Consequences of peatland disturbance for dissolved organic matter and nutrient transport and fate in northern catchments

by

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Abstract

Northern peatlands contain ~415 Pg of carbon (C) in soil organic matter and are significant sources of dissolved organic matter (DOM) in inland waters. DOM includes a range of molecules that are C-rich and may also contain nitrogen (N) and phosphorus (P). The escalating disturbance of peatlands due to climate and land use change disrupts DOM and nutrient composition, transport, and fate in inland waters. Dissolved organic C (DOC; the C component of DOM) plays a pivotal role in the global C cycle, and an overabundance of DOC, as well as excess N and P, can harm aquatic ecosystems and increase water treatment expenses. However, the impact of diverse peatland disturbances on DOM and nutrient export remains uncertain, as does the quality and bioavailability of DOM. Consequently, effectively managing peatland resources amidst changing conditions presents an ongoing challenge. This thesis employs field and lab investigations alongside literature synthesis to unravel the consequences of peatland disturbance on catchment and continental-scale C and nutrient export and fate.

In my first study (Chapter 2), I examined how industrial peat extraction influenced DOC and nutrient export and fate in western Canadian stream networks. Studying 55 nested subcatchments (ranging from <1–180 km^2), I analyzed solute concentration, DOM composition, and relative solute attenuation. Peat disturbance increased NH_4^+ concentration and stream turbidity, while diminishing PO_4^{3-} sink capacity compared to intact peatlands. Although DOC concentration correlated positively with overall peatland coverage, peatland disturbance had no significant impact. Hydrology, specifically stream flow and flowpaths, primarily governed DOM composition variability, showing minimal response to disturbance. An assessment of mass balance indicated inorganic nutrient attenuation across the stream network, with DOC acting conservatively, similar to base cations. Variable stream flow regulated solute attenuation;

dissolved inorganic N (DIN) and DOC experienced greater attenuation during low flows, while PO_4^{3-} was more attenuated during high flows. Therefore, downstream impact from disturbed peatlands depended on flow conditions.

Chapter 3 explored peatland disturbance's effect on DOM bioavailability for stream bacteria. Sampling three headwater peatland catchments over 12 months (intact, extracted, and burned), I evaluated DOM composition, biodegradability of DOC, DON, and DOP, and bioavailable C:N:P ratios. Across these catchments, DOM was primarily humic-like, with minimal bioavailability (<1% on average). Extracted peatlands had higher bioavailable DOC, yet bioavailable DON and DOP were rarely detected. Bioavailability of DOC and DON peaked during spring freshet, associated with reduced DOM aromaticity. While DON and DOP remained largely inaccessible to bacteria, inorganic N and P were abundant, particularly DIN in extracted peatlands and PO_4^{3-} in burned peatlands. Bacterial abundance and C:N:P ratios indicated increased C-limitation due to peatland disturbance.

Chapter 4 delved into northern peatlands' role and the impact of peatland disturbance on continental-scale DOC export and fate. A systematic review of DOC export from northern peatlands, coupled with a random forest model, predicted DOC concentration and yield above 45° N. The review revealed a bias toward wetter climates, overestimating northern peatland DOC export. Key predictors of DOC concentration and yield were peatland coverage, mean annual air temperature, and mean annual precipitation. High-latitude headwater peatland catchments exported ~29 Tg C yr^{-1} to inland waters and 20 Tg C yr^{-1} to oceans. While peatland drainage had minor impact on continental-scale DOC export, climate change is projected to increase DOC export by 12%–23% by 2100. This shift stems from higher DOC concentration and yield in present-day discontinuous permafrost regions.

This thesis underscores the impact of peatland disturbance on inorganic nutrient export in western Canada and the global significance of northern peatlands on DOC export to inland waters. By studying catchments in sub-boreal western Canada, my research helps advance the fields of biogeochemistry and ecosystem ecology by linking disturbance patterns to C, N, and P concentration and fate in nested stream networks. Chapter 4 highlights DOC concentration and yield variation across a climatic gradient in northern peatland catchments and underscores the need for research in cooler, drier climates, like those in sub-boreal western Canada. Further studies on novel disturbances and catchment C, N, and P dynamics in these underrepresented regions will help inform global biogeochemical models. This research is poised to guide water managers and policymakers in safeguarding peatlands and freshwater resources amid ongoing climate change and land disturbances.

Preface

Contributions of authors

All co-authored work presented in this dissertation follows the author order convention of first author is lead author, followed by authors in order of contribution, with the last author as the Principal Investigator. Each chapter in this thesis represents a collaborative, scientific effort resulting in manuscript publication or preparation for submission to peer-reviewed journals, as detailed below. For all chapters, R.J.F. designed the study with input from D.O. and coauthors; R.J.F. led field and laboratory work, data analysis, and manuscript writing; before publication, all co-authors contributed, or will contribute, to writing.

Chapter 2: Frei, R.J., Shewan, R., Cao, M., Abbott, B.W., Olefeldt, D. Boreal peat extraction affects inorganic nitrogen and phosphorus concentration and hydrology modulates downstream fate in sub-boreal nested catchments. A version of this paper has been submitted to *Water Resources Research*.

Chapter 3: Frei, R.J., Cao, M., Rulli, M., Mangal, V., Berggren, M., Olefeldt, D. Prevailing carbon-limitation for bacteria in disturbed headwater peatland streams. In preparation for submission to *Limnology & Oceanography.*

Chapter 4: Frei, R.J., Tank, S., Olefeldt, D. Refining current and future estimates of export and downstream attenuation of dissolved organic carbon (DOC) from northern peatlands. In preparation for submission to *Global Biogeochemical Cycles.*

and then once more still.
The salamanders,
like tiny birds, locked into formation,
fly down into the endless mysteries

of the transforming water,
and how could anyone believe
that anything in this world
is only what it appears to be—

that anything is ever final—
that anything, in spite of its absence,
ever dies
a perfect death?

An excerpt from "What Is It?" by Mary Oliver.

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I am also grateful for my network of friends and family. To Lynn and Tammy, thanks for bringing me into this world and teaching me to work and play hard. To my nine siblings, thanks for cheering me on. Many thanks to my friends in Edmonton and Salt Lake who have gotten me away from the computer and out in the beautiful landscapes that we love. I feel fortunate to have such a wonderful community of friends who challenge themselves at the office, in the community, and on the trails and peaks of the Rocky and Wasatch mountains. And of course, thank you to my partner, Scott, who has been my number one supporter in all facets of life. You're the best, I love you. And to our puppy dog, Nellie, you are the goodest girl.

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1. General Introduction

Northern peatland disturbance is increasing because of climate change and land use and land cover change (LULCC), which could substantially increase dissolved organic matter (DOM) export to inland waters. DOM is operationally defined as the amount of OM that passes through a 0.45 µm filter, and is produced in peatlands as the byproduct of incomplete OM decomposition (Thurman, 1985). The abundant organic matter within peatlands, along with their effective hydrological transport of DOM to inland waters, make them substantial sources of DOM (Rosset et al., 2022). To illustrate, despite covering merely 3% of the land area, peatlands contain almost 25% of the global soil organic matter (Yu, 2012). In the context of northern peatlands (distinct from tropical and southern hemisphere peatlands), which account for ~85% of global peatlands, soil organic matter contains approximately 415 Pg C, 10 Pg N, and 0.3 Pg P (Turetsky and St. Louis, 2006; Wang et al., 2015; Hugelius et al., 2020). Peatlands efficiently channel DOM towards inland waters, largely due to hydrological pathways that remain within organic soil, which do not adsorb as much DOM as mineral soils (Kaiser and Kalbitz, 2012; Kothawala et al., 2012). This is because, by definition, peatlands have deep organic soil layers of at least 30 cm, and average peat depth is between 1.3–2.3 m (Clymo et al., 1998; Limpens et al., 2008). The hydraulic conductivity in peat generally decreases with depth, thus routing dominant hydrologic flowpaths in near-surface peat (Holden, 2005). These northern peatlands have been forming since the early Holocene and have developed under mostly stable climate conditions and disturbance regimes (Yu et al., 2010). A growing concern is that changing peatland disturbance regimes (i.e., spatiotemporal dynamics of disturbances over an extended time period (Turner, 2010)) will change the C and nutrient balance of inland waters and exacerbate climate change and widespread nutrient pollution (Diaz and Rosenberg, 2008; Laine et al., 2013, 2014; Brown et al., 2015; Beaulieu et al., 2019).

Peatland disturbances are currently widespread, and are predicted to increase, with diverse consequences for aquatic ecosystems (see Figure 1). Climate change is a major threat to northern peatlands because of widespread permafrost thaw and wildfire, which are expected to affect at least half of northern peatlands (Turetsky et al., 2015; Hugelius et al., 2020). Direct human-caused disturbances such as peatland drainage affect ~11% of global peatlands, including ~50% of peatlands in Europe (Fluet-Chouinard et al., 2023). In some areas, human-caused peatland disturbances have stabilized (e.g., through restoration efforts), but few peatlands are protected, and large swaths of peatlands in northern Canada and Siberia are vulnerable to increased disturbances from resource extraction activities (Strack et al., 2019; Harris et al., 2022; Fluet-Chouinard et al., 2023). Altogether, these diverse disturbances endanger water supply for approximately 71.4 million people and threaten countless species endemic to peatlands and northern waters (Schindler, 1998; Xu et al., 2018). Specifically, peatland disturbances commonly increase DOM and nutrient export to inland waters (Marttila et al., 2018; Nieminen et al., 2020a), which increases the difficulty and cost of producing clean drinking water (Roulet and Moore, 2006; Kritzberg et al., 2020). Elevated DOM (and iron) in water causes "browning", which makes water a dark brown color that reduces light in the water column, decreases primary production, and endangers aquatic predators that rely on visual stimuli (Kritzberg et al., 2020). DOM also co-precipitates with contaminants such as heavy metals and methylmercury which bioaccumulate up the food chain (Wu et al., 2021; Thompson et al., 2023). Moreover, elevated nutrients can lead to eutrophication (an overabundance of nutrients), which causes harmful algal blooms and deadly hypoxic zones for aquatic life (McElarney et al., 2010; Le Moal et al., 2019). Though elevated DOM and nutrients in aquatic ecosystems are relatively well-studied phenomena, the contribution of peatland disturbances to the prevalence of these issues remains uncertain.

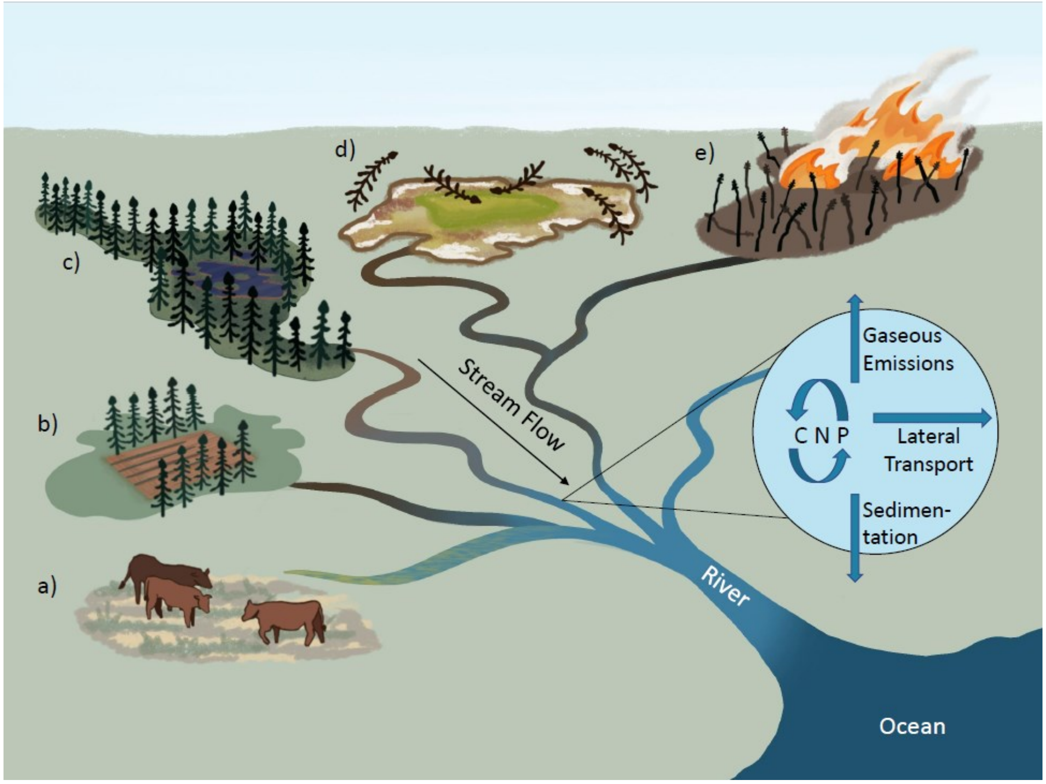

Figure 1. Conceptual diagram of the various impacts of peatland disturbances on surface water quality. Here, I show a fictitious landscape where an agricultural upland (scene a) is connected to the same stream network as different peatlands: b) an extracted and drained peatland, c) an intact peatland, d) a thawing permafrost peatland, and e) a burned peatland. I hypothesize that different peatland disturbances affect the quantity and type of dissolved organic matter and nutrients that are exported downstream, as reflected by the stream water color for various landscapes (i.e., darker color indicates elevated solute load compared to lighter colors, browning suggests more DOM export, and greening suggests more inorganic nutrient export). The inset shows that carbon (C), nitrogen (N), and phosphorus (P) are processed during lateral transport, resulting in some C and N loss to the atmosphere via gaseous emissions and some C, N, and P loss to sediments via flocculation and sedimentation processes. Thus, the fate of solutes exported from disturbed peatlands depends on their initial state and the physicochemical conditions that they encounter downstream.

Another key consideration for peatlands is their role in the global C cycle. Peatlands are large C pools that control major C fluxes both vertically to the atmosphere and laterally to inland waters (Yu et al., 2010; Loisel et al., 2021; Rosset et al., 2022). Peat accumulates over centuries and millennia as OM production exceeds decomposition. In northern peatlands, OM production is relatively slow, but cold, wet, and acidic conditions in addition to recalcitrant litter inputs from plants such as *Sphagnum* mosses contribute to even slower decomposition (Clymo et al., 1998; Chiapusio et al., 2018; Fudyma et al., 2019). Thus, peatlands are considered to be C "savings accounts", slowly accumulating and storing C at a rate of ~0.14 Pg C yr^{-1}, which offsets less than 1% of annual fossil fuel emissions (Limpens et al., 2008; Gallego-Sala et al., 2018). Though peatlands are currently a weak C sink (Gallego-Sala et al., 2018), destabilizing these ecosystems could result in large C losses to the atmosphere and to inland waters, where C may be degassed to the atmosphere, buried in sediments, or transported to oceans (Turetsky et al., 2015; Drake et al., 2018; Loisel et al., 2021; Qiu et al., 2021). However, the amount of DOM exported from disturbed peatlands and its fate in aquatic networks is highly uncertain and is poorly integrated into global biogeochemical models (Drake et al., 2018). Therefore, the magnitude of impact that disturbed peatlands have on DOM export and ecosystem function beyond their boundaries remains unclear.

1.1 DOM production and transport in pristine northern peatlands

To understand the potential impacts of peatland disturbance on DOM, we must first outline how DOM is produced and transported in pristine northern peatlands. As stated previously, DOM is produced as the byproduct of incomplete SOM decomposition. Peatlands have high water tables, which affect redox conditions and the mechanisms of SOM decomposition (i.e., aerobic vs. anaerobic) (Holden, 2005). Moreover, peatland SOM is vertically stratified, such that the top layer contains fresh litter inputs and plant exudates, and below the first 10–20 cm the peat is hundreds to thousands of years old and more humic-like (Chanton et al., 2008; Evans et al., 2014; Tfaily et al., 2014). However, most DOM exported from pristine peatlands is relatively young because incomplete aerobic decomposition in near surface peat breaks down fresh organic matter into DOM that moves laterally and vertically through the peat column (Chanton et al., 2008; Corbett et al., 2013; Tfaily et al., 2014). This young DOM fuels further aerobic and anaerobic decomposition at depth, therefore even deep hydrological flowpaths can transport DOM that is relatively young compared to the surrounding peat substrate (Chanton et al., 2008; Corbett et al., 2013). Vascular plants and mosses also release root exudates such as easily decomposable organic acids, sugars, and amino acids, in addition to extracellular enzymes that further stimulate decomposition (Jones et al., 2009; Basiliko et al., 2012; Mastný et al., 2021). Much of the DOM exported from peatlands is aromatic (Olefeldt et al., 2013), which is associated with anaerobic decomposition that selectively preserves aromatic organic compounds (Baldock et al., 1997; Verbeke et al., 2022).

Though C is the most common element in DOM molecules, other elements including N and P are also important, and their biogeochemical cycles are intrinsically linked (Schlesinger et al., 2011). For example, N and P modulate both primary production (i.e., C inputs) and organic matter decomposition (C outputs) (Bridgham et al., 1998; Salmon et al., 2021). Most nutrients are tied up in SOM and can be mineralized into bioavailable forms that are rapidly utilized (Bridgham et al., 1998). The nutrient content of peat is also vertically stratified, with C:N ratios increasing with depth whereas C:P decreases with depth (Wang et al., 2015). Most N and P exported from peatlands to inland waters is in dissolved organic forms, and inorganic nutrient export varies by peatland type, e.g. higher in minerotrophic fens and lower in ombrotrophic bogs (Rydin and Jeglum, 2013). Additionally, warming and water table drawdown have both been shown to increase inorganic N and P concentrations in porewater and inland waters (Laine et al., 2013; Marttila et al., 2018; Nieminen et al., 2020a; Iversen et al., 2023).

DOM transport in peatlands is a function of complex hydrological processes. Peatlands have high water tables that vary little in the first few decimeters where bulk density is low and hydraulic conductivity is high (Holden et al., 2012; Bourgault et al., 2018). Lateral water flow in peatlands is controlled by water table position, slope, and peat hydraulic properties, and highest lateral flow occurs when water table is high because of greater hydraulic conductivity (Waddington and Roulet, 1997). Thus, spring snowmelt and rainstorms produce the majority of annual catchment runoff and DOM export (Clark et al., 2007; Ågren et al., 2008). Lateral flow paths in near-surface peat also enhances DOM export because mineral soils preferentially adsorb aromatic DOM and substantially reduce DOM concentration in receiving waterbodies (Meier et al., 2004; Kothawala et al., 2012). But in peatlands, dominant water flow paths in near-surface peat reduces DOM contact with adsorbent mineral particles. Moreover, peatland DOM export to inland waters requires hydrological connectivity between the two ecosystems. Bogs and fens—the main peatland categories—are largely differentiated by groundwater connectivity, with bogs mostly disconnected from groundwater inputs while fens are groundwater-fed (Rydin and

Jeglum, 2013). Bogs are often intermittently connected to inland waters, especially during dry seasons. For example, hydrology in permafrost peatlands shows isolated flat bogs are disconnected most of the year except during spring snowmelt (Quinton et al., 2009). Therefore, hydrology is a key component of DOM export that affects water quality in peatlands and downstream ecosystems.

Temperature is also an important control on DOM production and transport in peatlands, dictating the rate of all chemical and biochemical reactions (Davidson and Janssens, 2006; Laudon et al., 2012). Many northern peatlands also experience seasonal and prolonged freezing conditions (i.e., permafrost, defined as perennially frozen ground), which slows decomposition and water movement. Seasonal changes in litter inputs and water flow paths also affect DOM concentration and quality in peat porewater and inland waters (Ågren et al., 2008; Leach et al., 2016). Climate change at high-latitudes is expected to warm faster than the global average, which will likely stimulate both primary production and organic matter decomposition in peatlands (Gallego-Sala et al., 2018; Verbeke et al., 2022). However, it remains uncertain how these competing processes will affect net ecosystem exchange and DOM export to inland waters (Wilson et al., 2016; Heffernan et al., 2020; Hugelius et al., 2020).

1.2 Peatland disturbance and water quality

Disturbance is an important component of ecosystem evolution and development, and I use the definition of disturbance from disturbance ecoclogy "A disturbance is any relatively discrete event that disrupts the structure of an ecosystem, community, or population, and changes resource availability or the physical environment." (White and Pickett, 1985; Turner, 2010). In the context of global biogeochemical cycles, discrete disturbance and recovery periods bring about changes in source and sink dynamics on yearly to decadal timescales, but may not have long-term impacts unless disturbance regimes shift (Luo and Weng, 2011). Peatlands, for example, have expanded and contracted over millennia in response to changing climate. However, in the context of anthropogenic climate change, rapid C loss from northern peatlands is considered irrecoverable because they are unable to recuperate their lost C at relevant timescales (i.e., in the next ~100 years) (Goldstein et al., 2020; Harris et al., 2022). Peatland disturbances also affect water quality for short timescales or may trigger regime shifts that fundamentally change aquatic ecosystem structure (Ritson et al., 2016; Kothawala et al., 2017; Kritzberg et al., 2020). Therefore, changing DOM export due to peatland disturbance is important at decadal and centennial timescales for global climate feedbacks, and at annual to decadal timescales for local water quality for aquatic organisms and human society.

Currently, northern peatlands face widespread disturbances due to climate change and LULCC that alter DOM production and transport. Direct climate change impacts include warming temperatures and altered precipitation regimes, and indirect impacts include wildfire and permafrost thaw (Tarnocai, 2009; Trenberth, 2011; Hugelius et al., 2020). LULCC disturbances in northern peatlands are legion, but the main disturbances include forestry, agriculture, urban infrastructure, peat harvesting for horticulture, and oil and gas exploration and extraction infrastructure (including pipelines, temporary and permanent well pads, seismic lines) (Poulin et al., 2004; Turetsky and St. Louis, 2006; Saraswati et al., 2019; Strack et al., 2019). These disturbances vary in their severity and extent, but all affect peatland hydrology and/or OM decomposition to some degree, and therefore affect how DOM is produced and transported.

Climate change is a major disturbance at high-latitudes where temperature is increasing 2–6 times faster than the global mean, precipitation regimes are intensifying, and wildfire and permafrost thaw are increasing across the landscape (Kelly et al., 2013; Gibson et al., 2018; Environment and Climate Change Canada, 2019; Hugelius et al., 2020). Mean annual air temperature (MAAT) and mean annual precipitation (MAP) control DOM production and transport in northern landscapes, and climate change will likely increase DOM export at continental scales (Frey and Smith, 2005; Laudon et al., 2012). Prolonged drought also lowers water table position, and many studies have reported a decrease in DOM concentration as DOM is immobilized due to increased acidity and ionic strength, followed by a pulse of DOM when water returns (Clark et al., 2011). Permafrost peatlands comprise nearly half of northern peatland area and C stocks, and permafrost thaw is expected to substantially increase C and N loss to inland waters as solutes and water from permafrost are liberated (Frey and Smith, 2005; Olefeldt et al., 2014; Hugelius et al., 2020). Moreover, climate change has increased wildfires across northern landscapes, and has doubled wildfire extent in boreal Canada (Gillett et al., 2004; Kasischke and Turetsky, 2006; Kelly et al., 2013). Water-logged conditions in peatlands usually create a wildfire buffer in the landscape, but warmer, drier conditions will expose more peat biomass to combustion and smoldering (Turetsky et al., 2015). Incomplete peat combustion leaves behind charred OM and elements that are not easily vaporized (such as P), which affects water quality for years to decades post-fire (Burd et al., 2018; Granath et al., 2021). However, wildfire has variable impacts on lateral C and nutrient export to inland waters (Brown et al., 2015; Granath et al., 2021).

LULCC disturbances in northern peatlands are patchier than climate-related disturbances, but have the potential to be major point sources of excess DOM and nutrients. The most studied effect of LULCC disturbance in peatlands is drainage, which has affected ~11% of global peatlands (Leifeld and Menichetti, 2018; Fluet-Chouinard et al., 2023). Drainage lowers the water table and exposes more peat to aerobic decomposition, increasing vertical and lateral C fluxes (Evans et al., 2016; Leifeld and Menichetti, 2018) as well as dissolved nutrients and other solute fluxes (Nieminen, 2004; Marttila et al., 2018; Nieminen et al., 2020a). A study comparing fluvial C from drained and re-wetted peatlands showed that DOC concentration and area-weighted yields increased by about 50% and 60% respectively due to drainage, and rewetting decreased DOC concentration and yield by about 25% and >100% respectively (Evans et al., 2016). However, a systematic review of DOC yield from peatlands found no significant difference between drained and undrained boreal peatlands (Rosset et al., 2022). Overall, research on disturbed peatlands is limited, geographically biased (i.e., most studies are on blanket bogs in the UK and afforested peatlands in Fennoscandia) (Rosset et al., 2022), and primarily focused on DOC. Therefore, more research in understudied regions (e.g., western North America and Siberia) and on a broader suite of water quality parameters are needed to understand the role of peatland disturbance on water quality for humans and aquatic ecosystems.

1.3 DOM attenuation in inland water networks

Once peatland DOM enters inland waters, it faces new biogeochemical contexts that will determine its fate. DOM fate is controlled by intrinsic molecular composition and extrinsic environmental conditions, such that DOM in one environment may become more or less reactive in a different context (Kothawala et al., 2020; Berggren et al., 2022). Moreover, the dominant control (e.g., molecular composition vs. environment) on DOM fate varies from soils to freshwater ecosystems (Kothawala et al., 2020). In soils, environmental conditions such as temperature, nutrient availability, and DOM adsorption to mineral surfaces are more important controls on DOM turnover than molecular composition (Kothawala et al., 2020). Whereas in freshwaters, DOM fate is largely related to its composition (Kellerman et al., 2015; Kothawala et al., 2017), which controls rates of bio- and photodegradation, flocculation, and co-cycling of these processes that degas CO_2, fuel primary production, and bury OM in sediments (Cory and Kling, 2018; Creed et al., 2018; Einarsdóttir et al., 2020). Current freshwater theory assumes that labile DOM is consumed first, and remaining DOM becomes more difficult to degrade (Kothawala et al., 2020). Therefore, previously stable peat DOM faces new biogeochemical processes as it is flushed into inland waters and travels downstream.

In headwaters, allochthonous or terrestrially-sourced DOM and nutrients are important nutritional subsidies to aquatic ecosystems (Marcarelli et al., 2011; Tanentzap et al., 2017; Berggren et al., 2018). DOM that is assimilable by aquatic organisms is considered bioavailable, which broadly means that DOM molecules can pass through cell walls and be used as a nutritional source. A large fraction of potentially bioavailable C, N, and P in inland waters are bound to large DOM molecules that do not pass cell membranes (Jones et al., 1988), but extracellular or membrane-associated enzymes can assist in decomposing DOM into smaller, assimilable molecules (Arnosti et al., 2014). Therefore, bioavailable DOM includes DOM that can potentially be assimilated by microbial communities, either directly or facilitated by enzymatic processing (Stepanauskas et al., 2002; Berggren et al., 2015). Bioavailable DOC is the most commonly studied form of bioavailable DOM, but DOM contains other elements including nitrogen (N) and phosphorus (P) which are essential nutrients for life and co-cycle with C (Schlesinger and Bernhardt, 2013). N and P are most readily bioavailable in their inorganic forms, but DON and DOP (the fraction of N and P in DOM) are usually the most abundant forms in northern peatland catchments, and their bioavailability depends on DOM composition and environmental conditions (Berggren et al., 2015; Soares et al., 2017; Rulli et al., 2022). The effect of global change on N and P transport from peatlands to inland waters is even more uncertain than C, with implications for aquatic primary productivity and algal blooms across freshwater and marine ecosystems (Hugelius et al., 2020; Terhaar et al., 2021).

Northern freshwaters also have strong seasonal cycles that affect species habitat and nutritional quality. For example, DOM bioavailability in boreal waters is generally highest during the spring snowmelt when bioavailable soil leachates are flushed to inland waters (Ågren et al., 2008). Species diversity in northern freshwaters is also lower than in temperate and tropical freshwaters, making them more sensitive to climate change and LULCC (Schindler, 1998). Thus, disturbances that affect the timing of DOM delivery to freshwaters could have ramifications for species survival and biodiversity (Mustonen et al., 2018). Because peatland disturbances affect OM degradation and pore water chemistry, and peatlands deliver large amounts of DOM to inland waters, peatland disturbance threatens the stability of northern freshwater ecosystems.

The consequences for water quality and biodiversity naturally propagate downstream with ramifications for large rivers, lakes, and coastal marine ecosystems. For example, DOM sources shift longitudinally downstream from allochthonous, terrestrial sources to autochthonous sources (Creed et al., 2015), which is reflected in the isotopic signature of respired CO_2 from riverine ecosystems (Hotchkiss et al., 2015). Light and flow conditions have also emerged as important environmental controls on DOM and inorganic nutrient turnover and primary production in freshwaters (Zarnetske et al., 2011; Bernhardt et al., 2022). As DOM travels through inland water networks, oxidized, aromatic, high-molecular weight DOM is preferentially lost over time, which is the main type of DOM exported from peatlands (Kellerman et al., 2015). Though there is some evidence to suggest preferential loss of peat DOC in freshwater ecosystems, the mechanisms controlling these processes across catchment and continental scales remain uncertain.

It is estimated that at least 5 times as much C enters inland waters as is exported to global oceans, and revisions continue to increase the estimated load of terrestrial C to inland waters (Drake et al., 2018). These estimates have refined our understanding of the global C cycle and the strength of the terrestrial C sink. However, the estimated C export from terrestrial ecosystems to inland waters does not include wetlands, such as peatlands, that likely disproportionately contribute C to inland waters, and could further refine our understanding of the C cycle (Rosset et al., 2022). Moreover, climate change and LULCC will likely increase C export (Regnier et al., 2013; Creed et al., 2018; Drake et al., 2018), making it extremely important to constrain current export and future change.

1.4 Research Objectives and Hypotheses

The purpose of this thesis is to understand the role of peatland disturbance on DOM and nutrient (N and P) export and attenuation in the terrestrial-aquatic continuum at catchment and continental scales. In this first chapter, I have introduced northern peatlands and their role in

DOM cycling in inland waters. Chapters two through four present primary research on the effects of peatland disturbance on DOM quantity, quality, and attenuation. Specifically, chapter two will investigate how peat drainage via industrial peat extraction affects DOM and inorganic nutrient yield and attenuation through two meso-scale (~150 km^2) stream networks. The third chapter focuses on the impact of peatland disturbance (wildfire and drainage) on DOC, DON, and DOP bioavailability and the implications for resource availability in peat porewater and headwater streams. The fourth chapter uses a spatially-explicit observation-based modelling approach to predict DOC concentration and area-weighted yield across northern peatland catchments and uses the model to predict future DOC concentration and yield due to climate change. Finally, the fifth chapter will summarize the main findings and propose future research directions.

Throughout this thesis, I hypothesize that climate change and peatland drainage will increase DOM export to inland waters because of changes in DOM production and hydrological transport, which will have ramifications for DOM cycling in inland waters. I predict that peat DOM will be preferentially removed from inland waters because aromatic DOM has higher rates of mineral adsorption and photo-degradation. Furthermore, I predict that drainage, drought, and permafrost thaw will release more bioavailable nutrients that will further stimulate heterotrophic respiration of bioavailable DOM. Therefore, I hypothesize that increased DOM export and increased attenuation of disturbed peatland DOM in inland waters will intensify the flux of C from inland waters to the atmosphere. Alternatively, if DOM export to inland waters increases, but net DOM attenuation remains approximately the same, then there will be little impact on the global C cycle.

2. Boreal peat extraction affects inorganic nitrogen and phosphorus concentration and hydrology modulates downstream fate in sub-boreal nested catchments

Abstract:

Land use and hydrology influence the transport and attenuation of dissolved organic carbon (DOC) and nutrients through river networks, influencing aquatic food webs, habitat, and water quality. Here, we studied how horticultural peat extraction affects DOC and nutrient dynamics in western Canada across a range of ice-free flow conditions. We sampled 55 subcatchments and analyzed solute concentration and export, dissolved organic matter (DOM) composition, and relative solute attenuation in the stream network. We found that the proportion of peatland disturbance significantly increased NH_4^+ concentration and turbidity, and reduced the PO_4^{3-} sink relative to intact peatland catchment cover. DOC concentration was elevated in extracted peatland drainage ditches relative to intact headwater catchments, but the disturbance effect was non-significant overall. DOM composition differed more by hydrology than land use, with high flows transporting more aromatic, humic-like DOM, and low flows transporting more fresh, autochthonous-like DOM to the stream network. Downstream fate of DOC and nutrients were also modulated by hydrology. Inorganic nutrients attenuated rapidly, while DOC acted conservatively, and attenuation of all solutes except PO_4^{3-} was greater during low flows compared to high flows. These results highlight the role of peatland disturbance in nutrient delivery to aquatic ecosystems, and the effect of hydrology on DOM composition and nutrient processing. This study provides essential data for a relatively understudied region within the peatland DOM and nutrient literature, and highlights the need for more research into effective water quality management for disturbed peatlands.

2.1 Introduction

Human land use and land cover change (LULCC) has drained at least 11% of global peatlands (Fluet-Chouinard et al., 2023), which have accumulated vast stocks of partially decomposed organic matter (OM) under waterlogged conditions (Clymo et al., 1998). Drainage lowers peatland water tables, exposing more peat OM to aerobic decomposition and hydrological transport, and increasing dissolved organic carbon (DOC), nitrogen (N), and phosphorous (P) concentration in inland waters (Holden, 2005; Holden et al., 2006; Marttila et al., 2018;

Nieminen et al., 2020a). Approximately 71.4 million people rely on peatland catchments for their water supply (Xu et al., 2018), and elevated DOC and nutrient concentrations and export threaten water security for these communities (Kritzberg et al., 2020). For example, elevated DOC concentration contributes to the pervasive water browning trend across many high-latitude watersheds (Roulet and Moore, 2006; Creed et al., 2018; Kritzberg et al., 2020), which is associated with decreased light penetration into the water column, increased toxic metal mobilization, and increased difficulty and cost of water treatment for human use (Kraus et al., 2010; Kothawala et al., 2017; Kritzberg et al., 2020). Moreover, elevated nutrient concentrations cause harmful algal blooms and remove oxygen in the water, creating hypoxic zones that kill aquatic life (Feuchtmayr et al., 2019). Therefore, understanding the controls on solute export and fate from disturbed peatlands is important to protect aquatic ecosystem function and manage freshwater resources.

Additionally, peatlands are just one part of the mosaic of a landscape, and different land uses contribute DOC and nutrients to freshwaters from various sources and at varying rates (Kincaid et al., 2020; Vaughn et al., 2021). For example, intact peatlands are major DOC sources compared to forests and agriculture (Koprivnjak and Moore, 1992; Creed et al., 2008; Olefeldt et al., 2013; Sebestyen et al., 2021). DOC concentration in stream water is positively correlated with soil organic carbon stocks, and carbon is abundant across the boreal landscape. As DOC is transported from C-rich soils to headwater streams, contact with mineral sediments in non-peatland ecosystems sorb DOC, removing it from the fluvial network (Kothawala et al., 2012; Nichols and Peteet, 2019). Because peatland headwaters often travel through organic sediments, a larger fraction of DOC is transported from peatland soils to inland waters. Though peatlands are DOC sources, their status as nutrient source or sink depends on their vegetation and hydrology, with bogs and poor fens more likely to be nutrient sinks in the landscape (Devito et al., 1989; Nieminen, 1998; Turetsky, 2003; Sponseller et al., 2018). In contrast, agriculture and urban areas are major sources of inorganic nutrients with large inputs from fertilizers, manure, atmospheric deposition, and waste water (Carpenter et al., 1998). Some peatland disturbances, such as industrial peat extraction and wildfire, may eliminate plant nutrient demand and lower the water table, increasing soil OM mineralization and producing more DOC and inorganic nutrients for downstream transport (Strack et al., 2008; Marttila et al., 2018). However, it is uncertain how impactful peatland disturbance will be on water quality in heterogeneous catchments with diverse DOC and nutrient sources.

As solutes travel from disturbed peatlands to downstream ecosystems, in-stream processes transform solutes through biotic and abiotic processes. DOC and nutrients are removed or attenuated in the stream network through processes such as microbial assimilation, denitrification, photodegradation, and sedimentation (Pinay et al., 2015; Jones et al., 2016; Cory and Kling, 2018; Zarnetske et al., 2018; Krause et al., 2022), and are produced through sediment resuspension, autochthonous DOC production, or nutrient mineralization from dissolved organic matter (DOM). As water mixes downstream, solutes from disturbed peatlands and other sources create ideal conditions for solute transformation (McClain et al., 2003; Bernhardt et al., 2017). For example, when previously inert DOC combines with dissolved inorganic N (DIN), the lower DOC to DIN ratio increases DOC bioavailability (Wickland et al., 2012; Abbott et al., 2014), though this is not always the case (see Wologo *et al* 2021). To monitor solute processing, stream water chemistry from spatially-explicit synoptic samplings is a common method to locate solute sources and sinks in a catchment and demonstrate how solutes propagate downstream (Abbott et al., 2018; Shogren et al., 2019). Previous research has shown that some subcatchments have a large influence, or disproportionate leverage on downstream water chemistry most or at least part of the time (Abbott et al., 2018; Frei et al., 2021; Gu et al., 2021). Thus, research has shown that disturbed peatlands are important control points in the landscape that negatively affect downstream water quality.

Hydrology also influences the quantity and quality of solutes from different sources (e.g., disturbed peatlands) that are transported to the inland water network, which determine whether solutes are processed locally or transported downstream (Raymond et al., 2016). Climate change is expected to intensify hydrological extremes (i.e., frequent drought and intense, infrequent storms), which change the timing and magnitude of river discharge (Barnett et al., 2005; Trenberth, 2011; Sinha et al., 2019; Hicke et al., 2022). Variable discharge regimes therefore affect how landscapes contribute solutes to inland waters (Moatar et al., 2017; Fellman et al., 2020). For example, deeper water flow-paths integrate different DOM sources because OM distribution in peatland and upland catchments are vertically stratified in the soil (Barnes et al., 2018; Tfaily et al., 2018). Hydrology also affects the connectivity of the landscape with inland waters (Ameli and Creed, 2017; Blaurock et al., 2021). Depending on flow conditions, hydrological connectivity limits the delivery of DOC and nutrients to stream waters, and concentrations increase with flow as the landscape becomes more connected (Moatar et al., 2017; Zarnetske et al., 2018; Fellman et al., 2020; Wen et al., 2020). However, high flows could also produce a dilution effect, which has been reported in some northern peatlands (Laudon et al., 2011; Fork et al., 2020). As solutes are delivered to the stream network, water residence time affects in situ solute processing. Low flows increase water residence time which decreases the ratio of reaction time to residence time resulting in more DOC and nutrient processing (Burt and Pinay, 2005; Oldham et al., 2013). Therefore, hydrology has an important role to play in DOC and nutrient dynamics at the catchment scale.

Here, we studied two meso-scale (~150 km^2) catchments at the transition between boreal and grassland biomes in central Alberta, Canada. The catchments had mixed land use, with both undisturbed peatlands and forests, as well as agriculture and horticultural peat extraction sites. We measured DOC, N, and P concentrations in 55 nested subcatchments, and estimated solute export and attenuation during contrasting wet (2020) and dry (2021) years. We investigated the following questions: (1) How does peat extraction affect C and nutrient concentration and export compared to other catchment land cover and land use? (2) What is the fate of disturbed peatland DOC and nutrients as they move through stream networks? And (3) How does hydrological variability affect peatland DOC and nutrient concentration and fate? We hypothesize that extracted peatlands increase aromatic, humic-like DOC and inorganic nutrient concentrations due to enhanced decomposition and nutrient mineralization following extraction. We hypothesize that the fate of these solutes will be hydrologically-dependent, because water residence time is an important factor in solute processing rates. Therefore, we predict that aromatic, humic-like DOM exported from extracted peatland headwaters will shift to aliphatic, fresher DOM near the catchment outlet, and that this shift in DOM composition will be more pronounced during prolonged low-discharge periods. Moreover, we predict that inorganic nutrients will be rapidly attenuated in these C-rich, nutrient-limited environments, especially during low-discharge periods. The results from this study will be important for watershed management and modeling studies to understand the interacting effects of land use and climate change.

2.2 Methods

2.2.1 Study area

This study was conducted in two meso-scale catchments in central Alberta, Canada with mixed landscapes of agriculture, upland forest, and peatlands (Figure 2). The climate in the region is subhumid continental. Mean annual temperature is 2.6°C and mean annual precipitation is 483 mm (2005–2021; ACIS Alberta). Most of the precipitation falls as rain (339.1 mm annual mean) and the rainiest month is typically July (95.6 mm). Mean annual snowfall is 118.3 cm, and January is the snowiest month on average (21.7 cm). Tomahawk Creek (outflow: 53.35°, -114.65°) has a 188 km^2 catchment dominated by agriculture (primarily hay production and cattle grazing), but with widespread peatlands in the headwaters. Deep Creek (53.34°, -114.82°) has a 132 km^2 catchment west of Tomahawk Creek, dominated by agriculture with smaller peatlands only in the eastern main tributary. Elevation ranges between 809–724 m and 906-733 m above sea level in the Tomahawk Creek and Deep Creek catchments respectively. Both streams flow into the North Saskatchewan River which is the main source of drinking water for the City of Edmonton (population 981,000) approximately 150 km downriver.

