga plains of western Canada

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Abstract

Catchment export of terrestrial dissolved organic matter (DOM) and its downstream degradation in aquatic ecosystems are important components of landscape scale carbon balances. In order to assess the influence of peatland permafrost on river DOM characteristics, we sampled 65 rivers along a 900 km transect crossing into the southern discontinuous permafrost zone on the Boreal and Tundra Plains of western Canada. Catchment peatland cover and catchment location north or south of the permafrost boundary were found together to have strong influences on dissolved organic carbon (DOC) concentrations and DOM chemical composition. River DOC concentrations increased with catchment peatland cover, but were consistently lower for catchments north of the permafrost boundary. In contrast, protein fluorescence (PARAFAC analysis), was unrelated to catchment peatland cover but increased significantly in rivers north of the permafrost boundary. Humic and fulvic acid contribution to DOM fluorescence was lower in rivers draining catchments with large lakes than in other rivers, consistent with extensive photodegradation, but humic and fulvic acid fluorescence were also lower in rivers north of the permafrost boundary than in rivers to the south. We hypothesize that shifts in river DOM characteristics when crossing the permafrost boundary are related to the influence of permafrost on peatland hydrological connectivity to stream networks, peatland DOM characteristics and differences in DOM degradation within aquatic ecosystems.

Keywords: dissolved organic matter, dissolved organic carbon, permafrost, peatlands, boreal, river, fluorescence

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1. Introduction

Downstream transport and aquatic mineralization of terrestrially derived dissolved organic matter (DOM) represents the fate of a large fraction of terrestrial net ecosystem productivity when considered over large spatial and temporal scales (Tranvik et al 2009). For individual boreal catchments, several factors are known to influence the concentrations and chemical composition of riverine DOM, including climate, topography, hydrogeology and land cover (Mattson et al 2005, Laudon et al 2011). Permafrost is common in high-latitude boreal catchments, and peatlands often are the only landscape units with permafrost in lowland regions of the southern discontinuous permafrost zone due to the thermal properties
of peat (Beilman et al. 2001, Ecosystems Classification Group 2007). While permafrost in upland catchments has been associated with increased stream concentrations of dissolved organic carbon (DOC) due to forced surficial hydrological flow-paths through organic-rich soil horizons (Petrone et al. 2006, Balcarczyk et al. 2009), it is less well understood how permafrost influences riverine DOM characteristics in catchments with extensive peatlands, and through which mechanisms (Frey and McClennand 2009).

Rivers draining catchments with extensive peatlands in boreal regions often have high DOC concentrations and high DOC aromaticity (Mattsson et al. 2005, Ågren et al. 2008). Peatlands generally have higher DOC export than upland ecosystems both due to large stores of DOC in thick organic soils and due to peatland runoff not being in contact with mineral soils where DOC otherwise is readily retained (Laudon et al. 2011, Kaiser and Kalbitz 2012). However, peatland DOC export varies significantly among regions with different climates and also depends on the local hydrological setting of individual peatlands (Creed et al. 2008, Olefeldt and Roulet 2012). The presence of permafrost in peatlands influences hydrological conditions, vegetation and C biogeochemistry (Johansson et al. 2006) and is therefore likely to also influence DOC export and DOM chemical composition. In western Canada, regions of widespread peatland permafrost are associated with ombrotrophic peatlands (peat plateaus) while minerotrophic peatlands (poor fens) dominate permafrost-free peatland areas further south (Vitt et al. 2000, Quinton et al. 2009). Recent climate change is causing deepening of the active layer and complete loss of permafrost in peatlands of the southern discontinuous permafrost zone in western Canada (Halsey et al. 1995, Quinton et al. 2009), and improved knowledge of the interactions between the presence of permafrost in peatlands and catchment DOC export is thus of importance for our understanding of the potential impacts of continued climate change on high-latitude C cycling.

