Dissolved organic carbon concentration and character in northern hardwood-dominated headwater catchments: A paired-catchment investigation of legacy harvesting impacts

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

This thesis is partially comprised (Chapters 2 and 3) of manuscripts intended, but not yet submitted, for publication. The remainder (Chapters 1 and 4) were not written with the intent of publication. Exceptions to sole authorship are outlined below as relates to Chapters 2 and 3.

Research presented in Chapter 2 is being prepared for publication as:

A. Gray, M. Stone, M. Emelko, K.L. Webster, J.A. Leach, and J.M. Buttle. Legacy harvesting effects and wetland position impact stream DOC concentrations in two northern hardwood-dominated headwater catchments.

This research was conducted at the University of Waterloo by Annie Gray under the co-supervision of Micheal Stone and Monica Emelko. Annie Gray was responsible for conceptualization, methodology, formal analysis, data curation, writing, review and editing, and project administration. Micheal Stone was responsible for conceptualization, methodology, formal analysis, resources, writing review/editing, supervision, project administration, and funding acquisition. Monica Emelko was responsible for conceptualization, writing review/editing, supervision, project administration, and funding acquisition. Kara Webster was responsible for conceptualization, resources, data curation, writing – review and editing, funding acquisition. Jason Leach was responsible for conceptualization, methodology, resources, data curation, writing – review and editing. James Buttle was responsible for conceptualization, methodology, writing – review and editing.

Research presented in Chapter 3 is being prepared for publication as:

A. Gray, M. Stone, M. Emelko, K.L. Webster, J.A. Leach, and J.M. Buttle. Wetland position and forest harvesting history influence event-scale dynamics of stream DOC concentration and character in northern hardwood-dominated headwater catchments.

This research was conducted at the University of Waterloo by Annie Gray under the co-supervision of Micheal Stone and Monica Emelko. Annie Gray was responsible for conceptualization, methodology, formal analysis, data curation, writing, review and editing, and project administration. Micheal Stone was responsible for conceptualization, methodology, formal analysis, resources, writing review/editing, supervision, project administration, and funding acquisition. Monica Emelko was responsible for conceptualization, methodology, writing review/editing, supervision, project administration, and funding acquisition. Kara Webster was responsible for conceptualization, resources, data curation, writing – review and editing, funding acquisition. Jason Leach was responsible for conceptualization, methodology, resources, data curation, writing – review and editing. James Buttle was responsible for conceptualization, methodology, writing – review and editing.

Abstract

The water quality of forested source water regions can be degraded by natural and anthropogenic landscape disturbances such as wildfires and forest harvesting, the latter an economically important primary industry in Canada and a proposed wildfire mitigation strategy. Harvesting practices can alter the chemistry and hydrologic connectivity of hillslope solute pools, thereby enhancing hillslope-stream transport and the downstream propagation of sediments and solutes, including those relevant to drinking water treatment operations such as dissolved organic carbon (DOC). Although many studies have evaluated the sub-decadal impacts of forest harvesting on the concentration, export, and character of stream DOC, less is known about the legacy (decadal-scale) impacts. The purpose of this thesis was to evaluate the legacy impacts of clearcut harvesting on the variability of stream DOC concentrations, export, and character at the Turkey Lakes experimental Watershed (TLW). Using a paired-catchment approach (unharvested reference vs. legacy (24 years post-) clearcut), inter- and intra-catchment variability in stream DOC concentrations and export was evaluated under a range of flow conditions. Stream DOC variability was related to the concentrations, spatial distribution, and hydrologic connectivity of hillslope solute pool DOC. Additionally, a subset of event-scale stream and hillslope solute pool samples were analyzed for DOC character using Liquid-Chromatography Organic Carbon Detection (LC-OCD). DOC character was expressed in terms of the specific UV absorbance at 254 nm (SUVA) and the relative contributions of LC-OCD-defined DOC fractions. Whereas stream DOC concentrations in the legacy clearcut catchment exceeded (+1.21 mg L^{-1}) and differed significantly ($p \leq 0.05$) from the unharvested reference catchment, inter-catchment differences in stream DOC export were inconsistent. No inter-catchment differences were observed in the DOC concentrations or hydrologic connectivity of the hillslope solute pools, despite the common association of these mechanisms with post-harvest increases in stream DOC concentrations. Significant ($p \leq 0.05$) inter-