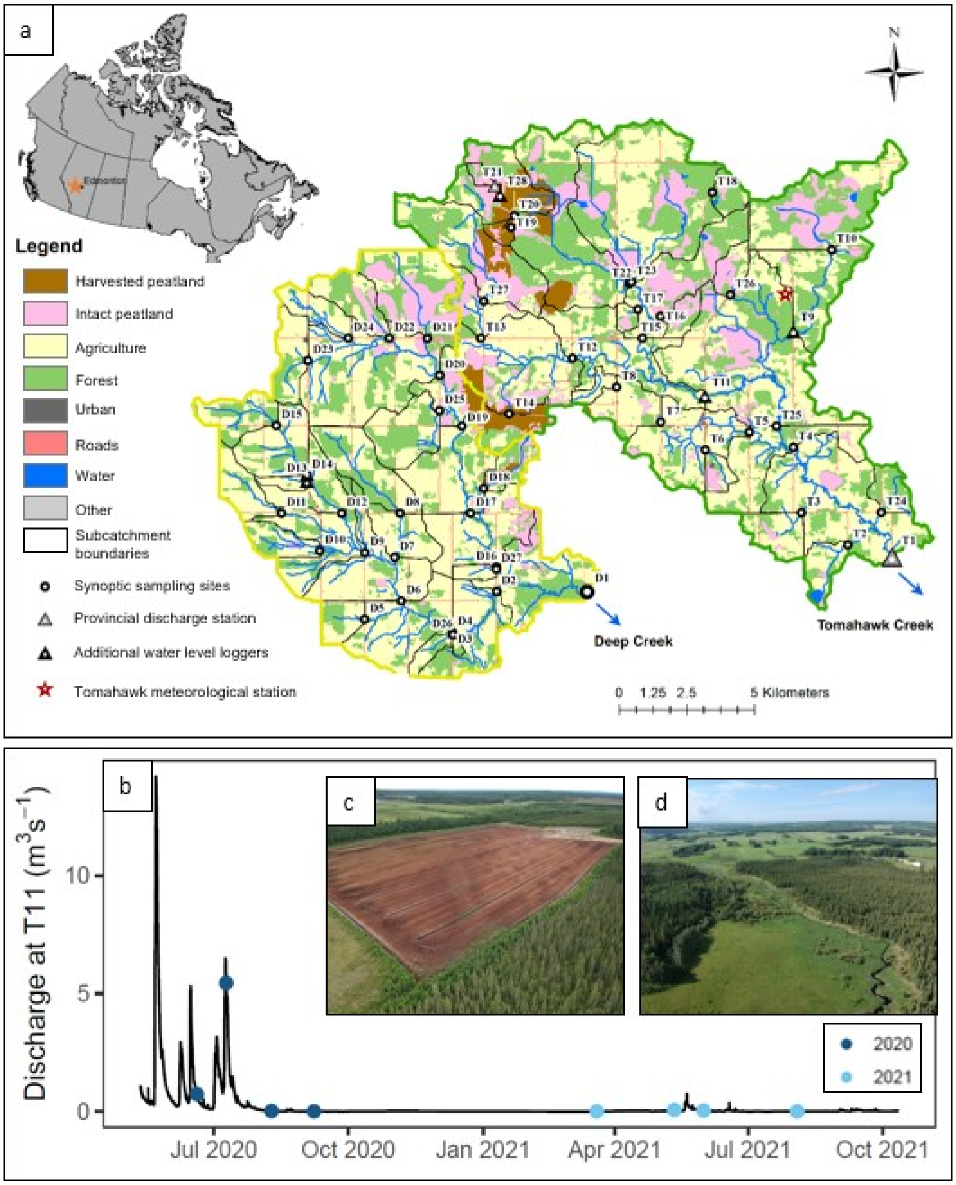

Figure 2. Map (a) of synoptic sampling locations in the Deep Creek (yellow outline) and Tomahawk Creek (green outline) catchments near Seba Beach, Alberta, Canada. Land cover and land use characteristics are shaded in the map. Fifty-five nested synoptic sampling sites are marked, with their catchment boundaries delineated. Provincial water and weather monitoring stations where we extracted hydroclimatic data are shown on the map. Plot b shows when the 8 sampling campaigns occurred in relation to the hydrograph at site T11. Drone photos (b and c) show aerial views of the landscape showing the diverse and heterogeneous nature of the area, including one of the extracted peatland sites (c, site T28).

The catchments are located within the Boreal Transition ecoregion, which forms the transition between the broader Boreal Plains and Prairie ecozones of Canada. The Boreal Transition ecoregion marks the northern limit of agricultural land, and much of it is used for grazing. Upland forests are primarily comprised of trembling aspen (*Populus tremuloides*), balsam poplar (*Populus balsamifera*), and a thick understory of mixed herbs and tall shrubs. Surficial geology is mostly Cretaceous shale, and the hummocky plains are covered by calcareous, glacial till and significant inclusions of relatively level lacustrine deposits. Rougher morainal deposits are associated with a large number of small lakes, ponds, and sloughs that occupy shallow depressions. Well-drained to imperfectly drained Gray Luvisols and Dark Gray Chernozemic soils are predominant (The Ecological Framework of Canada, 2014). Wildfires are uncommon in this rural landscape, but after a dry winter a 15.7 km^2 section of the Tomahawk and Deep Creek catchments caught fire in May 2021 and burned forest, peatlands, and agricultural land. However, we observed no difference in solute concentration or DOM optical properties post-fire, therefore we do not include fire in our subsequent analysis.

Wetlands in the region are found in depressions, along watercourses, and on flat lacustrine plains, and include all wetland classes. Peatlands, i.e., bogs and fens with deep peat soils (greater than 4 m in some places), are the most common wetlands, and are characterized by open-canopy black spruce (*Picea mariana*) and tamarack (*Larix laricina*) forests. Twenty-four percent of the wetlands in the study catchments have been used for industrial peat extraction, which has been ongoing since 1975 (Wind-Mulder et al., 1996), with the majority located within the Tomahawk Creek catchment. The extracted peatlands have been leveled, drained, and vacuum extracted so that only bare peat remains. Extraction sites are at different stages of production: some sites have been drained and actively extracted for more than 30 years, while other fields were leveled and drained for about 15 years. Because these are not recent operations, drainage ditches from extracted peatlands flow directly into headwater streams without retention ponds or overland flow (which have become best management practices for water drainage in newer extraction sites in Canada (Canadian Sphagnum Peat Moss Association, personal communication)). A few extracted sites are undergoing ecological restoration, but we were not able to quantify the spatial coverage of these sites with our GIS analysis (see section 2.2.4).

2.2.2 Water sample collection and chemical analysis

We collected water samples from 4 drainage ditches at peat extraction sites and 51 streams within the Tomahawk Creek (28 sites; T1–T28) and Deep Creek catchments (27 sites; D1–D27; Figure 2). In total, we collected 361 water samples during eight synoptic surveys in 2020 and 2021 to capture seasonal and temporal variability in DOC and nutrient concentration. We captured 97% of the hydrological variability during our study period, including the spring freshet (2021 only), summer baseflow, and storm events. Each synoptic sampling took 2–3 days to complete. During the summer months, some headwater streams flowed intermittently. Water samples were collected from flowing streams, and we sampled from the midpoint of small streams and 1 m out from the banks of larger streams. We measured pH, electrical conductivity, and water temperature *in situ* using a handheld multiparameter probe (Hanna, USA) that was calibrated daily. We also measured turbidity in the field using a portable 2020i Turbidity Meter (LaMotte, USA), calibrated daily.

We collected filtered samples for laboratory analysis of DOC concentration and composition, nutrients, base cations (the sum of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} concentrations), and other dissolved solutes. We filtered samples using 0.7 µm Whatman GF/F filters into pre-rinsed, acid-washed 60 mL glass amber bottles (for solute concentration) and 30 mL HDPE scintillation vials (for DOC optical properties). Samples were kept cool in transit to the lab, and were refrigerated at 4ºC until analysis. DOC concentration samples were acidified using 2 M HCl within 12 hours of collection. Solute concentration samples were analyzed within one week by the University of Alberta Natural Resources Analytical Lab using standard methods. DOC samples were analyzed on a Shimadzu TOC-L CPH Model Total Organic Carbon Analyzer with an ASI-L and TNM-L (Shimadzu, Japan). Dissolved ions (SO_4^{2-}, NO_3^{-}, NO_2^{-}, Cl^{-}, PO_4^{3-}, and NH_4^{+}) were analyzed with a Thermo Gallery Plus Beermaster Autoanalyzer (Thermo Fisher Scientific, Finland). Dissolved metals (Na, K, Ca, Mg, Fe, B, Mn, Zn, and Cu), TS, and TP were analyzed with a Thermo iCAP6300 Duo inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo Fisher Corp., United Kingdom). Analytes below detection limits were assigned half the detection limit value.

DOC optical properties were analyzed at the University of Alberta Catchment and Wetland Sciences Lab for absorbance and fluorescence. Absorbance was analyzed on filtered samples using a 1 cm quartz cuvette in a Shimadzu UV-1280 UV-vis spectrophotometer (Shimadzu, Japan). We measured absorbance spectra from 200–750 nm at 1 nm increments. To measure DOM fluorescence, we used a Horiba Aqualog spectrofluorometer (Horiba, Japan) using a 1 cm quartz cuvette with 1 second integration. If absorbance at 254 nm was > 4 cm^{-1} then we diluted the samples with Milli-Q water (Kothawala et al., 2013). All fluorescence data were blank-subtracted using Milli-Q water. We used Naperian absorbance at 254 nm to calculate specific UV absorbance ($SUVA_{254}$), and used fluorescence to compute the humification index (HIX (Ohno, 2002)), the autochthonous productivity index or freshness index (BIX (Wilson and Xenopoulos, 2009; Fellman et al., 2010)), and fluorescence peaks including humic-like peaks A, C, and M, and protein-like peaks B and T (Coble, 1996; Fellman et al., 2010). These peaks measure fluorescence intensity at different excitation and emission wavelengths, so we combined the fluorescence peaks into a Peak Ratio, i.e. the sum of peaks A and C divided by the sum of peaks T and B, to avoid autocorrelation with DOM concentration. Fluorescence indices and peaks were computed using the *staRdom* package in R (Pucher et al., 2019).

2.2.3 Hydrological data

Hydrological data were obtained from two government monitoring sites: one along the mainstem (T11; Station #: 05DE009; data available since 1984) and one near the outlet to the North Saskatchewan River (T1; Station #: 05DE930; data available since 2019). Provisional data were retrieved from https://rivers.alberta.ca (data available for T1 and T11 from 2019–2021) and https://wateroffice.ec.gc.ca/ (data available for T11 from 1984–2020). Data were checked for quality and used to estimate differences in flow conditions across sampling campaigns (e.g., we used discharge at T11 (Q_{T11}) in our statistical analyses to account for changes in hydrology) and to estimate catchment runoff from the Tomahawk Creek catchment.

2.2.4 Catchment delineation and land use

To relate hydro-biogeochemical data to LULCC, we delineated our 55 subcatchments and extracted LULCC and surficial geology data in ArcGIS Pro. Catchments were delineated using 25 m digital elevation models from Government of Alberta Open Data. Automated catchment delineations were then QA/QCd based on field observations. We used the Human Footprint Index and Wetlands Inventory spatial data products from Alberta Biodiversity Monitoring Institute to extract land use and land cover characteristics for each subcatchment. We also used

Surficial Geology of Alberta from Government of Alberta Open Data to extract surficial geology (Figure S1).

2.2.5 Statistical analysis and calculations

We used correlation and linear regression analyses to determine the effect of peatland disturbance on water quality. To control for seasonal and hydrological effects, we calculated mean values for our suite of water chemistry parameters (DOC, DON, NO_3^-, NH_4^+, DOP, PO_4^{3-}, SO_4^{2-}, base cations, Fe, Mn, Zn, and Cu). Then we used Spearman correlations to identify water quality parameters that were significantly correlated with disturbed and intact peatland cover (*Figure S3*). We regressed the significant variables with disturbed and intact peatland cover for catchments with at least 1% total peatland cover (n = 37). To test for significant differences between regression coefficients, we calculated the p-value using the z-statistic from a normal distribution (Clogg et al., 1995).

To investigate the influence of land use, seasonality, and hydrological conditions on solute concentration, we used Random Forest models to predict solute concentration from catchment characteristics, daily specific discharge from T11, and water temperature measured *in situ* at each site. Random forest models build a forest of regression trees from random subsets of data to create many predictions of the dependent variable that are then averaged for the final estimate (Breiman, 2001). Unlike other multivariate regression models, Random Forest does not require independent data, is less sensitive to correlated predictor variables, and is able to model non-linear relationships. We used the *ranger* package in R to run the model, and used $n_{tree} = 500$, and tuned the number of variables tried at each split in a tree (m_{try}) for each model using the GridSearchCV algorithm. The data was split into 80/20 training and test data sets (i.e., the model was trained on 80% of the data and tested on the remaining 20%) using stratified random sampling for equal variance in solute concentration between the training and test data. To assess model performance, we calculated out-of-bag R-squared and the root mean squared error (RMSE) to express the average model prediction error in units of the dependent variable (solute concentration). To interpret the models, we show predictor importance and partial dependence plots. Predictor importance plots show the predictor variables ranked in order of importance, with the most important predictors having a value of 1, and less important predictors having a value of <1. Partial dependence plots show the relationship (which can be non-linear) between a single predictor and the dependent variable.

We used redundancy analysis (RDA) to understand the relationships among DOM composition (response variables) and hydrological, water chemistry, and land cover variables (explanatory variables). All data was standardized before analysis using the *decostand* function in the *vegan* package in R (Oksanen et al., 2022). RDA is an extension of multiple regression by modelling how an explanatory matrix X affects a response matrix Y. To achieve this, an ordination of Y is conducted to derive ordination axes, which represent linear combinations of the variables within matrix X (Legendre and Legendre, 2012). The DOM composition response variables included $SUVA_{254}$, HIX, BIX, and the Peak Ratio. We selected hydrological, land cover, and water chemistry explanatory variables initially based on ecological significance. We then reduced dimensionality, especially for the land cover and water chemistry variables, using the *ordiR2step* function also from the *vegan* package. The final suite of explanatory variables included hydrological proxy variables: specific discharge at T11, *in situ* water temperature, sulfate concentration, and the sum of base cation concentrations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}); catchment characteristics: intact peatland cover, disturbed peatland cover, cropland cover, and distance from subcatchment outlet to the main catchment outlet; and water chemistry variables: ammonium (NH_4^{+}), total iron (Fe), dissolved organic N (DON, and phosphate (PO_4^{3-}) concentrations. To disentangle the impacts of different groups of variables, partial Redundancy Analysis (pRDA) partitioned variance among hydrological, catchment, and water chemistry variables. We examined potential issues with multicollinearity and non-linear relationships by investigating univariate correlations (*Figure S3*) and linear regressions among explanatory and response variables in the RDA models.

To assess solute attenuation through the stream network, we employed an innovative metric to qualitatively appraise solute mass balance, as outlined by Abbott *et al.* (2018). This metric assigns a percent leverage value to each subcatchment, akin to statistical leverage, and is computed through the following formula:

[1]
$$Subcatchment\ Leverage = (C_S - C_O) \times A_S/A_O \times Q_S/Q_O$$

Here, C signifies concentration, A denotes area, Q represents specific discharge, and S and O respectively stand for subcatchment and catchment outflow, as adapted from Abbott et al.'s framework. Because of limited subcatchment discharge data, the calculation of subcatchment leverage was reliant solely on concentration and area, similar to work by others (Shogren et al., 2019; Frei et al., 2021). For each of our main solutes (DOC, DIN, and PO_4^{3-}), we used the average of all subcatchment leverage values to interpret catchment mass balance. In instances where the mean leverage was close to zero, we interpreted the mass balance for the corresponding solute to be neutral, implying conservative mixing with no net production or removal. We interpreted positive mean leverage to indicate net attenuation, signifying a greater solute flux in the headwaters of a catchment than could be accounted for at the outlet. Conversely, a negative mean leverage signaled in-network production. By considering the central tendency of subcatchment leverage values, we used this metric to gain insights into the catchment mass balance, a reflection of diverse biological and physical attenuation and production mechanisms.

In our subcatchment leverage calculation (outlined above), we assumed uniform specific discharge out of logistical necessity (i.e., we did not have the ability to measure discharge across our 55 subcatchments). However, we acknowledge that this assumption likely does not hold (Karlsen et al., 2016), and therefore we assessed the sensitivity of our mass balance assessment to artificial variation in specific discharge. For one experiment, we induced variation in specific discharge by peatland cover because peatlands have been observed to have higher runoff generation than upland forests in boreal landscapes (Galster, 2007; Lyon et al., 2012; Devito et al., 2017). In another experiment, we induced random variation in specific discharge to simulate unpredictable contributions from groundwater discharge and disturbances such as wildfire, resource extraction, and water withdrawal (Galster, 2007). For the peat-weighted discharge scenario, we used total peatland area (intact and disturbed) multiplied by 10 as a proxy for specific discharge. For the randomly-weighted discharge scenario, we randomly generated specific discharge coefficients for each subcatchment over four orders of magnitude (0.1–100) and used those coefficients to calculate leverage for each subcatchment. We used these different discharge scenarios to test for significant differences among mean leverage values by solute (DOC, DIN, and PO_4^{3-}) using one-way analysis of variance.

Data analysis was carried out in R version 4.0.5.

2.3 Results

2.3.1 The effect of peatland disturbance on water quality

Peatland disturbance significantly influenced water quality compared to intact peatland dynamics. In our four disturbed headwater (< 10 km^2) peatland sites (samples collected from drainage ditches; sites T14, T19, T20, and T28) DOC concentration was 82 mg L^{-1} on average (range: 45–144 mg L^{-1}), NH_4^+ was 1.4 mg L^{-1} on average (0.03–4.5 mg L^{-1}), PO_4^{3-} was 0.18 mg L^{-1} on average (below detection to 0.98 mg L^{-1}), and turbidity was 45 NTU on average (3 to >200 NTU). In comparison, in our four intact headwater peatland catchments (T16, T21, T26, and D21), DOC concentration was 65 mg L^{-1} on average (range: 30–117 mg L^{-1}), NH_4^+ was 0.15 mg L^{-1} on average (0.02–0.66 mg L^{-1}), PO_4^{3-} was 0.11 mg L^{-1} on average (below detection to 0.73 mg L^{-1}), and turbidity was 9 NTU on average (below detection to 74 NTU). In catchments with more than 1% total peatland cover, peatland disturbance exhibited positive relationships with turbidity and NH_4^+, explaining 32% and 29% of the variance, respectively ($p < 0.001$; *Figure 3*). In contrast, intact peatland cover was negatively associated with turbidity (explaining only 17% of the variance), and had no significant relationship with NH_4^+. For PO_4^{3-}, intact peatland cover had a negative relationship, explaining 10% of the variance ($p = 0.03$), but disturbance showed no significant relationship ($p = 0.23$). The regression coefficients between the disturbed and intact models for turbidity, NH_4^+, and PO_4^{3-} were significantly different ($p < 0.05$). Disturbed peatland cover explained 34% of the variance in DOC concentration, and increased DOC by around 5 mg L^{-1} compared to intact peatlands, but the regression coefficients were not significantly different ($p = 0.06$). Though pH, base cations, and some DOM composition parameters were correlated with disturbed and intact peatland cover, no significant effects emerged between the peatland types.

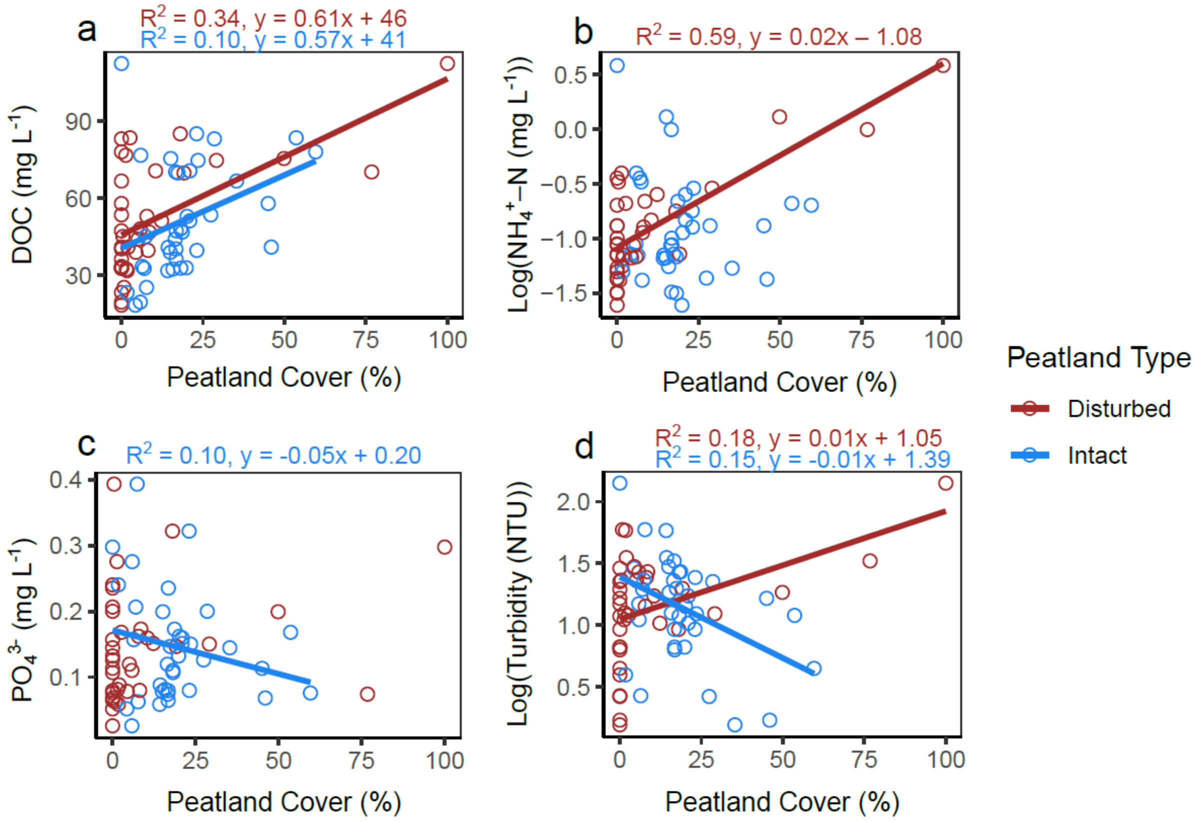

Figure 3. Significant effects ($p < 0.05$) of peatland disturbance compared to intact peatlands for key water chemistry parameters: dissolved organic carbon (DOC, plot a), the freshness index (BIX, plot b), ammonium (NH_4^+, plot c), and turbidity (plot d). Linear regression results are reported above the respective plots for disturbed peatland and intact peatland cover.

2.3.1 Land cover and hydrologic variability on DOC and nutrient concentrations

The disturbed peatland headwaters were part of heterogeneous, sub-boreal catchments, and we used random forest models to understand the role of peatland disturbance within the broader catchment dynamics. Across the 55 subcatchments and eight sampling campaigns, DOC concentration ranged from 4.7 to 150 mg L^{-1}, averaging 44 mg L^{-1}. Notably, significant positive correlations emerged between DOC concentration and intact peatlands, disturbed peatlands, and organic deposits (0.56, 0.50, and 0.61 respectively). Conversely, negative correlations were observed between DOC and agriculture and moraine deposits (-0.58 and -0.53 respectively; Figure S2). All of these correlations were statistically significant ($p < 0.05$). A random forest model explained 71% of the variability in DOC concentration, with the most influential predictors being intact peatlands, agriculture, and disturbed peatlands (variable importance scores = 1, 0.91, and 0.67 respectively; Figure 4d). DOC and agriculture exhibited an inverse relationship, with elevated concentrations evident in subcatchments featuring less than 25% agricultural coverage (Figure 4g). Both intact and disturbed peatland covers displayed positive correlations with DOC concentration, with a notable surge in DOC concentration occurring at a 25% catchment cover (Figure 5a and 5d).

The range of total N spanned from 0.24 to 7.6 mg L^{-1}, with an average of 1.6 mg L^{-1}. Dissolved organic N emerged as the primary N form, accounting for 82% of total N on average (Figure S4). NH_4^+ and NO_3^- constituted 12% and 6% of TN on average, respectively. Across all sites and samplings, NH_4^+–N concentration varied between below detection levels and 4.5 mg L^{-1}, averaging at 0.19 mg L^{-1}. NH_4^+ exhibited positive correlations with NO_3^-, PO_4^{3-}, disturbed peatland cover, and organic deposits (Spearman correlations = 0.46, 0.39, 0.23, and 0.23 respectively). Conversely, negative correlations were evident with forest cover, agricultural cover, human infrastructure, and moraine surficial geology (Spearman correlations = -0.09, -0.27, -0.27, -0.28; Figure S2), all of which were statistically significant ($p < 0.05$). A random forest model explained 75% of the variance in NH_4^+ concentration (root mean squared error = 0.47 mg L^{-1}). Key variables contributing to this model were peatland disturbance, forest cover, and catchment area (variable importance scores = 1, 0.22, and 0.20; Figure 2). The influence of peatland disturbance on NH_4^+ was distinctly evident from partial dependence plots, showing substantial increases around 40% and 80% disturbed peatland coverage. Moreover, intact peatland cover, while the least influential predictor in the NH_4^+ model (importance score = 0.03), displayed a linear increase in NH_4^+, thereby emphasizing the role of peatlands as NH_4^+ sources, further exacerbated by disturbance by an order of magnitude (Figure 5b and 5e).

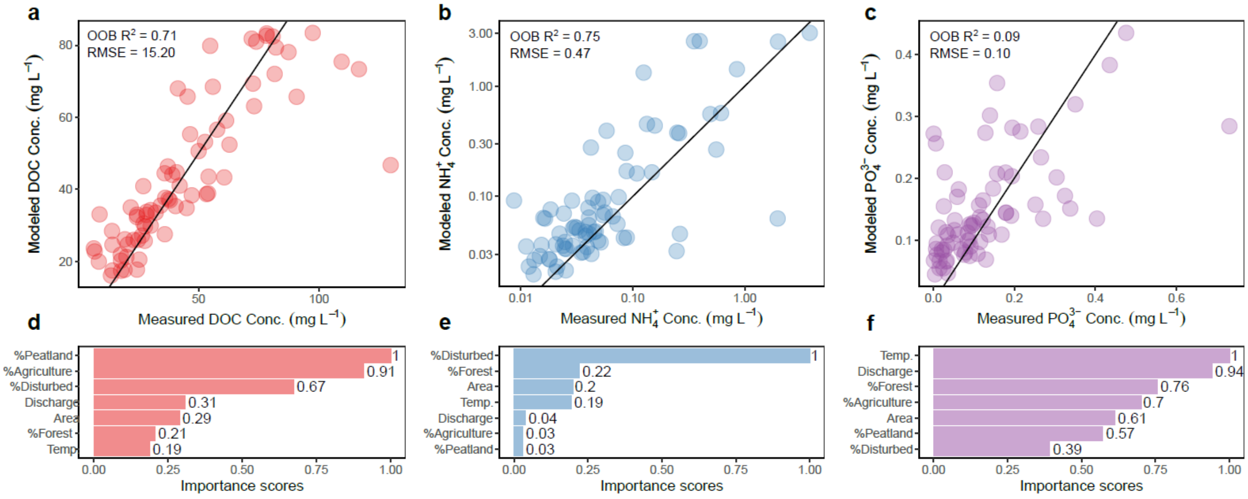

Figure 4. Random forest models predicting DOC and inorganic nutrient concentrations using land use and climate variables. Plots a-c show modeled vs. measured solute concentrations, and he trendline is a 1:1 line. Plots d-f show relative importance scores in descending order. OOB = out-of-bag. RMSE = root mean squared error.

The concentration of total P ranged from levels below detection to 2.0 mg L^{-1}, with a mean concentration of 0.20 mg L^{-1}. Notably, inorganic P (PO_4^{3-}) proved to be more prevalent than organic P, comprising 68% of total P on average (Figure S4). The observed PO_4^{3-} concentration spanned from below detection to 1.8 mg L^{-1}, averaging at 0.14 mg L^{-1}. The PO_4^{3-} random forest model accounted for only 9% of the variation in PO_4^{3-} concentration (with a root mean squared error of 0.10 mg L^{-1}). The three primary predictors were *in situ* water temperature, stream discharge (measured at T11), and forest cover (variable importance scores = 1, 0.94, and 0.76; Figure 2). In comparison, intact and disturbed peatlands exerted relatively minor influences on the model (variable importance scores = 0.57 and 0.39 respectively), but these variables displayed contrasting relationships. Specifically, PO_4^{3-} exhibited a positive relationship with peatland disturbance, with step-wise increases around 20% and 80% peatland disturbance coverage. However, intact peatlands had little effect on PO_4^{3-}, except when intact peatland coverage was low (i.e., < 1%) and PO_4^{3-} concentration was ~0.06 mg L^{-1} higher on average (Figure 5c and 5f).

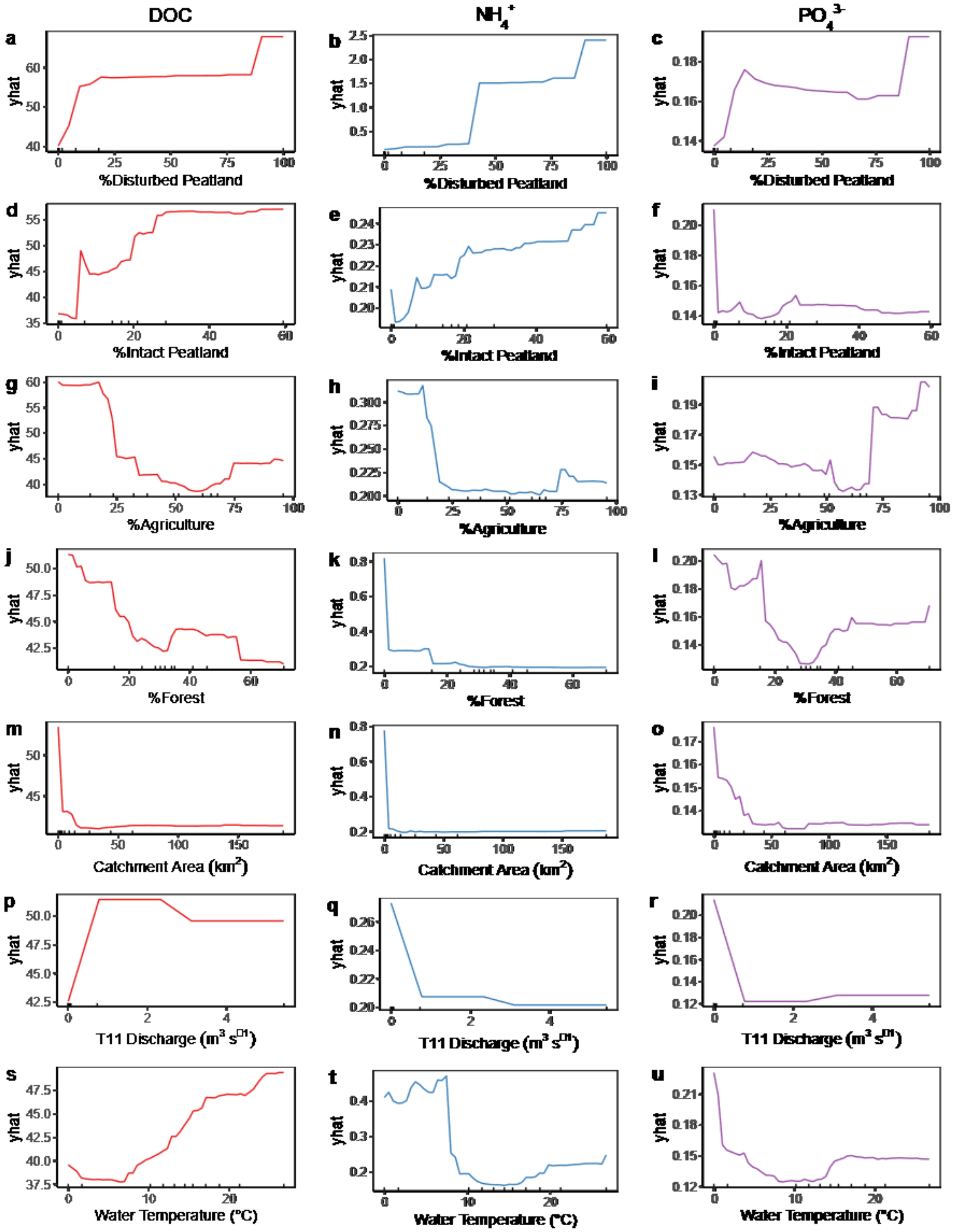

Figure 5. Partial dependence plots for DOC, NH_4^+, and PO_4^{3-} Random Forest models. Rug plots (tick marks along the x-axis) shows data deciles.

Across sampling campaigns, variations in hydrology measured by T11 discharge revealed broad, annual-scale concentration-discharge relationships for DOC, NH_4^+, and PO_4^{3-}. In the DOC model, discharge's relative importance was 0.31. During summer storms, moderate flow raised DOC, while high flows slightly decreased it, suggesting enrichment then dilution at high flows (*Figure 5*p). In the NH_4^+ model (relative importance: 0.04), higher discharge in summer storms led to NH_4^+ reduction, indicating dilution (*Figure 5*q). With a high relative importance of 0.94 in the PO_4^{3-} model, increasing summer storm discharge consistently lowered PO_4^{3-} levels, highlighting a dilution pattern (*Figure 5*r). These insights underscore the influence of hydrological variability on water quality indicators.

2.3.2 Spatiotemporal dynamics of DOM composition: hydrological variability and subcatchment characteristics

We examined the effect of hydrochemistry and catchment characteristics (including peatland disturbance) on the observed variation in DOM composition using RDA. DOM composition metrics were colinear with each other: $SUVA_{254}$ was positively correlated with HIX and the Peak Ratio (0.74 and 0.73 respectively), HIX and the Peak Ratio were strongly positively correlated (0.98), and BIX was negatively correlated with $SUVA_{254}$, HIX, and the Peak Ratio (-0.65, -0.71, -0.71; *Figure S3*). Average $SUVA_{254}$ across sites and sampling campaigns was 3.64 L mg^{-1} C m^{-1} (range: 0.96–5.80), average HIX was 0.92 (0.79–0.96), average Peak Ratio was 7.39 (1.95–17.5), and average BIX was 0.60 (0.44–0.88) (the Peak Ratio, HIX, and BIX are unitless values based on fluorescence). In the RDA, 62% of the variance in DOM composition was explained by the suite of hydrochemical variables and catchment characteristics ($p < 0.001$; Figure 6, Table S1). Notably, the primary RDA axis (RDA1) predominantly contributed to this variation, explaining 53% of the DOM composition variance primarily due to fluctuations in hydrochemistry. Through variance partitioning, the specific impact of hydrochemistry remained prominently influential. While controlling for catchment characteristics, hydrochemical factors (e.g., discharge variability across samplings; in situ water temperature; and concentrations of base cations, SO_4^{2-}, DON, NH_4^+, PO_4^{3-}, and Fe) were highly significant, explaining 51% of the variation in DOM composition (82% of the explained variance of the full model; Table S1). High-flow conditions, warmer water, and higher DON and Fe concentrations were associated with more aromatic, humic-like DOM; whereas low-flow conditions with higher nutrient, SO_4^{2-}, and base cation concentrations were associated with fresher, more autochthonous DOM. While catchment characteristics were also significant factors, they accounted for only 6% of variance in DOM composition (10% of the full model's explained variance). Notably, the distance between subcatchments and the catchment outlet correlated with distinct land cover and DOM composition patterns. Greater peatland land cover, both intact and disturbed, was associated with increased distance from the outlet, aligning with a prevalence of aromatic, humic-like DOM. In contrast, catchments closer to the outlet exhibited heightened cropland cover and a corresponding abundance of fresh, autochthonous-like DOM.

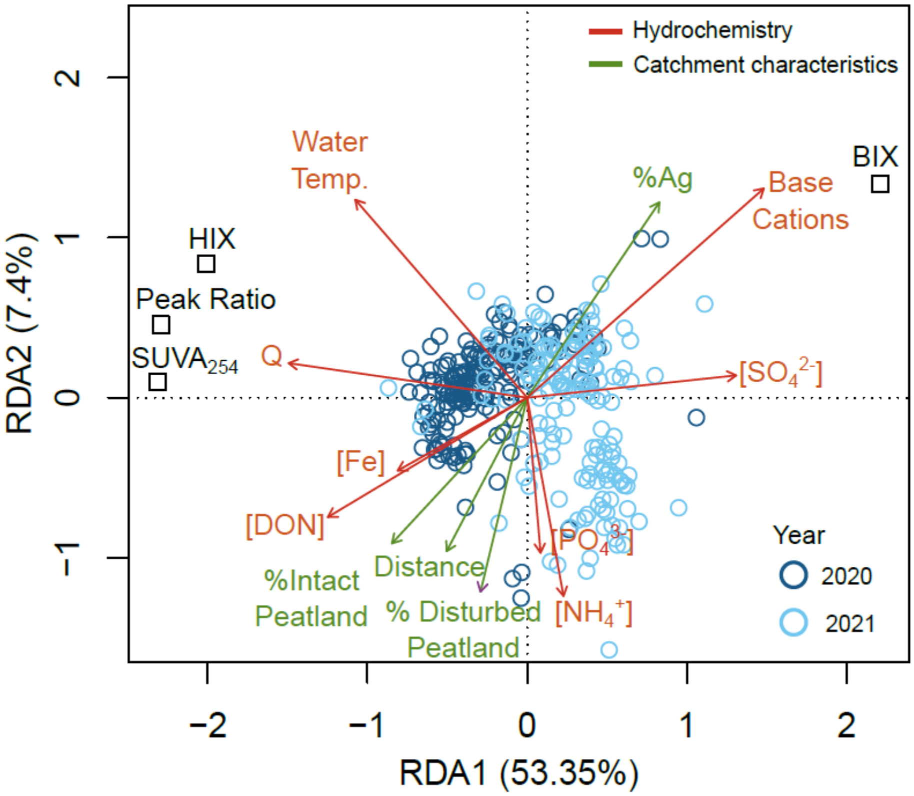

Figure 6. Triplot of the redundancy analysis (RDA) to show relationships between the suite of DOM composition variables and explanatory variables (hydrological variables, catchment characteristics, and water chemistry). Points represent water samples collected across sites and sampling campaigns, and are colored by year to show interannual differences between contrasting wet (2020) and dry (2021) years.

2.3.3 Subcatchment leverage and solute attenuation

Subcatchment leverage analysis showed that DOC and nutrients attenuated as they moved through the stream network, but that attenuation differed both between solutes and between contrasting hydrological years (Figure 7). We used mean leverage values to measure nutrient production or attenuation along the stream network between wet and dry years. Mean subcatchment leverage for DOC in the both the wet and dry year were near zero (2.15% and 5.96% respectively), indicating a neutral mass balance (i.e., conservative mixing). The mean was slightly higher (more positive) during the dry year, indicating modest net DOC attenuation during drought and low-flow conditions. Mean DIN leverage was strongly positive (12% and 30% for 2020 and 2021 respectively), indicating net DIN attenuation through the stream network. Moreover, dry years had even greater positive leverage values and therefore higher attenuation rates. Mean PO_4^{3-} leverage was also strongly positive, but attenuation rates were greatest during the wet year (80% and 39% in 2020 and 2021 respectively). Base cations, which we would expect to act conservatively through the stream network, had mean leverage values near 0 (-1.7% and -1.7% for 2020 and 2021 respectively), suggesting a neutral mass balance with no change between hydrological conditions.

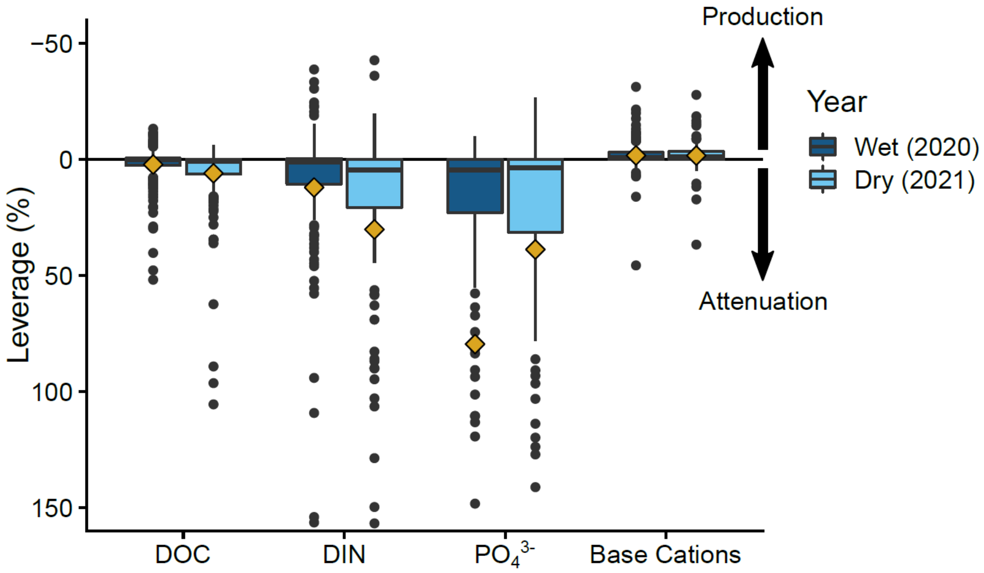

Figure 7. Boxplots of subcatchment leverage show differences in solute fate between wet (2020) and dry (2021) years. Boxplots show the median and 95% confidence interval of subcatchment leverage values. Yellow diamonds indicate the mean. Negative mean leverage indicates solute

production and positive mean leverage indicates solute attenuation through the stream network. We have flipped the y-axis to visually agree with the concepts of solute production (an increase and generally associated with ‘up’) and removal (a decrease and generally associated with ‘down’). Base cations = the sum of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} concentrations.