The chemical composition of DOM varies among different terrestrial sources (Wickland et al. 2007), and rates of biodegradation, photodegradation and sedimentation of DOM in aquatic ecosystems have been associated with DOM chemical composition. For example, protein fractions of the DOM pool are rapidly mineralized microbially, while humic and fulvic acids generally are poorly biodegradable but can be mineralized, sedimented or transformed into bioavailable compounds through photochemical processes (Kalbitz et al. 2003, von Wachenfeldt et al. 2008, Sulzberger and Durisch-Kaiser 2009). Long water residence times in lakes allows for a substantial removal of terrestrial-source DOM and is accompanied by changes in aquatic DOM composition as a result of preferential removal of different types of organic compounds (Weyhenmeyer et al. 2012). Absorbance and fluorescence spectroscopy of DOM represents rapid and precise approaches for characterizing complex DOM mixtures (Weishaar et al. 2003, Stedmon and Bro 2008). Not all organic compounds have optical properties, fluorescence is for example primarily linked either to aromatic structures found in humic/fulvic acids or to specific amino acids, but the use of DOM absorbance and fluorescence characteristics can yield information on the origin, subsequent processing and biogeochemical properties of aquatic DOM (Fellman et al. 2010).

The objective of this study was to assess DOC concentrations and DOM chemical composition as assessed through optical properties among 65 rivers sampled along a transect crossing the permafrost boundary. The study region is located within a peatland-rich region in western Canada and the rivers were sampled during summer base-flow. We were primarily interested in exploring the potential interactions between catchment peatland cover and the presence or absence of permafrost in governing river DOM characteristics, but influences of catchment size and the presence of large lakes were also expected. By assessing the influence of permafrost on river DOM characteristics, this study yields information relevant for understanding how permafrost affects linkages between terrestrial and aquatic C cycling at high-latitude boreal catchments under current and future climates.

2. Study area

The study area is located within the Boreal and Taiga Ecoszones of Canada (Marshall et al. 1999) and stretches ~900 km between 54°N and 62°N (figure 1). The region has a sub-humid climate where annual precipitation (300–550 mm) is close to potential evapotranspiration (Devito et al. 2005), yielding low average annual catchment runoff (50–200 mm) with high inter-annual variation (HYDAT database, maintained by Environment Canada, www.ec.gc.ca). Mean annual air temperatures range between 1.0 °C in the south and −4.0 °C in the north. The region is located on sedimentary bedrock and its surface geology is dominated by thick tills and glaciolacustrine deposits. Upland forests transition from mixed forests into coniferous forests in the northern part, and common stand-forming species are white spruce (Picea glauca), balsam poplar (Populus balsamifera), balsam fir (Abies balsamea) and trembling aspen (Populus tremuloides). Peatlands in the region are either non-treed or dominated by open canopy black spruce (Picea mariana) or tamarack larch (Latrix laricina) stands. Peatlands north of the permafrost boundary shown in figure 1 are generally a mosaic of permafrost peat plateaus and non-permafrost bogs and fens (Hugelius et al. 2013, Ecosystems Classification Group 2007) while permafrost in peatlands is much less common further south where nutrient poor fens are the most common peatland type (Beilman et al. 2001, Vitt et al. 2000). Permafrost thaw has been occurring in the study area in response to increases in air temperatures since the end of the Little Ice Age with recent acceleration, and is associated with the conversion of peat plateaus into bogs and fens (Halsey et al. 1995, Quinton et al. 2009).

3. Methods

A total of 65 rivers were sampled at road crossings between the 14th and 20th of August of 2011, all rivers were sampled during summer base-flow conditions following a wetter than normal July (figure 1). Electrical conductivity (Ec), pH and temperature were measured in the field using a calibrated YSI.
Figure 1. Map of the study region (a), and hydrographs with the 2011 sampling date indicated for four catchments along the sampling transect (b–e). Runoff data is from the HYDAT database, maintained by Environment Canada, www.ec.gc.ca. The permafrost boundary is based on the Northern Circumpolar Soil Carbon Database (Hugelius et al 2013), see text for further details.

Professional Plus meter. Water samples (250 ml) were filtered through 0.7 µm glass fiber filters (Macherey Nagel) in the field and stored cool and dark for two weeks in pre-washed amber glass bottles prior to analysis.