catchment differences in the fractional composition of stream DOC were observed at the event-scale but may be related to the presence of a wetland near the outlet of the unharvested reference catchment, rather than a harvesting impact. Wetland position was identified as a key factor in the variability of both DOC concentration and character in the unharvested reference catchment. Overall, the results of this thesis suggest that while forest harvesting practices may result in long-term increases in stream DOC concentration in northern hardwood-dominated headwater catchments, the effects may be limited at decadal-scales and likely do not pose a reasonable threat to downstream drinking water treatment operations.

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Chapter 1. Introduction

1.1 Research Context

The provision of high-quality drinking water supplies is a critical ecosystem service provided by forested watersheds, accounting for three-quarters of the global accessible freshwater supply (FAO, 2018). In the conterminous United States, forested watersheds serve approximately 60 million people despite accounting for only 38% of the land area (Liu et al., 2021) and in Canada, forested watersheds account for a large proportion of the surface water resources that serve approximately two-thirds of the population (Natural Resources Canada, 2021). Additionally, as forests typically provide high quality source water (Dudley & Stolton, 2003), the costs of drinking water treatment and supply are reduced (Abildtrup et al., 2013; Lopes et al., 2019; Warziniack et al., 2017). However, the quality of forest-sourced waters is necessarily linked to the characteristics of the contributing landscapes and is thus vulnerable to degradation by natural and anthropogenic landscape disturbances (Emelko et al., 2011; Gartner et al., 2014).

Natural and anthropogenic landscape disturbances including insect outbreaks (Brouillard et al., 2016; Mikkelson et al., 2013; Su et al., 2017), climate-exacerbated extreme weather events (Chang et al., 2020; Zou et al., 2023), wildfires (Robinne et al., 2019, 2020), and forest harvesting (Kreutzweiser et al., 2008) can disrupt critical catchment biogeochemical and hydrologic mechanisms related to water interception, storage, and filtration (Neary et al., 2009), potentially leading to source water quality degradation. In Canada, forest harvesting practices are a major stand-replacing agent of disturbance (Kreutzweiser et al., 2008) and constitute a key component of the national economy (Bogdanski, 2008; Brandt et al., 2013). In 2021, the Canadian forestry sector (comprised of forestry and logging operations, pulp and paper manufacturing, and wood product manufacturing) accounted for $34.8 billion CAD (1.5%) of Canada’s nominal GDP and represented $44.9 billion CAD in export value (Natural Resources Canada, 2022). Additionally, forest harvesting practices have been proposed as a wildfire mitigation and source water protection strategy in response to predicted, climate-exacerbated increases in wildfire magnitude and frequency (Dale et al., 2001; Deval et al., 2021; Gannon et al., 2019; Webb, 2012). However, the wildfire mitigation and associated source water protection benefits offered by forest harvesting practices may be tempered by the potential hydrologic and biogeochemical impacts of forest harvesting itself (Buttle et al., 2018; Erdozain et al., 2018; Martin et al., 2000), especially with respect to water quality parameters relevant to drinking water treatment operations such as the concentration and character of dissolved organic carbon (DOC) (Emelko et al., 2011). Accordingly, a robust understanding of the magnitude and duration of forest harvesting impacts on the concentration and character of DOC is necessary for the sustainable management of forested watersheds for the ecosystem service of source water provision.