To assess the sensitivity of the central tendency of subcatchment leverage values (i.e., our qualitative solute attenuation analysis), we conducted a sensitivity experiment where we artificially changed the stream discharge component in the leverage calculation. Because boreal peatlands in subhumid catchments have been found to generate more runoff than other land cover units (e.g., the boreal forest, see Devito *et al* 2017), we increased specific discharge in subcatchments proportional to their peatland cover. We also inserted random variation to simulate effects of unaccounted groundwater influence. We found that varying specific discharge across the catchments by peatland area and random variation generally increased mean leverage, i.e. greater attenuation, compared to the control (i.e., the unweighted, uniform discharge scenario) for all solutes (DOC, DIN, and PO_4^{3-}). However, the only significant effect was observed for DOC concentration in the peat-weighted discharge scenario (one-way ANOVA, $p = 0.003$), but not for any other discharge scenario or solute (Figure S5).

2.4 Discussion

This study showed that peatland disturbance by industrial peat extraction significantly affected NH_4^+ and PO_4^{3-} concentrations and turbidity compared to intact peatlands. For DOC, highest concentrations were observed in the drainage ditches from actively extracted peatlands, but overall the disturbance effect was not significant. Across the meso-catchment-scale (i.e., ~150 km^2), disturbed peatland cover was the most important predictor variable in a random forest model that explained 75% of the variance in NH_4^+, but disturbance was less important in the PO_4^{3-} and DOC models. Disturbance had little effect on DOM composition, and most of its variability was explained by hydrochemical changes across flow conditions. Additionally, in our qualitative estimate of catchment mass balance, the evidence suggested that DIN and PO^{3-} were attenuated in the stream network, while DOC and base cations acted more conservatively. Changes in stream flow affected attenuation for solutes in different ways, likely affecting the mass flux and reach of solutes downstream. We further discuss the implications of this research in the following paragraphs.

2.4.1 DOC export in the net ecosystem carbon balance of extracted peatlands

Extracted peatlands are significant sources of greenhouse gas emissions to the atmosphere (Sundh et al., 2000; Wilson et al., 2015; Rankin et al., 2018; He et al., 2023). Many studies have indicated that draining peatlands enhances dissolved organic carbon (DOC) export (Moore and Clarkson, 2007; Strack et al., 2008; Evans et al., 2016; Menberu et al., 2017), but some studies have reported little effect (Moore, 1997; Rosset et al., 2022). Prior research demonstrated that fluvial carbon export, wherein DOC is a pivotal component, can constitute up to 30% of the net ecosystem carbon balance (NECB) in extracted boreal peatlands (Evans et al., 2016). Nevertheless, our present study on sites in continental western Canada suggests that DOC export's significance for the NECB is much less. We approximated DOC export from the extracted peatlands by utilizing the mean DOC concentration from drainage ditches in the disturbed sites (82 mg L^{-1}) and twice the mean annual runoff of larger mixed catchments (see Table S*2*). Our estimation of double the mean annual runoff is conservative, considering the smaller size of extracted peatland catchments and the evidence of higher runoff in peatland catchments in the boreal plains of western Canada compared to upland catchments (Devito et al., 2017). Consequently, we inferred that the yearly DOC export was <10 g C m^{-2} yr^{-1} in the wetter year (2020) and <2 g C m^{-2} yr^{-1} in the drier year (2021). While literature on greenhouse gas exchange in extracted peatlands remains limited, it's evident that these peatlands emit substantial CO_2 and some methane from the exposed peat surface, with measurements ranging from 70 to 300 g C m^{-2} yr^{-1} (Sundh et al., 2000; Waddington et al., 2010; Wilson et al., 2015; Rankin et al., 2018; Clark et al., 2023; He et al., 2023). As such, in this subhumid region characterized by limited runoff, DOC export is probably a minor constituent of the NECB for extracted peatlands. However, its role could potentially be more significant in wetter climates.

2.4.2 The effect of peatland disturbance on water quality

Disturbed peatlands significantly increased NH_4^+ concentrations in inland waters compared to intact peatlands. The decomposition of peat organic matter (OM) in intact peatlands leads to the mineralization of N to NH_4^+. This NH_4^+ is taken up by biota and recycled into organic matter, resulting in relatively low inorganic nitrogen concentrations in inland waters (Wang et al., 2015). However, in extracted peatlands, the removal of plants reduces biotic nutrient uptake, and drainage operations lower the water table and accelerate peat OM decomposition (Nieminen, 1998). This altered environment fosters elevated NH_4^+ production, which is subsequently transported to inland waters (Nieminen, 1998, 2004; Laine et al., 2013; Tuukkanen et al., 2017; Nieminen et al., 2020a). Moreover, some investigations have also documented elevated levels of NO_3^- in drained peatlands (Nieminen, 1998, 2004; Marttila et al., 2018; Nieminen et al., 2020a). However, NO_2^- and NO_3^- concentrations were low in these sites, with several possible explanations for this phenomenon. Notably, the biological process of ammonium oxidation, or nitrification, carried out by nitrifying bacteria and archaea, converts NH_4^+ to NO_2^- and NO_3^- (Li et al., 2018). Acidic conditions have been found to hinder this process (Li et al., 2018; Shi et al., 2021), aligning with our observed negative correlation between peatland disturbance and pH levels (though the disturbance effect was non-significant). Other processes such as nitrite-dependent anaerobic methane oxidation, anaerobic ammonium oxidation (anammox), denitrification, and dissimilatory nitrate reduction to ammonium may play a role in reducing NO_3^- and decreasing its concentration (Shi et al., 2021). However, given the high NH_4^+ concentration compared to low concentrations of NO_3^- and NO_2^- in disturbed peatlands, the overall significance of these NO_3^- reducing processes appears limited. Consequently, peat extraction was a major source of NH_4^+ for this landscape, but drained peatlands in other regions could have less of an impact on DIN concentrations depending on fertilizer application, atmospheric N deposition, peat OM quality, and N content (Shi et al., 2021).

For PO_4^{3-}, there was a significant difference between trends for disturbed and intact peatlands. PO_4^{3-} concentrations decreased as intact peatland cover increased, but increasing peatland disturbance had no significant effect. This phenomenon can be attributed to rapid phosphorus cycling in the upper peat layers of intact peatlands, particularly ombrotrophic bogs, which maintain low levels of PO_4^{3-} in inland waters (Wang et al., 2015). However, in extracted peatlands, organic P can be mineralized to PO_4^{3-}, but oxidized conditions can co-precipitate P with other compounds such as Fe and Mn (Zak et al., 2004). Therefore, the response of PO_4^{3-} is modulated by redox conditions and concentrations of co-precipitating compounds, resulting in an unclear PO_4^{3-} relationship with peatland disturbance. Notably, other studies have reported increasing PO_4^{3-} concentrations from both drained and rewetted peatlands, highlighting the intricate role of redox chemistry across diverse peatland disturbance and restoration processes (Zak et al., 2004; Zak and Gelbrecht, 2007; Nieminen et al., 2020a).

We hypothesized that inorganic N and P export from agricultural subcatchments would be much greater than from disturbed peatlands, and that the influence of peat extraction in mixed agricultural catchments would be marginal. However, extracted peatlands were the main DIN source and land use had no effect on inorganic P concentration. This is likely explained by the fact that agriculture in our study region consisted of mostly low-density grazing and hay production, both of which result in low N and P inputs from fertilizer and manure. Additionally, the relatively high DOC concentration in agriculture subcatchments suggests that many uplands in this region are also rich in SOM, and nutrients are likely retained within the soil (Taylor and Townsend, 2010). Nevertheless, PO_4^{3-} was abundant in both peatlands and upland catchments, suggesting that other factors beyond land use control P cycling in this study region. Unfortunately, we do not have detailed N and P inventories like other regions (Eshleman and Sabo, 2016; Sabo et al., 2019; Frei et al., 2020) and more research is needed to understand nutrient cycling in the Boreal Transition ecozone.

Disturbed and intact peatland cover had contrasting relationships with turbidity. Peatland drainage increased erosion of particulate matter into inland waters, whereas intact peatlands acted as water filters (St-Hilaire et al., 2006; Wilson et al., 2011). The influence of drainage on particulate loading of inland waters has prompted the peat extraction industry in Canada to adopt sediment settling ponds in newer extraction sites to help reduce sediment transport downstream (St-Hilaire et al., 2006; Hafdhi et al., 2020). Our headwater extracted peatland sites are located on older extraction sites and therefore their drainage network has been left free-flowing.

Though DOC concentrations were elevated in inland waters draining disturbed headwater peatlands relative to intact headwater peatlands (< 10 km^2), there was no significant effect of disturbance in our regression analysis. The DOC random forest model supported this assessment, suggesting that peatland cover in general was the most important driver of DOC concentration across the meso-scale catchments (~150 km^2). Evidence from NH_4^+ concentrations, and companion studies on vertical C fluxes from the peat surface and ditches (Hunter, *in review,* and work from eastern Canada: Clark *et al* 2023, He *et al* 2023) suggest that peat OM decomposition was elevated in the extracted peatlands, but this did not translate to significantly higher DOC concentrations in the stream network. DOM composition was not significantly affected by disturbance, and was mainly affected by changes in hydrology. This data is critically important to support the broader research on disturbed peatland DOM dynamics across ecosystems and climatic gradients (Rosset et al., 2022).

2.4.3 Influence of hydrology on DOC and nutrient processing and attenuation in the stream network

Hydrological variability modulates solute attenuation and catchment nutrient dynamics, affecting the downstream reach of solutes from disturbed peatlands. Generalized concentration-discharge relationships showed that both N and P exhibited dilution patterns with rising stream discharge, suggesting that these nutrients were production-limited across the catchment. However, their attenuation rates in response to contrasting hydrological conditions were opposite. During prevailing dry conditions in 2021, DIN exhibited higher attenuation while PO_4^{3-} had lower attenuation. These attenuation patterns suggest divergent processes removing DIN and P from the water column such as redox chemistry and biological nutrient demand (i.e., differences in prevailing nutrient limitation) (Zak and Gelbrecht, 2007). This data indicates that the effect of peatland disturbance on downstream water quality and nutrient delivery is modulated by hydrology and redox chemistry. Sedimentation impounds and ditch blocking may retain a large portion of eroded sediments and nutrients during low flows, but high flows overwhelm their retention capacity (St-Hilaire et al., 2006; Hafdhi et al., 2020). Therefore, more research is needed to develop the tools and assessments necessary for more responsible watershed management. Moreover, peatlands are widespread in northern regions and peat extraction is just one type of peatland disturbance. Thus, more research is needed on the generalizability of the impacts of peatland disturbance on water quality across northern regions in the context of global biogeochemical cycles (Rosset et al., 2022).

DOC displayed enrichment during moderate flows and slight dilution during high flows, consistent with patterns in other peatland systems (Fork et al., 2020; Bass et al., 2023). Though hydrology was a less important factor in the DOC random forest model, it was a major factor controlling DOM composition. Redundancy analysis showed that hydrochemistry exerted a more substantial influence on dissolved organic matter (DOM) composition than land cover, highlighting the interconnectedness between water flux, hydrological flowpaths, and DOM sources (Broder et al., 2017; Sebestyen et al., 2021). However, it's worth noting that hydrochemical indicators, such as base cation and sulfate concentrations, were correlated with land cover due to differences in hydrological flowpaths between peatland and upland systems. Higher stream flow increased aromatic, humic-like DOM into the stream network, associated with less DOC attenuation. Conversely, low flow conditions were linked with greater DOC attenuation. Low flows were also associated with elevated base cations and sulfate concentrations, indicating increased groundwater influence (Abbott et al., 2016), resulting in fresher and more autochthonous-like DOM. This shift in DOM composition from aromatic to fresher forms signifies a combination of processes, including mineral adsorption, photo- and bio-degradation, autochthonous DOM production, and the infusion of fresh DOM as catchments transition from peat-dominated headwaters to agricultural landscapes near the outlet (Broder et al., 2017; Fork et al., 2020).

Our findings emphasize the complexity of solute dynamics and the critical role of hydrological variability in shaping them. It's important to note that while our qualitative assessment of solute mass balance makes certain assumptions about uniform specific discharge across the study area, future research involving catchment-scale hydrological modeling and mass balance studies is crucial for determining precise rates and mechanisms of solute attenuation (e.g., Wen *et al* 2020). As we anticipate the continued impact of human development and climate change on northern peatlands (Hugelius et al., 2020; Loisel et al., 2021; Fluet-Chouinard et al., 2023), understanding and managing DOM and nutrient export from disturbed peatlands while preserving intact peatlands is increasingly imperative (St-Hilaire et al., 2006; Hafdhi et al., 2020; Harris et al., 2022). This work aids in mitigating potential downstream consequences and provides evidence to support broader efforts in peatland conservation and sustainable management (Loisel et al., 2021; Harris et al., 2022).

2.5 Conclusions

Peatland disturbance has the potential to disrupt water quality far beyond the boundaries of the initial disturbance. In this study, subcatchments draining extracted peatlands without sediment impoundments affected inorganic N and P concentration and turbidity in inland waters relative to intact peatlands. DOC concentrations were elevated in drainage ditches relative to headwater peatland catchments, but this effect was not significant across the study region. In context of the net ecosystem carbon balance, we estimated that DOC flux from extracted peatlands was a minor component due to low runoff in this subhumid climate. As such, peatland DOC export in our study region is lower than in more humid regions such as eastern Canada. Additionally, we estimated that inorganic nutrients were attenuated as they moved downstream, with divergent patterns in response to stream discharge. DOC acted conservatively through the stream network, but changes in DOM composition were associated with hydrochemical indicators suggesting that differences in hydrological flowpaths and water residence time influenced DOM fate.

3. Prevailing carbon-limitation for bacteria in disturbed headwater peatland streams

Abstract

Peatlands are abundant in northern landscapes and are significant sources of water and dissolved organic matter (DOM) to inland waters. DOM consists of diverse molecules that contain carbon (C), nitrogen (N), and phosphorous (P) that are essential nutrients for aquatic organisms in relative ratios. Disturbances in northern peatlands, such as wildfire and resource extraction, may influence the magnitude and bioavailability of C, N, and P that are produced in peatlands and transported to inland waters. Yet, the impact and relevance of peatland disturbance for aquatic ecosystems remain understudied. Here, we investigated how wildfire and industrial peat extraction affected nutrient limitation for bacteria in three headwater peatland catchments in central Alberta, Canada. We sampled peatland porewater and headwater streams four times over a year and measured dissolved C, N, and P concentration; DOM molecular properties; and performed bacterial regrowth lab incubations to estimate dissolved organic C (DOC), DON, and DOP bioavailability. Our results suggest that peatland disturbance had no significant effect on DOM bioavailability, which was <1% on average, because recalcitrant molecular structures precluded heterotrophic bacterial uptake. However, the spring freshet produced a spike in bioavailable DOC and DON which was associated with a decrease in DOM aromaticity. Inorganic nutrients were significantly affected by peatland disturbance, with dissolved inorganic N (DIN) increasing in the extracted peatland, and phosphate (PO_4^{3-}) increasing in the burned peatland. Consequently, bacterial abundance and stoichiometric ratios of bioavailable C:N:P suggested that headwater peatland streams were C-limited, exporting recalcitrant DOC and reactive nutrients downstream.

3.1 Introduction

The molecular composition and bioavailability of DOM exported from disturbed northern peatlands are subject to change due to climate change, land use alterations, and land cover changes (Creed et al., 2018). This DOM contains essential nutrients, including nitrogen (N), phosphorous (P), and other elements that support the productivity and function of northern aquatic ecosystems (Tanentzap et al., 2017; Berggren et al., 2018). Peatland disturbances release older, stored organic matter, altering the quantity, composition, and reactivity of DOM entering northern water bodies (Butman et al., 2015; Burd et al., 2018). Because northern ecosystems generally exhibit lower biodiversity compared to temperate and tropical regions, they are more sensitive to disruptions in food resources that could destabilize ecosystem structure (Schindler, 1998). Consequently, peatland disturbances could have profound implications for aquatic biogeochemistry, nutrient cycling, and ecosystem health (Berggren et al., 2015; Creed et al., 2018).

Despite the well-recognized significance of peatland DOM export, our understanding of the effects of peatland disturbance on DOM bioavailability in northern aquatic ecosystems remains limited (Hulatt et al., 2014a; Berggren et al., 2015). Previous studies have predominantly focused on gaseous and bulk aquatic fluxes of C (Evans et al., 2016), largely overlooking the complex dynamics of DOM and its bioavailability. Peatland disturbance likely affects DOM composition and bioavailability because of changes in vegetation, water table position, water flow paths, and DOM production rates (Holden et al., 2006; Laine et al., 2014). Deeper water flow paths transport DOM from older peat, reintroducing ancient C into the contemporary C cycle (Hulatt et al., 2014b; Butman et al., 2015). The relationship between DOM age and bioavailability is murky (Butman et al., 2012; Hulatt et al., 2014a; Bogard and Butman, 2018), but older peat DOM suggests that DOM is sourced from deeper peat, which is associated with more humic-like DOM with higher N:P ratios (Wang et al., 2015; Tfaily et al., 2018). Moreover, research on drained and burned peatlands has shown increased DOC and inorganic N and P concentrations in peat porewater and connected streams (Strack et al., 2008; Brown et al., 2015; Nieminen et al., 2017; Ritson et al., 2017; Burd et al., 2018; Wu et al., 2022). Increasing nutrient availability in soils has been connected with increasing DOC bioavailability, an effect known as nutrient priming which may also occur in aquatic ecosystems (Wologo et al., 2021). Yet, few studies have measured the synergistic effects of DOM bioavailability and nutrient concentrations in disturbed peatlands (Hulatt et al., 2014a; Burd et al., 2018).

Only a fraction of natural DOM is bioavailable for consumption by aquatic organisms, which is determined by the interaction of molecular composition and environmental conditions (Kothawala et al., 2020; Berggren et al., 2022). For example, molecular composition determines the thermodynamic favorability of DOM for mineralization, which factors in bond energies, chemical structure, functional groups, and oxidations state (Kothawala et al., 2020).

Environmental conditions (e.g., temperature, redox, nutrient availability) modulate the rate of reactions, allowing labile DOM to persist for centuries or nonlabile DOM to react rapidly (Kothawala et al., 2020; Berggren et al., 2022). Therefore, bioavailability is an operational term that measures the amount of an element potentially assimilable by biota, either directly or via enzymatic processing (Stepanauskas et al., 2002; Berggren et al., 2015).

While northern DOM-rich waters contain abundant DON and DOP, their bioavailability remains understudied compared to DOC (Berggren et al., 2015). Recent research in Scandinavia employing bacterial regrowth bioassays suggests that bioavailable DON (BDON) and DOP (BDOP) might be more accessible than BDOC, with %BDOC < %BDON < %BDOP (Stepanauskas et al., 2002; Soares et al., 2017; Rulli et al., 2022). However, these studies have primarily focused on fresh DOM from relatively pristine boreal catchments, leaving the bioavailability of DOC, DON, and DOP from disturbed peatlands unexplored. Consequently, understanding the impact of peatland disturbances on bioavailable resource stoichiometry (C:N:P ratio) for aquatic heterotrophic bacteria remains challenging (Berggren et al., 2015). Because aquatic bacteria have specific but variable requirements for consuming C, N, and P (Fagerbakke et al., 1996; Vrede et al., 2002), insufficient access to these resources significantly decreases species abundance, potentially leading to cascading effects on aquatic food webs and alterations in aquatic biogeochemistry (Creed et al., 2018).

Here, we investigated the effect of peatland disturbance on DOM molecular structure, and on C, N, and P bioavailability and stoichiometry. To this end, we studied porewater and stream water in three headwater peatland catchments: one intact, one extracted, and one burned. We measured DOM molecular composition using UV-Vis and fluorescence spectroscopy and radiocarbon (14C-DOC) analysis. We hypothesized that extraction and wildfire would lead to the downstream export of older, more humic-like, and less bioavailable DOM, due to lowered water table and removal of vegetation and the relatively increased transport of DOM derived from deeper and older peat layers. Therefore, we predicted that disturbed peatlands would be C-limited compared to the intact peatland because of lower DOM bioavailability (particularly BDOC). And if so, disturbed peatlands would export more inorganic nutrients and recalcitrant DOM to downstream ecosystems. Overall, this research seeks to contribute to our knowledge of northern peatland dynamics, offering valuable insights into the effects of disturbance on dissolved organic matter bioavailability and its repercussions on the intricate balance of northern aquatic ecosystems.

3.2 Methods

3.2.1 Study sites

The study was carried out in three headwater peatland catchments located near Seba Beach, Alberta, Canada (53° 28’ N, 114° 51’ W; Figure 8). We selected one intact, one extracted, and one burned headwater peatland catchment based on catchment characteristics (Table 1) and site accessibility. These catchments were located in the Canadian Boreal Transition ecoregion, where the Prairie ecoregion transitions into the Boreal Plains (The Ecological Framework of Canada, 2014). The study sites were all, at one point, treed bogs with vegetation dominated by *Sphagnum spp*., *Rhododendron groenlandicum*, and *Picea mariana*. We used GIS analysis in ArcGIS Pro to delineate catchments and quantify land cover extent. Catchments were delineated using the Government of Alberta’s Provincial Digital Elevation Model at 25 m resolution. Land cover data was extracted from the Alberta Biodiversity Monitoring Institute’s Human Footprint Index and Wetlands Inventory. Catchment characteristics are reported in Table 1. Briefly, the intact peatland catchment was adjacent to the extracted one but disturbance was negligible. In the extracted peatland catchment, 100% of the catchment was extracted and natural vegetation had been completely removed (see Figure 8). The burned peatland catchment caught fire in May 2021 in the Parkland Fire, and burned to the extent that most vegetation was incinerated and only charred tree trunks remained. These headwater catchments drained into Tomahawk Creek and Deep Creek, which are tributaries to the North Saskatchewan River approximately 150 km upriver from Edmonton, Alberta. The river is the city’s primary drinking water source. Regional surficial geology is dominated by moraines and glaciolacustrine deposits, and peatlands have formed over hundreds of years in flat regions underlain by fine-grained, glaciolacustrine deposits.

Table 1. Land cover information for the three headwater peatland catchments.

Site	Area (km^2)	Total wetland (%)	Extracted peat (%)	Burned (%)	Forest (%)	Agri-culture (%)
Intact Peatland	0.50	56	3	0	43	0
Extracted Peatland	0.04	100	100	0	0	0
Burned Peatland	8.68	45	0	29	30	23

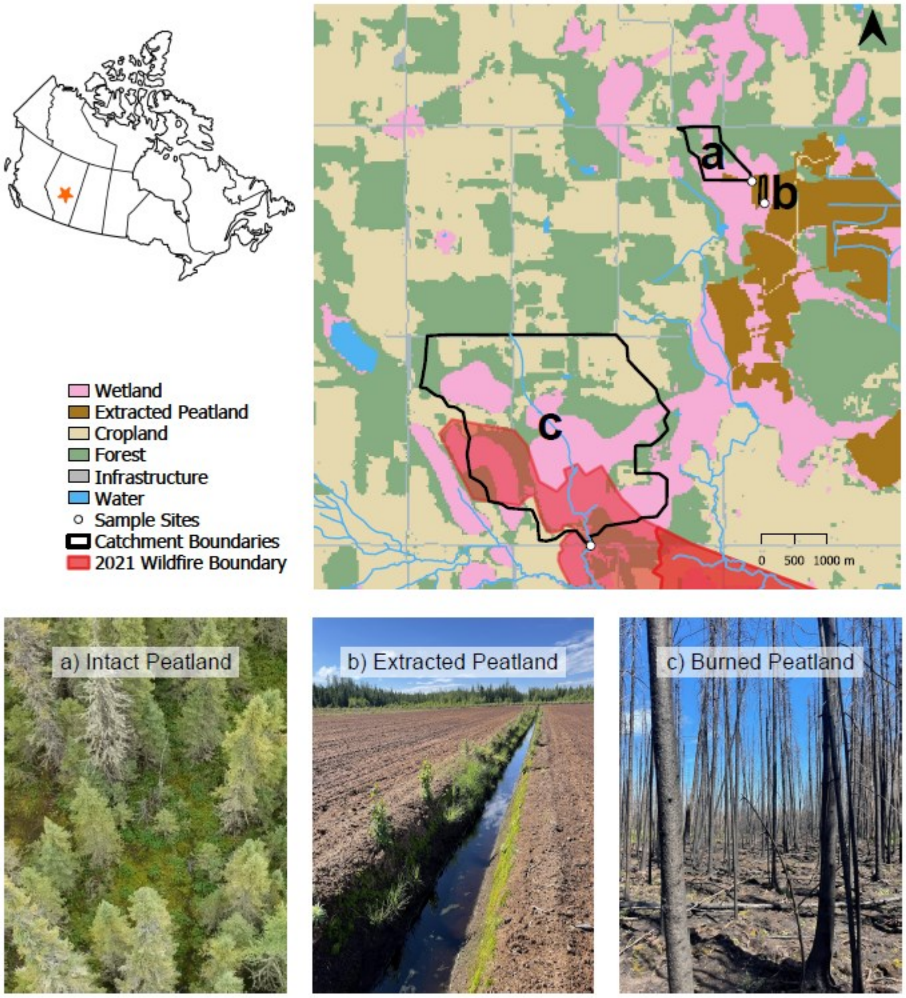

Figure 8. Map of study sites in the Tomahawk and Deep Creek Catchments. Photos show conditions in intact (a), extracted (b), and burned (c) headwater peatland catchments.

3.2.2 Sample collection and analysis

We collected porewater and stream water samples from the three sites to understand the effect of peatland disturbance on DOM bioavailability, stoichiometry, and molecular composition. We sampled porewater twice and stream water four times from August 2021 to August 2022 to capture seasonal and hydrological variability. The samplings occurred during summer base flow conditions (August 2021 and 2022), the spring freshet (March 2022), and a summer storm (July 2022). Peat porewater samples were collected in July and August 2022 by digging two or three ~30 cm pits in the peat until groundwater began seeping in. To reduce the disturbance effect of digging on pore water DOM, we waited for the pits to fill with water for 10–30 mins (depending on flow rate), and removed most of the water and then waited for the pits to refill. Equal volumes were collected from each pit and combined to form a representative porewater sample for each site. Stream water samples were collected from headwater streams near the center of the stream. Pore and stream water samples were filtered in the field for water chemistry analysis.

3.2.2.1 DOM concentration and other water chemistry parameters

We collected *in situ* data and grab samples from the headwater peatland catchments to determine DOM and nutrient concentrations and general water chemistry. We measured water temperature, pH, and electrical conductivity using an *in situ* multiparameter probe (Hanna). We collected filtered stream water samples to analyze for DOC, nutrients, and other elements. Samples were filtered using pre-rinsed 0.7 µm glass fiber filters (GFF) into 60 ml glass amber bottles (for DOC) and 60 ml HDPE bottles (for nutrients, ions, and metals). Samples were transported back to the laboratory on ice. DOC samples were acidified to pH 2 using standard-grade 2M HCl, and all samples were stored in the dark at 4°C until analysis. Samples were analyzed for DOC, dissolved ions, and metals at the University of Alberta Natural Resources Analytical Lab. DOC samples were analyzed on a Shimadzu TOC-L CPH Model Total Organic Carbon Analyzer with an ASI-L and TNM-L (Shimadzu, Japan). Dissolved ions (SO_4^{2-}, NO_3^-, NO_2^-, Cl^-, PO_4^{3-}, and NH_4^+) were analyzed with a Thermo Gallery Plus Beermaster Autoanalyzer (Thermo Fisher Scientific, Finland). Dissolved metals (Na, K, Ca, Mg, Fe, B, Mn, Zn, and Cu), TS, and TP were analyzed with a Thermo iCAP6300 Duo inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo Fisher Corp., United Kingdom).

3.2.2.2 DOM molecular composition

To determine DOM molecular composition, we collected porewater and stream water samples from the headwater peatland catchments for UV-Vis and fluorescence spectroscopy. We syringe-filtered samples in the field using 0.7 µm GFF into 20 ml plastic scintillation vials. Samples were stored in the dark at 4°C until analysis. In the lab, we measured absorbance from 200–750 nm at 1 nm increments using a 1 cm quartz cuvette with a Shimadzu UV-1280 UV-vis spectrophotometer (Shimadzu, Japan). We used a Horiba Aqualog spectrofluorometer (Horiba, Japan) to measure fluorescence excitation and emission using a 1 cm quartz cuvette with an integration time of 0.5 second. If absorbance at 254 nm was > 4 cm^{-1} then we diluted samples by a factor of 2 with Milli-Q water. Fluorescence excitation and emission matrices (EEMs) were blank-subtracted in MATLAB using Milli-Q blanks.

To measure DOM age and source, we collected samples for radiocarbon analysis (^{14}C-DOC) during the July and August 2022 samplings. Radiocarbon samples were vacuum-filtered in the field using 0.7 µm GFF and stored in sterile 500 ml HDPE bottles wrapped in aluminum foil and were frozen until analysis. Samples were analyzed at the University of Ottawa A. E. Lalonde AMS Laboratory. Radiocarbon analyses were performed on an Ionplus AG MICADAS (Mini Carbon Dating System). Data are reported following conventions recommended by Millard (2014). The fraction modern carbon, F14C, was calculated according to the ratio of the sample ^{14}C/^{12}C to the standard ^{14}C/^{12}C (Ox-II) measured in the same data block. Radiocarbon ages are calculated as -8033ln(F14C) and reported in 14C years before present (BP=AD 1950), as described by Stuiver and Polach (1977).

3.2.3 DOM bioavailability bioassays

3.2.3.1 Concentration change bioassays

To determine DOM bioavailability, we used two different methods: concentration change (Vonk et al., 2015) and bacterial regrowth incubations (Stepanauskas et al., 2000; Soares et al., 2017; Rulli et al., 2022). Concentration change incubations are commonly used in freshwater studies to determine DOC bioavailability (Abbott et al., 2015; Vonk et al., 2015; Wologo et al., 2021). This method uses the change in DOC concentration at the beginning and end of the incubation to determine DOC bioavailability. Bioavailable DON and DOP can theoretically also be measured by this method, but concentration changes are commonly within instrument error margins. During the 2022 season, we used 7- and 28-day concentration change incubations following Vonk *et al* (2015) to estimate BDOC. In the field, we collected unfiltered samples in acid-washed 4 L LDPE cubitainers. Back at the lab, we vacuum-filtered the samples using 0.7 µm GFF (Whatman) within 12 hours. We added 150 ml of porewater and stream water to acid-washed 250 ml borosilicate glass amber bottles in triplicate. Samples were incubated in the dark at 20°C for 28 days, and were aerated at least once a week to prevent anoxia. Subsamples (20 ml) were collected at the beginning (T0), after 7 days (T7), and after 28 days (T28), and were acidified to pH 2 with 2M HCl. After the full 28-day incubation, subsamples were analyzed together for DOC on a Shimadzu TOC-L analyzer.

3.2.3.2 Bacterial regrowth bioassay

The second incubation method we used was a bacterial regrowth bioassay to measure concurrent bioavailability of DOC, DON, and DOP in the three headwater peatland streams (Stepanauskas et al., 2000; Soares et al., 2017; Rulli et al., 2022). To briefly overview the method, bacteria are removed from stream water samples and then reintroduced to bioassays to measure bacterial regrowth (via bacterial abundance) over a seven-day incubation period. Three subsets of the bioassays target bacterial consumption of bioavailable DOC, DON, and DOP respectively to facilitate bacterial regrowth. Thus, bacterial abundance is used to estimate bioavailable fractions of DOC, DON, and DOP.

In the lab, we conducted four controlled bacterial regrowth bioassays in the laboratory over one year following an adapted protocol based on the methods from Rulli *et al. (*2022). We collected 4 L of unfiltered stream water from each site in acid-washed LDPE cubitainers. To remove bacteria, we vacuum-filtered these samples within 24 hours using 0.2 µm nylon membrane filters (Whatman). The filtered water for each sample was divided into 12 replicates—each in a 250 ml acid-washed glass bottle with a polypropylene cap (Duran) for a final incubation volume of 150 ml. We also prepared a control incubation by following the same steps above but with Milli-Q water instead of stream water. We then added bacteria back to the incubation bottles using 2% (v/v) standard inoculum—water collected from throughout the Tomahawk catchment stream network and vacuum-filtered using 1.2 µm membrane filters (Millipore) to remove particulate matter and large bacterivores. Next, we added 5% (v/v) of modified Bold's Basal Medium (excluding N and P) which contains the micronutrients and trace metals necessary for bacterial growth. During lab trials, we found that we needed to raise pH in the incubation samples to reduce bacterial shock due to naturally acidic conditions in the headwater peatland streams (pH ~5). Therefore, we amended the pH in each sample to pH 7 using an autoclaved calcium carbonate solution to imitate natural pH in the mainstem of Tomahawk Creek where these headwaters drain. Total amounts of calcium carbonate solution added to each sample depended on initial pH, which varied by season and hydrological conditions, but was <5% (v/v) of incubation volume.

To encourage bacteria to utilize bioavailable organic matter for growth, we induced strong C-, N-, or P-limitation in a subset of the incubation bottles. For example, for each water sample consisting of 12 replicate bottles, we induced C-limitation in a third of the bottles, N-limitation in another third, and P-limitation in the final third by adding non-limited nutrients in excess. For example, in the C-limited subset, we added N (as NH_4NO_3; amount added 2000 µg N L^{-1}) and P ($NaH_2PO_4 \bullet H_2O$; amount added 200 µg P L^{-1}). In the N-limited subset, we added C ($C_6H_{12}O_6$; amount added 20 mg C L^{-1}) and P ($NaH_2PO_4 \bullet H_2O$; amount added 200 µg P L^{-1}). In the P-limited subset, we added C ($C_6H_{12}O_6$; amount added 20 mg C L^{-1}) and N (as NH_4NO_3; amount added 2000 µg N L^{-1}). To verify that we induced nutrient limitation, and to estimate average nutrient content in bacteria cells, we added a spike of the limiting nutrient in half of the samples. Specifically, in two of the four C-limited samples we added a spike of C (final concentration in bioassay: 1000 µg C L^{-1}); in two of the four N-limited samples we added a spike of N (final concentration in bioassay: 100 µg N L^{-1}); and in two of the four P-limited samples we added a spike of P (final concentration in bioassay: 10 µg P L^{-1}).

Samples were incubated in the dark at 20°C for 7 days. Every 24 hours, we collected two one-ml subsamples from each incubation bottle and stored them in sterile 1.5 ml Eppendorf tubes. We immediately fixed the subsamples with filtered (0.2 µm) glutaraldehyde (3% v/v) and stored them at 4°C until analysis for bacterial abundance.

Bacterial abundance was determined by flow cytometry within one week of subsampling. Flow cytometry is optimal for measuring bacterial abundance because it enables rapid and automated sample analysis with high accuracy. Flow cytometry uses fluorescence spectroscopy and fluid focusing to count thousands of individual cells per second. We prepared our samples by staining the fixed subsamples with diluted fluorescent SYTO-13 dye. We also prepared flow cytometry controls for each sample run, which consisted of pure Milli-Q water and Milli-Q water stained with SYTO-13. After the subsamples were stained, they were stored in the dark for 15 minutes, and then analyzed on an Attune NxT flow cytometer. Raw bacterial count data were post-processed using FlowJo v10.7.2 software to quality check the data and remove nonviable cell counts. Final bacterial abundance was calculated as concentration of cells ml^{-1}.

3.2.4 Calculations and statistical analyses

3.2.4.1 Absorbance and fluorescence spectroscopy and modelling

We used UV-Vis and fluorescence spectroscopy to measure DOM molecular composition. UV-Vis spectra were used to calculate indices that estimate DOM aromaticity and molecular weight.

We estimated DOM aromaticity by calculating specific UV absorbance at 254 nm ($SUVA_{254}$; L mg^{-1} C m^{-1}) by dividing the Naperian absorbance value at 254 nm by DOC concentration (Weishaar et al., 2003). To estimate molecular weight, we calculated the slope ratio (S_R) using the *staRdom* package in R (Helms et al., 2008; Pucher et al., 2019). S_R is calculated by dividing the slope from 275–295 nm by the slope from 350–400 nm, and is inversely correlated with DOM molecular weight (Helms et al., 2008). We calculated fluorescence indices using the *pickpeaks* function in the drEEM toolbox in MATLAB. First, we corrected the EEMs by removing noisy data, normalizing to Raman Units, and correcting for inner filter effects. The *pickpeaks* function calculated the Freshness Index and Humification Index (HIX) to estimate fractions of fresh and humic-like DOM. The Freshness Index is used to estimate biological activity in inland waters, and is measured by dividing the emission at 380 nm by the emission maximum between 420 and 435 at the excitation at 310 nm. The HIX is correlated with humic-like, recalcitrant DOM, and is measured as the area under the emission spectra from 435–480 nm divided by the peak area at 300–345 nm and 435–480 nm in the excitation spectra at 254 nm (Ohno, 2002). Used together, these indices provide information about DOM molecular composition, including molecular weight, aromaticity, and source.

Additionally, we used parallel factor (PARAFAC) analysis to further characterize DOM molecular composition based on fluorescence signals unique to our dataset. PARAFAC decomposes EEMs into a series of statistical, tri-linear components, which explain the variability of fluorescence characteristics in DOM. To run PARAFAC analysis, we used the drEEM toolbox in MATLAB (Murphy et al., 2013). Using the same corrected EEMs from the peak picking exercise above, we created initial PARAFAC models. Next, we identified and removed outliers, adjusted model parameters to minimize sum of squares residuals, and identified the appropriate number of components, randomly initializing with 10 iterations. Finally, we validated the model using split-half analysis. The final validated model had four components, and the relative fluorescence intensity was expressed as a percentage of the sum of all four component intensities. To interpret the components, we compared our four components to other published PARAFAC components in the OpenFluor database (Murphy et al., 2014).

3.2.4.2 Bioavailable DOC, DON, and DOP calculations

We measured bioavailable DOC using two methods: through concentration change and bacterial regrowth incubations. Using the concentration change method, we estimated the fraction of bioavailable DOC by calculating the proportion of DOC lost over the 7-day ($BDOC_{cc7}$) and 28-day ($BDOC_{cc28}$) incubation periods.

Bioavailable DOC, DON, and DOP were estimated from the bacterial regrowth incubations. For most samples, bacterial abundance peaked after 3 days (Figure S9). Secondary peaks were common as bacterial abundance increased during the second half of the incubation. Our goal was to identify the primary bacterial abundance peak so we could use a spike-and-response approach from Stepanauskas *et al* (2000) with a fixed timeframe to estimate the fraction of DOC, DON, and DOP that is readily bioavailable to bacteria (Soares et al., 2017). Therefore, we used bacterial abundance from day 3 to estimate nutrient bioavailability.

To calculate bioavailable fractions of DOC, DON, and DOP from the bacterial regrowth incubation, we made the following three assumptions as explained in detail in Rulli *et al* (2022). First, we assumed that the added spike of limiting nutrients was 100% bioavailable and assimilated during the incubation. Second, bioavailable C, N, and P compounds produced an equal increase in bacterial biomass per mol of C, N, or P. Lastly, all bioavailable C, N, and P were exhausted when the bacterial growth reached a primary peak—representing only readily bioavailable nutrients.

First, we calculated nutrient content per cell ($Nutrient_{cell}$) in Equation 1:

$$Nutrient_{cell} = \frac{s}{A_{spike} - A_{stream}}$$

Where s is the concentration of C (as glucose), N (as ammonium nitrate), or P (as phosphate) spike added to the C-, N-, and P-limited spike samples respectively. A_{spike} is the average bacterial abundance in the spiked samples (cells ml^{-1}), and A_{stream} is the average bacterial abundance in the unspiked stream and control samples (cells ml^{-1}). Concentrations of BDOC, BDON, and BDOP (in µg L^{-1}) were calculated using Equation 2:

$$B = (Nutrient_{cell} \times A_{stream}) - I$$

Where I is the concentration of inorganic nutrients (in μg L^{-1}). The inorganic fraction of C was ignored. The dissolved non-bioavailable fraction (D_n) of C, N, or P (in μg L^{-1}) was calculated in Equation 3:

$$D_n = T - B - I$$

Where T is the total dissolved concentration of that particular nutrient.

3.2.4.3 Stoichiometric C:N:P ratios

We compared total (DOC:TDN:TDP), inorganic (DOC:DIN:DIP), and bioavailable (BDOC:DIN+BDON:DIP+BDOP) resource fractions to identify the limiting nutrients for the headwater catchments across seasonal and hydrological conditions. We report C:N:P ratios as log-transformed molar ratios, which is the best practice in ecosystem stoichiometry studies to avoid data bias that favors P-limitation (Isles, 2020). We compared stream water sample stoichiometry to the log-transformed Redfield ratio (log(106:16:1)) to estimate nutrient limitation for bacteria in headwater peatland streams.

3.2.4.4 Statistical analysis

To test for significant differences among headwater peatlands and sampling periods, we used one-way ANOVAs. We tested assumptions of normality and equal variance using q-q plots and the Levene's Test respectively. Differences among groups were determined using the Tukey Honest Significant Differences test. We used linear discriminant analysis, a multivariate, rotation-based analysis, to maximize the spread of DOM molecular composition indices among headwater peatlands. Discriminant analysis can be affected by the scale of predictor variables (Legendre and Legendre, 2012), so we standardized the data so that the mean and standard deviation for each DOM analyte would be 0 and 1 respectively. We performed the analysis using the candisc package in R (Friendly and Fox, 2021).

We used multiple linear regression models to assess the effect of intrinsic and extrinsic controls on DOM bioavailability. We constructed two models with $BDOC_{br}$ and $BDON_{br}$ concentration as the respective response variables. Because of a large number of zeros in the $BDON_{br}$ concentration data, we ran a zero-inflated regression model. Due to our small sample size (n = 11), we chose four explanatory variables: $SUVA_{254}$, S_R, DIN, and PO_4^{3-}. Prior to statistical modelling, we standardized the data and log-transformed variables as needed.