Samples were analyzed for DOC concentrations using a Shimadzu TOC-V. Four point calibration curves over the range 1–100 mg l$^{-1}$ were established using standards and MilliQ-water. Each sample run included one standard (100 mg C l$^{-1}$) along with at least four MilliQ-water samples. All samples (25 ml) were acidified prior to analysis (0.1 ml, 2 N HCl) and sparged for 2 min to remove dissolved inorganic C. Sample UV–vis absorbance between 200 and 600 nm (1 nm steps) was measured on a Varian Cary 100 in a 10 mm quartz cuvette, with MilliQ-water used as blank. Absorbance at 254 nm divided by the sample DOC concentration yields specific UV absorbance (SUVA), which increases linearly 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. Samples were diluted prior to fluorescence scans with MilliQ-water so that absorbance at 254 nm was 15 ± 0.2 m$^{-1}$ ($±$1 standard deviation) in order to avoid strong primary and secondary inner filter effects (Ohno 2002). After correction for inner filter effects, all fluorescence intensities were multiplied by the dilution factor to represent the fluorescence intensities of whole samples. Fluorescence excitation/emission matrices (EEMs) were collected over an excitation range from 240 to 400 nm (5 nm increments) and an emission range from 300 to 550 nm (2 nm increments), using 0.25 s averaging times. Fluorescence intensities were normalized the area of the Raman peak, thus fluorescence intensities were expressed in Raman Units (RU). A parallel factor (PARAFAC) analysis was performed (Stedmon and Bro 2008) using a total of 416 EEMs, which in addition to the 65 river samples from this study also included similarly collected EEMs from dark and UV incubated peatland and upland surface soil leachates, and samples from lakes, peatland wells and mineral wells—all originating from the Utikuma Lake region located in the southern part of the study transect (Olefeldt et al 2013a, 2013b). Samples from 5 rivers (Hay River, Caribou River, Ponton River and Indian Cabins River) were excluded from the final PARAFAC model, as they had EEMs that were clearly disturbed by large scatter peaks associated with visually turbid samples. The PARAFAC analysis validated a six component ($C_C, C_X, C_M, C_A, C_T$ and $C_T$) model using a split-half
Table 1. Descriptions of fluorescence components in emission/excitation matrices identified through PARAFAC analysis.

| Component | Em. (nm) | Ex. (nm) | Fluorescence association | Peak name | Origin | Molecular weight | Bio-lability | UV-lability |
|-----------|---------|---------|--------------------------|-----------|--------|----------------|-------------|------------|
| C_C       | 452     | <240, 340 | Humic/fulvic acids      | C         | T      | High           | Low         | High       |
| C_X       | 520     | 255     | Humic/fulvic acids      | —         | T      | High           | Low         | High       |
| C_M       | 404     | <240, 305 | Humic/fulvic acids      | M         | T/A/M  | Low            | Low         | High       |
| C_A       | 436     | <240     | Fulvic acids            | A         | T      | High           | Low         | Low        |
| C_T       | 332     | <240, 275 | Tryptophan, free or bound in protein | T         | T/A/M  | Low            | High        | Low        |
| C_Ty      | <300    | 270     | Tyrosine, free or bound in protein | B         | T/A/M  | Low            | High        | Low        |

a Peak emission and excitation wavelengths. Secondary excitation wavelengths in italics.
b Fluorophore description follows Coble (1996), and Fellman et al (2010) where origin abbreviations stand for terrestrial sources (T), autochthonous production (A) and microbial processing (M).

Draft. Relative losses of component fluorescence during biodegradation (Bio) and UV exposure (UV), see Olefeldt et al (2013a, 2013b).

approach. Peak regions of each component corresponded well with previously identified fluorophores and inspection of residuals suggested that no fluorophores were unaccounted for (table 1 and supplementary data available at stacks.iop.org/ERL/9/035005/mmedia). Individual component fluorescence is reported as a percentage (%) of the sum of fluorescence intensities of all six components.