3.3 Results

3.3.1 The effect of peatland disturbance on C, N, and P concentrations and bioavailability

Peatland disturbance had little effect on DOC, DON, and DOP concentrations, but increased inorganic N and P concentrations (Figure 9). Highest DOC, DON, and DOP concentrations occurred in disturbed peatlands, but differences among peatland catchments were not statistically significant ($p > 0.05$; See Figure 9 and Table S4). Porewater and stream water DOC concentrations averaged 178 ± 36 (standard error) mg L^{-1} and 84 ± 8 mg L^{-1} respectively; DON concentrations in porewater and stream water averaged 2.6 ± 0.50 mg L^{-1} and 1.7 ± 0.13 mg L^{-1} respectively; and DOP concentrations in porewater and stream water averaged 0.16 ± 0.09 mg L^{-1} and 0.09 ± 0.02 mg L^{-1} respectively (Table S3). Inorganic nutrients were more affected by disturbance than their organic counterparts. Porewater and stream water DIN concentrations averaged 3.4 ± 1.4 mg L^{-1} and 0.80 ± 0.43 mg L^{-1} respectively, with highest concentrations coming from the disturbed peatland. DIN in the extracted peatland was significantly higher than the burned and intact peatlands ($p = 0.004$; Figure 9 and Table S4). Porewater and stream water PO_4^{3-} concentrations averaged 1.9 ± 1.2 mg L^{-1} and 0.13 ± 0.04 mg L^{-1} respectively, with highest concentrations coming from the burned peatland. However, there was no significant effect of peatland disturbance on PO_4^{3-} ($p = 0.18$, Table S4).

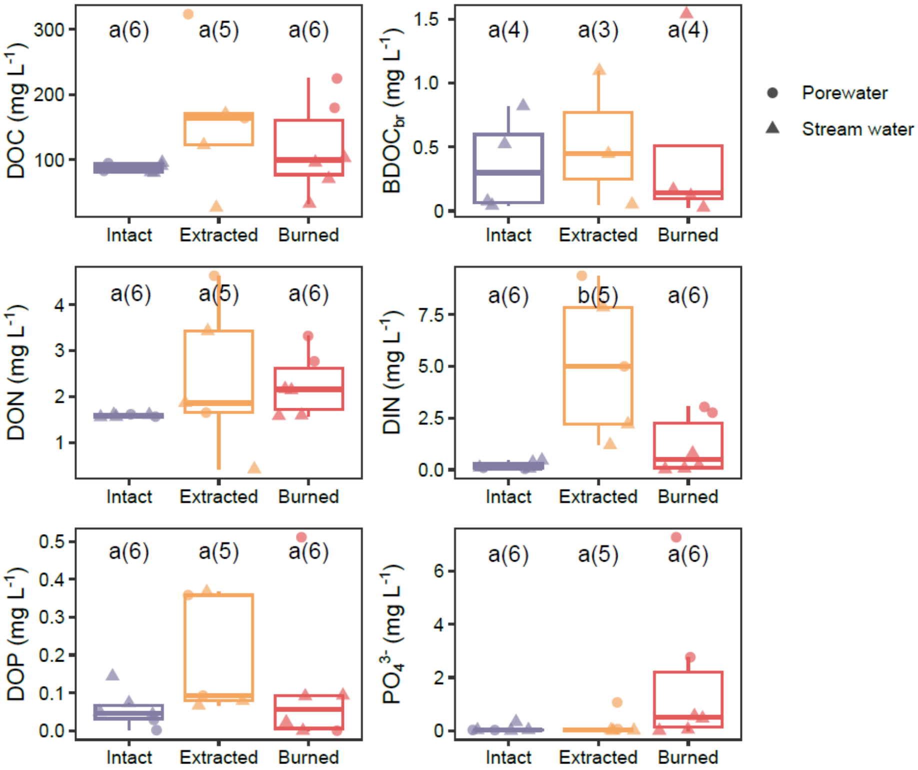

Figure 9. Boxplots of C, N, and P concentrations showing the interquartile range (box) about the median (mid-line) for each headwater peatland catchment. Different shapes for the jittered sample points show differences in porewater and stream water samples. In the text above the boxplots, the first letter is the compact letter display to show significant differences among catchments ($p < 0.05$), and the integer in parentheses shows the total number of samples.

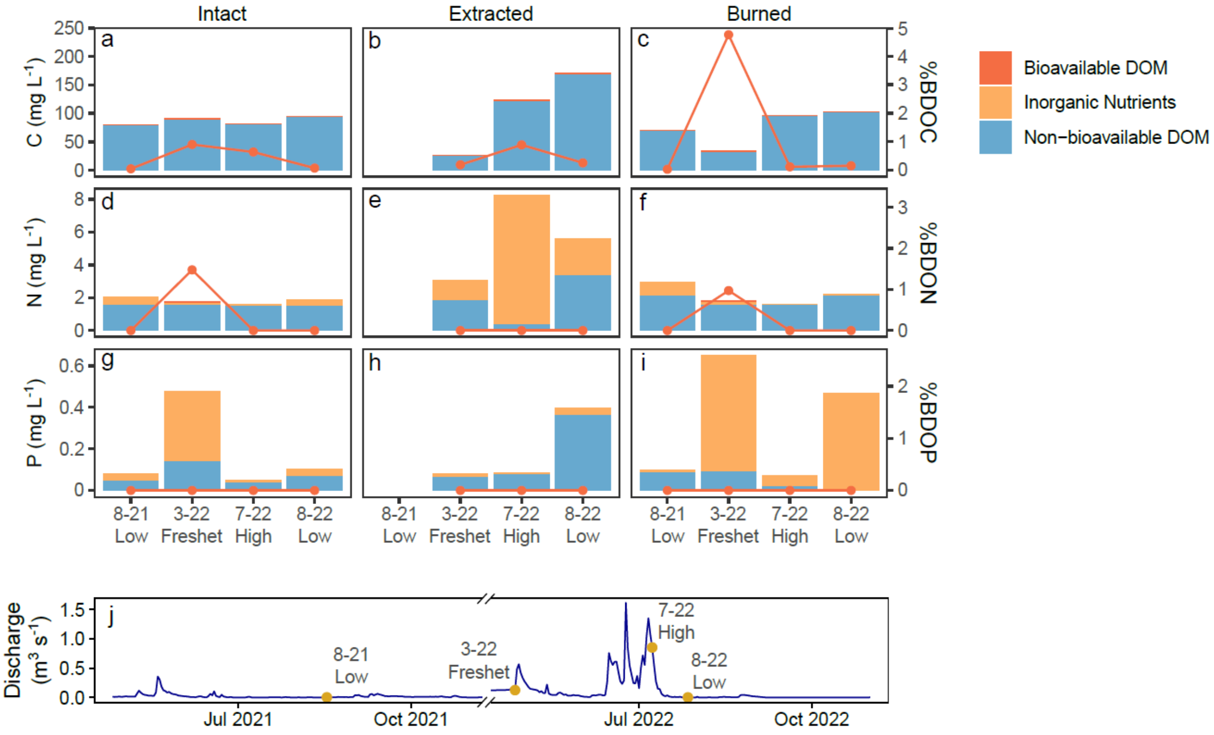

Figure 10. Stacked bar plots of C, N, and P concentrations in stream water samples (plots a–i). Stacked bars show differences in bioavailable and non-bioavailable organic matter and inorganic nutrients (left-hand y-axis). Percent bioavailable DOC, DON, and DOP is shown by the line plot, with the corresponding right-hand y-axis. Stream discharge (plot j) measured ~10 km downstream of the headwater sites shows change in hydrology over the four sampling periods.

Less than 5% of DOC, DON, and DOP were bioavailable in the headwater streams (Figure 10). $BDOC_{br}$ ranged from 0.04% to 4.77%, and was 0.74 ± 0.41% on average (Figure 10, Table 2). In the intact and burned peatlands, $BDOC_{br}$ peaked during the spring freshet (0.91% and 4.77% respectively), but in the extracted peatland $BDOC_{br}$ peaked during the summer high flow sampling (0.90%). $BDON_{br}$ was undetectable during all samplings except during the spring freshet when $BDON_{br}$ was 3.7% and 2.4% in the intact and burned streams respectively (Table 2). $BDOP_{br}$ was undetectable throughout the study. There were no significant effects on bioavailable resource fractions or concentrations among headwater peatlands using one-way ANOVA (Figure 9; $p > 0.05$). Moreover, there were no significant relationships between inorganic nutrients and $BDOC_{br}$ and $BDON_{br}$ (Figure S8). We compared the $BDOC_{br}$ results with results from the 7-day change in concentration incubation ($BDOC_{cc7}$), and the data were significantly positively correlated (Figure S7, $R^2 = 0.99$, $p < 0.001$). The BDOC$_{cc28}$ results were not well correlated with the 7-day BDOC$_{br}$ results ($R^2 = 0.18$).

Table 2. Bioavailable dissolved organic carbon (BDOC), nitrogen (BDON), and phosphorus (BDOP) concentrations in headwater peatland catchments over the four sampling dates.

Headwater Peatland Catchment	Aug 2021 Low Flow	Mar 2022 Freshet	Jul 2022 High Flow	Aug 2022 Low Flow	Aug 2021 Low Flow	Mar 2022 Freshet	Jul 2022 High Flow	Aug 2022 Low Flow
	BDOC (µg C L^{-1})				**BDOC (%)**			
Intact	42	820	523	75	0.05	0.91	0.64	0.08
Burned	26	1539	118	166	0.04	4.77	0.12	0.16
Extracted		51	1096	447		0.19	0.90	0.26
	BDON (µg N L^{-1})				**BDON (%)**			
Intact	0	63	0	0	0	3.70	0	0
Burned	0	43	0	0	0	2.44	0	0
Extracted		0	0	0		0	0	0
	BDOP (µg P L^{-1})				**BDOP (%)**			
Intact	0	0	0	0	0	0	0	0
Burned	0	0	0	0	0	0	0	0
Extracted		0	0	0		0	0	0

3.3.2 The effect of peatland disturbance on DOM molecular composition

DOM molecular composition was mostly aromatic, humic-like, and high molecular weight across the study sites (Table S3). There was little variation in DOM composition across study sites and water sources (e.g., pore and stream water), except for S$_R$ which was significantly higher in burned peatland samples than extracted peatland samples ($p = 0.03$). However, S$_R$ from the burned and extracted peatland samples were not significantly different from the intact peatland samples ($p > 0.05$; Figure S10, Table S4). SUVA$_{254}$ was statistically lower during the spring freshet than other samplings ($p < 0.001$; Figure S11, Table S5). But S$_R$ was not significantly affected by the spring freshet and we did not measure DOM fluorescence for that sampling due to instrument malfunction.

Parallel Factor (PARAFAC) analysis resulted in 4 components that corresponded with humic- and fulvic-like organic material, all of which corresponded with fluorophores described in previous studies (Figure S13). Component 1 (C1) contributed the most to overall fluorescence, ranging from 34% to 58% (mean: 41 ± 1.3%). C1 was similar to terrestrially-sourced, humic-like fluorescence with an excitation maximum <300 nm and emission maximum at 414 nm, and PCA showed that C1 and SUVA$_{254}$ were negatively correlated (Figure S12). Components 2 (C2; ex:

335 nm, em: 461 nm) and 3 (C3; ex: 360 nm, em: 447 nm) contributed 24 ± 4% (range: 0–51%) and 19 ± 3% (range: 0–35%) of total fluorescence respectively, and were similar to terrestrially-sourced, humic-like fluorescence in catchments that have been anthropogenically altered. PCA showed that C2 was negatively associated with BIX, and C3 was negatively associated with S_R. Component 4 (C4; ex: 400 nm, em: >500 nm) accounted for 17 ± 1% (range: 10–23%) of total fluorescence on average, and was similar to microbially altered humic- and fulvic-acids. C4 was also positively associated with BIX (Figure S12). Importantly, PARAFAC analysis did not identify a component that corresponded with protein-like fluorophores which are associated with DOM bioavailability. There were no significant effects of season, hydrology, or peatland disturbance on PARAFAC components ($p > 0.05$; Figure S10, Figure S11).

DOM age was significantly older in the extracted peatland than the intact and burned peatlands ($p < 0.001$; Figure S10, Table S4). Radiocarbon samples were only collected in July and August 2022, and there were no significant effects based on one-way ANOVA between the two samplings ($p = 0.95$; Figure S11, Table S5). Porewater DOC age in the extracted peatland was 1016 ± 24 years before present, and stream water DOC age was 619 ± 25 years before present (mean F14C: 0.90 ± 0.02). Porewater and stream water DOC ages in the intact and burned peatlands were both modern and enriched with ^{14}C (mean F14C: 1.09 ± 0.003 and 1.07 ± 0.005 respectively).

We used linear discriminant analysis to test the extent that DOM molecular composition was affected by peatland disturbance in July and August 2022 samples (Figure 11). The first canonical variate accounted for 98.1% of the variation among peatland groups, and the second accounted for only 1.7% ($p = 0.07$). The total structure coefficients for the two canonical variates indicated that the variables that best accounted for among-group variation were F14C, $SUVA_{254}$, and S_R (first variate); and C4% and HIX (second variate).

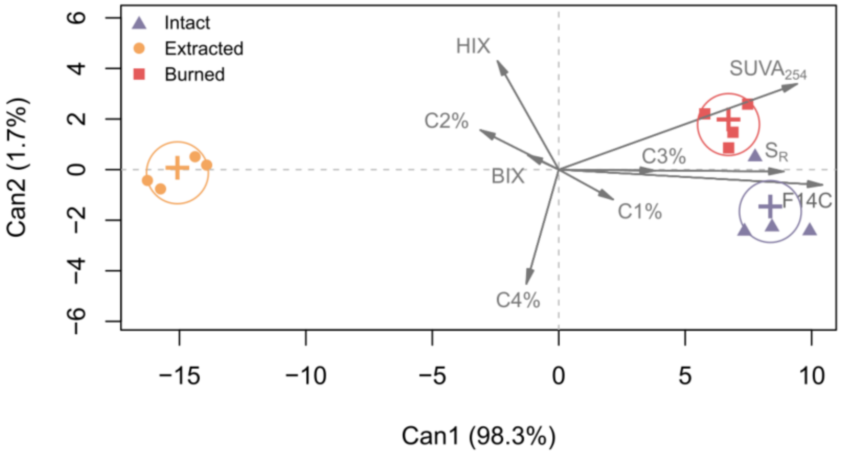

Figure 11. Linear discriminant analysis showing which DOM optical properties best account for differences among peatland groups. Points show variant scores for each porewater and stream water sample, and crosses show the centroid variant scores for each group. Circles show the 95% confidence interval about the group centroids.

3.3.3 Stoichiometry and nutrient limitation in headwater peatland streams

Total resource stoichiometry and inorganic stoichiometry, which are commonly used to study nutrient limitation (Berggren et al., 2015), consistently overestimated C:N and C:P ratios in our study streams. Thus, total and inorganic resource ratios suggested that N and/or P were the limiting nutrients (Figure 12). However, factoring in resource bioavailability in stoichiometric ratios significantly decreased C:N and C:P ratios ($p < 0.05$), indicating that C predominant limiting nutrient. Interestingly, N:P ratios exhibited no significant differences among the resource pools (i.e., total, inorganic, and bioavailable N:P), with average inorganic and bioavailable N:P ratios approximating the Redfield ratio. This finding provides further evidence that N and P were not major limiting nutrients. Bacterial abundance from the regrowth incubations further supported these conclusions on resource limitation. Specifically, bacterial abundance was significantly lower in the C-limited samples compared to the N-limited and P-limited samples across all sites and samples (Figure S15; $p < 0.001$). Moreover, there were no significant differences in bacterial abundance between N-limited and P-limited samples ($p > 0.05$).

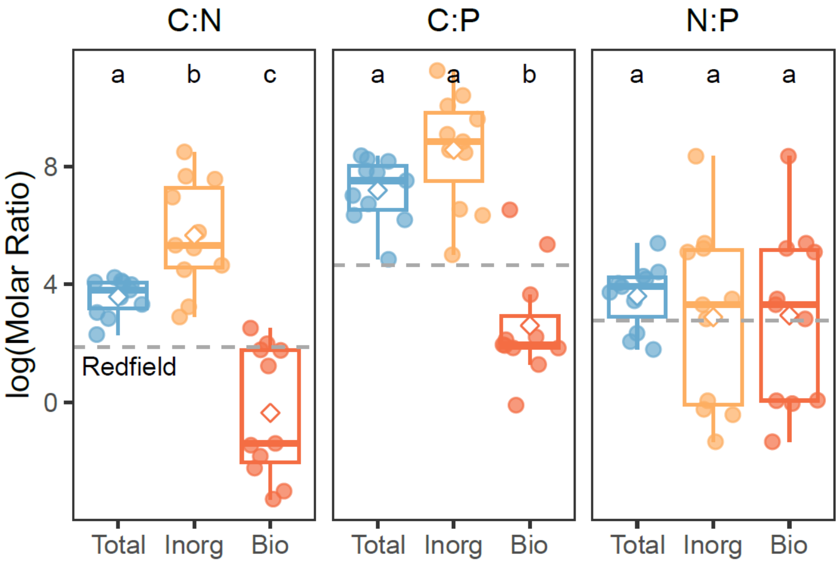

Figure 12. Stoichiometry of stream water calculated by total resource pools (DOC:TDN:TDP), inorganic resource pools (DOC:DIN:DIP), and bioavailable resource pools (BDOC:BDON+DIN:BDOP:DIP). The boxplots show the interquartile range (the box) about the median (the horizontal line), and the diamonds show the mean. The dashed horizontal lines show the log-transformed Redfield Ratio compared to resource pool stoichiometry. Statistically significant differences ($p < 0.05$) among resource pools are shown in compact letter display above the boxplots.

We then examined the impact of peatland disturbance on bioavailable nutrient stoichiometry and nutrient limitation among streams (Figure 13). There were no significant differences in bioavailable C:N and C:P ratios among headwater peatland streams ($p > 0.05$). However, we observed higher bioavailable N:P ratios in the extracted peatland compared to the burned peatland ($p < 0.05$), though neither differed significantly from intact peatland N:P. Higher bioavailable N:P in the extracted peatland was driven by elevated DIN concentration, and lower bioavailable N:P in the burned peatland was driven by higher PO_4^{3-} concentration. Comparing these ratios with the Redfield ratio, the intact peatland was generally C-limited, the extracted peatland was co-limited by C and P, and the burned peatland was co-limited by C and N.

Bioavailable nutrient stoichiometry also varied across seasons and flow conditions, though are sample size is limited (Figure 13). Headwater peatlands had bioavailable C:N ratios below Redfield on average, but increased during freshet and summer high flow events for intact and burned peatlands. The extracted peatland had consistently low C:N ratios. Burned peatland C:N values were closer to intact peatland values, except during the 2022 summer low flow sampling. Average bioavailable C:P was below Redfield. Burned peatland C:P was consistently low, while intact and extracted peatland C:P increased above Redfield during the summer high flow event. Bioavailable N:P varied widely among disturbed peatlands and over time. Extracted peatlands had consistently high N:P values, while intact and burned peatlands fluctuated. The highest observed N:P values occurred during the summer high flow event in the extracted peatland and during the 2021 summer low flow sampling for intact and burned peatlands (when the extracted peatland stream was dry). Notably, during the 2022 summer low flow sampling, burned peatland N:P was at its lowest, and intact peatland N:P was similar to the 2021 value.

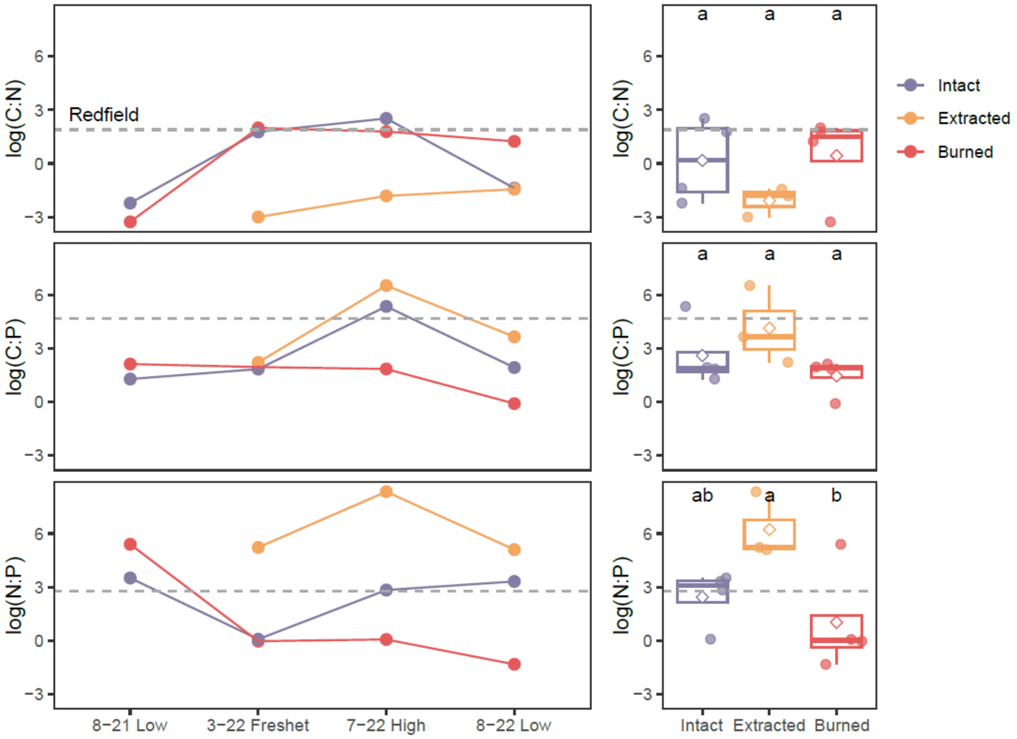

Figure 13. Stream water bioavailable stoichiometry time series and boxplots. The time series show differences in stoichiometry across seasons and flow conditions. The boxplots show differences in stoichiometry among peatland disturbances, with the box representing the interquartile range about the median (the horizontal line) and the diamond representing the mean. The dashed gray line indicates the log-transformed Redfield molar ratio. Statistically significant

differences ($p < 0.05$) among peatland headwaters are shown in compact letter display above the boxplots.

3.4 Discussion

Contrary to our original hypothesis, peatland disturbance had little effect on DOM molecular composition and bioavailability most of the year in headwater peatland streams. DOM was mostly humic-like and recalcitrant in all peatland porewater and streams. The largest changes in DOM bioavailability and DOM composition were observed in the extracted peatland, whereas DOM patterns in the burned peatland were similar to the intact peatland. Drainage ditches in the extracted peatland increased the age (~500 years BP) and proportion of high molecular weight DOM in the porewater and stream samples, but we found no significant relationship among radiocarbon age, DOM size, and DOM bioavailability similar to other studies (McCallister and del Giorgio, 2012; Casas-Ruiz et al., 2016). Despite complete and partial combustion of peatland vegetation in the burned catchment, DOM composition and bioavailability were similar to the intact peatland. Yet, elevated PO_4^{3-} values in the burned peat porewater and stream water suggest that the water sources from the burned areas of the catchment were significant (Figure 9). Fire mineralizes organic P in peat during combustion, but P has no significant gaseous component like C and N (Neff et al., 2005). Therefore, these results suggest that peatland wildfire had little influence on DOM composition and bioavailability, but increased inorganic P availability, similar to findings from other studies (Evans et al., 2017; Burd et al., 2018; Davidson et al., 2019).

The spring freshet was the only notable seasonal/hydrological period that significantly changed DOM molecular composition and bioavailability (Figure 10). Many studies across ecosystems have observed increased DOM bioavailability during the freshet (Agren et al., 2008; Broder et al., 2017). This increase in bioavailability is attributed to flushing reactive DOM that accumulated over winter (Agren et al., 2008). Increasing DOC and DON bioavailability during the freshet was negatively associated with $SUVA_{254}$. However, $SUVA_{254}$ values in the extracted peatland decreased similarly to those in the intact and burned peatlands, but was not accompanied by an increase in DOM bioavailability. This further highlights the result that $SUVA_{254}$ was not strongly correlated with BDOC in general (Figure S14, Figure S6). This suggests that water flow paths in the extracted peatland similarly flowed through surface peat, but there were no fresh DOM inputs from plants, such as sphagnum mosses which contribute bioavailable DOM (Fenner et al., 2004; Wickland et al., 2007). Instead, BDOC spiked in the extracted peatland during the summer high flow event, when some colonizing plants may have contributed bioavailable DOM along unmaintained ditches (based on qualitative field observation).

Previous studies conducted in the boreal region emphasized the significance of BDON and BDOP as nutrient sources in DOM-rich aquatic ecosystems (Stepanauskas et al., 2000; Jansson et al., 2012; Soares et al., 2017; Rulli et al., 2022). Consequently, we initially hypothesized that BDON and BDOP would demonstrate higher bioavailability compared to BDOC. But our findings mostly contradicted this assumption, as we observed minimal BDON and BDOP overall. Though BDON and BDOP were commonly below detection, BDOC was always detectable, suggesting that microbes preferentially consumed DOM without N and P compounds (Kothawala et al., 2014; Kellerman et al., 2015). The absence of protein- and amino acid-like compounds in our PARAFAC model further suggests that the bioavailable DOM compounds were likely simple sugars that were a minor fraction of the total DOM pool. The exception to this pattern was during the spring freshet in intact and burned peatland streams when BDOC and BDON levels were at their highest (see Figure 10). To interpret these results, several possible explanations were considered. One likely scenario is that due to the recalcitrant molecular structure of DOM and the abundance of inorganic nutrients, it was more energetically favorable for microbes to utilize inorganic nutrients than to mine for BDON and BDOP. During the spring freshet, the DOM exhibited reduced aromaticity and increased bioavailability, suggesting that more labile molecular compounds were accessible for microbes, and they were therefore able to utilize BDON as a nutrient source even with ample DIN available.

Additionally, the contrasting nutrient conditions in the two disturbed peatlands acted as a natural case study of the effect of nutrient priming on DOM bioavailability. Inorganic N was elevated in the extracted peatland and PO_4^{3-} was elevated in the burned peatlands (Figure 9), yet inorganic nutrients had no observable effect on DOM bioavailability. Despite evidence of nutrient priming in other freshwater catchments (Bianchi et al., 2015; Rosemond et al., 2015), our results show no evidence for nutrient priming in these disturbed peatland streams similar to results from others (Catalán et al., 2015; Textor et al., 2018, 2019; Wologo et al., 2021). Our data supports the hypothesis that DOM turnover in freshwater ecosystems is primarily controlled by molecular composition and to a lesser extent by environmental conditions (Kothawala et al., 2014, 2020; Kellerman et al., 2015; Berggren et al., 2022). Therefore, despite abundant DOC and inorganic nutrients in disturbed peatland streams, the recalcitrant molecular structure limited heterotrophic respiration of these compounds.

In order to accurately infer nutrient limitation from stoichiometric ratios in DOM-rich waters, we must include bioavailable resource fractions of C, N, and P (i.e., BDOC, BDON, and BDOP) (Berggren et al., 2015; Graeber et al., 2021). Indeed, our results showed that stoichiometric ratios based on total, inorganic, and bioavailable resource fractions led to different conclusions about limiting nutrients (Figure 12). Because bulk DOC concentrations were so large, inferring nutrient limitation from total and inorganic resource fractions suggested that N and P were the limiting nutrients. However, because most of the DOC in these streams was molecularly recalcitrant, bacterial abundance and stoichiometric ratios suggested that these peatlands are C-limited most of the year (Figure 13, Figure S15), as has been reported in other studies (Soares et al., 2017).

Our results show that peatland disturbance affects the timing and magnitude of bioavailable C, and inorganic N and P for aquatic ecosystems. As with bioavailability and molecular composition, peat extraction and wildfire significantly altered N:P stoichiometry due to changes in inorganic nutrient concentrations. These findings are consistent with global syntheses of CNP stoichiometry that have found that anthropogenic disturbances are major disruptors to stoichiometric ratios (Taylor and Townsend, 2010; Wymore et al., 2021). Because of persistent C-limitation across peatland catchments during low flow (regardless of disturbance), these headwater streams likely act as conveyors of recalcitrant DOM and reactive N and P downstream (Kothawala et al., 2015), and may contribute to water quality issues downstream.

3.5 Conclusions

Peat extraction and wildfire minorly affected DOM concentration, composition, and bioavailability and significantly increased inorganic N and P concentrations in stream and porewater. Overall, DOM molecular composition was aromatic, humic-like, and high molecular weight and disturbances shifted DOM molecular composition even more in that direction. By integrating detailed DOM composition analysis with bioavailability incubations, we were able to show that DOM molecular structure limited uptake by heterotrophic bacteria. These results suggest that as peatland disturbance increases due to climate change, land cover, and land use changes, more recalcitrant DOM and inorganic nutrients will be exported to inland waters.

4. Refining current and future estimates of export and downstream attenuation of dissolved organic carbon (DOC) from northern peatlands

Abstract

Northern peatlands are significant sources of dissolved organic carbon (DOC), but uncertainties remain regarding their current and future export into freshwater ecosystems, attenuation along river networks, and contribution to continental-scale DOC export into oceans. In the face of rapid, ongoing climate change, understanding controls on peatland DOC export is crucial for peatland carbon balance, water quality, aquatic ecosystems, and carbon flux across the terrestrial-aquatic continuum. Here, we present a synthesis of observation-based DOC export from catchments with northern peatlands (≥45°N). Using machine learning coupled with spatial datasets of peatland distribution, we assessed peatland influence on riverine DOC concentration and export across various catchment scales and climates. Our analysis revealed significant variability in DOC concentration and yield across peatland regions, driven by permafrost conditions and annual precipitation. Average peatland DOC yield from headwaters was 8.5 g C m^{-2} yr^{-1}, ranging from 5 to 15 g C m^{-2} yr^{-1}. Total peatland DOC export into headwaters was 29 Tg C yr^{-1}, representing 26% of all headwater DOC export despite covering only 9% of the study area. We project a 12–23% increase in peatland DOC export by the end of the century, particularly for peatlands in the current discontinuous permafrost zone. Peatland DOC was found to attenuate more rapidly than non-peat DOC along river networks to the ocean, but further research is needed to understand the underlying mechanisms and responses to climate change. Our model suggests that previous research has overestimated northern peatland DOC export to oceans by 45%, leading us to revise the estimate of global peatland DOC export to inland waters from ~91 to ~67 Tg C yr^{-1}. These results underscore the importance of peatlands in lateral carbon transport, and the role of climate in modulating DOC concentration and yield across high-latitudes.

4.1 Introduction

Northern peatlands (>45 deg N) are known to be substantial dissolved organic carbon (DOC) sources to aquatic ecosystems, but there have been few attempts to understand the factors controlling current and future DOC concentrations and yields from peatland-rich catchments at the continental scale (Laudon et al., 2012; Rosset et al., 2022). Peatland-derived DOC plays a crucial role in shaping northern ecosystems, necessitating a deeper understanding of its significance. For example, DOC's contribution to the net carbon balance of peatlands may be relatively small compared to productivity or respiration, but its magnitude is comparable to the net ecosystem exchange of CO_2, and is therefore a significant component of the long-term peatland soil carbon balance (Dinsmore et al., 2010; Olefeldt et al., 2012; Yu, 2012; D′Acunha et al., 2019). DOC concentration in inland waters determines light conditions (e.g., productivity, habitat, thermal stratification (Roulet and Moore, 2006; Karlsson et al., 2009; Kritzberg et al., 2020), co-transport of organic nutrients and contaminants such as methylmercury (Broder and Biester, 2015; Nieminen et al., 2020b; Thompson et al., 2023), and influences lake greenhouse gas emissions (Cole et al., 2007; Tranvik et al., 2009). Moreover, the export of riverine DOC into oceans determines nutrient availability and productivity in marine ecosystems (Terhaar et al., 2021), but the magnitude of DOC export to oceans may increase with climate change (Holmes et al., 2021). Given the rapid climate change at high latitudes (e.g., warming and permafrost thaw), and expanding human disturbances in peatlands (Turetsky et al., 2015; Fluet-Chouinard et al., 2023), understanding how these disturbances control peatland DOC export is important to accurately assess carbon fluxes within peatlands and along the terrestrial-aquatic continuum.

Peatland DOC concentrations (mass per volume) and area-weighted yields (mass per unit area per unit time) are higher than those of adjacent ecosystems due to the unique biogeochemical and hydrological characteristics of these habitats. One key factor is the substantial soil carbon storage within peatlands (Yu, 2012; Hugelius et al., 2020), where DOC is produced as an intermediate step during soil decomposition. DOC production generally increases with temperature, and is also modulated by soil water content (Freeman et al., 2001; Neff and Asner, 2001; Clark et al., 2009). Warmer temperatures that increase soil DOC concentration do not always coincide with hydrologic transport, and therefore temperature alone does not accurately predict stream water concentration and yield (D'Amore et al., 2015). Another key factor that increases DOC export from peatlands is hydrological flow paths in organic peatland soils that reduce DOC adsorption to mineral soils, facilitating the rapid transfer of DOC to nearby waters (Meier et al., 2004; Kaiser and Kalbitz, 2012; Kothawala et al., 2012). Mineral adsorption also preferentially removes aromatic DOC, thus peatland DOC often exhibits higher aromaticity and color compared to DOC from other terrestrial ecosystems, and is more susceptible to photodegradation (Olefeldt et al., 2013; Anderson et al., 2019).

There is significant regional variability in headwater peatland DOC export, ranging from less than 5 g C m^{-2} yr^{-1} to over 20 g C m^{-2} yr^{-1}, which complicates our understanding of how climate change and human disturbances affect peatland DOC export to aquatic networks. For instance, peatland catchments in Finland, the UK, and eastern Canada exhibit considerably higher DOC concentrations and yields than those observed in permafrost peatland catchments (Frey and Smith, 2005; Olefeldt et al., 2014). Further investigation into these climatic controls on peatland DOC export between regions is crucial to comprehending and predicting the dynamics of this important C flux.

Current estimates suggest that approximately 80% of terrestrially derived DOC does not reach coastal oceans, i.e., it is attenuated during transit (Drake et al., 2018). DOC is attenuated via multiple interacting pathways including microbial degradation, photodegradation, flocculation, and sedimentation. These processes are controlled by DOC molecular composition and environmental factors such as temperature, microbial community, nutrient availability, and water residence time (Battin et al., 2008; Bertuzzo et al., 2017; Kothawala et al., 2020; Berggren et al., 2022). Most aquatic C is attenuated via rapid degassing of dissolved, terrestrially-derived CO_2 and mineralization of organic C within aquatic networks (Raymond et al., 2013; Hotchkiss et al., 2015; Drake et al., 2018). These same pathways apply in peatland-dominated catchments, though flocculation and sedimentation may play a larger role because DOC molecular composition and environmental conditions make peat DOC more susceptible to photochemical reactions, microbial processing, and chemical reactions modulated by pH and temperature (Wachenfeldt et al., 2009; Attermeyer et al., 2018; Einarsdóttir et al., 2020). However, whether peatland DOC is more or less attenuated in aquatic networks than DOC from other sources remains uncertain (Einarsdóttir et al., 2020).

Climate change is occurring rapidly in the north, with potentially profound implications for peatland DOC export and attenuation—though the net effect remains largely unknown (Frey and Smith, 2005; Olefeldt et al., 2014; Hugelius et al., 2020). In particular, temperature will likely impact DOC export to aquatic networks through processes such as permafrost thaw, temperature-dependent DOC sorption/desorption, net DOC production (heterotrophic respiration), leachates and root exudates from plant productivity, and changes in plant species composition (Neff and Asner, 2001; Hedwall et al., 2017; McPartland et al., 2019; Hugelius et al., 2020). Additionally, climatic shifts in precipitation, particularly its influence on runoff generation and the water balance (including evapotranspiration), will also likely affect peatland DOC dynamics (Holden, 2005; de Wit et al., 2016; Holmes et al., 2021). Notably, climate change effects may manifest rapidly as current ecosystems respond to warming and thaw, but there may also be long-term trends in peatland formation and loss as regions become wetter or drier (Treat et al., 2019; Loisel et al., 2021). Thus, understanding the various climate change factors and their impacts on peatland DOC export and attenuation is essential to grasp the broader consequences of ongoing environmental changes in the northern peatlands.

Disturbances from land use and land cover change will also likely have consequences for DOC export from northern peatlands. For example, land conversion across ecosystems has increased global DOC export to aquatic networks by ~1 Pg C yr^{-1} since the industrial revolution (Regnier et al., 2013), and has increased the age of DOC in river systems (Butman et al., 2015). Part of this shift in DOC age is attributed to peatland drainage, which affects ~11% of global peatlands with largest losses in western Europe where nearly 50% of peatlands have been drained (Fluet-Chouinard et al., 2023). A recent systematic review found that global peatland disturbance significantly increased DOC export to inland waters, though tropical peatlands were the main drivers of this effect (Evans et al., 2014; Rosset et al., 2022). Many studies have examined the effect of disturbances on northern peatland hydrology and biogeochemistry (Turetsky et al., 2002; Holden et al., 2006; Nieminen et al., 2021), but much of this research has occurred in western Europe and the implications for understudied regions are unclear (Rosset et al., 2022).

Here, our objectives were to understand how northern peatlands affect current and future DOC concentration, yield, and attenuation across high-latitude catchments. We conducted a systematic review of DOC concentration and area-weighted yield from northern peatland catchments (≥45°N), and used random forest machine learning to predict DOC concentration and yield across the study region. With this analysis, we investigated the following questions: 1) what controls DOC concentration and yield in northern catchments at continental scales (e.g. climatic variables, catchment cover, disturbance), and how significant are peatlands to overall DOC export? 2) How much peatland and non-peatland DOC is lost in transit to coastal oceans? And 3) how will climate change affect future peatland DOC export? We hypothesize that peatland coverage will be the most important predictor of DOC concentration and yield, but that climate and catchment size will also be important predictors because of their role in DOC production, transport, and attenuation processes. Thus, we predict that peatlands will have an outsized effect on DOC export across scales, and that climate change will increase DOC export.

4.2 Methods

4.2.1 Systematic Review

We conducted a systematic literature review to compile empirical data from high-latitude peatland catchments. To gather relevant studies, we searched Web of Science using various terms for DOC, peat, catchment, and runoff, as detailed in the Supplemental Information. From the search results, we extracted data from studies that met the following criteria: 1) data were from field observations of streams and rivers with delineated catchments, 2) catchments were located above 45°N latitude, and 3) data included estimates of mean annual DOC concentration and/or yield. Throughout our study, we define export as the DOC mass over time, while DOC yield is mass over time divided by watershed area.

Next, we constructed a dataset that included DOC concentration, annual DOC yield, annual runoff (i.e., water yield as measured by field observations), catchment area, catchment land use and land cover (e.g., percent coverage of peatlands, forests, lakes, etc.), wetland type (as classified by the study authors), peatland disturbance type (as classified by study authors and then binned into three broad categories: drainage, fire, and permafrost thaw), mean annual precipitation (MAP), and mean annual air temperature (MAAT; Table S10). When available, long-term averages of MAAT and MAP were recorded as reported in individual studies. Additionally, we collected ancillary water chemistry data and catchment data when available, including catchment slope, pH, base cations, inorganic nitrogen and phosphorous concentrations, and specific ultraviolet absorbance at 254 nm. However, the reporting of such data was inconsistent, as such they were not used in our analysis. At least 20% of the studies did not report catchment peatland coverage, and even more studies did not report other land cover characteristics such as percent peatland disturbance, lake, forest, agriculture, and human infrastructure coverage. To fill in these data gaps, we estimated the values using Google Earth imagery. For missing MAAT and MAP data, we extracted values from WorldClim v2.1 at the catchment outflow (Fick and Hijmans, 2017).

After the systematic review was completed, we identified that data was sparse from Siberia and western Canada. Hence, we expanded the search for these regions by searching for catchment DOC studies specifically in Canada and Russia. This yielded an additional 16 studies that were not picked up in the initial search because they mentioned wetlands and permafrost instead of peatlands. We also included data from 3 currently unpublished studies in western Canada, which will be included in the final published dataset. Overall, our data was structured so that each row represented a unique catchment. Therefore, repeat observations from the same catchment over different years were combined into average values for all variables (e.g., catchment characteristics, DOC data, ancillary water chemistry, etc.).

4.2.2 Statistical Analysis and predictions from random forest analysis

We investigated univariate relationships among climate variables, catchment characteristics, and DOC concentration and yield using spearman rank correlations, two-sample t-tests, and linear regression. For each analysis, we checked the data for normality, heteroscedasticity, and multicollinearity. Because catchment area was skewed, we used log-transformed area in statistical and machine learning analyses.

We used random forest models (Breiman, 2001) to investigate drivers and predict DOC concentration and yield in high-latitude catchments for current and future climate scenarios. The models were implemented using the ranger package in R (Wright and Ziegler, 2017), using climate and catchment characteristics as explanatory variables for predicting DOC concentration and yield. Models were trained using repeated, stratified cross-validation (k = 5, repetitions = 3) with data split into 80% training data and 20% testing data, stratified by DOC concentration and yield. The model parameters were set to ntree = 500, and an optimal mtry was selected using GridSearchCV, a common algorithm for tuning hyper-parameters in machine learning models. We used an iterative approach to feature selection, and in preliminary models we used all land cover variables, MAAT, MAP, and catchment area as features. We used relative feature importance scores to guide our feature selection, and all land cover variables except peatland cover had low (<10%) relative feature importance scores. Therefore, we omitted these features from our model and used peatland coverage, MAAT, MAP, and catchment area as predictor features in our DOC concentration and yield upscaling models. Though peatland drainage had low relative feature importance, we included this feature in our driver attribution model (see Figure 15) to assess the effect of drainage on DOC concentration and yield.