The catchments for each river sampling location were delineated and characterized with respect to their size, lowland cover, presence of lakes and whether they were located north or south of the permafrost boundary. Catchment limits and size were determined from topography with GreenKenue 3.3.10 hydrological modeling software, using Canadian Digital Elevation Data (1:250 000 scale), but required manual adjustments of catchment limits in some areas of low hydrological gradients in order to achieve agreement with the National Hydro Network (Canadian Council on Geomatics, www.geobase.ca). Slope was calculated by the slope tool in the ArcGIS 10.1 software. This utilizes a rise over run calculation of the average maximum height difference in a 3 × 3 window of the digital elevation data. Catchment lowland cover was defined as the fraction of the catchment with an average slope <1%, excluding the areas of 6 lakes larger than 250 km². Peatlands are very common in lowland areas within the study region (Vitt et al 2000, Ecosystems Classification Group 2007), and catchment lowland cover is thus assumed proportional to catchment peatland cover (cf Creed et al 2008). We classified five catchments as lake catchments, as they were sampled downstream of lakes that covered 5–15% of the catchment area and were the recipients of most catchment runoff. Hiset belt distribution, i.e. landscape cover of peatland permafrost soils, is mapped in the Northern Circumpolar Soil Carbon Database (a polygon dataset with 1:1 000 000 scale, Hugelius et al 2013). Hiset distribution is mapped as >40% north of the boundary shown in figure 1, while it is mapped as 0% south of the boundary; hence we used this boundary to classify catchments as being located north or south of the permafrost boundary.

We generated regression models with DOC concentration, SUVA and the six PARAFAC components as dependent variables (MatLab R2011b). Independent variables included two continuous variables; catchment size and lowland cover, and two binary variables; catchment location north or south of the permafrost boundary and presence or absence of large lakes. Interactions between the variables were included. Model ranking and selection was done with the Akaike Information Criteria with bias adjustment for small sample sizes.

4. Results

Catchments varied in size from 20 to 50 000 km², but 43 of 65 catchments were between 100 and 1000 km² in size. Catchment lowland cover ranged from 3 to 100%. Extensive lowland cover north of the permafrost boundary led to higher average catchment lowland cover than for catchments south of the permafrost boundary, 87 ± 12% versus 55 ± 27% (figure 2). Median river Ec was 413 µS cm⁻¹, ranged from 111 to 1830 µS cm⁻¹ and increased with catchment lowland cover (linear regression with log₁₀ transformed river Ec: \( R^2 = 0.29, p < 0.01 \)), but did not differ between catchments north and south of the permafrost boundary. All rivers had pH between 7.4 and 8.5, and river pH was not significantly related to catchment lowland cover (\( R^2 = 0.06, p = 0.11 \)). All individual river data on catchment characteristics and water chemistry are found in the supplemental data (available at stacks.iop.org/ERL/9/035005/mmedia).

The most parsimonious regression model for river DOC concentrations had an adjusted \( R^2 \) of 0.45 (table 2). River DOC concentrations varied from 13 to 65 mg C l⁻¹, and increased with catchment lowland cover. However, river DOC concentrations were lower in catchments north of the permafrost boundary (table 2, figure 2(a)). Catchment size and lake presence were not included in the most parsimonious model for river DOC concentrations, River SUVA, which ranged from 1.24 to 3.95 l mg C⁻¹ m⁻¹, indicated that DOC aromaticity decreased with greater lowland cover and in lake catchments but was unaffected by the permafrost boundary (table 2, figure 2(b)). In order to isolate the influence of the permafrost boundary on river DOM characteristics in catchments with high lowland cover, we also compared non-lake catchments with >70% lowland cover—including 15 catchments north of the permafrost boundary and 14
to the south. These two groups of catchments had similar average lowland cover (88 ± 8%) and river size (390 ± 520 km$^2$) and river Ec (510 ± 230 μS cm$^{-1}$) (t-tests: $p = 0.12$, 0.91 and 0.10, respectively), but catchments north of the permafrost boundary had lower DOC concentrations (33 ± 12 mg C l$^{-1}$ versus 44 ± 6, t-test: $p < 0.01$) and SUVA (2.04 ± 0.411 mg C$^{-1}$ m$^{-1}$ versus 2.45 ± 0.36, t-test: $p = 0.01$) than those without.