To assess model performance, we computed the out-of-bag R^2, a measure similar to linear regression R^2, where values closer to 1 indicate greater model accuracy. Additionally, we calculated the root mean squared error (RMSE), representing the average difference between the actual and predicted values. To interpret the relationship between the explanatory variables and response variables, we generated partial dependence plots for continuous variables and individual conditional expectation (ICE) plots for the discrete peatland disturbance variable. These plots helped unravel complex multivariate relationships, displaying the average relationship of each explanatory variable with the response variable in the case of partial dependence plots, and the modeled relationship for each individual observation in ICE plots. ICE plots, in particular, allowed us to consider the effects of climate and catchment area on the impact of disturbance on DOC concentration and yield.

Random forest models generally perform well when given enough data, but data sparsity, or imbalanced data, can lead to inaccurate results. In our systematic review dataset, 65% of the data originated from catchments in western Europe, a climatically distinct region compared to most northern catchments. To assess the impact of this data bias on model performance, we conducted an experiment with a random 80% split of the non-western European data, followed by prediction using a model trained on the remaining 20% test dataset of non-western European data. We then trained a random forest model on a random 80% split of the full DOC yield data (including western Europe) and used that model to predict the same 20% test dataset of non-western European data. The overabundance of western European data had a marginal effect on model performance (out-of-bag $R^2 = 0.72$ vs. 0.60), so we proceeded with a full model trained as described earlier.

Moreover, we observed data imbalance towards catchments smaller than 10,000 km^2, and our model had poor accuracy, which resulted in inaccurate predictions of DOC yield and export from the largest Arctic rivers (millions of km^2). Because random forest models are designed to reduce overall prediction error, models trained on imbalanced datasets may fail to accurately predict underrepresented data (He and Garcia, 2009; López et al., 2013). Therefore, in fractal river networks where headwater catchments outnumber large rivers (Tarboton et al., 1988), the predictive power of data-driven regression models excel for headwater catchments, but are limited at large scales. To address this limitation, we employed the SMOGN pre-processing algorithm. The algorithm involved random under-sampling of small watersheds and artificial oversampling of large watersheds (using the SMOTER algorithm combined with Gaussian noise) to improve accuracy for predictions of DOC yield (Branco et al., 2017)). This process aimed to enhance the model's ability to predict DOC yield across different watershed scales. The implementation of SMOGN was carried out using the UBL R package (Branco et al., 2016), where we defined a relevance function to oversample catchments larger than 10^5 km^2 with a threshold relevance of 0.5. The resultant SMOGN-balanced dataset was similar in size as the original, and artificial data was within plausible ranges for large high-latitude watersheds. However, we recognize the pitfalls of relying on synthetic data to model real-world processes, and we interpret the large river yield results with caution.

Overall, by utilizing random forest models and employing the SMOGN pre-processing algorithm, we addressed data imbalances and sought to provide accurate predictions of DOC concentration and yield in high-latitude catchments for different climate scenarios.

4.2.3 Spatial upscaling and calculations

We used our random forest models to predict DOC concentration and yield across high-latitude catchments. To estimate attenuation processes through the stream network, we modeled DOC yield for headwaters, in addition to terrestrial export to oceans via large rivers and coastal catchments. We coarsely delineated headwater catchments by using 2.5 degree-minute pixels (~10 km^2) across the study region. This pixel size was the finest resolution from our spatial data products, and allowed us to estimate headwater processes at the smallest spatial scale possible. For modelling terrestrial export to oceans (i.e., export from large rivers and coastal catchments), we used catchment delineations from the HydroBasin dataset which models global watershed boundaries (Linke et al., 2019). Specifically, we used HydroBasin Level 3 polygons, which include large rivers and aggregated coastal catchments, and filtered out endorheic basins. Catchments that were cutoff along the southern boundary (45°N) were still included, but we only estimated their contribution to oceans north of the boundary.

For each “catchment” (pixels and HydroBasin polygons), we calculated average peatland coverage, MAAT, and MAP. We used the northern peatland map from Hugelius et al. (2020) to estimate peatland cover in each catchment. Climate variables (MAAT and MAP) were estimated from current and future climate scenarios in the WorldClim v2.1 database to estimate MAAT and MAP across watershed scales (Fick and Hijmans, 2017). Current climate in WorldClim v2.1 spanned 1970–2000, and future climate scenarios from the Coupled Model Intercomparison Project Phase 6 (CMIP6) were available for four time periods: 2021–2040, 2041–2060, 2061–2080, and 2081–2100. Future climate was aggregated under four Shared Socio-economic Pathways (SSPs): SSP1-2.6, SSP2-4.5, SSP3-7.0, and SSP5-8.5, which estimate low, intermediate, high, and very high emissions scenarios respectively. For all four SSP scenarios, temperature increased across high-latitudes. In the moderate climate change scenario (SSP2-4.5°C), MAAT was projected to increase by 4.8°C on average, ranging from +1.6°C in the south to +11.4°C in the far north (Figure 19a). MAP was more spatially variable, with less precipitation expected in western Europe (by as much as -27 mm), and substantial increases in precipitation in coastal regions (usually > 100 mm).

To estimate DOC concentration and yield for the high-latitude region for current and future climate scenarios, we predicted DOC concentration and yield for each headwater catchment (2.5 degree-minute pixels, ~10 km^2), in addition to catchment yield to the ocean (i.e., DOC yield from large rivers and aggregated coastal catchments (HydroBasin Level 3 polygons)). To understand changing DOC dynamics across northern headwater catchments, we used random forest models trained on the full dataset to predict DOC concentration and yield. To assess the central tendency and range of peatland DOC concentration and yield specifically, we modeled DOC concentration and yield in headwater catchments with at least 5% peatland cover, but told the model that peatland cover was 100%. For terrestrial export to the oceans, we used the pre-processing SMOGN algorithm to balance our dataset, and then used the balanced dataset to train the model and predict yield in large watersheds (we did not predict DOC concentration at this scale). We also used an ensemble of 20 upscaling models that used 20 randomly resampled subsets of the data (80% of the datasets) to calculate 95% confidence intervals. To determine relationships among spatial patterns, we computed spatial correlations among upscaled DOC concentration and yield, the predictor variables, and permafrost coverage (Obu et al., 2019).

We estimated DOC export (DOC_E) from headwaters and from large watersheds using the following equation:

Eq. 1

$$\mathrm{DOC_E} = \mathrm{DOC_Y} \times \mathrm{A}$$

where DOC_Y is the modeled DOC yield in g C m^{-2} yr^{-1}, and A is the area of the catchment in km^2. To estimate DOC export across the study domain, we summed export from individual catchments.

To specifically estimate peatland DOC export (DOC_{EP}) from each catchment, we predicted peatland DOC yield (DOC_{YP}) by assuming that each catchment had 100% peatland cover and multiplied the yield by actual peatland area (A_P) as shown in Eq. 2:

Eq. 2

$$\mathrm{DOC_{EP}} = \mathrm{DOC_{YP}} \times \mathrm{A_P}$$

In this way, catchments with 0% peatland coverage had a peatland export of 0.

Finally, we estimated DOC loss by attenuation in inland water networks by calculating the percent loss between DOC export from headwaters (DOC_{EH}) and catchment export to oceans (DOC_{EO}) in the following equation:

$$\mathrm{DOC_{loss}} = \frac{\mathrm{DOC_{EH}} - \mathrm{DOC_{EO}}}{\mathrm{DOC_{EH}}} \times 100$$

Conceptually, this calculation estimates stream network attenuation by estimating what DOC export would be if each headwater catchment piped its DOC straight to the ocean versus the amount of DOC actually exported to oceans by large rivers and coastal catchments. We did not attempt to model how DOC is routed along the terrestrial-aquatic continuum, and we assume that all headwater pixel “catchments” contributed to inland water flow. In this way, we calculated DOC attenuation for the full study region and also for large Arctic rivers. We also calculated 95% confidence intervals for DOC attenuation based on results from the random forest ensemble of 20 models.

We compared our modeled results to observational data in northern large rivers and countries. Additionally, to compare our modeled results to reported literature values, we downloaded watershed polygons for the six largest Arctic rivers and country shapefiles from public repositories (Holmes et al., 2012a; ESRI, 2022).

4.3 Results

4.3.1 Controls on DOC concentration and yield in northern catchments at continental scales

Our systematic review gathered DOC concentration data from 566 catchments and DOC yield data from 701 catchments. Among them, 562 catchments reported both DOC concentration and yield. The median DOC concentration was 10.6 mg L^{-1}, ranging between 2.5 and 32.9 mg L^{-1} (5th and 95th percentiles). The median DOC yield was 4.7 g C m^{-2} yr^{-1}, varying between 1.1 and 21.5 g C m^{-2} yr^{-1}. The central tendency and range of catchment characteristics and climate variables associated with the DOC concentration and yield data are presented in Table 3.

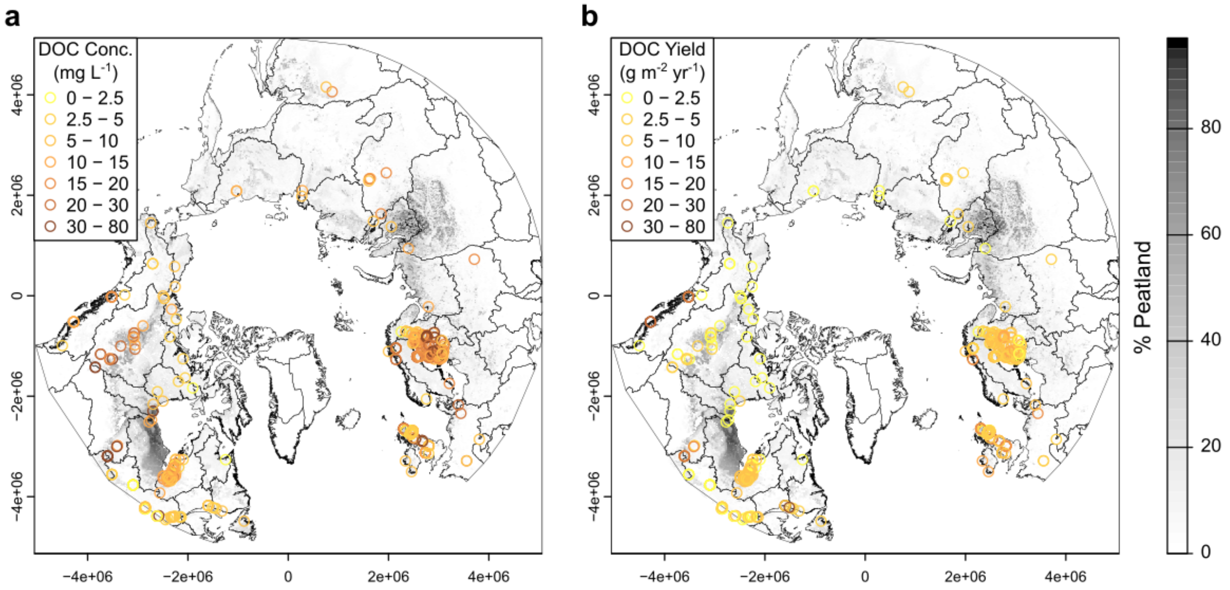

Figure 14. Maps of DOC concentration and yield from the systematic literature review (n = 566 and 701 respectively). Points are colored by observed DOC concentration (plot a) and yield (plot b). Peatland coverage is shaded in grey (data from Hugelius et al. 2020). Lines show modeled delineations of large river basins and aggregated coastal watersheds (data from Linke et al. 2019).

Table 3. Central tendency and range of systematic review data used in the random forest models to upscale DOC concentration and yield.

	DOC concentration random forest model input data (n = 566)			DOC yield random forest model input data (n = 701)		
	Median	5% CI	95% CI	Median	5% CI	95% CI
DOC concentration (mg L^{-1})	10.6	2.5	32.9	10.6	2.5	32.9
DOC Yield (g m^{-2} yr^{-1})	4.5	1.2	20.1	4.7	1.1	21.5
Area (km^2)	15	0.03	61,000	14	0.03	51,000
%Peatland	17	0	100	16	0	100
MAP (mm)	671	363	1631	693	376	1641
MAAT (°C)	3.1	-5.8	8.0	3.8	-5.2	8.4

Note: CI = Confidence Interval

Regarding the distribution of data among countries, Great Britain had the most extensive representation with 226 data points, followed by Canada, Finland, and Sweden with 181, 153, and 65 data points, respectively (Figure S18). Canada, covering 26% of the study region and 35% of high-latitude peatlands, accounted for 26% of the DOC concentration and yield data. The other three countries combined (Great Britain, Finland, and Sweden) contributed 63% of the DOC data but covered only 2.8% and 3.8% of the study region and peatland area, respectively. Notably, Russia, spanning 44% of the study region and 54% of high-latitude peatlands, accounted for less than 3% of the DOC data.

The concentration of DOC was positively associated with peatland coverage, and negatively associated with catchment area (all relationships $p < 0.05$). The Spearman correlations ranged from 0.29 to 0.56 (Figure S19), and R^2 values varied between 0.09 and 0.22 (Figure S20). Furthermore, the DOC yield demonstrated an increase with peatland coverage, MAAT, and MAP. Conversely, it showed a decrease with catchment area (all relationships $p < 0.05$). The Spearman correlations for these associations ranged from 0.22 to 0.56 (Figure S19), while the R2 values varied between 0.06 and 0.31 (Figure S20). Regarding the predictor variables (catchment area, peatland coverage, MAAT, and MAP), Spearman correlations among them were generally low, ranging from 0.02 to 0.37 for all variables. However, the correlation between MAAT and MAP stood out with a higher value of 0.71 (Figure S19).

The random forest models exhibited considerable explanatory power, accounting for 65% of the variation in DOC concentration and 72% in DOC yield (out-of-bag R^2), utilizing peatland coverage, MAAT, MAP, catchment area, and peatland drainage as predictor variables (Figure 15). Peatland coverage demonstrated a positive association with both concentration and yield (Figure 16a-b) and emerged as the most influential predictor for concentration (relative importance score = 1) and the second most significant predictor for yield (relative importance = 0.95). MAP ranked as the most crucial predictor for yield but was fourth for concentration (relative importance = 1 and 0.61, respectively). The relationship between MAP and DOC yield was positive, whereas the association between MAP and DOC concentration exhibited a non-linear, negative pattern with a drop observed at approximately 1000 mm yr^{-1} (Figure 16c-d). MAAT was the second and fourth most important predictor for DOC concentration and yield (relative importance = 0.77 and 0.43, respectively). The relationship between MAAT and DOC concentration was unimodal with a peak around 3°C, while the relationship between MAAT and DOC yield was bimodal, displaying a primary peak around 7°C and a secondary peak around 1°C (Figure 16e-f). Catchment area ranked as the third most important predictor for both concentration and yield (relative importance = 0.66 and 0.47, respectively) and demonstrated negative correlations with both DOC parameters, displaying declines in DOC concentration and yields when catchments exceeded approximately 1 km^2 and 10 km^2, in the respective models (Figure 16g-h). Peatland drainage had the least impact as a predictor in both models (relative importance = 0.07 for both concentration and yield). The ICE data for peatland drainage revealed a significant average increase of 1.23 mg L^{-1} ($p = 0.03$) in DOC concentration in drained versus undrained peatland catchments. However, there was no significant difference between DOC yield ICE values for drained and undrained peatlands ($p = 0.5$; Figure 16i-j).

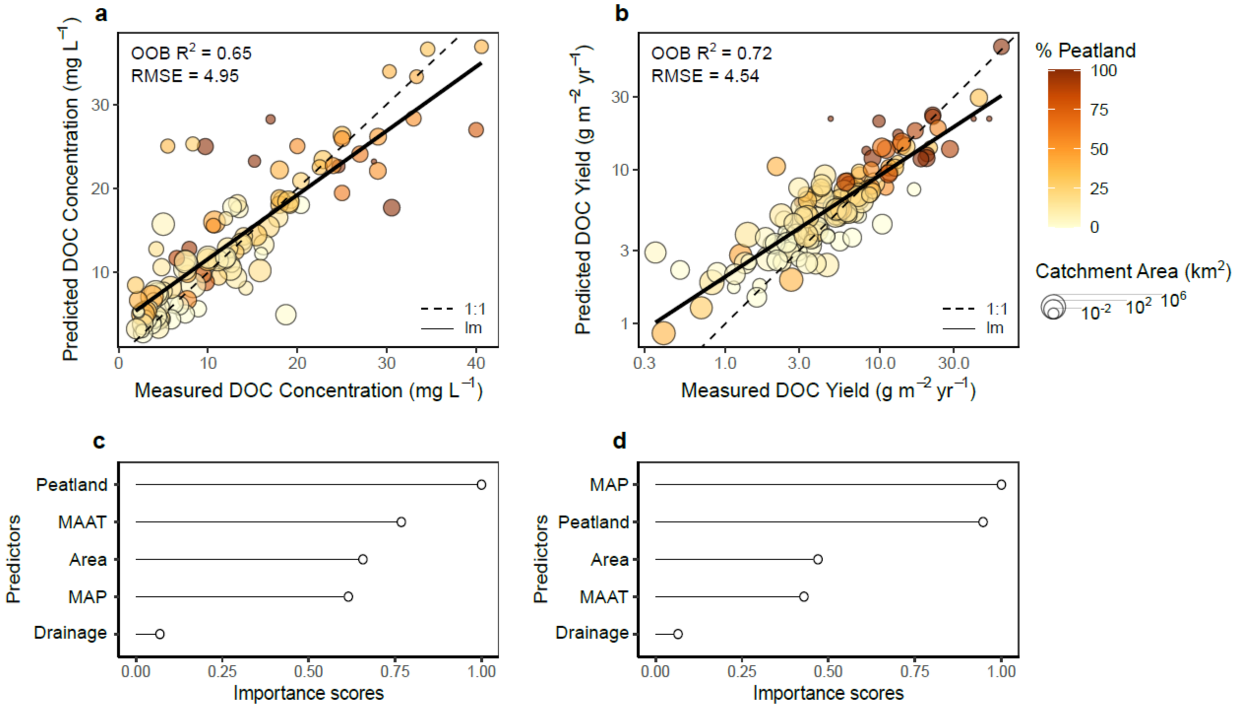

Figure 15. Random forest model predictions of DOC concentration and yield for the test data (20% of the data set) left out of the models. We compared predicted and measured values using a line of best fit (simple linear regression) and a 1:1 line. Plots c and d show predictor importance scores for the respective concentration and yield models. Predictors are ordered from most important to least.

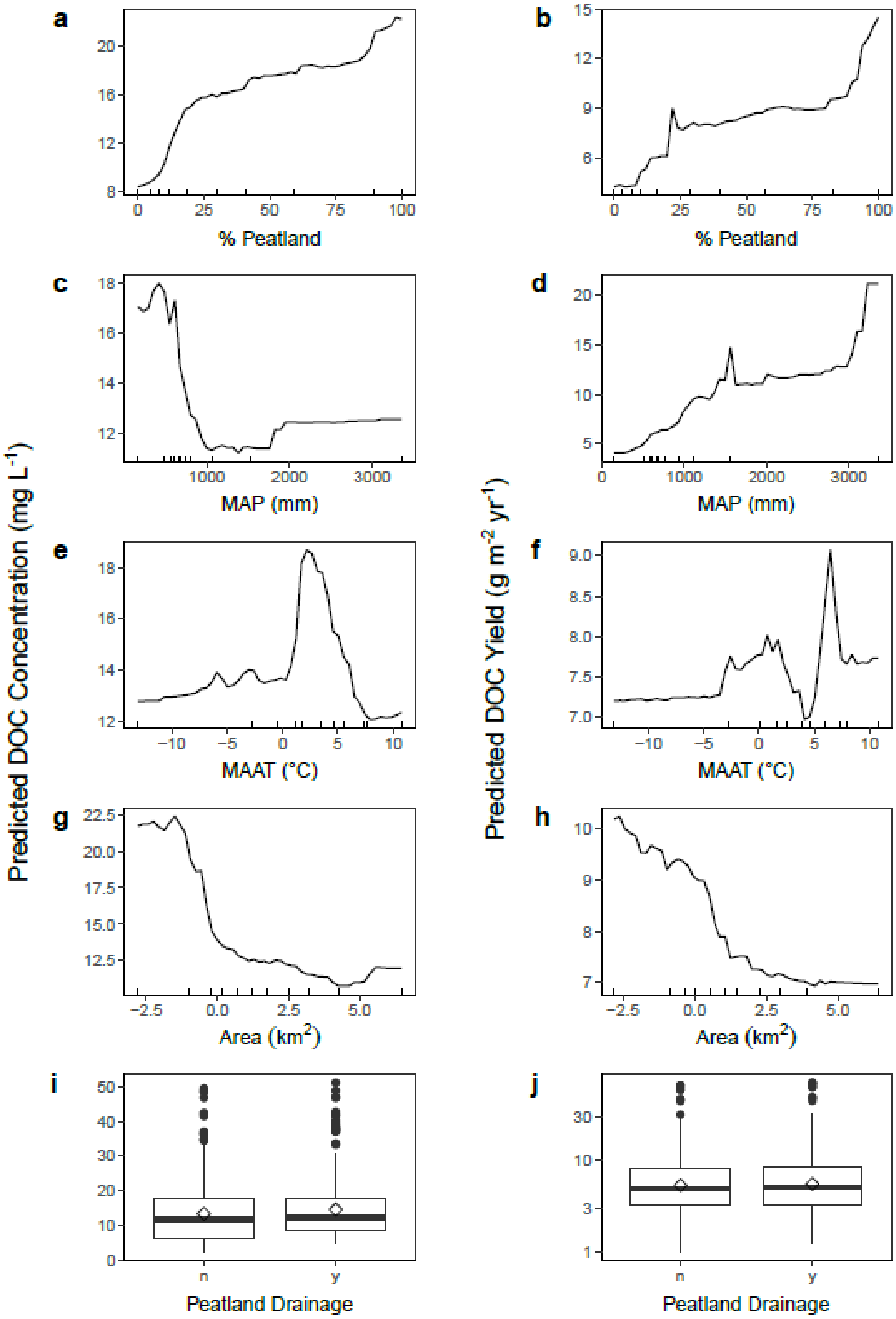

Figure 16. Partial dependence plots for random forest models predicting DOC concentration (plots a, c, e, g, i) and yield (plots b, d, f, h, j). Plots are ordered by predictor relevance. Plots i and j show individual conditional expectation (ICE) plots, showing the range in expected predictions for each observation. Note that the y-axis for plot j is on a $\log_{10}$ scale.

We examined the interactions between climate, peatland coverage, and catchment size on DOC concentrations and yields within the random forest model. Notably, modeled results for headwater peatland catchments (peat coverage = 80%, area = 10 km^2) showed that within the MAAT range of -10°C to 0°C and MAP of approximately 200 to 800 mm, DOC concentration and yield varied by less than 5 mg L^{-1} and less than 1 g C m^{-2} yr^{-1}, respectively. However, as the temperature increased from 0°C to 5°C (where permafrost disappears across the landscape), there was a substantial increase in both DOC concentration (>5 mg L^{-1}) and yield (~2 g C m^{-2} yr^{-1}) (Figure 18a-b). Moreover, the model revealed differences in DOC attenuation rates with peatland coverage across catchment scales (Figure 18c-d). In an average climate (MAAT = 5°C, MAP = 800 mm yr^{-1}), when catchments had high peatland cover (>70%), DOC concentration and yield were substantially higher than catchments with low peatland cover (<30%), especially in headwater catchments (<10 km^2). Moreover, the rate of change in DOC yield between the headwaters and the catchment outlet (an indicator of stream network attenuation) varied slightly by peatland coverage, where DOC yield decreased by 40% for peatland-dominated catchments, and by 34% for low-peatland coverage catchments.

4.3.2 Upscaling DOC concentration and yield in high-latitude catchments

Using random forest models to upscale DOC yield to high-latitude catchments, we estimate that median area-weighted DOC yield was 8.5 g C m^{-2} yr^{-1} from northern headwater peatland catchments. Thus, we estimate that northern peatlands exported 29 (27–37) Tg C yr^{-1} to aquatic networks, or 26 (24–34)% of total terrestrial DOC flux to inland waters (Table 4). For terrestrial DOC export to oceans, we estimate that northern peatlands contributed 20 (19–26) Tg C yr^{-1}, or 23 (22–30)% of total DOC export though northern peatlands covered on 11% of the study area. Our estimates of large-scale catchment export into oceans agreed well with empirical DOC export from the literature for large Arctic rivers and northern countries (R^2 = 0.98; Figure S21).

Table 4. DOC export estimates from high-latitude catchments.

			High-Latitude Peatlands (≥45°N)			**All High-Latitude Catchments**	
	Study area (10^6 km^2)	% peatland cover*	DOC export (Tg C yr^{-1})	% of total export	% DOC Attenuation	DOC export (Tg C yr^{-1})	% DOC Attenuation
Headwater (~10 km^2) export	38.05	9.01%	29 (27–37)	26% (24%–34%)		111 (97–125)	

Terrestrial export to oceans	38.05	9.01%	20† (19–26)	23%† (22%–30%)	31%†	88 (82–95)	21%

Note: data in parentheses shows the 95% confidence interval.
*Peatland cover data is from (Hugelius et al., 2020).
†Prediction is based on the SMOGN-balanced model and is more speculative than our other results.

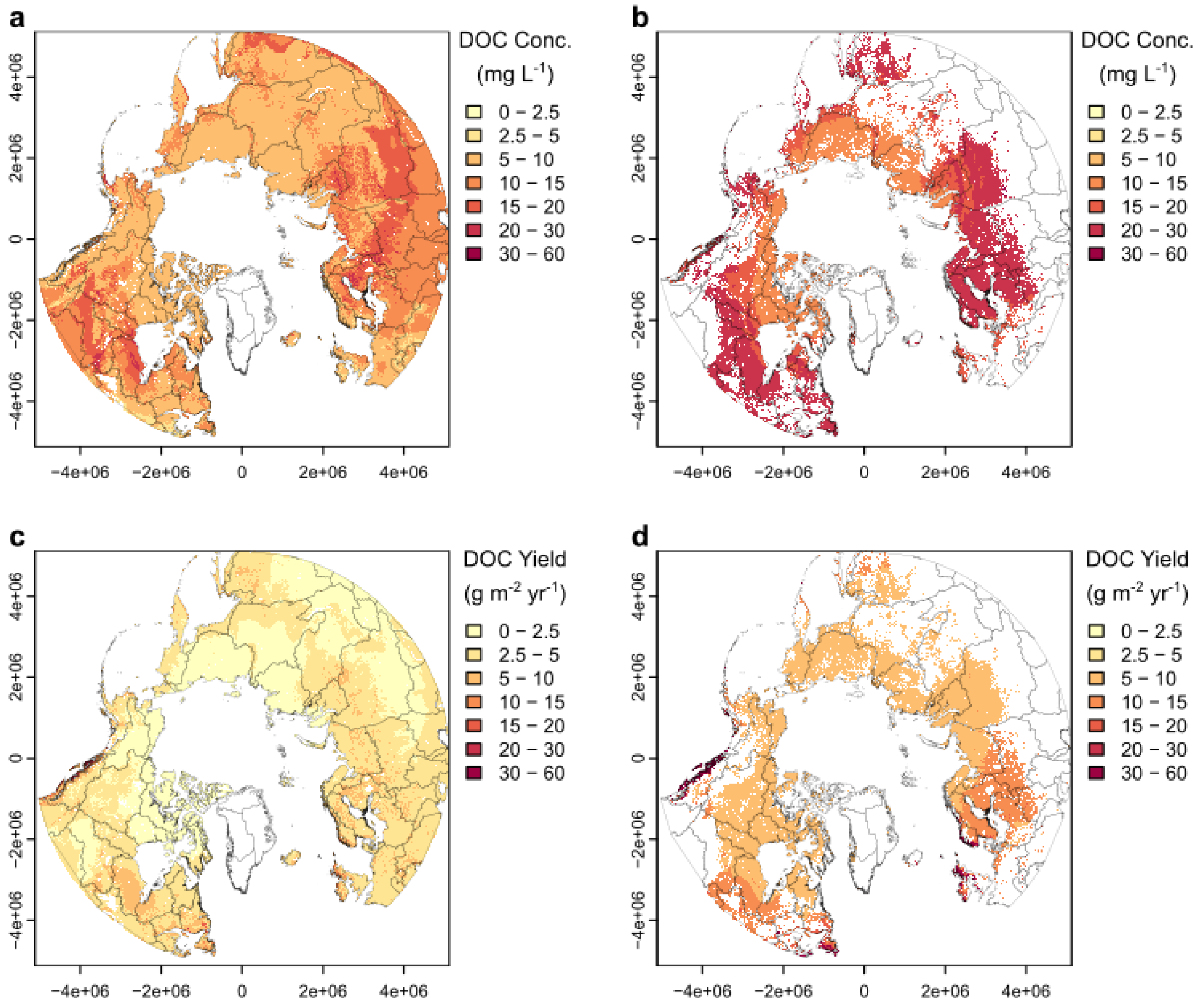

Figure 17. Peatland DOC concentration (plots a-b) and yield (plots c-d) predicted for headwater catchments (i.e., 2.5 degree-minute cells, ~10 km^2). Plots a and c show concentration and yield values for all high-latitude catchments based on peatland cover and climate. Plots b and d show variability in DOC concentration and yield when controlling for peatland cover by constraining predictions to catchments with ≥ 5% peatland coverage and setting peatland cover to 100%. Basin boundaries are shown for HydroBasin Level 3 polygons for large river catchments and aggregated coastal watersheds.

DOC concentration and yield upscaling revealed a pronounced climate control on lateral C production and transport across the high-latitude regions, and specifically from peatlands (Figure 17). Modelled DOC concentration showed high concentrations (>20 mg L^{-1}) in peatland-dominated regions such as the West Siberian and Hudson Bay Lowlands, as well as relatively warm and dry catchments in Siberia and western Canada. In contrast, DOC yield was highest (> 15 g C m^{-2} yr^{-1}) in wetter catchments, particularly in coastal catchments on the west coasts of Canada, Great Britain, and Fennoscandia. Arctic catchments, many of which are underlain by permafrost ground, had among the lowest estimated concentrations and yields (~5 mg L^{-1} and <2.5 g C m^{-2} yr^{-1}).

4.3.3 Peatland DOC attenuation in inland water networks

In our investigation of DOC attenuation in inland water networks, we used modeled DOC export results between “headwater” pixel catchments and coastal export to oceans. Our results showed a 31% reduction in peatland DOC export (~9 Tg C yr^{-1}) between headwaters (~10 km^2) and terrestrial export to oceans (Table 4). For total DOC, there was a 21% reduction in DOC export (~23 Tg C yr^{-1}) between headwaters and terrestrial export to oceans, suggesting that peatland DOC was preferentially lost along the stream network. These findings were further supported by the model results depicted in Figure 18d, which showed a larger reduction in DOC yield for catchments dominated by peatlands (>70% cover) compared to those with less peatland cover. However, Figure 18d shows that the largest reductions in DOC yield occur before 10 km^2, which is the catchment size used in our upscaling exercise. Therefore, this suggests that our upscaled DOC export estimates underestimate DOC attenuation in inland water networks.

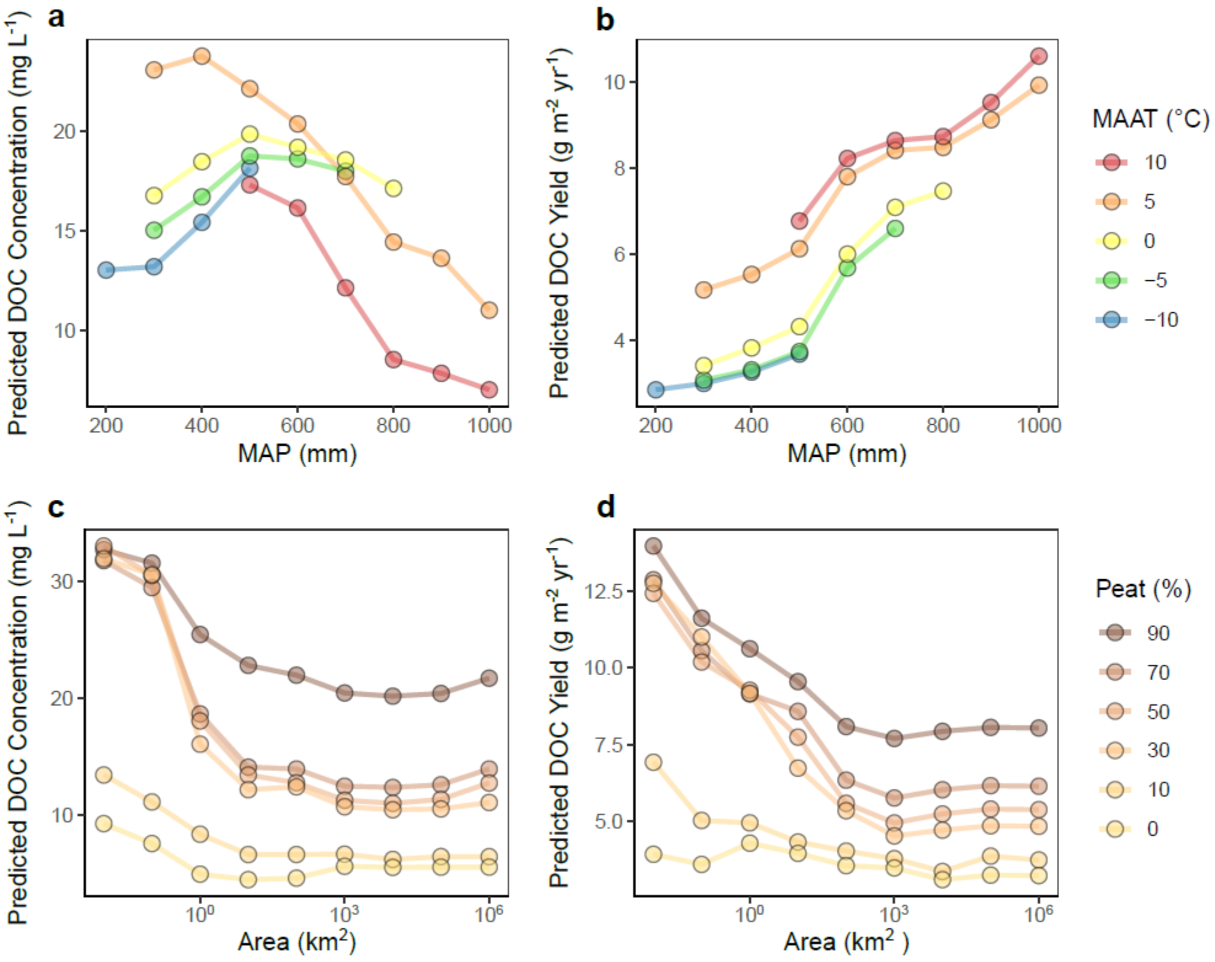

Figure 18. Modeled relationships among DOC, mean annual precipitation (MAP), and mean annual air temperature (MAAT; plots a-b); and DOC, catchment area, and peatland coverage (plots c-d). For plots a and b, peatland coverage was set to 80% and catchment area to 10 km^{2}. For plots c-d, MAP was fixed at 800 mm (~average MAP for the data set) and MAAT to 5 degrees (~average MAAT).

4.3.4 Climate change projections for peatland DOC export

To examine the impact of climate change on inland water DOC concentration and yield, we modeled DOC dynamics for high-latitude catchments under future climate scenarios. Our findings revealed that DOC concentration increased by 0.64 mg L^{-1} on average by the end of the century in the moderate climate change scenario (SSP2-4.5°C). However, the change in DOC concentration showed substantial variation across the study region (CV = 615). The largest increases in DOC concentration occurred in catchments where MAAT transitioned from cold (<

0°C) to moderately warm (0°–5°C), which coincided with the present-day discontinuous permafrost zone (Figure 19a). Conversely, where climate change increased MAAT past 5°C or substantially increased MAP (e.g., by >200 mm yr^{-1}), DOC concentration was predicted to decrease by up to 19 mg L^{-1}. However, the overall spatial patterns in changing DOC concentrations were not strongly correlated with the future changes in MAAT and MAP (Pearson correlations = 0.08 and -0.05, respectively).

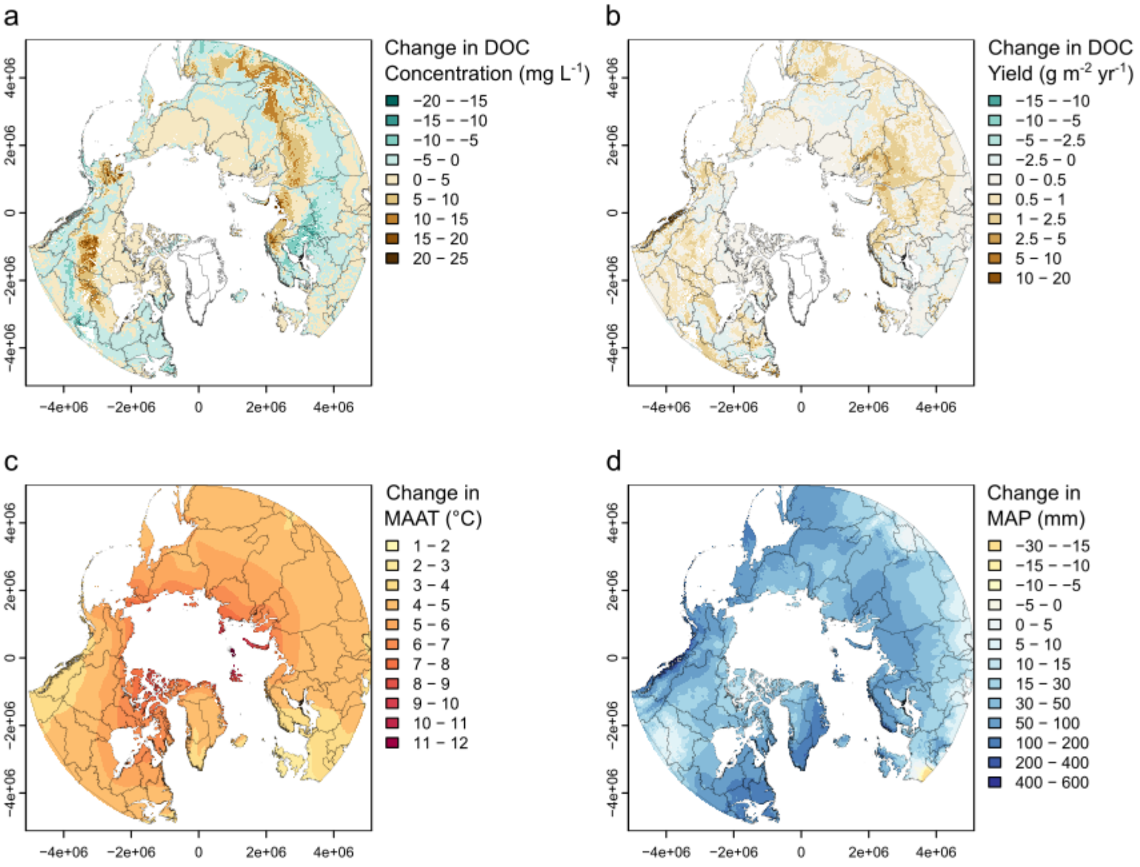

Figure 19. Spatial changes in DOC concentration (plot a), DOC yield (plot b), MAAT (plot c), and MAP (plot d) by the end of the century for SSP2-4.5°C. Future change in DOC concentration and yield were predicted by this study based on predicted changes in MAAT and MAP from CMIP6.

Regarding DOC yield, the moderate climate scenario displayed less variability than DOC concentration (CV = 190), and the average catchment yield change was +0.38 g C m^{-2} yr^{-1} (Figure 19b). Projections indicated that DOC yield could increase by as much as 16 g C m^{-2} yr^{-1} on the west coast of Canada, while decreasing by up to 14 g C m^{-2} yr^{-1} in eastern Canada. In general, spatial patterns of DOC yield were positively correlated with future changes in MAP and DOC concentration (Pearson correlations = 0.20 and 0.32, respectively).

Based on our modeled future climate scenarios, we anticipate that climate change will lead to an increase in peatland headwater DOC export by 12–23% by the year 2100 relative to current levels (Figure 20a). Additionally, overall DOC export from high-latitude catchments is projected to rise by 6–10% due to climate change (Figure 20b). These trends in increasing DOC export are attributed to the warmer and wetter conditions across high latitudes, which enhance DOC production and transport (Figure 19).

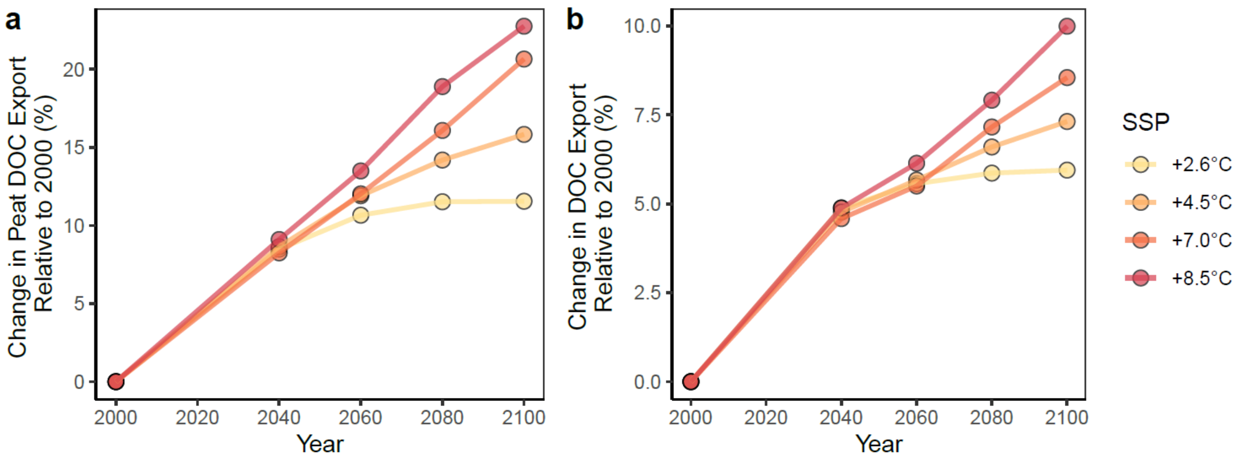

Figure 20. Predicted future change in peatland DOC export (plot a) and overall high-latitude DOC export from headwater catchments (plot b). Note the difference in scales on the y-axes.

4.4 Discussion

Our study confirms that northern peatlands are hotspots for mobilization of terrestrial DOC into aquatic ecosystems. Moreover, our analysis provides new insights into DOC mobilization from northern peatlands, revealing differences in export among regions with varying climates. We found that peatland-derived DOC is selectively attenuated along the aquatic continuum before reaching marine ecosystems. Additionally, our research suggests that climate change will induce distinct responses in DOC concentrations and yields across the study region. Particularly, regions experiencing permafrost thaw are likely to have substantial increase in DOC yields from peatlands. We expand on these points below.

4.1.1 Mobilization of DOC from peatlands in different climates

Peatland catchment cover was the most important factor determining watershed DOC concentration (Hope et al., 1997; Aitkenhead-Peterson et al., 2007; Olefeldt et al., 2014; Williamson et al., 2021). However, the model also revealed the additional influence of MAAT and MAP on DOC concentrations (Laudon et al., 2012; de Wit et al., 2021; Williamson et al., 2021; Bass et al., 2023). For small catchments dominated by peatlands (>80%), our analysis showed that DOC concentrations peaked for MAAT around 3°C, while MAP decreased DOC concentrations in wetter climates. The effect of temperature on DOC concentration likely stems from microbial heterotrophic processes that impact the balance between DOC production and degradation in peat soils (Laudon et al., 2012). Therefore, our results suggest a high net production of DOC in climates with MAAT around 3°C, while warmer climates may favor DOC degradation. Where MAAT is below 0°C, lower DOC concentrations suggest weaker peatland hydrological connectivity to stream networks because of permafrost (Quinton et al., 2009; Laudon et al., 2012). The negative relationship between MAP and DOC concentration might simply arise from dilution in wetter climates (de Wit et al., 2016). Overall, for small peatland-dominated headwaters, our model indicates higher DOC concentrations in Europe and western Russia (~30 mg L^{-1}), whereas colder and drier regions in western Canada and eastern Russia exhibit lower DOC concentrations (~10 mg L^{-1}; Figure 17b).

Watershed peatland cover had a considerable impact on DOC yield, ranking just below MAP in importance. Because DOC yield represents the combination of DOC availability and mobility, we consider peatland cover to strongly influence DOC availability while MAP is a proxy for mobility and downstream transport (de Wit et al., 2016). Moreover, our analysis revealed that MAAT strongly influenced DOC yields, particularly in small watersheds dominated by peatlands (see Figure 16). The sensitivity of DOC yields to MAAT was particularly evident near the threshold of 0°C, which often represents the southern limit for permafrost in peatlands (Frey and Smith, 2005; Olefeldt et al., 2014). However, we couldn't determine whether the influence of MAAT on peatland DOC yields was due to increased DOC production in thawed soils, or increased hydrological connectivity as permafrost barriers degrade (Quinton et al., 2009). Our study area exhibited substantial variation in peatland DOC yields within headwater catchments across different regions. For instance, permafrost regions in western interior Canada and eastern

Russia had DOC yields of approximately 6 g C m^{-2} yr^{-1}, while Scandinavia and eastern Canada exhibited yields of approximately 10 g C m^{-2} yr^{-1}. In warm climates, such as the west coast of Canada and the UK, coastal peatlands demonstrated DOC yields exceeding 15 g C m^{-2} yr^{-1} (Edwards et al., 2021).

Peatland drainage marginally affected DOC concentration and yield across high-latitude catchments in this study. Random forest ICE plots showed a significant increase in DOC concentration due to drainage, but no significant difference in DOC yield (similar to Rosset et al 2022). Though many catchment studies have reported significant increases in DOC concentration and yield from drained peatland catchments (including my own, see Chapter 2), our systematic review was limited by a few key factors. First, peatland drainage data was concentrated in western Europe, limiting the transferability of this data to other climates. Second, we included many different types of peatland drainage (e.g., peat extraction, afforestation, agriculture, etc.) that range in extent and severity, and we were not able to quantify these differences in our model. Thus, drainage had limited explanatory power in our model. As a result, more extensive research is necessary on the hydrology and lateral C transport in drained peatlands, particularly in drier climates. These investigations are vital to improve the accuracy of regional water quality predictions and enhance global biogeochemical models (Fluet-Chouinard et al., 2023).

4.4.2 DOC export and attenuation

Based on our upscaling approach, headwater DOC export to inland waters is estimated to be 29 Tg C yr^{-1}, or an average of 8.5 g C m^{-2} yr^{-1}, from the 3.4 million km^{2} of northern peatlands above 45°N. This represents 26% of the total headwater DOC export to aquatic networks, despite peatlands covering only 9% of the area. Notably, our estimate of northern peatland DOC export is 45% smaller compared to a previous study (Rosset et al., 2022). The difference can be primarily attributed to our inclusion of DOC yield from extensive permafrost peatlands, which have been underrepresented in the literature. Thus, we revise the previous estimate of peatland DOC export to global inland waters from ~91 to ~67 Tg C yr^{-1} (Rosset et al., 2022).

Several lines of evidence from our model suggested that DOC was substantially attenuated along inland water networks, and that more peatland DOC was attenuated than DOC from other landscape sources. For all DOC, catchment size had a strong influence on both concentration and yield in our model, with lower concentrations and yields for larger catchments (see Figure 16). When we examined average model behavior for headwater peatland yield across scales, we found that peatland DOC yield decreased at a higher rate (40% decrease) than non-peat DOC yield (34% decrease) (see Figure 18). Additionally, we assessed attenuation by calculating the difference between headwater DOC export and large coastal catchment export to oceans for the full study region. From that analysis, we estimated that peatland DOC export to the ocean was 20 Tg C yr^{-1}, i.e. an attenuation from 10 km^2 headwaters of ~30%, while the overall DOC export to the ocean was estimated to be 91 Tg, i.e. an overall attenuation of 20%. Preferential attenuation of peatland DOC may be linked to its composition, particularly that it is more aromatic than DOC from other sources (Olefeldt et al., 2013). More aromatic DOC is more likely to be affected by photochemical processes that directly photo-mineralize DOC into CO_2, degrade DOC into more bioavailable compounds, and/or result in increased flocculation that transfers DOC into aquatic sediments (Attermeyer et al., 2018; Creed et al., 2018; Bowen et al., 2019; Einarsdóttir et al., 2020). Additionally, peatlands are often located in low relief, flat catchments, and thus drain poorly and slowly, such that DOC may have a longer residence time and thus more time for attenuation compared to high-relief watersheds (McGuire et al., 2005; Moody et al., 2013).

4.4.3 Climate change impacts on DOC concentration and yield

Using a space for time approach, we predicted changes in DOC concentration and yield for the study domain as a result of future changes in MAAT and MAP. Our analysis suggested that DOC concentration in headwaters is likely to increase substantially (by 10 to 20 mg L^{-1}) in peatland-rich regions that currently have sporadic and discontinuous permafrost, such as northernmost Europe, the west Siberian Lowlands, and the interior plains of western Canada. This prediction is supported by several regional studies that have shown strong trends in DOC with mean annual temperature (Frey and Smith, 2005; Olefeldt et al., 2014). This could have consequences for aquatic functions, and availability of co-precipitating toxins such as methylmercury (Creed et al., 2018; Thompson et al., 2023). Conversely, large, non-permafrost boreal regions are predicted to experience reduced DOC concentrations as MAAT exceeds the unimodal peak at ~5°C (as suggested previously, see Laudon et al., (2012)).

Changes in headwater DOC yields were not uniform, and followed similar spatial patterns as DOC concentration (Figure 19). Areas with increasing DOC yield were predicted to occur primarily in peatland regions with current-day discontinuous permafrost, and regions predicted to experience decreasing DOC yield were mostly in southern regions predicted to become even warmer (i.e., were heterotrophic respiration will outpace lateral DOC export). By summing peatland DOC export across the study region, our analysis suggested that peatland DOC export from headwaters to inland water networks would increase by between 12% (SSP 2.6) and 23% (SSP 8.5; see Figure 20). Overall DOC export to inland waters were predicted to be marginal (6–10%), in line with recent work that has shown that DOC export to the ocean from the 6 largest Arctic rivers has remained mostly static over the past 20 years (Tank et al., 2023). Therefore, our results suggest modest increases in DOC export to inland waters, which may be attenuated more rapidly to maintain DOC export to the ocean (Tank et al., 2023). Additionally, our results do not support large lateral DOC fluxes to inland waters as suggested previously (Plaza et al., 2019; Hugelius et al., 2020).

However, our model only considers the influence of MAAT and MAP, and thus there are limitations to using this space for time approach. For example, shifts in DOC concentrations and yields are currently strongly influenced by the recovery from acidification of the late 20th century in eastern Canada and Europe (Monteith et al., 2007, 2023), and these effects are not considered in our model. Our model also cannot account for changes in DOC concentration and yield that are related to slower landscape processes, such as changes in soil organic matter storage (loss or expansion of current peatlands) or vegetation composition (Neff and Hooper, 2002; McPartland et al., 2019). Therefore, our model assumes that a peatland that exists in the current climate in northern Sweden will become like a peatland southern Sweden in a matter of decades, but there is a mismatch in timescales that we cannot account for using our space for time approach. However, it is reasonable to assume that changes in temperature and water fluxes will affect DOC dynamics (e.g., Laudon et al 2012, de Wit et al 2016), and this study is the first to estimate the amount of DOC export from northern peatlands using a spatially-explicit, observation-based approach.

4.5 Conclusions

Our study highlights the significant role of northern peatlands as hotspots for mobilizing terrestrial DOC into aquatic ecosystems. Our spatially-explicit model provided new insights into the variability of peatland DOC mobilization, highlighting differences in export among regions with varying climates. Our model also suggests that peatland-derived DOC undergoes selective attenuation along the aquatic continuum before reaching marine ecosystems. The research also indicates distinct responses in DOC concentrations and yields across the study region due to climate change, particularly with permafrost thaw leading to substantial increases in DOC yields from peatlands. Our results regarding peatland drainage were inconclusive, and more research is needed to determine the influence of peatland drainage and other disturbances on peatland DOC dynamics. Future climate change will likely increase DOC concentration and yield in peatland-rich regions experiencing sporadic and discontinuous permafrost. Conversely, non-permafrost boreal regions are predicted to experience reduced DOC concentrations where rising temperatures may shift soil organic matter from net accumulation to net loss. Overall, this study provides valuable insights into the dynamics of DOC export from northern peatlands and highlights the complex interactions between climate, peatland cover, and aquatic ecosystems.

5. Summary, Conclusions, and Directions for Future Research

5.1 Summary of findings

My research has focused on how peatland disturbance affects C, N, and P export to inland waters and the implications for local water quality, ecosystem health, and global biogeochemical cycles. Peatlands are the world's C savings accounts, but climate change and LULCC are forcing peatlands to withdraw more C than they deposit (Turetsky et al., 2015; Loisel et al., 2021). Some of the C lost is in the form of DOM exported to inland waters, which also includes N and P. Moreover, peatland disturbances, particularly drainage, mineralize peat OM to inorganic N and P that have consequences for aquatic ecosystem function. The fate of DOM and nutrients from disturbed peatlands depends on complex biogeochemical processes that are interconnected. Most of our understanding of DOM and nutrient export from disturbed peatlands relies on data from western Europe and eastern Canada (Rosset et al., 2022), which are climatically distinct from most northern peatland catchments (Frey and Smith, 2005; Olefeldt et al., 2014). Therefore, my work helps to address this data gap by studying disturbed peatland catchments in western Canada, and collates data from understudied catchments across the high-latitude region to improve our understanding of continental-scale DOC processes and export (more work is needed before a similar synthesis can be done for N and P).

In my first study (Chapter 2), I examined how industrial peat extraction affected DOC and inorganic nutrient concentration and export in two meso-scale catchments (~150 km^2) in sub-boreal Alberta, Canada. These drained and extracted peatlands significantly increased NH_4^+ concentration relative to intact peatlands and all other land uses. Peatland drainage also increased turbidity compared to intact peatlands, and disturbance reduced the PO_4^{3-} sink function of intact peatlands. DOC concentration was elevated in drainage ditches, compared to intact headwater peatlands, but these differences were not significant across the nested stream network. We used a qualitative assessment of solute attenuation to show that DIN and DIP were substantially attenuated along the stream network, but that net DOC attenuation was low. In other words, DOC acted conservatively through the stream network, similar to base cations. However, shifts in DOM composition to more fresh, autochthonous sources suggested that "conservative" DOC was actually balanced by gains and losses of DOC along the stream network. Furthermore, variability in stream discharge influenced DOC and nutrient fate by modulating stream network attenuation. This work provides important observations in a relatively data-poor region in the peatland catchment literature (Rosset et al., 2022), and provides critical insights into the fate of solutes exported from disturbed peatlands.

In my second study (Chapter 3), I examined how peat extraction and wildfire affected C, N, and P resource bioavailability for headwater stream bacteria. DOC bioavailability is relatively well-studied in peat-fed streams, but concurrent measurements of bioavailable DOC, DON, and DOP are rare (Berggren et al., 2015; Soares et al., 2017; Rulli et al., 2022). Given the abundance of DOM in these streams, organic nutrients could potentially be important nutrient sources for bacteria (Stepanauskas et al., 2002; Berggren et al., 2015), but my research suggests that this is not the case in headwater peatland streams. Overall, DOM was less than 1% bioavailable and DON and DOP were undetectable most of the time. DOM bioavailability (DOC and DON) peaked during the spring freshet (Stepanauskas et al., 2000; Ågren et al., 2008), which was associated with a decrease in DOM aromaticity. Though disturbance did not significantly affect DOM bioavailability, it did affect inorganic nutrient concentrations and stoichiometric ratios of bioavailable resources (C:N:P). Thus, peatland disturbances exacerbated C-limitation in headwater streams, which could destabilize aquatic ecosystems for at least a couple years (e.g., wildfire), and potentially for decades (in the case of decades-long peat extraction activities).

In my third study (Chapter 4), I zoomed out to examine the role of northern peatlands in the aquatic C cycle at continental scales. I employed a systematic review to synthesize available published research from high-latitude catchments, and highlighted the role of climate (MAAT and MAP) on DOC concentration and area-weighted yields. (Though my original goal was to include N and P in this study, during the systematic review it was clear that the literature was not yet sufficient to support robust upscaling.) One of the key findings was that most peatland catchment research to date is biased toward western Europe and eastern Canada, which are climatically distinct regions that support higher DOC concentration and yield. Therefore, previous estimates of northern peatland DOC export have relied on this biased data and have overestimated northern peatland DOC export. To ameliorate this issue, we used a spatially-explicit, observation-based modelling approach, and estimated that northern peatlands contribute 29 Tg C yr^{-1} to inland water networks and 20 Tg C yr^{-1} to oceans, suggesting that at least 31% of peatland DOC is attenuated in inland waters. We attempted to estimate the influence of peatland drainage on DOC export across high-latitude catchments, and model results suggest that peatland drainage significantly increased DOC concentration by 1.23 mg L^{-1} on average, but had negligible effects on DOC yield. However, the systematic review data for peatland drainage was limited and geographically biased. We also estimated that climate change will increase DOC export across northern peatland headwater catchments by 12% (SSP1-2.5°C) to 23% (SSP5-8.5°C) by 2100. Spatial projections suggest that the largest increases in DOC concentration and yield will occur in the present-day discontinuous permafrost region. Our estimate is a couple orders of magnitude lower than a previous speculative estimate for northern peatlands (Hugelius et al., 2020). This research significantly improves our understanding of northern peatland catchments in context of the global C cycle, and suggests that climate change will increase the flux of peatland C from inland waters to the atmosphere. However, this flux remains a small component of global C flux, especially in comparison to fossil fuel emissions.

The findings presented across different chapters of my research reveal an interesting contradiction for the amount of DOM attenuation. In Chapter 2, I reported relatively low DOM attenuation rates within headwater streams and meso-scale stream networks of approximately 150 km^2. In contrast, Chapter 4 presented substantial ~30% DOM attenuation across high-latitude catchments, with the model even suggesting potentially higher attenuation rates within smaller headwater catchments less than 10 km^2. The apparent discrepancy in these results can be explained through a combination of factors that emphasize the complex nature of DOM dynamics. Firstly, regional disparities in climate and water residence time may be significant contributors. As highlighted in Chapter 4, peatland-derived DOM is controlled by the specific climate conditions and peatland coverage of each region. Moreover, the study sites in chapter 2 were highly eutrophic, low-relief, sub-boreal catchments that are unique from other study sites in the literature. Another key consideration, and the crux of this research, is the impact of peatland drainage. The random forest model in Chapter 4 struggled to precisely define the effects of drainage on DOM dynamics, and therefore the projected DOC attenuation from the model may not apply to drained peatland catchments. The combined results from Chapters 2 and 3 emphasized that peatland drainage not only released more refractory DOM into the stream network but also contributed higher levels of DIN. The stream network analysis from Chapter 2 suggested that DOM behaved conservatively within the stream network. Nevertheless, multiple lines of evidence indicated some degree of DOM processing, such as downstream shifts in DOM to more aliphatic-like DOM, and attenuation of nutrients implying active plant uptake and primary production. Therefore, the observed contradictions in DOM attenuation outcomes across chapters underscore the interplay of local conditions, climate, hydrology, and anthropogenic disturbances in shaping the complex dynamics of dissolved organic matter within these ecosystems.

5.2 Management implications

My research in disturbed peatland catchments in Alberta revealed significant alterations in nutrient concentrations and stoichiometry in surface waters (see Chapters 2 & 3). Specifically, peat extraction increased NH_4^+ concentrations, and was even greater than NH_4^+ in nearby agricultural catchments. Similar patterns have been observed in Northern Europe (Vassiljev and Blinova, 2012), where nearly 50% of peatlands have been drained or destroyed since 1700 CE (Fluet-Chouinard et al., 2023). Consequently, drained peatlands have become diffuse nutrient sources in the landscape, requiring specialized management to ensure compliance with the European Union Water Framework Directive (Marttila et al., 2018; Nieminen et al., 2018, 2020a). In Canada, peatland policies have focused more on C sequestration, and less on the adverse effects of nutrient pollution from disturbed peatlands (Government of Alberta, 2014). This is notable because approximately 13% of Canada is covered by peatlands, and in Alberta that number increases to nearly 20% (Yu, 2012). Consequently, my research underscores the urgent need for more extensive and long-term monitoring efforts in peat-rich regions of Canada to promote healthy aquatic function and enhance wetland policy.

At extracted peatland sites, the current best management practice is to install sedimentation ponds in the drainage ditch network of new extraction sites before releasing water downstream (St-Hilaire et al., 2006; Hafdhi et al., 2020). My research suggests that, in addition to monitoring sediment yields from extracted sites, other dissolved water chemistry parameters should also be monitored, particularly nutrients. Water chemistry is critical for the health of aquatic ecosystems, and few studies have assessed the effectiveness of sedimentation ponds for managing elevated dissolved solutes from extracted peatland sites (St-Hilaire et al., 2006). However, research in Northern Europe suggests that sedimentation ponds are less effective than other interventions such as wetland buffers, ditch breaks, and adjustments in ditch depth and spacing for mitigating sediment and nutrient yields (Nieminen et al., 2018). Therefore, more research is needed to determine if current sedimentation ponds are effective for managing broader water quality.

Additionally, I recommend expanding water quality monitoring in disturbed peatland catchments in Alberta and across Canada to manage current and future change. Climate and LULCC disturbances in peatlands are increasing, and evidence from disturbed peatland catchments in Europe show widespread adverse effects for water quality (Nieminen et al., 2020a). Therefore, a Canadian peatland water monitoring program should focus on understanding the scope of the issue and providing evidence to shape future water policy. Long-term monitoring projects (e.g., multiple decades) at the landscape scale would be particularly useful to detect water quality changes across interannual and decadal hydrological cycles. Moreover, water quality monitoring downstream of restored peatlands should be included to assess how restoring the C sink capacity of disturbed peatlands affects water quality. Together, these interventions and monitoring frameworks will help improve stewardship of the vast C and nutrient stores in northern peatlands for current and future generations.

5.3 Directions for future research

To advance our knowledge of peatland DOM and nutrient export, future research should focus on one of two areas: first, future research should include field studies on DOM and nutrient export and fate in understudied regions—particularly in permafrost peatlands and disturbed peatlands in Siberia and North America. Secondly, more process-based research is needed to examine DOM and nutrient fate in northern waters using field techniques, lab experiments, mesocosm simulations, and reactive transport models. Because DOC export is a significant component of the net ecosystem C balance in northern peatlands, it is critical to understand how disturbances may affect the magnitude of peatland DOC export (Evans et al., 2014), the interaction with nutrient export, and the fate of peatland DOM in inland water networks.

Currently, we lack basic field research on the magnitude and composition of DOM export from northern peatland catchments in understudied regions. For example, 63% of the data in the systematic review in Chapter 4 originated from catchments in western Europe that encompassed less than 4% of northern peatland area. Consequently, there is substantial uncertainty in our understanding of DOM export and fate for a large proportion of northern peatland catchments in climatically and geologically distinct regions as pointed out by my research and others (Tank et al., 2020; Pugh et al., 2021; Zolkos et al., 2022). Future research is needed in understudied areas such as permafrost peatlands and peatlands with novel disturbances (e.g., linear oil and gas disturbances) so that we can close the data gap between peatlands in Northern Europe and the remaining high-latitude region. For example, permafrost affects ~50% of northern peatlands (Hugelius et al., 2020), yet most permafrost research has occurred in upland permafrost landscapes (e.g., the North Slope of Alaska). Additionally, widespread linear disturbances for oil and gas exploration made by seismic lines and roads affect the hydrology and vegetation of northern landscapes in Canada and Siberia (Braverman and Quinton, 2016; Saraswati et al., 2019; Strack et al., 2019), but the influence on DOM and nutrient export and DOM composition remains unquantified. As climate change advances, permafrost thaw will affect large swaths of northern peatlands, particularly in the discontinuous permafrost zone, and resource extraction activities may increase in the north as the climate becomes more accessible. The consequences of these disturbances for water quality and aquatic ecosystem health are highly uncertain (Plaza et al., 2019; Hugelius et al., 2020), but are extremely important for northern communities that rely on local water supplies and fisheries in peatland catchments.

To improve understanding of aquatic OM attenuation in permafrost peatland catchments, I propose several lines of investigation for future research across stream reach, catchment, and regional scales. First, future research should quantify the sensitivity and rates of OM degradation in permafrost peatland stream reaches using geochemical tracers (Abbott et al., 2016; Harms et al., 2019; Rodríguez-Cardona et al., 2020). The results from these efforts should be compared to coupled laboratory experiments and published results in attempt to harmonize results from field and laboratory studies (Plont et al., 2022). Second, future research at the catchment scale should incorporate nested high-frequency in situ analyzers to measure rates of network attenuation of permafrost peatland DOM (Wollheim et al., 2015, 2017). High frequency time series can be used to detect seasonal trends and model network attenuation. Finally, I propose using remote sensing to detect change in permafrost peatland landscapes and riverine DOM export over longer time frames (e.g., multiple decades) (Ross et al., 2019). The goal of this research would be to assess legacy effects of climate and landscape change on DOM export and composition (Camill and Clark, 2000; Huang et al., 2017). Therefore, these future research directions would improve our understanding of DOM attenuation in peatland catchments across scales which would help inform process-based models and the flux of C from inland waters to the atmosphere.

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Appendices

Appendix 1. Supporting information for Chapter 2

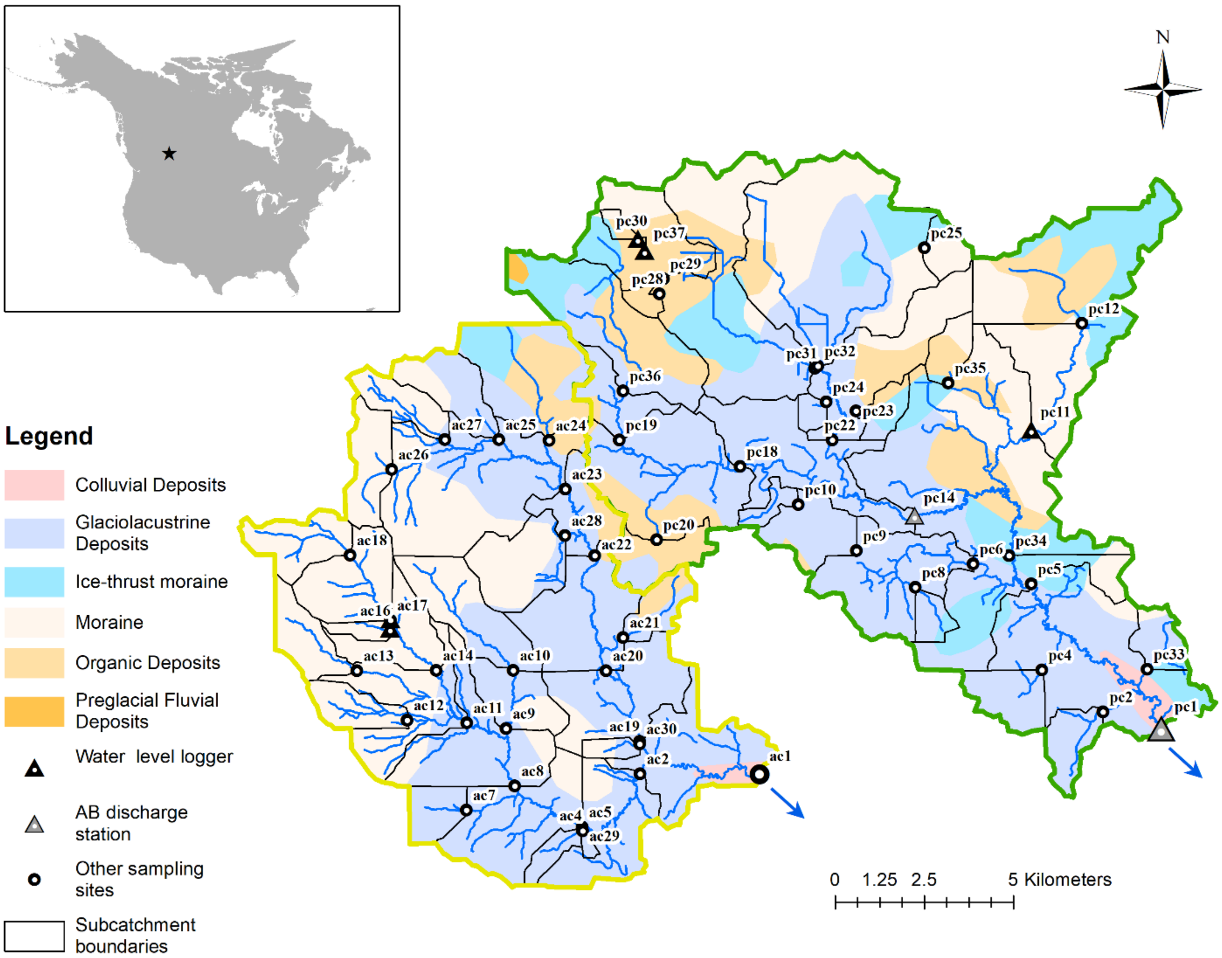
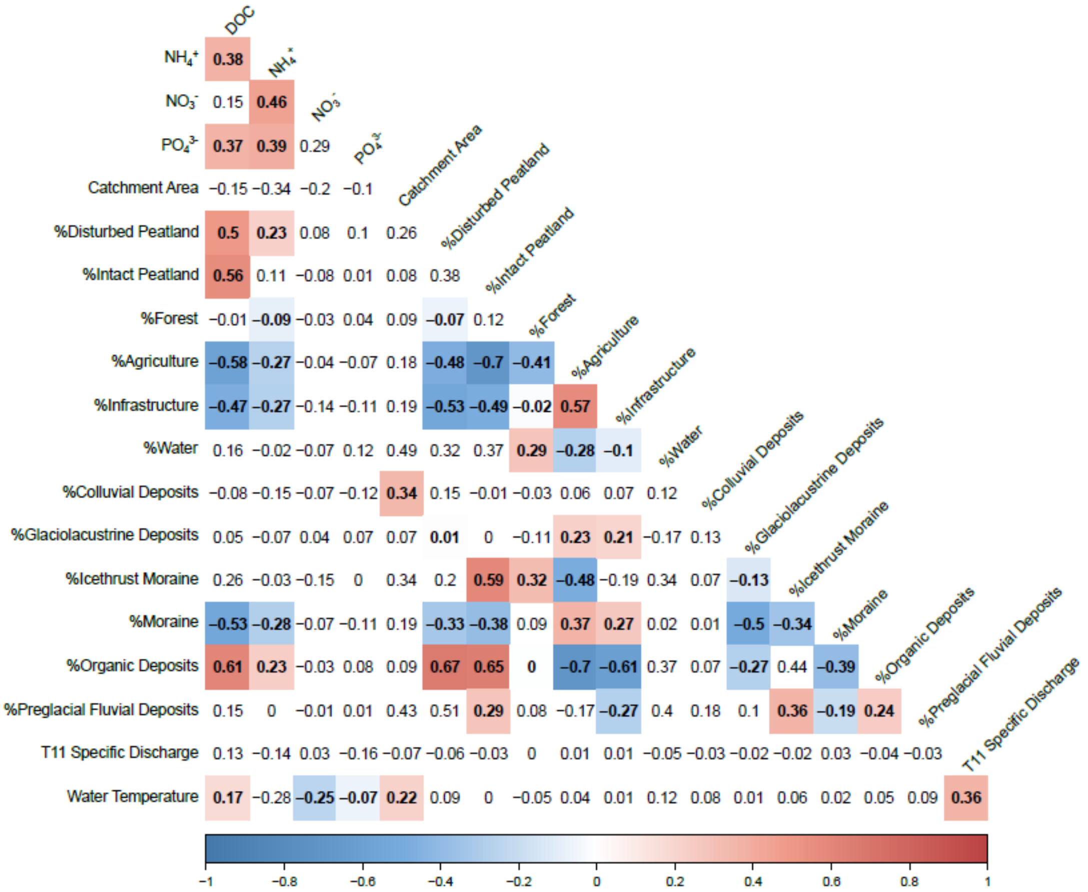
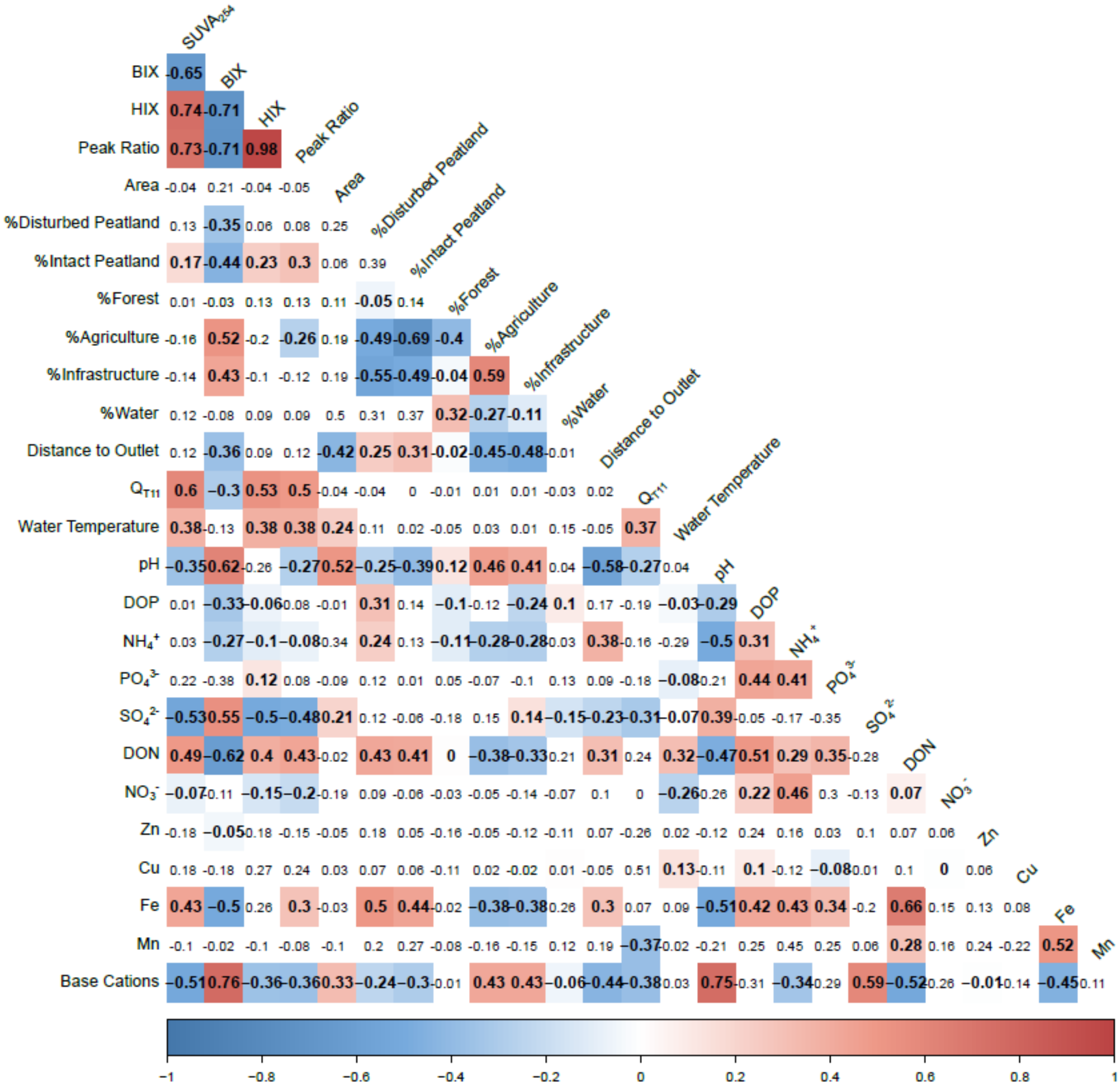


Figure S1. Map of surficial geology for the 55 subcatchments.



	DOC	NH_4^+	NO_3^-	PO_4^{3-}	Catchment Area	%Disturbed Peatland	%Intact Peatland	%Forest	%Agriculture	%Infrastructure	%Water	%Colluvial Deposits	%Glaciolacustrine Deposits	%Icethrust Moraine	%Moraine	%Organic Deposits	%Preglacial Fluvial Deposits	T11 Specific Discharge
NH_4^+	**0.38**																	
NO_3^-	0.15	**0.46**																
PO_4^{3-}	**0.37**	**0.39**	0.29															
Catchment Area	−0.15	−0.34	−0.2	−0.1														
%Disturbed Peatland	**0.5**	**0.23**	0.08	0.1	0.26													
%Intact Peatland	**0.56**	0.11	−0.08	0.01	0.08	0.38												
%Forest	−0.01	**−0.09**	−0.03	0.04	0.09	**−0.07**	0.12											
%Agriculture	**−0.58**	**−0.27**	−0.04	−0.07	0.18	**−0.48**	**−0.7**	**−0.41**										
%Infrastructure	**−0.47**	**−0.27**	−0.14	−0.11	0.19	**−0.53**	**−0.49**	**−0.02**	**0.57**									
%Water	0.16	−0.02	−0.07	0.12	0.49	0.32	0.37	**0.29**	**−0.28**	**−0.1**								
%Colluvial Deposits	−0.08	−0.15	−0.07	−0.12	**0.34**	0.15	−0.01	−0.03	0.06	0.07	0.12							
%Glaciolacustrine Deposits	0.05	−0.07	0.04	0.07	0.07	**0.01**	0	−0.11	**0.23**	**0.21**	−0.17	0.13						
%Icethrust Moraine	0.26	−0.03	−0.15	0	0.34	0.2	**0.59**	**0.32**	**−0.48**	−0.19	0.34	0.07	**−0.13**					
%Moraine	**−0.53**	**−0.28**	−0.07	−0.11	0.19	**−0.33**	**−0.38**	0.09	**0.37**	**0.27**	0.02	0.01	**−0.5**	**−0.34**				
%Organic Deposits	**0.61**	**0.23**	−0.03	0.08	0.09	**0.67**	**0.65**	**0**	**−0.7**	**−0.61**	0.37	0.07	**−0.27**	0.44	**−0.39**			
%Preglacial Fluvial Deposits	0.15	0	−0.01	0.01	0.43	0.51	**0.29**	0.08	−0.17	**−0.27**	0.4	0.18	0.1	**0.36**	**−0.19**	**0.24**		
T11 Specific Discharge	0.13	−0.14	0.03	−0.16	−0.07	−0.06	−0.03	0	0.01	0.01	−0.05	−0.03	−0.02	−0.02	0.03	−0.04	−0.03	
Water Temperature	**0.17**	−0.28	**−0.25**	**−0.07**	**0.22**	0.09	0	−0.05	0.04	0.01	0.12	0.08	0.01	0.06	0.02	0.05	0.09	**0.36**

Figure S2. Correlation matrix (spearman correlations) of primary solutes, land use, surficial geology, specific discharge, and water temperature. Significant correlations ($p < 0.05$) are bolded and have background color.



	SUVA$_{254}$	BIX	HIX	Peak Ratio	Area	%Disturbed Peatland	%Intact Peatland	%Forest	%Agriculture	%Infrastructure	%Water	Distance to Outlet	Q_{T11}	Water Temperature	pH	DOP	NH_4^+	PO_4^{3-}	SO_4^{2-}	DON	NO_3^-	Zn	Cu	Fe	Mn
BIX	**-0.65**																								
HIX	**0.74**	**-0.71**																							
Peak Ratio	**0.73**	**-0.71**	**0.98**																						
Area	-0.04	0.21	-0.04	-0.05																					
%Disturbed Peatland	0.13	**-0.35**	0.06	0.08	0.25																				
%Intact Peatland	**0.17**	**-0.44**	**0.23**	**0.3**	0.06	0.39																			
%Forest	0.01	-0.03	0.13	0.13	0.11	**-0.05**	0.14																		
%Agriculture	-0.16	**0.52**	-0.2	**-0.26**	0.19	**-0.49**	**-0.69**	**-0.4**																	
%Infrastructure	-0.14	**0.43**	-0.1	-0.12	0.19	**-0.55**	**-0.49**	**-0.04**	**0.59**																
%Water	0.12	-0.08	0.09	0.09	0.5	0.31	0.37	**0.32**	**-0.27**	**-0.11**															
Distance to Outlet	0.12	**-0.36**	0.09	0.12	**-0.42**	**0.25**	**0.31**	**-0.02**	**-0.45**	**-0.48**	-0.01														
Q_{T11}	**0.6**	**-0.3**	**0.53**	**0.5**	-0.04	-0.04	0	-0.01	0.01	0.01	-0.03	0.02													
Water Temperature	**0.38**	-0.13	**0.38**	**0.38**	**0.24**	0.11	0.02	-0.05	0.03	0.01	0.15	-0.05	**0.37**												
pH	**-0.35**	**0.62**	-0.26	**-0.27**	**0.52**	**-0.25**	**-0.39**	**0.12**	**0.46**	**0.41**	0.04	**-0.58**	**-0.27**	0.04											
DOP	0.01	**-0.33**	**-0.06**	0.08	-0.01	**0.31**	0.14	**-0.1**	-0.12	**-0.24**	**0.1**	0.17	-0.19	**-0.03**	**-0.29**										
NH_4^+	0.03	**-0.27**	**-0.1**	**-0.08**	0.34	**0.24**	0.13	**-0.11**	**-0.28**	**-0.28**	0.03	**0.38**	-0.16	-0.29	**-0.5**	**0.31**									
PO_4^{3-}	0.22	-0.38	**0.12**	0.08	-0.09	0.12	0.01	0.05	-0.07	-0.1	0.13	0.09	-0.18	**-0.08**	0.21	**0.44**	**0.41**								
SO_4^{2-}	**-0.53**	**0.55**	**-0.5**	**-0.48**	**0.21**	0.12	-0.06	-0.18	0.15	**0.14**	**-0.15**	**-0.23**	**-0.31**	**-0.07**	**0.39**	-0.05	-0.17	-0.35							
DON	**0.49**	**-0.62**	**0.4**	**0.43**	-0.02	**0.43**	**0.41**	**0**	**-0.38**	**-0.33**	0.21	**0.31**	0.24	**0.32**	**-0.47**	**0.51**	**0.29**	**0.35**	-0.28						
NO_3^-	**-0.07**	-0.11	**-0.15**	**-0.2**	-0.19	0.09	-0.06	-0.03	-0.05	-0.14	-0.07	0.1	0	**-0.26**	0.26	**0.22**	**0.46**	0.3	-0.13	**0.07**					
Zn	-0.18	**-0.05**	0.18	-0.15	-0.05	0.18	0.05	-0.16	-0.05	-0.12	-0.11	0.07	-0.26	0.02	-0.12	0.24	0.16	0.03	0.1	0.07	0.06				
Cu	0.18	-0.18	0.27	0.24	0.03	0.07	0.06	-0.11	0.02	-0.02	0.01	-0.05	0.51	**0.13**	-0.11	**0.1**	-0.12	**-0.08**	0.01	0.1	**0**	0.06			
Fe	**0.43**	**-0.5**	0.26	**0.3**	-0.03	**0.5**	**0.44**	-0.02	**-0.38**	**-0.38**	0.26	**0.3**	0.07	0.09	**-0.51**	**0.42**	**0.43**	**0.34**	-0.2	**0.66**	0.15	0.13	0.08		
Mn	-0.1	-0.02	-0.1	-0.08	-0.1	0.2	0.27	-0.08	-0.16	-0.15	0.12	0.19	**-0.37**	-0.02	-0.21	0.25	0.45	0.25	0.06	**0.28**	0.16	0.24	-0.22	**0.52**	
Base Cations	**-0.51**	**0.76**	**-0.36**	**-0.36**	**0.33**	**-0.24**	**-0.3**	-0.01	**0.43**	**0.43**	**-0.06**	**-0.44**	**-0.38**	0.03	**0.75**	-0.31	**-0.34**	0.29	**0.59**	**-0.52**	0.26	**-0.01**	0.14	**-0.45**	0.11

Figure S3. Correlation matrix (spearman correlations) of DOM composition variables, hydrological variables, catchment characteristics, and water chemistry variables that were fed into the initial RDA model before we reduced dimensionality with the *ordiR2step* function in the *vegan* R package. Significant correlations ($p < 0.05$) are bolded and have background color.