River DOM fluorescence exhibited trends across samples, both with regards to fluorescence intensity (reported in RU) and the contribution of individual components to total fluorescence intensity (reported in %). Rivers draining catchments with large lakes had low total fluorescence intensity (figure 3). Lake presence was associated with higher $C_{Ty}$ and $C_{Tr}$ and lower $C_C$, $C_X$ and $C_M$ fluorescence contribution in multiple regression models, while lake presence had no influence on $C_A$ contribution (table 2, figure 3). When comparing fluorescence characteristics between non-lake catchments with >70% lowland cover located north or south of the permafrost boundary, we found that total fluorescence intensity was lower north of the permafrost boundary (figure 3) and that rivers north of the permafrost boundary had higher $C_{Ty}$ contribution to total fluorescence (16 ± 7 versus 6 ± 3%, t-test: $p < 0.001$) while $C_C$, $C_A$ and $C_X$ were lower (t-tests, all $p < 0.01$, see figure 3 for comparisons). Catchment location north or south of the permafrost boundary was included in multiple regression models for all fluorescence components (table 2). In addition to the strong influences from lake presence and catchment location north or south of the permafrost boundary, we further found that $C_C$, $C_X$ and $C_M$ component contribution decreased while $C_{Ty}$ increased as catchment size increased (table 2). Catchment lowland cover had a less clear influence on component fluorescence contribution in river samples (table 2). Overall, the multiple regression models showed that variation in component $C_C$, $C_X$ and $C_M$ contributions could be well described ($R^2 > 0.57$) and had similar dependencies (decreasing north of permafrost boundary, with lake presence and with catchment size). In contrast, component $C_A$ could not be well described by the regression analysis ($R^2 = 0.18$) while component $C_{Ty}$ contribution exhibited opposite pattern from the other components (increasing north of permafrost boundary, with lake presence and with catchment size).

River samples from this study along with terrestrial-source and lake DOM samples from the Utikuma region in the southern (non-permafrost) part of the study area (Olefeldt et al 2013a, 2013b) were found to occupy discrete regions in a

Figure 2. Scatterplots between catchment lowland cover and river DOC concentrations (a) and SUVA (b) Fitted lines are significant ($p < 0.05$) linear regression for rivers north of the permafrost boundary (figures (a) and (b)) and south of the permafrost boundary (figure a only). Multiple regression models for DOC concentrations and SUVA are presented in table 2.

Table 2. Descriptions of the most parsimonious regression models for stream DOC concentration, SUVA and fluorescence contributions of PARAFAC component.

| Model$^a$ | Adj. $r^2$ | $F$ |
|-----------|------------|-----|
| DOC (mg C l$^{-1}$ = 19.1 − 15.5 × PFB + 0.32 × Low | 0.45 | 25.13 |
| SUVA (l mg C$^{-1}$ m$^{-1}$ = 3.40 − 0.65 × Lake − 0.013 × Low | 0.46 | 26.41 |
| $C_C$ (%) = 23.5 − 2.9 × PFB − 6.1 × Lake − 0.9 × Size | 0.79 | 76.16 |
| $C_X$ (%) = 27.1 − 1.5 × PFB − 3.1 × Lake − 0.04 × Low − 0.8 × Size | 0.57 | 21.10 |
| $C_M$ (%) = 17.7 − 1.9 × PFB − 1.4 × Lake + 0.2 × Low − 0.4 × Size | 0.58 | 21.47 |
| $C_A$ (%) = 27.0 − 2.4 × PFB + 0.04 × Low | 0.18 | 7.61 |
| $C_{Tr}$ (%) = 3.5 − 0.5 × PFB + 4.0 × Lake | 0.58 | 42.79 |
| $C_{Ty}$ (%) = 0.7 + 9.5 × PFB + 5.0 × Lake + 2.3 × Size | 0.58 | 28.17 |

$^a$ Model selection was done using the Akaike information criterion, where all potential model combinations of lowland proportion (Low, %), size (Size, log$_{10}$ (km$^2$)), lake presence (Lake, yes = 1/no = 0), catchment location north of permafrost boundary (PFB, yes = 1/no = 0).
The two-dimensional space defined by SUVA and the component ratio C_C/(C_C + C_A) (figure 4). Both C_C and C_A fluorescence is associated with terrestrially derived and poorly biodegradable humic and fulvic acids, but differ in that C_C is more sensitive to photochemical degradation which thus causes C_C/(C_C + C_A) to decrease. Terrestrial DOM samples (samples from peatland pore-water wells and leachates from live Sphagnum moss and upland organic soils) had C_C/(C_C + C_A) that was generally higher than that of river samples, which in turn was generally higher than that of lake samples. Samples from deep mineral groundwater wells had high variability in C_C/(C_C + C_A) but consistently low SUVA. Results from dark incubation show that microbial degradation causes increases in SUVA, while dark incubations appear to cause a convergence of C_C/(C_C + C_A) to values in the range 0.4–0.5, i.e. roughly equal contributions from C_C and C_A to total sum of component fluorescence. River DOM characteristics were intermediate to other DOM sources with regards to both SUVA and C_C/(C_C + C_A), with river samples from catchments north of the permafrost boundary closer in appearance to lake and mineral groundwater DOM sources and further from the appearance of peatland well DOM and organic soil DOM leachates (figure 4).