Table S1. The influence of hydrology, catchment characteristics, and water chemistry on DOM composition across the stream network decomposed with partial redundancy analysis (pRDA). Inertia is analogous to variance. The proportion of explainable variance represents the total constrained variation explained by the full model.

Partial RDA models	**Inertia**	***Adj. R^2***	***p* (>*F*)**	**Proportion of explainable variance**	**Proportion of total variance**
Full model: *DOM ~ hydrochem. + catch.*	4.00	0.62	0.001***	1	0.64
Pure hydrochemistry model: *DOM ~ hydrochem. | (catch.)*	2.04	0.51	0.001***	0.82	0.51
Pure catch. characteristics model: *DOM ~ catch. | (hydrochem.)*	0.24	0.06	0.001***	0.10	0.06
Confounded hydrochemistry/catchment characteristics	0.80			0.20	0.13
Total unexplained	1.45				0.36
Total inertia	6.25				1.00

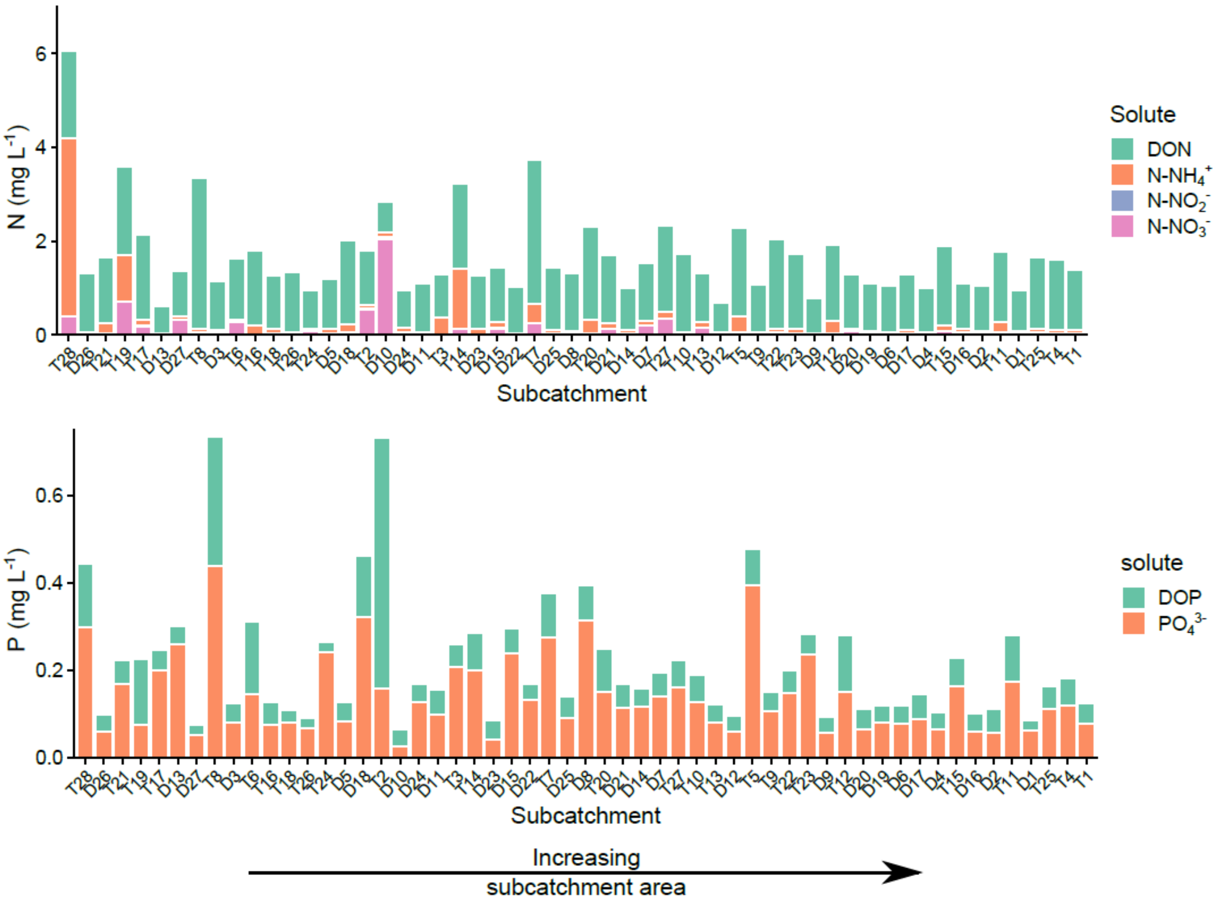


Figure S4. Summary of different species of N and P.

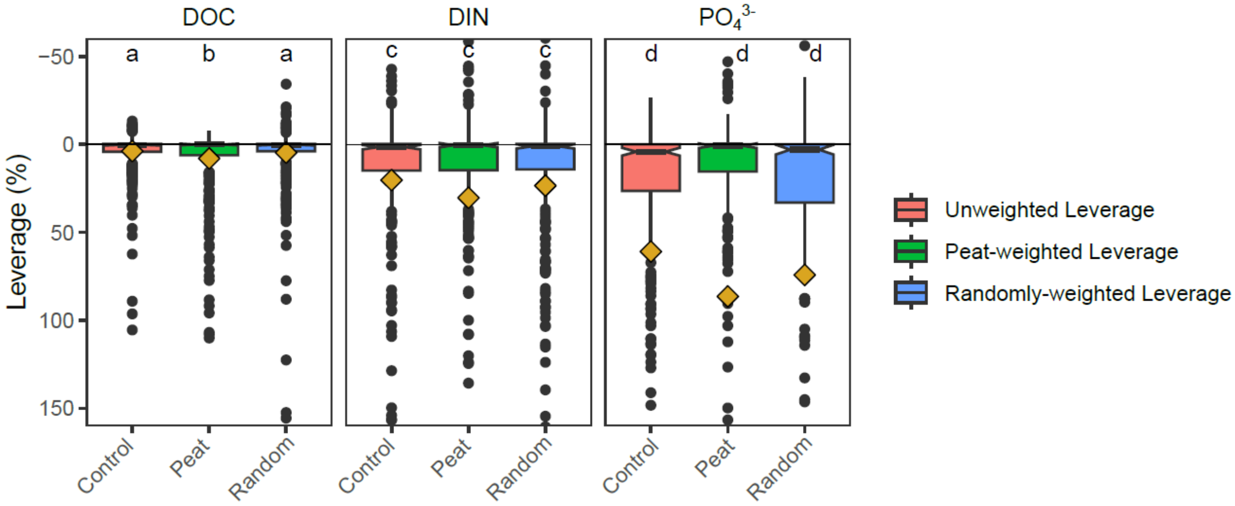


Figure S5. Leverage sensitivity analysis showing differences in the central tendency for leverage values in response to specific discharge variability. Yellow diamonds indicate the mean and boxplots show the median and 95% confidence interval about the median. Unweighted leverage values indicate leverage values assuming equal specific discharge across subcatchments. Peat-weighted leverage assumes specific discharge is a function of peatland cover (i.e., 10 * total peatland cover). Randomly-weighted leverage assumes random variation (from 0.1 to 100 m^3 s^{-1} km^{-2}) in specific discharge across subcatchments. Compact letter display shows statistical differences among discharge assumptions (i.e., unweighted (control), peat-weighted, and randomly-weighted).

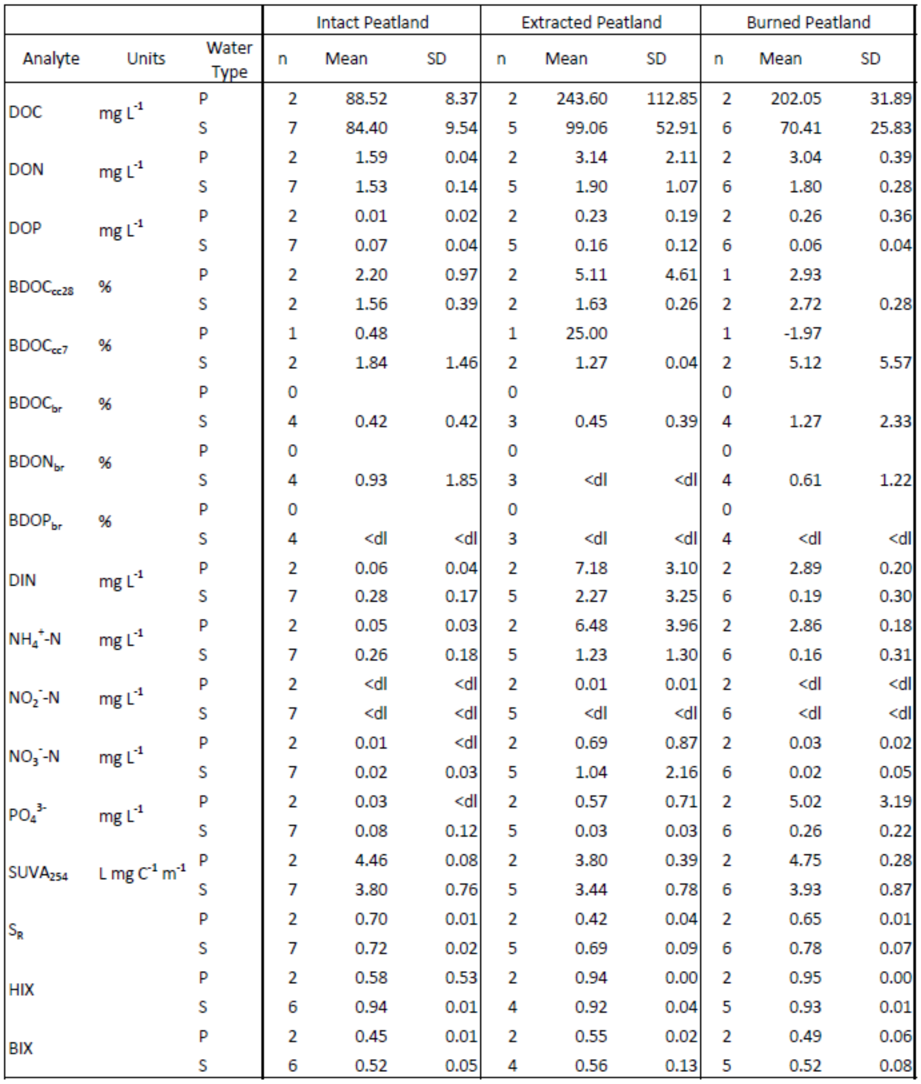
Table S2. Solute export and runoff for sites T1 (Tomahawk Creek catchment outlet) and T11. Discharge was measured by Alberta Environment and Parks.

Site	Year	Land cover	Area km^2	Runoff mm yr^{-1}	DOC	N-NH$_4^+$	N-NO$_3^-$	PO$_4^{3-}$
					Annual yield (g m^{-2} yr^{-1})			
T1	2020	Mixed Land Use	187.83	108	5.83	0.0043	0.0028	0.0086
T11	2020	Mixed Land Use	96.85	100	6.99	0.0027	0.0050	0.013
T1	2021	Mixed Land Use	187.83	10	0.26	0.00031	0.000046	0.0011
T11	2021	Mixed Land Use	96.85	4.9	0.17	0.00013	0.00010	0.00017

Note: yields were calculated using 'method 5' (Littlewood, 1995): $Flux = K\frac{\sum_i Ci*Qi}{\sum_i Qi}Q_T$ where Ci and Qi represent instantaneous concentration and discharge, Q_T is mean river discharge during the period, and K is a conversion factor.

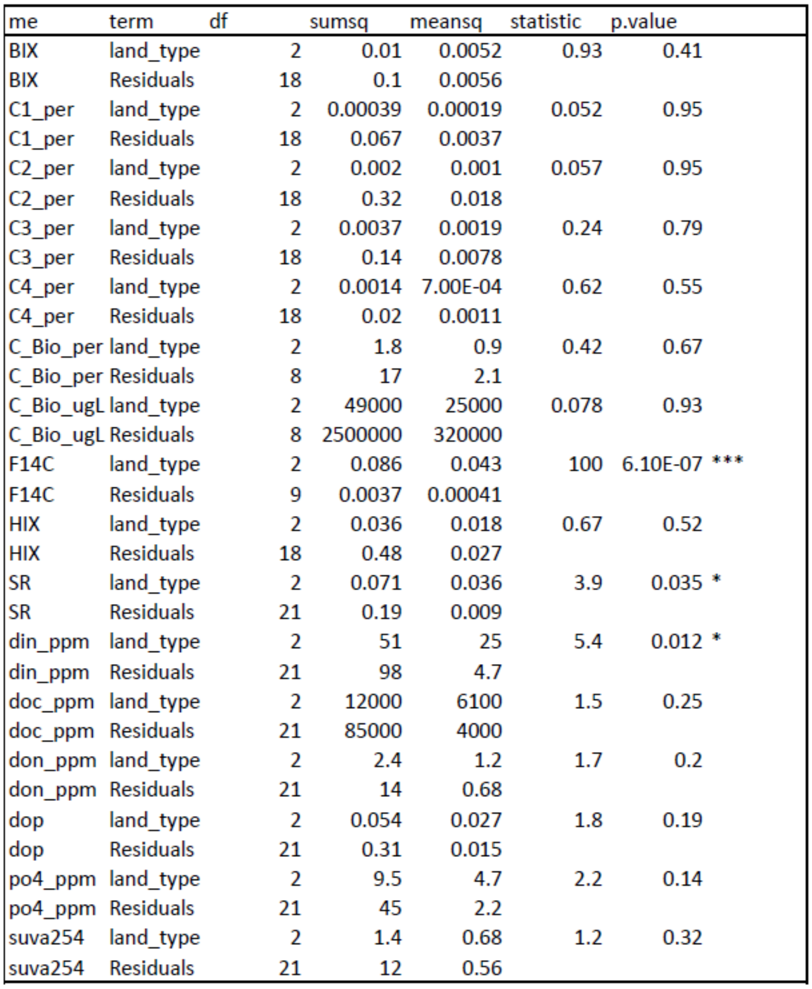
Appendix 2. Supporting information for Chapter 3

Table S3. Summary statistics for porewater (P) and stream water (S) samples.



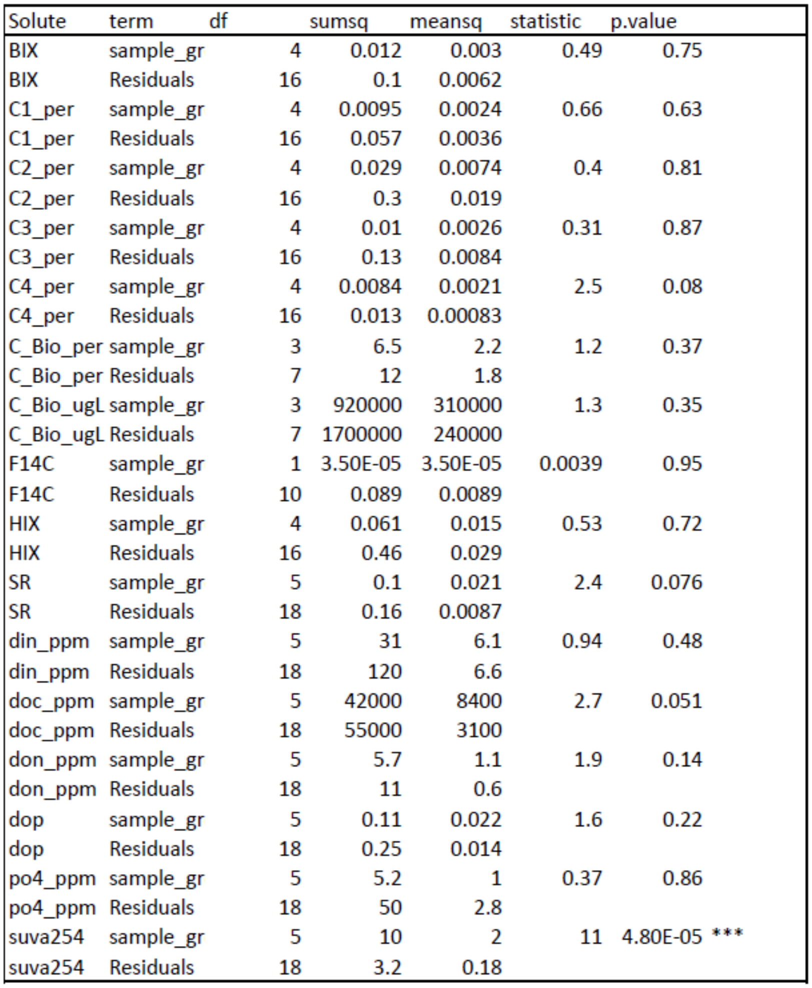
			Intact Peatland			Extracted Peatland			Burned Peatland		
Analyte	Units	Water Type	n	Mean	SD	n	Mean	SD	n	Mean	SD
DOC	mg L^{-1}	P	2	88.52	8.37	2	243.60	112.85	2	202.05	31.89
		S	7	84.40	9.54	5	99.06	52.91	6	70.41	25.83
DON	mg L^{-1}	P	2	1.59	0.04	2	3.14	2.11	2	3.04	0.39
		S	7	1.53	0.14	5	1.90	1.07	6	1.80	0.28
DOP	mg L^{-1}	P	2	0.01	0.02	2	0.23	0.19	2	0.26	0.36
		S	7	0.07	0.04	5	0.16	0.12	6	0.06	0.04
$BDOC_{cc28}$	%	P	2	2.20	0.97	2	5.11	4.61	1	2.93	
		S	2	1.56	0.39	2	1.63	0.26	2	2.72	0.28
$BDOC_{cc7}$	%	P	1	0.48		1	25.00		1	-1.97	
		S	2	1.84	1.46	2	1.27	0.04	2	5.12	5.57
$BDOC_{br}$	%	P	0			0			0		
		S	4	0.42	0.42	3	0.45	0.39	4	1.27	2.33
$BDON_{br}$	%	P	0			0			0		
		S	4	0.93	1.85	3	<dl	<dl	4	0.61	1.22
$BDOP_{br}$	%	P	0			0			0		
		S	4	<dl	<dl	3	<dl	<dl	4	<dl	<dl
DIN	mg L^{-1}	P	2	0.06	0.04	2	7.18	3.10	2	2.89	0.20
		S	7	0.28	0.17	5	2.27	3.25	6	0.19	0.30
NH_4^+-N	mg L^{-1}	P	2	0.05	0.03	2	6.48	3.96	2	2.86	0.18
		S	7	0.26	0.18	5	1.23	1.30	6	0.16	0.31
NO_2^--N	mg L^{-1}	P	2	<dl	<dl	2	0.01	0.01	2	<dl	<dl
		S	7	<dl	<dl	5	<dl	<dl	6	<dl	<dl
NO_3^--N	mg L^{-1}	P	2	0.01	<dl	2	0.69	0.87	2	0.03	0.02
		S	7	0.02	0.03	5	1.04	2.16	6	0.02	0.05
PO_4^{3-}	mg L^{-1}	P	2	0.03	<dl	2	0.57	0.71	2	5.02	3.19
		S	7	0.08	0.12	5	0.03	0.03	6	0.26	0.22
$SUVA_{254}$	L mg C^{-1} m^{-1}	P	2	4.46	0.08	2	3.80	0.39	2	4.75	0.28
		S	7	3.80	0.76	5	3.44	0.78	6	3.93	0.87
S_R		P	2	0.70	0.01	2	0.42	0.04	2	0.65	0.01
		S	7	0.72	0.02	5	0.69	0.09	6	0.78	0.07
HIX		P	2	0.58	0.53	2	0.94	0.00	2	0.95	0.00
		S	6	0.94	0.01	4	0.92	0.04	5	0.93	0.01
BIX		P	2	0.45	0.01	2	0.55	0.02	2	0.49	0.06
		S	6	0.52	0.05	4	0.56	0.13	5	0.52	0.08

Table S4. Statistics from one-way ANOVA tests across peatland sites for combined stream and porewater samples.



me	term	df	sumsq	meansq	statistic	p.value	
BIX	land_type	2	0.01	0.0052	0.93	0.41	
BIX	Residuals	18	0.1	0.0056			
C1_per	land_type	2	0.00039	0.00019	0.052	0.95	
C1_per	Residuals	18	0.067	0.0037			
C2_per	land_type	2	0.002	0.001	0.057	0.95	
C2_per	Residuals	18	0.32	0.018			
C3_per	land_type	2	0.0037	0.0019	0.24	0.79	
C3_per	Residuals	18	0.14	0.0078			
C4_per	land_type	2	0.0014	7.00E-04	0.62	0.55	
C4_per	Residuals	18	0.02	0.0011			
C_Bio_per	land_type	2	1.8	0.9	0.42	0.67	
C_Bio_per	Residuals	8	17	2.1			
C_Bio_ugL	land_type	2	49000	25000	0.078	0.93	
C_Bio_ugL	Residuals	8	2500000	320000			
F14C	land_type	2	0.086	0.043	100	6.10E-07	***
F14C	Residuals	9	0.0037	0.00041			
HIX	land_type	2	0.036	0.018	0.67	0.52	
HIX	Residuals	18	0.48	0.027			
SR	land_type	2	0.071	0.036	3.9	0.035	*
SR	Residuals	21	0.19	0.009			
din_ppm	land_type	2	51	25	5.4	0.012	*
din_ppm	Residuals	21	98	4.7			
doc_ppm	land_type	2	12000	6100	1.5	0.25	
doc_ppm	Residuals	21	85000	4000			
don_ppm	land_type	2	2.4	1.2	1.7	0.2	
don_ppm	Residuals	21	14	0.68			
dop	land_type	2	0.054	0.027	1.8	0.19	
dop	Residuals	21	0.31	0.015			
po4_ppm	land_type	2	9.5	4.7	2.2	0.14	
po4_ppm	Residuals	21	45	2.2			
suva254	land_type	2	1.4	0.68	1.2	0.32	
suva254	Residuals	21	12	0.56			

Table S5. Statistics from one-way ANOVA across sampling dates for combined stream and porewater samples.



Solute	term	df	sumsq	meansq	statistic	p.value	
BIX	sample_gr	4	0.012	0.003	0.49	0.75	
BIX	Residuals	16	0.1	0.0062			
C1_per	sample_gr	4	0.0095	0.0024	0.66	0.63	
C1_per	Residuals	16	0.057	0.0036			
C2_per	sample_gr	4	0.029	0.0074	0.4	0.81	
C2_per	Residuals	16	0.3	0.019			
C3_per	sample_gr	4	0.01	0.0026	0.31	0.87	
C3_per	Residuals	16	0.13	0.0084			
C4_per	sample_gr	4	0.0084	0.0021	2.5	0.08	
C4_per	Residuals	16	0.013	0.00083			
C_Bio_per	sample_gr	3	6.5	2.2	1.2	0.37	
C_Bio_per	Residuals	7	12	1.8			
C_Bio_ugL	sample_gr	3	920000	310000	1.3	0.35	
C_Bio_ugL	Residuals	7	1700000	240000			
F14C	sample_gr	1	3.50E-05	3.50E-05	0.0039	0.95	
F14C	Residuals	10	0.089	0.0089			
HIX	sample_gr	4	0.061	0.015	0.53	0.72	
HIX	Residuals	16	0.46	0.029			
SR	sample_gr	5	0.1	0.021	2.4	0.076	
SR	Residuals	18	0.16	0.0087			
din_ppm	sample_gr	5	31	6.1	0.94	0.48	
din_ppm	Residuals	18	120	6.6			
doc_ppm	sample_gr	5	42000	8400	2.7	0.051	
doc_ppm	Residuals	18	55000	3100			
don_ppm	sample_gr	5	5.7	1.1	1.9	0.14	
don_ppm	Residuals	18	11	0.6			
dop	sample_gr	5	0.11	0.022	1.6	0.22	
dop	Residuals	18	0.25	0.014			
po4_ppm	sample_gr	5	5.2	1	0.37	0.86	
po4_ppm	Residuals	18	50	2.8			
suva254	sample_gr	5	10	2	11	4.80E-05	***
suva254	Residuals	18	3.2	0.18			

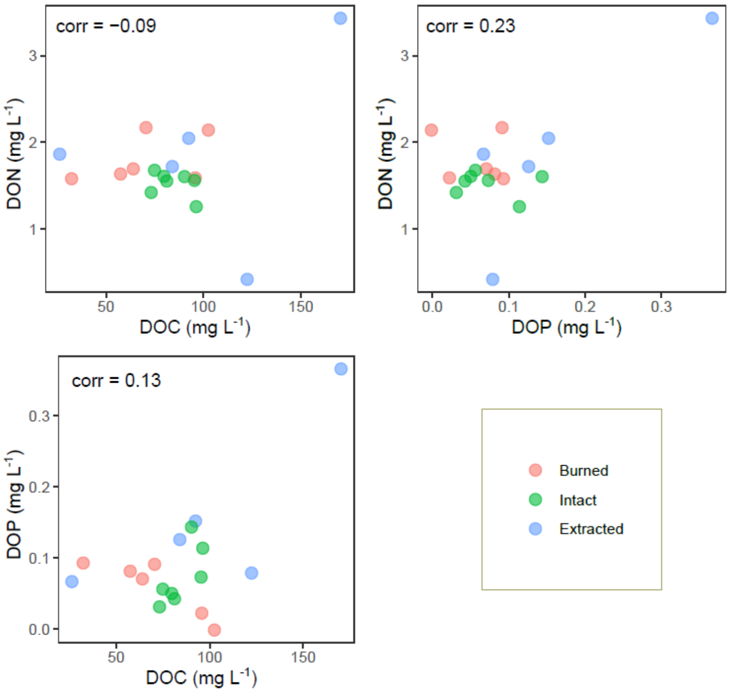


Figure S6. Correlations among bulk DOC, DON, and DOP concentrations showing differences in DOM molecular composition among disturbed and intact peatlands.

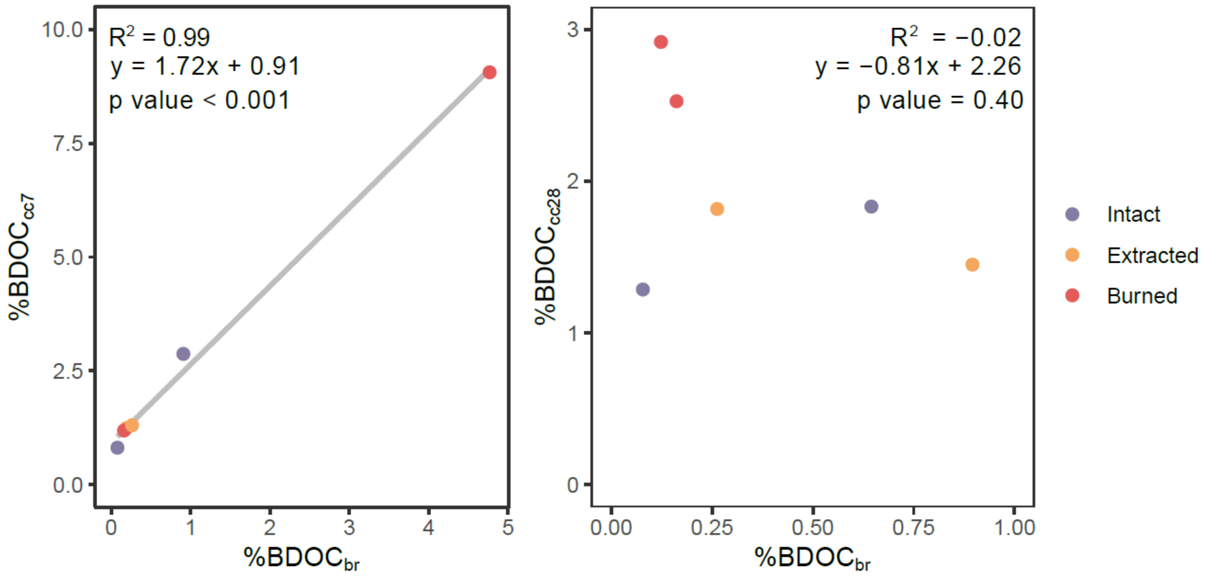


Figure S7. Relationship between results from different lab incubations to measure % bioavailable DOC (BDOC). Results from the 7-day bacterial regrowth incubation are on the x-axis, and results from the concentration change incubations are on the y-axis. The plot on the left shows results from the 7-day concentration change incubation ($BDOC_{cc7}$), while the plot on the right shows results from the 28-day concentration change incubation ($BDOC_{cc28}$).

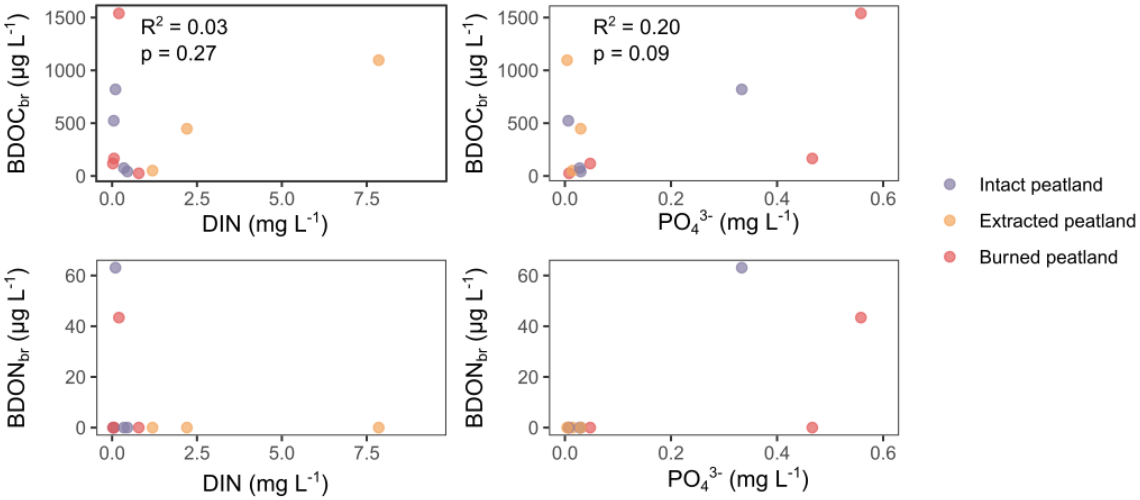


Figure S8. Relationships between stream water inorganic N and P and BDOC and BDON.

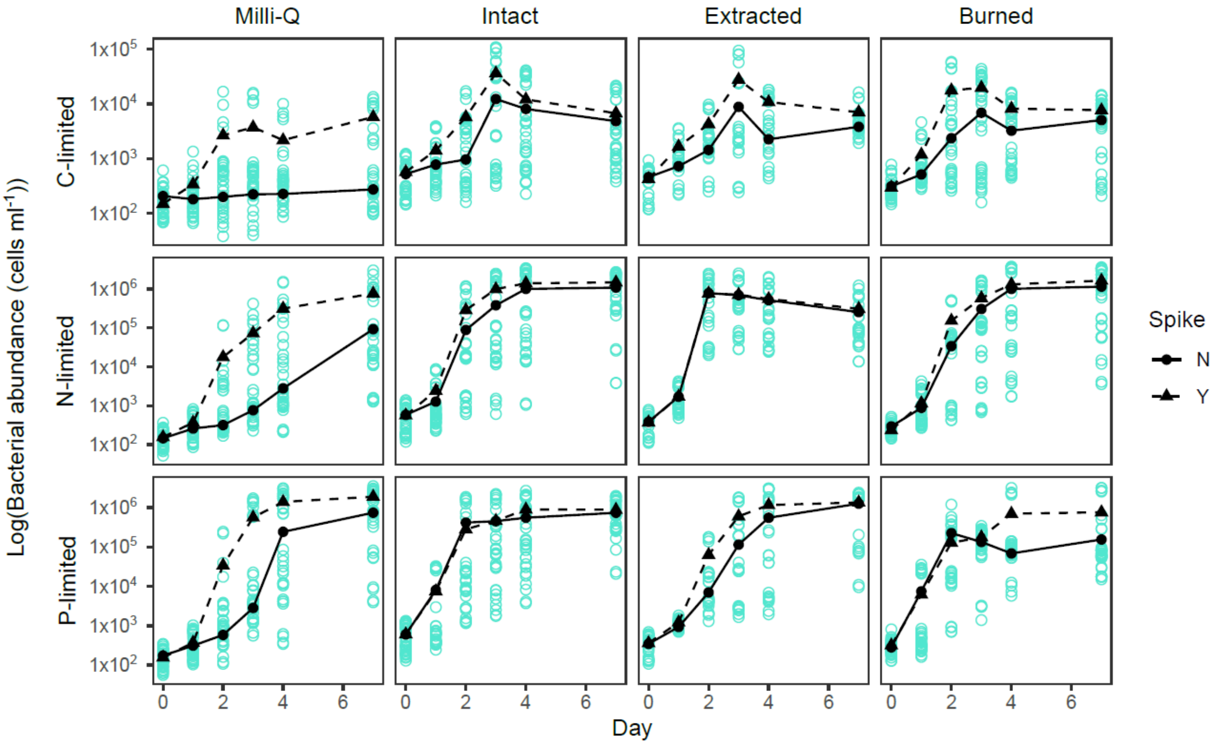


Figure S9. Bacterial abundance in headwater peatland samples (and the Milli-Q control) across all four sampling campaigns. The solid line shows average bacterial abundance in the unspiked samples over time, and the dashed line shows average bacterial abundance in spiked samples over time.

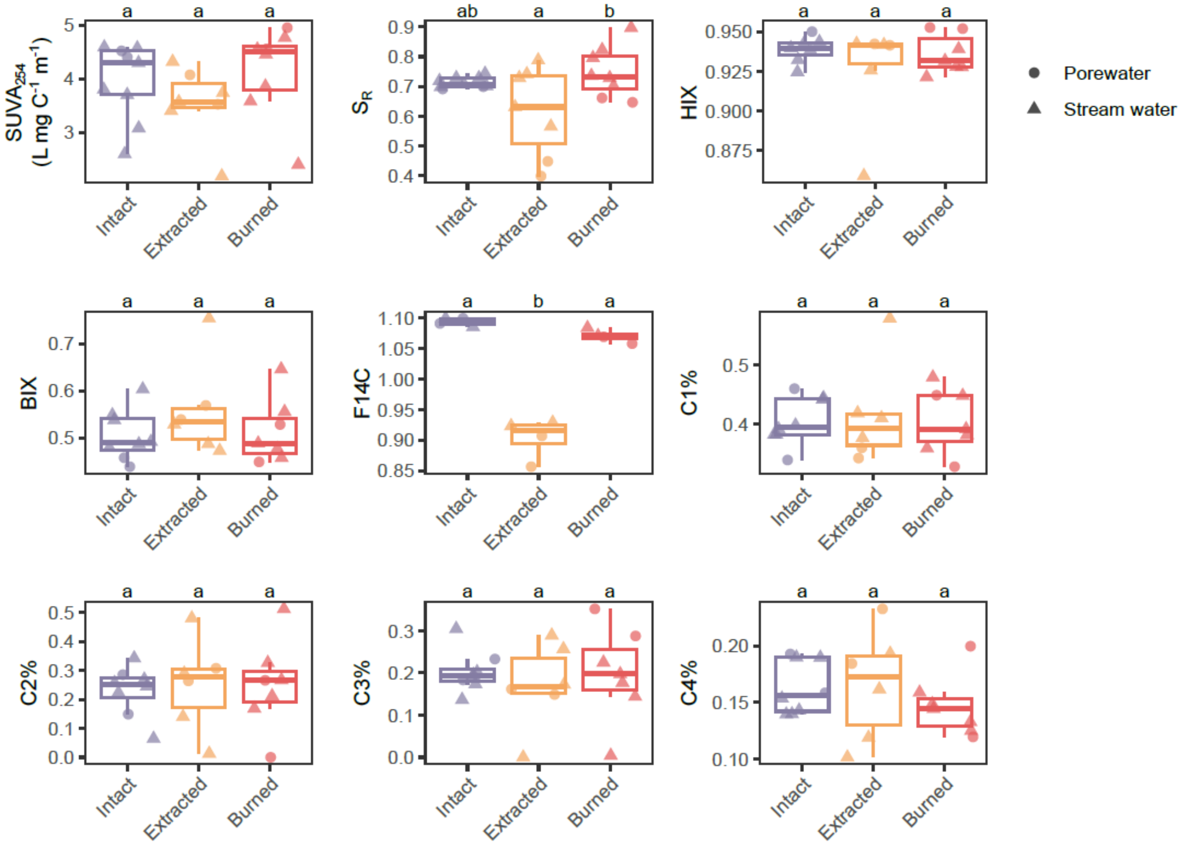


Figure S10. Boxplots of DOM composition analytes across headwater peatlands. Compact letter display shows significant differences across sampling campaigns.

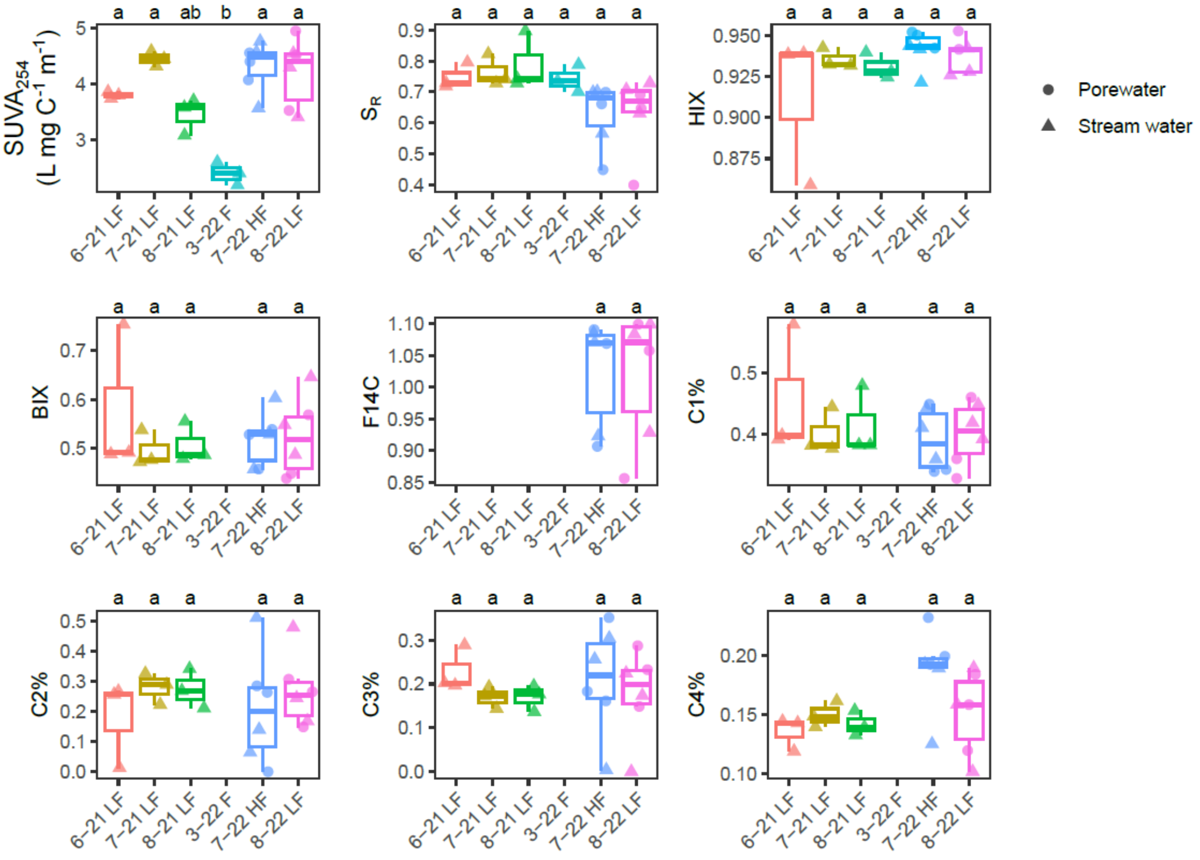


Figure S11. Boxplots of DOM composition analytes across samplings. Compact letter display shows significant differences across sampling campaigns.