5. Discussion and conclusions

Aquatic C cycling is important for our understanding of C cycling at the catchment or landscape level, and aquatic C cycling is intrinsically linked to upstream terrestrial ecosystems through their delivery of DOM (Tranvik et al 2009). Aquatic DOC concentration and DOM composition influence catchment C export (Mattson et al 2005) and aquatic atmospheric gaseous C exchange (Roehm et al 2009b, Stutter et al 2013). Here our objective was to assess the influence of permafrost on DOM characteristics among rivers along a 900 km transect. Our results showed that catchment location north or south of the permafrost boundary together with catchment peatland cover influenced several aspects of river DOM characteristics.

Catchment peatland cover was a primary control on river chemistry and DOM characteristics. As in many boreal regions (Ågren et al 2008, Olefeldt et al 2013c), we found that river DOC concentrations increased with catchment lowland cover. Peatlands are often important catchment sources of DOC to aquatic ecosystems since, particularly during base-flow periods when runoff from upland ecosystems is routed through mineral soils with high adsorptive capacity. However, in contrast to other studies and to our expectations, we found...
that greater catchment lowland cover was also associated with lower DOC aromaticity (SUVA) and higher river Ec. Peatland runoff is often characterized by higher DOC aromaticity and lower Ec than that of mineral soil groundwater sources (Olefeldt et al. 2013c, Kothawala et al. 2012a). The reason for this discrepancy is unclear, but we hypothesize two potential mechanisms that could cause the observed patterns. The western Boreal/Tundra Plains have deep, heterogeneous glaciated substrates that are known to cause complex surface and groundwater interactions (Devito et al. 2005), and higher Ec and lower aromaticity could be a sign that lowland areas are locations for discharge of regional groundwater sources. Alternatively, given the dry climate of the study region it is possible that surface water in lowland areas has long residence times that enhance both evaporative enrichment of Ec and selective photochemical degradation of aromatic DOC (Sulzberger and Durisch-Kaiser 2009, Weyhenmeyer et al. 2012). We also note that river Ec was not influenced by whether catchments were located north or south of the permafrost boundary, suggesting that the permafrost cover in the southern discontinuous permafrost zone is not sufficient to act as an aquitard for groundwater interactions at the catchment level as found for studies in the northern discontinuous permafrost zone (Walvoord et al. 2012).

We found significant differences in river DOM characteristics between catchments north and south of the permafrost boundary. Rivers north of the permafrost boundary had lower DOC concentrations, lower aromaticity, lower total fluorescence intensity (sum of components) and lower humic/fulvic acid contribution to the total fluorescence, while protein fluorescence was greater. These differences were apparent also when comparing a subset of the catchments that were similarly sized catchments with >70% lowland cover and no lakes. The question is whether these shifts in DOM characteristics are due to permafrost conditions in peatlands or due to other factors. Fire regime, bedrock characteristics and dominant surface geology do not shift near the permafrost boundary and are thus unlikely to cause the shifts in river DOM characteristics (The Atlas of Canada, maintained by Natural Resources Canada, www.nrcan.gc.ca). There is a concurrent shift from mixed to coniferous forest that occurs near the peatland permafrost boundary, but this is unlikely to have been the main reason since shifts in river DOM characteristics were primarily associated with catchments dominated by peatlands rather than uplands. Along the north–south gradient there is also an increase in the average annual runoff generation, from ~50–100 mm in the south to 100–200 mm in the north. Increased runoff generation could cause shifts in relative contribution from mineral and organic soil DOM sources to rivers. However, shifts in river DOM characteristics in this study occurred at a similar climatological threshold, the boundary of peatland permafrost, as reported for DOC concentrations among rivers in the peatland-rich West Siberian lowlands (Frey and McClelland 2009), suggesting that peatland permafrost conditions are central to river DOM characteristics. Studies at smaller scales have shown that permafrost in peatlands of the discontinuous permafrost zone has a strong influence on hydrological connectivity between different peatland ecosystems and aquatic ecosystems (Quinton et al. 2009, Olefeldt and Roulet 2012). Peat plateaus are elevated and act as hydrological barriers that channel runoff through spatially discrete and highly minerotrophic channel fens, while simultaneously ensuring that non-permafrost bogs are poorly connected to the stream network. As a result of differences in hydrological connectivity during summer, fens have been shown to be stronger DOC sources than peat plateaus or bogs (Olefeldt and Roulet 2012). As fens become more abundant relative to ombrotrophic peatland types such as bogs or peat plateaus south of the permafrost boundary (Vitt et al. 2000), we hypothesize that lower river DOC concentrations in rivers north of the permafrost boundary during summer is a result of decreased hydrological connectivity between peatlands and adjacent stream networks.