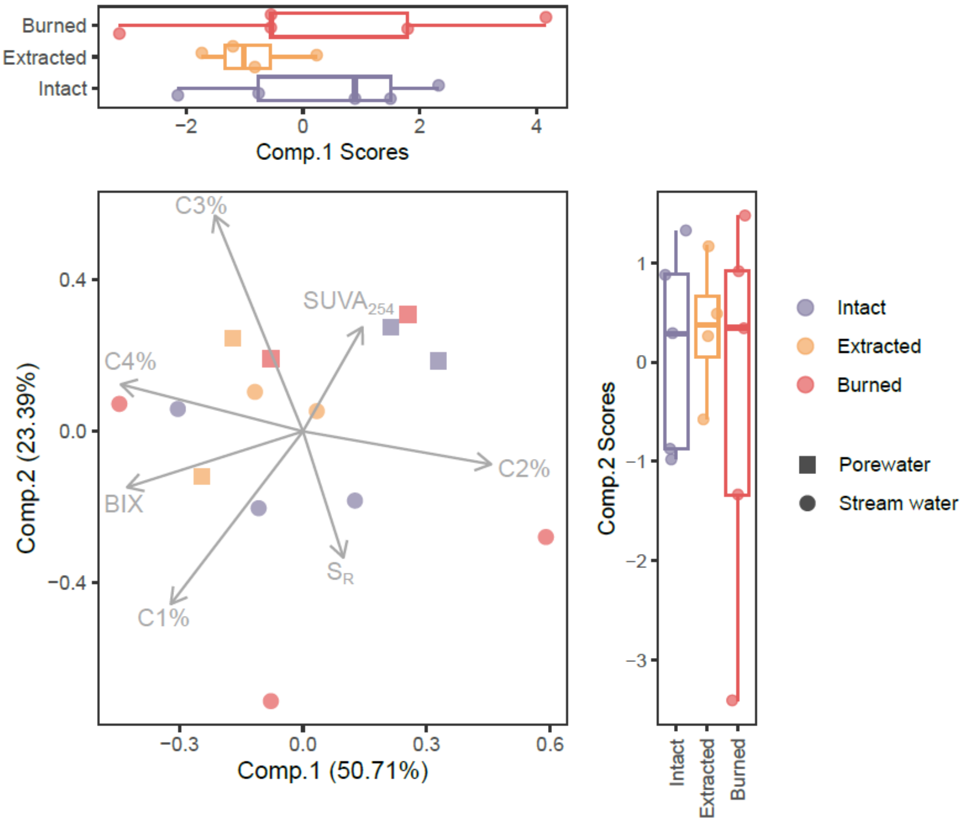


Figure S12. Principal component analysis of DOM molecular composition as measured by optical properties. Boxplots show differences in component scores among the headwater peatlands.

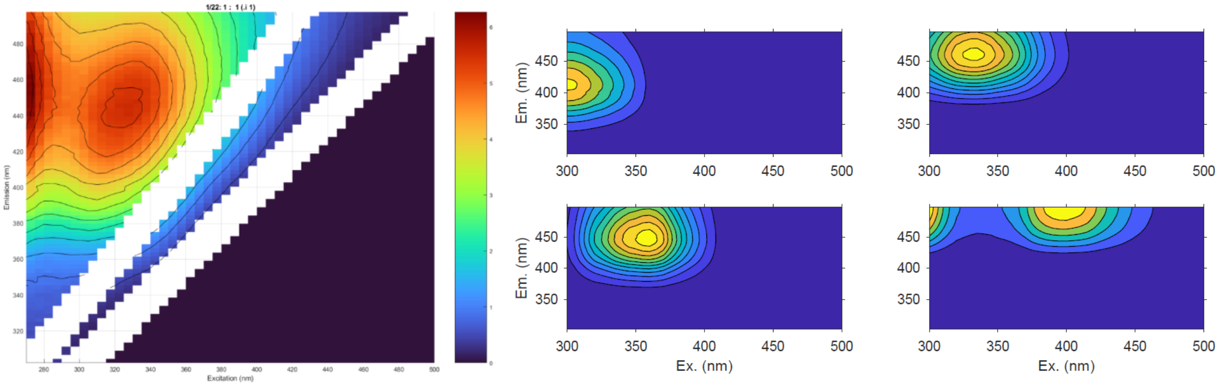


Figure S13. Representative EEM from this study and the fingerprint of the validated 4-component PARAFAC model.

Table S6. PARAFAC component information.

PARAFAC Component	Peak location	Coble Peak Classification	Description	Similar fluorophores from Openfluor
C1	Ex: <300 nm Em: 414 nm	A, M	Humic, terrestrial, allochthonous	C2 - (Cohen et al., 2014)
C2	Ex: 335 nm Em: 461 nm	C	Humic-like, terrestrial, anthropogenic, agriculture	C6 - (Wheeler et al., 2017)
C3	Ex: 360 nm Em: 447 nm	C	Humic-like, terrestrial, anthropogenic, agriculture	Model G C3 - (Shutova et al., 2014)
C4	Ex: 400 Em: >500 nm	NA	Humic- and fulvic acid, terrestrial, autochthonous	C3 - (Kothawala et al., 2014)

Table S7. Spearman rank correlations between $BDOC_{br}$ and $BDON_{br}$ concentrations (n = 11) and water chemistry variables.

	$BDOC_{br}$	$BDON_{br}$	Temp	EC	pH	DOC	DOP	DON	DIN	NH4	Cl	NO2	PO4	SO4	NO3	Na	K
$BDOC_{br}$	1.00	0.64	-0.29	-0.25	-0.05	-0.06	0.18	-0.35	0.36	0.20	-0.30	-0.26	0.53	0.18	0.44	-0.05	0.53
$BDON_{br}$	0.64	1.00	-0.65	-0.22	-0.02	-0.26	0.15	-0.12	-0.22	-0.33	-0.16	-0.15	0.67	0.03	-0.13	-0.07	0.71
Temp	-0.29	-0.65	1.00	0.15	0.09	0.81	0.22	0.32	0.29	0.40	-0.41	-0.44	-0.29	0.04	0.19	0.14	-0.32
EC	-0.25	-0.22	0.15	1.00	0.75	-0.11	-0.07	0.16	-0.05	0.02	0.21	-0.25	-0.12	-0.23	-0.09	0.94	0.21
pH	-0.05	-0.02	0.09	0.75	1.00	-0.32	-0.35	0.06	-0.27	-0.32	0.17	-0.21	0.30	-0.02	-0.20	0.81	0.52
DOC	-0.06	-0.26	0.81	-0.11	-0.32	1.00	0.58	0.33	0.39	0.53	-0.60	-0.52	-0.26	-0.06	0.26	-0.11	-0.27
DOP	0.18	0.15	0.22	-0.07	-0.35	0.58	1.00	0.66	0.19	0.51	-0.08	-0.09	-0.12	-0.05	-0.05	0.06	-0.01
DON	-0.35	-0.12	0.32	0.16	0.06	0.33	0.66	1.00	-0.41	-0.02	0.13	0.04	0.02	-0.09	-0.63	0.24	-0.01
DIN	0.36	-0.22	0.29	-0.05	-0.27	0.39	0.19	-0.41	1.00	0.91	-0.05	0.00	-0.32	-0.25	0.96	-0.06	-0.41
NH4	0.20	-0.33	0.40	0.02	-0.32	0.53	0.51	-0.02	0.91	1.00	0.06	0.07	-0.43	-0.29	0.75	0.03	-0.50
Cl	-0.30	-0.16	-0.41	0.21	0.17	-0.60	-0.08	0.13	-0.05	0.06	1.00	0.88	-0.21	-0.28	-0.12	0.23	-0.30
NO2	-0.26	-0.15	-0.44	-0.25	-0.21	-0.52	-0.09	0.04	0.00	0.07	0.88	1.00	-0.20	-0.24	-0.05	-0.25	-0.48
PO4	0.53	0.67	-0.29	-0.12	0.30	-0.26	-0.12	0.02	-0.32	-0.43	-0.21	-0.20	1.00	0.07	-0.21	0.04	0.68
SO4	0.18	0.03	0.04	-0.23	-0.02	-0.06	-0.05	-0.09	-0.25	-0.29	-0.28	-0.24	0.07	1.00	-0.20	-0.09	0.39
NO3	0.44	-0.13	0.19	-0.09	-0.20	0.26	-0.05	-0.63	0.96	0.75	-0.12	-0.05	-0.21	-0.20	1.00	-0.11	-0.31
Na	-0.05	-0.07	0.14	0.94	0.81	-0.11	0.06	0.24	-0.06	0.03	0.23	-0.25	0.04	-0.09	-0.11	1.00	0.38
K	0.53	0.71	-0.32	0.21	0.52	-0.27	-0.01	-0.01	-0.41	-0.50	-0.30	-0.48	0.68	0.39	-0.31	0.38	1.00
Mg	-0.29	-0.20	0.25	0.94	0.81	-0.04	-0.13	0.19	-0.10	-0.06	0.19	-0.26	-0.03	-0.24	-0.12	0.93	0.21
Zn	0.62	0.25	-0.08	-0.27	-0.37	0.23	0.20	-0.54	0.87	0.71	-0.13	-0.01	-0.06	-0.23	0.89	-0.23	-0.13
S	0.20	0.13	0.08	0.76	0.87	-0.19	-0.01	0.21	-0.19	-0.17	0.04	-0.37	0.39	0.16	-0.19	0.90	0.67
Ca	-0.30	-0.17	0.13	0.90	0.87	-0.20	-0.20	0.15	-0.12	-0.09	0.37	-0.06	-0.02	-0.25	-0.12	0.91	0.22
Cu	0.37	0.34	-0.48	-0.49	-0.18	-0.38	0.21	0.06	-0.04	0.00	0.47	0.62	0.12	0.12	-0.07	-0.29	0.09
B	0.18	-0.25	0.47	0.59	0.33	0.40	0.18	-0.13	0.59	0.57	-0.16	-0.45	-0.35	-0.15	0.55	0.61	-0.02
Fe	-0.37	-0.20	0.11	0.98	0.72	-0.13	-0.10	0.19	-0.15	-0.07	0.27	-0.18	-0.17	-0.29	-0.18	0.90	0.16
Mn	-0.12	0.15	0.06	0.69	0.68	-0.10	-0.15	0.23	-0.23	-0.23	0.10	-0.23	0.43	-0.44	-0.20	0.70	0.31

Mg	Zn	S	Ca	Cu	B	Fe	Mn
-0.29	0.62	0.20	-0.30	0.37	0.18	-0.37	-0.12
-0.20	0.25	0.13	-0.17	0.34	-0.25	-0.20	0.15
0.25	-0.08	0.08	0.13	-0.48	0.47	0.11	0.06
0.94	-0.27	0.76	0.90	-0.49	0.59	0.98	0.69
0.81	-0.37	0.87	0.87	-0.18	0.33	0.72	0.68
-0.04	0.23	-0.19	-0.20	-0.38	0.40	-0.13	-0.10
-0.13	0.20	-0.01	-0.20	0.21	0.18	-0.10	-0.15
0.19	-0.54	0.21	0.15	0.06	-0.13	0.19	0.23
-0.10	0.87	-0.19	-0.12	-0.04	0.59	-0.15	-0.23
-0.06	0.71	-0.17	-0.09	0.00	0.57	-0.07	-0.23
0.19	-0.13	0.04	0.37	0.47	-0.16	0.27	0.10
-0.26	-0.01	-0.37	-0.06	0.62	-0.45	-0.18	-0.23
-0.03	-0.06	0.39	-0.02	0.12	-0.35	-0.17	0.43
-0.24	-0.23	0.16	-0.25	0.12	-0.15	-0.29	-0.44
-0.12	0.89	-0.19	-0.12	-0.07	0.55	-0.18	-0.20
0.93	-0.23	0.90	0.91	-0.29	0.61	0.90	0.70
0.21	-0.13	0.67	0.22	0.09	-0.02	0.16	0.31
1.00	-0.32	0.76	0.96	-0.49	0.59	0.95	0.82
-0.32	1.00	-0.28	-0.30	0.16	0.37	-0.34	-0.27
0.76	-0.28	1.00	0.75	-0.17	0.42	0.68	0.64
0.96	-0.30	0.75	1.00	-0.31	0.49	0.93	0.76
-0.49	0.16	-0.17	-0.31	1.00	-0.36	-0.49	-0.45
0.59	0.37	0.42	0.49	-0.36	1.00	0.53	0.26
0.95	-0.34	0.68	0.93	-0.49	0.53	1.00	0.73
0.82	-0.27	0.64	0.76	-0.45	0.26	0.73	1.00

Table S8. Spearman rank correlations between $BDOC_{br}$ and $BDON_{br}$ concentrations (n = 11) and UV-Vis indices.

	$BDOC_{br}$	$BDON_{br}$	SUVA254	a254	a300	E2:E3	E4:E6	S275:295	S350:400	S300:700	SR
$BDOC_{br}$	1.00	0.64	-0.44	-0.23	-0.21	0.10	-0.32	-0.55	0.17	0.11	-0.46
$BDON_{br}$	0.64	1.00	-0.58	-0.47	-0.46	-0.22	-0.16	-0.20	-0.14	-0.17	-0.02
SUVA254	-0.44	-0.58	1.00	0.74	0.73	0.29	0.71	0.34	0.34	0.36	-0.16
a254	-0.23	-0.47	0.74	1.00	1.00	0.68	0.57	0.16	0.69	0.72	-0.56
a300	-0.21	-0.46	0.73	1.00	1.00	0.67	0.56	0.11	0.69	0.71	-0.58
E2:E3	0.10	-0.22	0.29	0.68	0.67	1.00	0.17	0.30	0.97	0.97	-0.73
E4:E6	-0.32	-0.16	0.71	0.57	0.56	0.17	1.00	0.15	0.30	0.34	-0.25
S275:295	-0.55	-0.20	0.34	0.16	0.11	0.30	0.15	1.00	0.18	0.21	0.36
S350:400	0.17	-0.14	0.34	0.69	0.69	0.97	0.30	0.18	1.00	1.00	-0.84
S300:700	0.11	-0.17	0.36	0.72	0.71	0.97	0.34	0.21	1.00	1.00	-0.82
SR	-0.46	-0.02	-0.16	-0.56	-0.58	-0.73	-0.25	0.36	-0.84	-0.82	1.00

Table S9. Spearman rank correlations between $BDOC_{br}$ concentrations (n = 8) and fluorescence indices.

	$BDOC_{br}$	B	T	A	M	C	N	FI	FreshIX	BIX	HIX	C1_per	C2_per	C3_per	C4_per
$BDOC_{br}$	1.00	0.08	-0.08	-0.01	-0.03	-0.02	-0.02	-0.07	0.03	0.04	0.37	0.04	-0.31	0.31	0.38
B	0.08	1.00	0.76	0.85	0.80	0.82	0.83	0.03	0.02	0.03	-0.30	0.10	0.39	-0.46	-0.42
T	-0.08	0.76	1.00	0.97	0.99	0.98	0.98	0.07	-0.06	-0.06	0.07	-0.09	0.28	-0.34	-0.09
A	-0.01	0.85	0.97	1.00	0.99	1.00	1.00	-0.07	-0.17	-0.17	-0.03	-0.08	0.39	-0.45	-0.25
M	-0.03	0.80	0.99	0.99	1.00	1.00	1.00	-0.02	-0.13	-0.13	0.03	-0.10	0.34	-0.40	-0.17
C	-0.02	0.82	0.98	1.00	1.00	1.00	1.00	-0.05	-0.15	-0.16	0.00	-0.10	0.37	-0.43	-0.21
N	-0.02	0.83	0.98	1.00	1.00	1.00	1.00	-0.02	-0.13	-0.13	0.00	-0.07	0.35	-0.42	-0.21
FI	-0.07	0.03	0.07	-0.07	-0.02	-0.05	-0.02	1.00	0.95	0.95	0.42	0.54	-0.78	0.74	0.59
FreshIX	0.03	0.02	-0.06	-0.17	-0.13	-0.15	-0.13	0.95	1.00	1.00	0.27	0.72	-0.79	0.72	0.50
BIX	0.04	0.03	-0.06	-0.17	-0.13	-0.16	-0.13	0.95	1.00	1.00	0.26	0.70	-0.78	0.71	0.50
HIX	0.37	-0.30	0.07	-0.03	0.03	0.00	0.00	0.42	0.27	0.26	1.00	-0.03	-0.71	0.76	0.87
C1_per	0.04	0.10	-0.09	-0.08	-0.10	-0.10	-0.07	0.54	0.72	0.70	-0.03	1.00	-0.55	0.44	0.02
C2_per	-0.31	0.39	0.28	0.39	0.34	0.37	0.35	-0.78	-0.79	-0.78	-0.71	-0.55	1.00	-0.99	-0.81
C3_per	0.31	-0.46	-0.34	-0.45	-0.40	-0.43	-0.42	0.74	0.72	0.71	0.76	0.44	-0.99	1.00	0.84
C4_per	0.38	-0.42	-0.09	-0.25	-0.17	-0.21	-0.21	0.59	0.50	0.50	0.87	0.02	-0.81	0.84	1.00

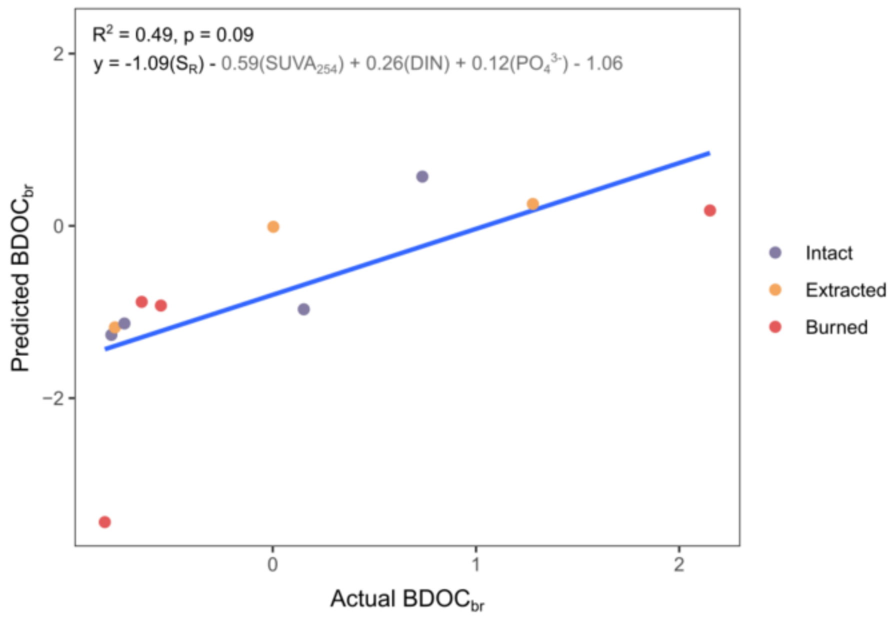


Figure S14. Predicted $BDOC_{br}$ concentration results from a multiple linear regression model compared to actual $BDOC_{br}$ concentration. Plotted results are shown for standardized and log-transformed variables.

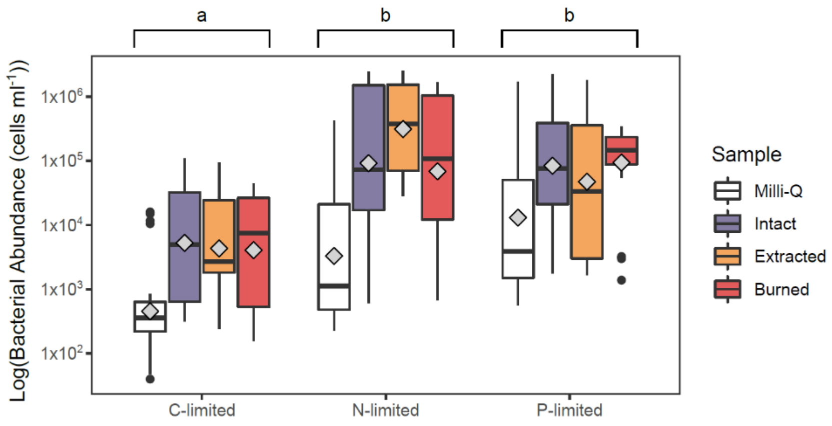


Figure S15. Bacterial abundance on day 3 of bacterial regrowth incubations shows differences among nutrient treatments and samples. Boxplots show the interquartile range about the median of bacterial abundance values, and the grey diamonds show the mean. Compact letter display shows significant differences ($p < 0.05$) in bacterial abundance among nutrient treatments.

Appendix 3. Supporting information for Chapter 4

Web of Science search query:

(“dissolved organic carbon” OR “DOC” OR “dissolved organic matter” OR “DOM”) AND (peat* OR mire OR fen OR bog) AND (catchment* OR watershed* OR basin*) AND (runoff OR discharge OR export) NOT (tropic* OR China)

Table S10. Description of the systematic review data that was used to train a random forest model to predict DOC concentration and yield.

Meta data	Description
DOC concentration	Mean annual DOC concentration (mg L^{-1}): average DOC concentration reported at the site, typically spanning high and low flow conditions and multiple seasons.
DOC yield	Mean annual DOC yield during the ice-free season (g m^{-2} yr^{-1}). We estimated yield for studies that reported annual runoff and mean annual DOC concentration but not DOC yield.
Runoff	Annual catchment runoff (mm) reported from studies.
Catchment area	Catchment area (km^2) reported from studies.
Catchment land use and land cover	% Peatland: proportion of catchment covered by peatlands/wetlands. % Disturbed peatland: proportion of catchment covered by disturbed peatlands % Forest: proportion of catchment covered by forests. % Lakes: proportion of catchment covered by lakes/ponds/reservoirs. % Agriculture: proportion of catchment covered by agriculture. % Urban: proportion of catchment covered by human development including towns, cities, roads, etc.

	If values were not reported in the study then we estimated them using Google Earth imagery.
Wetland type	General wetland classification including bogs, fens, palsas, etc.
Peatland disturbance	General disturbance classification including drained, permafrost thaw, and wildfire.
Climate	Mean annual air temperature (MAAT; °C) reported from the study or estimated using Worldclim v2.1 data from the sampling location. Mean annual precipitation (MAP; mm) reported from the study or estimated using Woldclim v2.1 data from the sampling location.

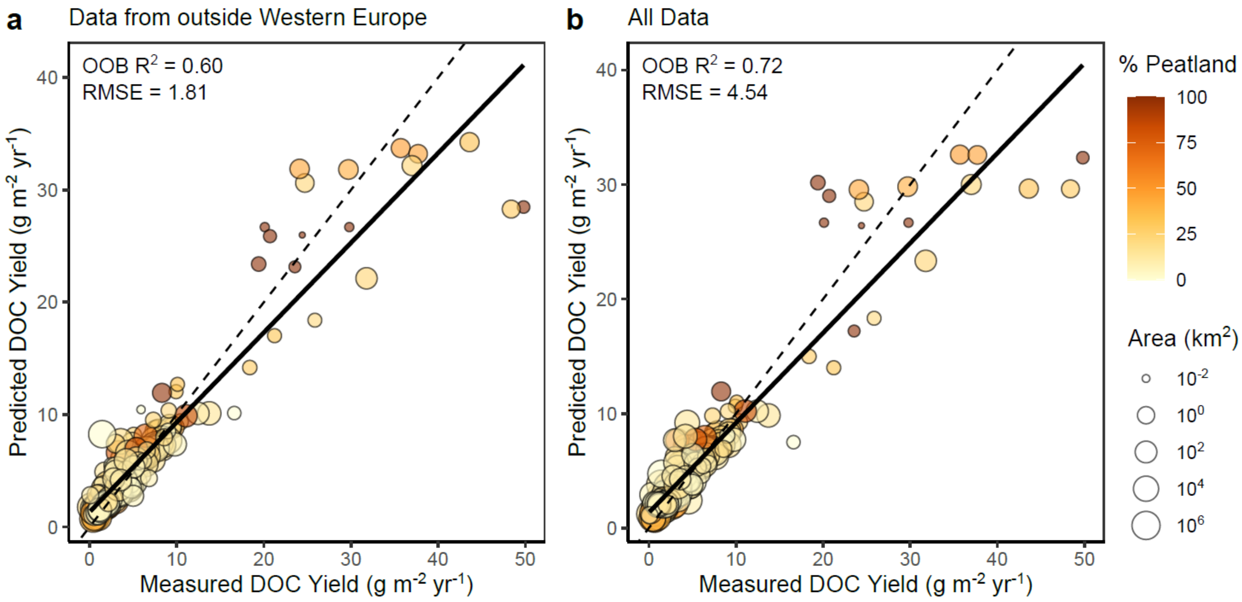


Figure S16. Modelling exercise to show the effect of the western European data bias on model performance. Plot a shows model performance for a model trained on data from outside western Europe (i.e., North America, Eastern Europe, and Siberia) and predicting DOC yield for the same region. Plot b shows model performance for a model trained on all DOC yield data (including western Europe) predicting DOC yield for catchments outside of western Europe. The solid black line indicates the linear regression line of best fit and the dashed line indicates a 1:1 relationship.

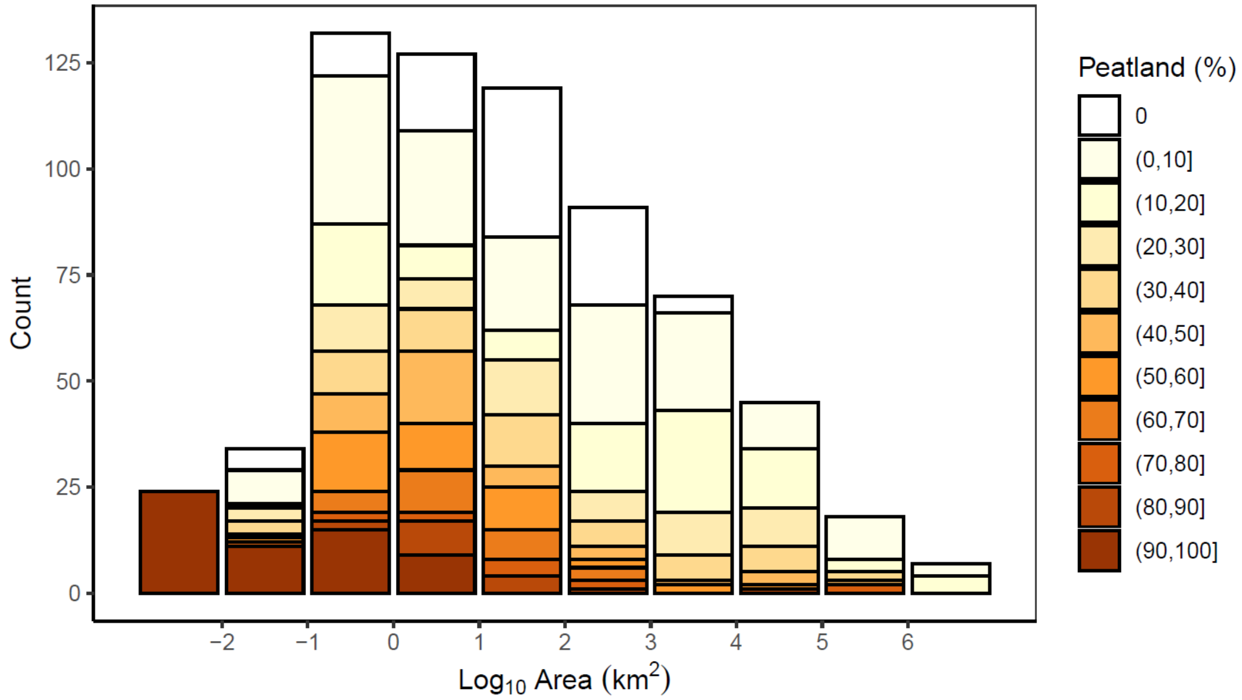


Figure S17. Histogram of catchment area from systematic review data. Histogram bars are shaded into % peatland cover to show range in values across catchment sizes.

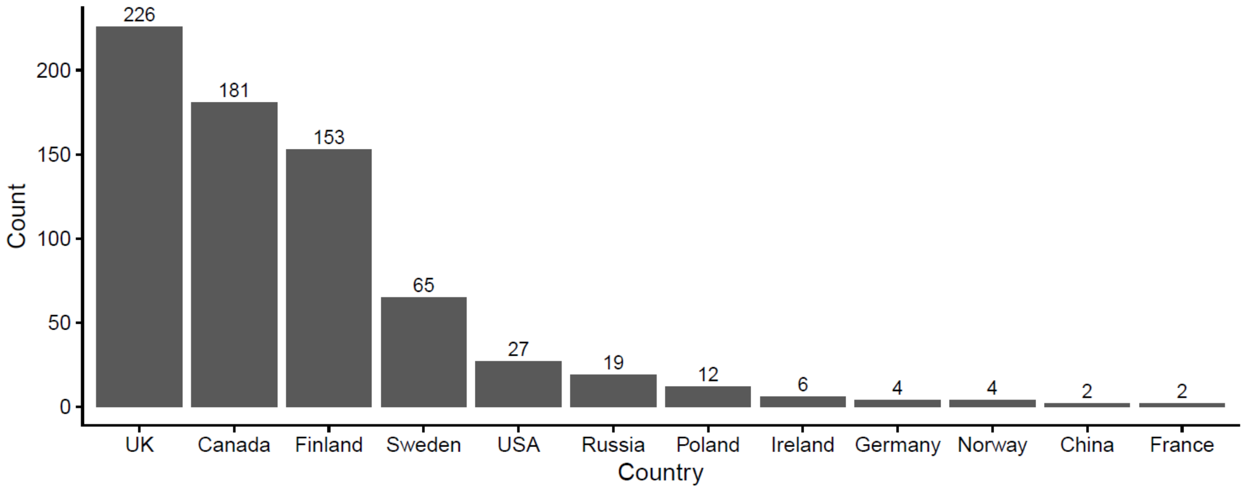
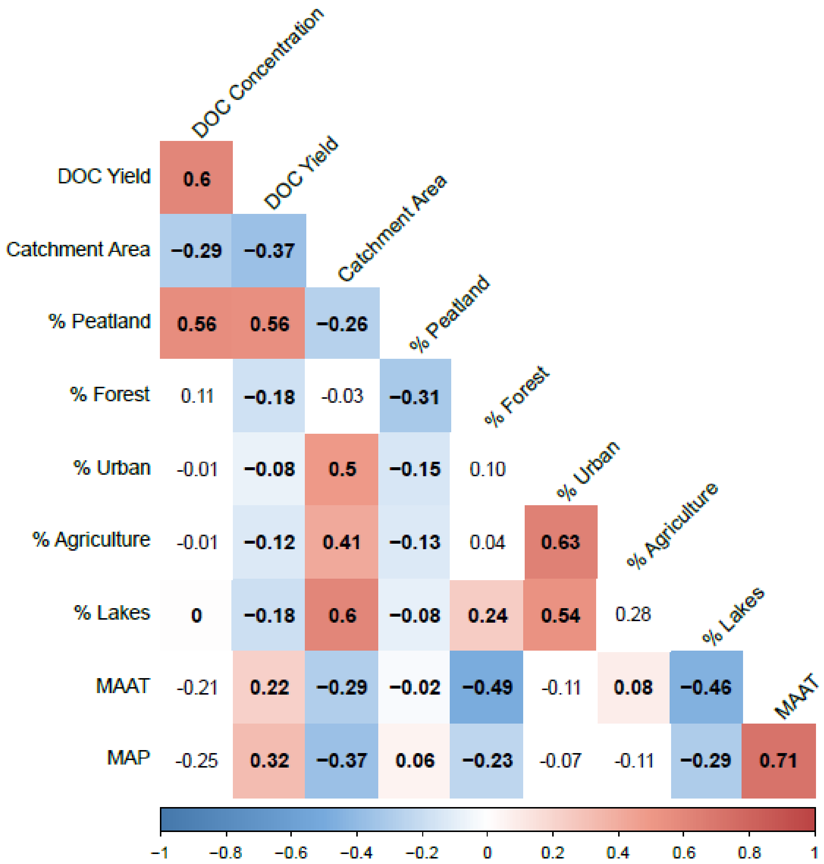


Figure S18. Histogram of catchments by country from the systematic review data.



	DOC Concentration	DOC Yield	Catchment Area	% Peatland	% Forest	% Urban	% Agriculture	% Lakes	MAAT
DOC Yield	**0.6**								
Catchment Area	**−0.29**	**−0.37**							
% Peatland	**0.56**	**0.56**	**−0.26**						
% Forest	0.11	**−0.18**	-0.03	**−0.31**					
% Urban	-0.01	**−0.08**	**0.5**	**−0.15**	0.10				
% Agriculture	-0.01	**−0.12**	**0.41**	**−0.13**	0.04	**0.63**			
% Lakes	**0**	**−0.18**	**0.6**	**−0.08**	**0.24**	**0.54**	0.28		
MAAT	-0.21	**0.22**	**−0.29**	**−0.02**	**−0.49**	-0.11	**0.08**	**−0.46**	
MAP	-0.25	**0.32**	**−0.37**	**0.06**	**−0.23**	-0.07	-0.11	**−0.29**	**0.71**

Figure S19. Spearman correlations among DOC concentration, DOC export, and landscape and climate characteristics from synthesis data. Significant correlations ($p < 0.01$) are shown in bold and have background color.

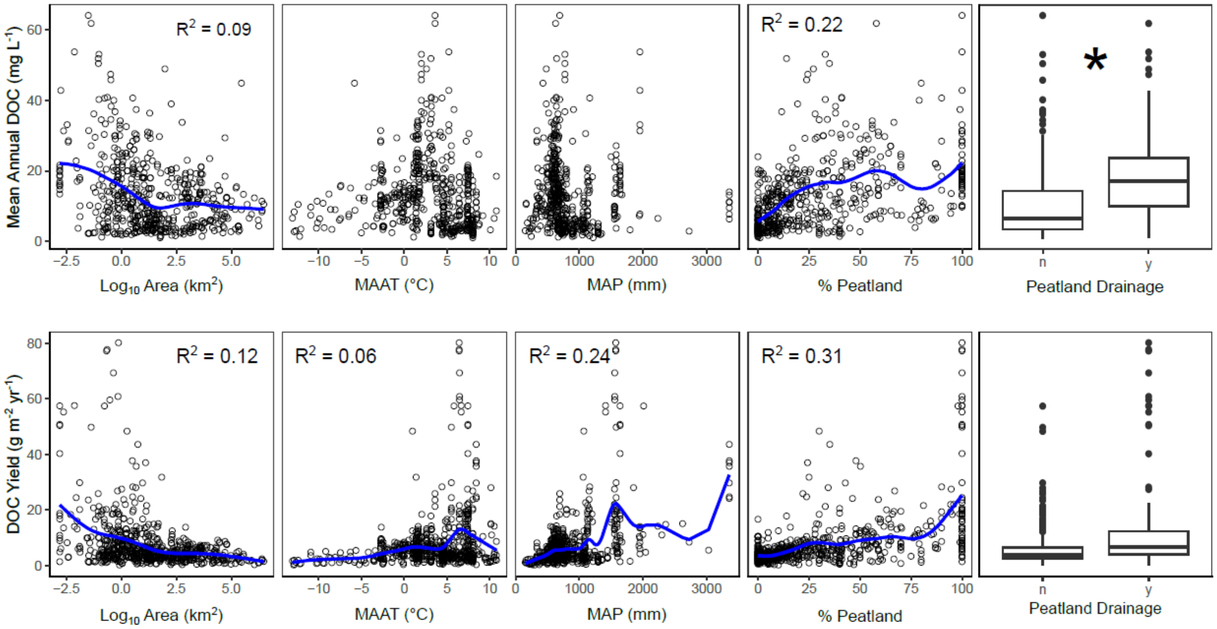


Figure S20. Univariate relationships among DOC concentration, yield, and random forest predictor variables (area, MAAT, MAP, peatland cover, and peatland drainage). Significant linear regression relationships ($p < 0.05$) are reported in the biplots and the blue spline function line shows non-linear relationships. Boxplots of peatland drainage show the median and 95% confidence interval, and asterisks show significant differences based on a two-sample t-test.

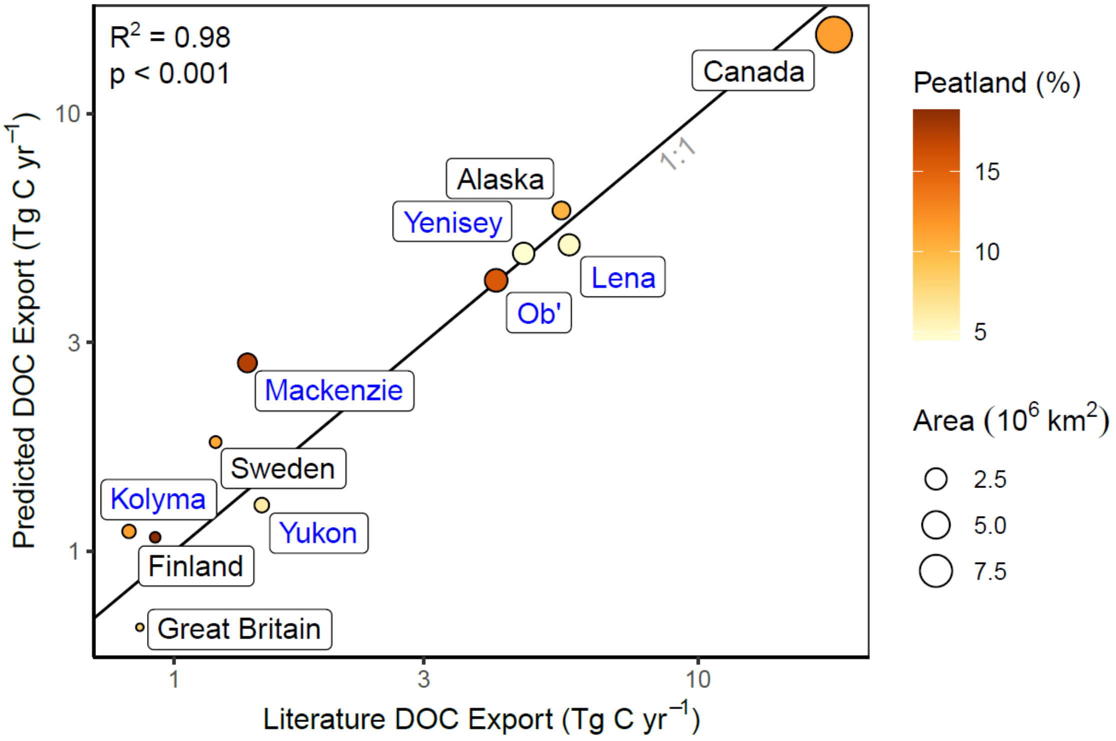


Figure S21. Comparing modeled DOC export versus literature values for political regions (black font) and large Arctic rivers (blue font). Literature values were gathered from the following studies: (Holmes et al., 2012b), (Clair et al., 2013), (Stackpoole et al., 2017), (Worrall et al., 2018), (Humborg et al., 2010), (Raike et al., 2012).

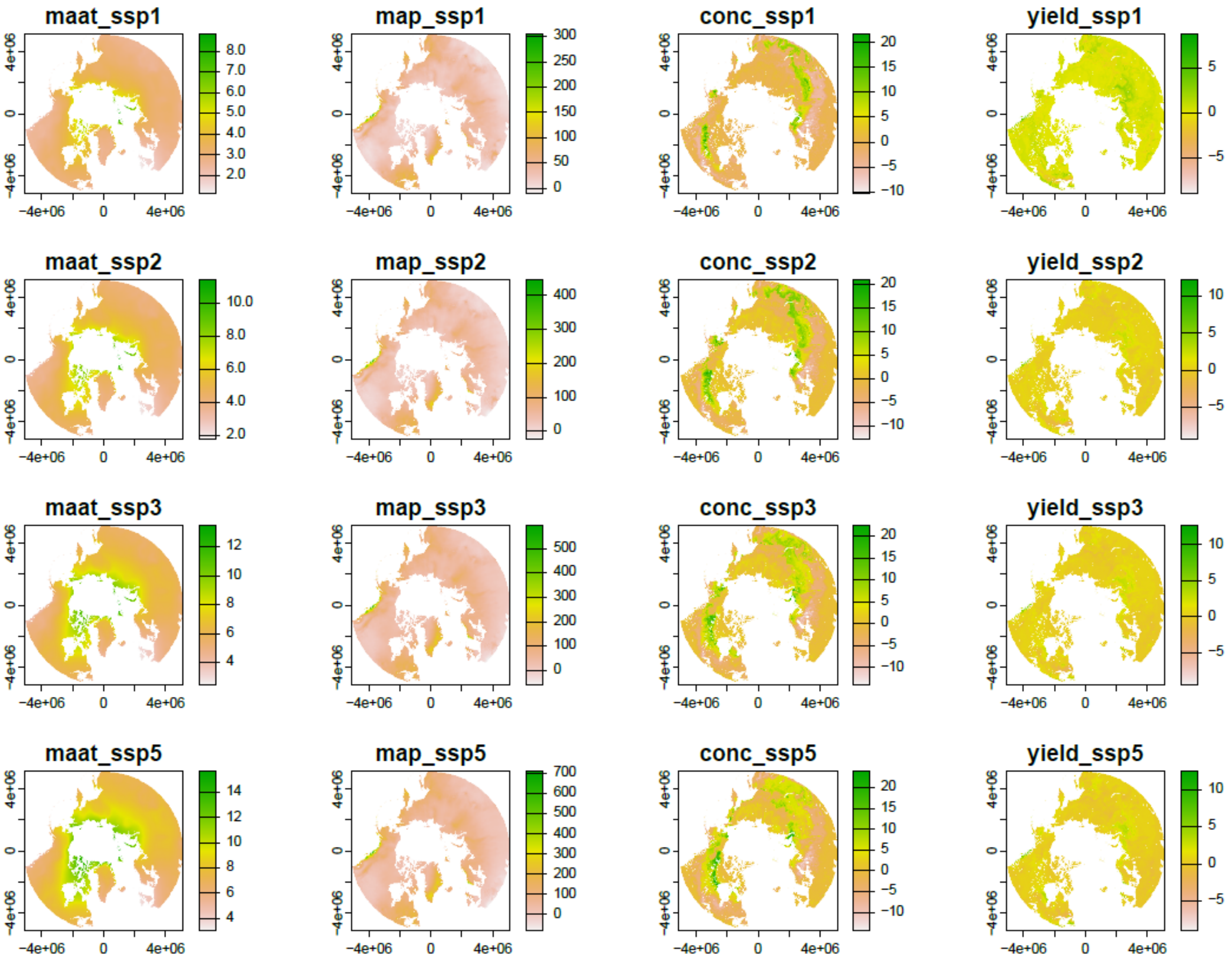


Figure S22. Spatial differences between current (1970–2000) and future climate (2080–2100). Column 1 shows differences in MAAT in °C, column 2 shows differences in MAP in mm yr^{-1}, column 3 shows differences in DOC concentration in mg L^{-1}, and column 4 shows differences in DOC yield in g C m^{-1} yr^{-1}. Each row shows spatial differences for the four SSP scenarios.