Observed shifts in river DOM composition across the permafrost boundary may also be related to differences in DOM delivery from different peatland types. Different peatland types are known to have differences in pore-water DOM composition (Tityl et al. 2013), e.g. it is known that DOM in nutrient-rich channel fens in the discontinuous permafrost zone is less aromatic than that in peat plateaus (Roehm et al. 2009a). Lower aromaticity and higher protein contribution in DOM samples from rivers north of the permafrost boundary would thus be consistent with a greater relative importance of DOM sources from highly productive nutrient-rich channel fens (Ström and Christensen 2007, Roehm et al. 2009a) while contribution of highly aromatic DOM from peat plateaus and bogs is restricted due to poor hydrological connectivity during summers. Lower aromaticity and higher protein contribution is associated with higher DOM biodegradability (Balcarczyk et al. 2009), and may thus influence the rate and degree to which terrestrial DOM is degraded in aquatic ecosystems. The release of previously frozen soil organic matter as DOM into rivers following thaw likely comprises a small fraction of the riverine DOM pool (Guo and Macdonald 2006), but DOM from destabilized permafrost soils has been shown to be sensitive to both microbial and photochemical processes (Cory et al. 2013, Vonk et al. 2013) and could possibly contribute to the observed trends in DOM composition among rivers in this study.

Shifts in DOM composition across the permafrost boundary may stem not only from differences in terrestrial DOM source dynamics, but also be related to differences in the degradation and transformation of terrestrial DOM in aquatic ecosystems. Microbial degradation act primarily on non-aromatic DOM, hence lower water temperatures in rivers further north is likely to result in slowed and less extensive microbial enrichment of aromatic DOM (Berggren et al. 2009). Alternatively, lower aromaticity and Ec fluorescence in rivers north of the permafrost boundary could be due to increased photochemical degradation. As the Ec component has been associated reduced organic compounds, the ratio Ec/(C_C + C_A) may represent an index of DOM oxidation (Kothawala et al. 2012b). Due to particularly rapid photochemical loss of C_C fluorescence (Olefeldt et al. 2013a), river DOM samples had values of C_C/(C_C + C_A) that were lower than for terrestrial sources but higher than lake samples, and rivers
draining catchments north of the permafrost boundary had characteristics with greater similarity to lake samples than catchments without. Increased photochemical processing of DOM in aquatic ecosystems north of the permafrost boundary could be as results of the lower DOC concentrations, whereby an equal rate of photochemical processing would affect a greater proportion of the DOM pool. Ultimately, it is not possible from this study to definitively attribute the shifts in DOM characteristics across the peatland permafrost boundary to specific processes, but our data on DOM composition has yielded information that can be used as basis for future studies.

In conclusion, our study shows that there are significant shifts in river DOC concentrations and DOM composition for lowland catchments across the permafrost boundary during summers. While identifying specific mechanisms responsible for the shifts in river DOM characteristics need further research, it is likely that they are linked to the influence of permafrost on peatland structure and hydrological connectivity. Future research is also needed to assess whether these differences remain throughout the year or are only apparent during summers. Observed higher river DOC concentrations, higher aromaticity and lower protein contribution to DOM fluorescence in rivers without peatland permafrost suggest that ongoing climate change and permafrost thaw is likely to alter both aquatic C cycling and DOC export in permafrost catchments.

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