Dissolved organic carbon in forested systems is a by-product of the decomposition and biogeochemical processing of litterfall, root exudates, plant litter, microbial biomass, and soil organic matter (Kalbitz et al., 2000). Dissolved organic carbon can serve as a vector for the transport of metals (Porvari et al., 2003) and persistent organic pollutants (Bergknut et al., 2010) in terrestrial and aquatic systems and regulates light penetration in aquatic systems (Schindler & Curtis, 1997). In a drinking water treatment context, increases in the concentration of source water DOC can result in higher coagulant and disinfectant demands, can promote the formation of harmful disinfection by-products, and can result in taste and odour problems (Emelko et al., 2011; Löfgren et al., 2009). The molecular character of DOC can further influence the choice of treatment methodology and materials required to safely treat water for consumption (Chow et al., 2008; Fabris et al., 2008; Krzeminski et al., 2019; Sharp et al., 2006). DOC character is often described in terms of biodegradability, molecular weight distribution, hydrophobicity, aromaticity and ultra-violet (UV) absorbance at various wavelengths (MWH, 2012). DOC character defined as the specific UV absorbance at 254 nm (SUVA, L mg^{-1} m^{-1}) is a commonly used proxy for DOC aromaticity and reactivity in the drinking water treatment industry (Edzwald, 1993), especially as changes in SUVA can impact the efficacy of organic matter removal through coagulation (MWH, 2012). Overall, both the concentration and the character of source water DOC are relevant to the methods, materials, and predicted outcomes of drinking water treatment operations (Edzwald, 1993; MWH, 2012).

The concentration and character of DOC exported from forested source watersheds are influenced by interrelationships between catchment properties such as soil type and vegetation, soil biogeochemical processes that regulate soil solute concentrations, and catchment moisture conditions that control the differential connectivity of hillslope solute DOC pools and their subsequent transport to receiving waters (Christ & David, 1996; Hope et al., 1994; Kalbitz et al., 2000; Wen et al., 2020). Notably, the mobilization and export of DOC in forested systems is highly flow-driven and predominantly occurs during high-flow conditions such as the spring freshet and precipitation events (Hinton et al., 1997; Morison et al., 2022). Under high-flow conditions, rising water tables can saturate organic-rich, upper riparian and hillslope soil horizons with relatively high DOC concentrations, thus mobilizing DOC in surface runoff and lateral subsurface flow that enhances the transfer of hillslope DOC pools to receiving surface waters (Hood et al., 2006; Vidon et al., 2008). Accordingly, the observed temporal variability in stream DOC concentrations and export from forested watersheds is a function of the concentrations, character, spatial distribution, and hydrologic connectivity of hillslope solute pool DOC (Inamdar et al., 2004; McGlynn & McDonnell, 2003).

Forest harvesting can alter soil moisture, hydrological flowpaths, and biogeochemical processes that are key drivers of DOC variability in streams (Kreutzweiser et al., 2008; Schelker et al., 2013). The removal of forest canopy cover and understory vegetation can reduce interception and soil evapotranspiration (Oda et al., 2021). Changes in vegetation over the short term (<10 years) can increase soil moisture content and water table location (Hotta et al., 2010). Additionally, the decomposition of soil organic matter and harvest residues is enhanced and post-harvest hillslope solute pool DOC concentrations can increase (Kreutzweiser et al., 2008; Piirainen et al., 2007). Furthermore, harvesting machinery can compact forest soils, thus reducing soil porosity and infiltration capacity (Cambi et al., 2015). Reductions in soil infiltration capacity can lead to the formation of preferential near-surface flowpaths (Buttle et al., 2018; Kreutzweiser et al., 2008; Monteith et al., 2006b). Such conditions have generally been related to post-harvest increases in water tables, the magnitude and frequency of peak flows, and total streamflow (Wei et al., 2022; Wei & Zhang, 2010) but some contradictory results have been reported (Goeking & Tarboton, 2020; Goodbrand et al., 2022). The combination of harvest-induced changes to the concentrations and hydrologic connectivity of hillslope solute pool DOC can ultimately result in changes to the concentrations and export of stream DOC in harvested catchments (Kreutzweiser et al., 2008).

Stream DOC responses to forest harvesting are inconsistent and range from post-harvest increases in stream DOC concentrations (Laudon et al., 2009; Pinel-Alloul et al., 2002; Schelker et al., 2012; Webster et al., 2022) to post-harvest decreases in stream DOC concentrations (Meyer & Tate, 1983). In other cases, no post-harvest response was observed in stream DOC concentrations (Knoepp & Clinton, 2009; Lepistö et al., 2014). Although these studies have advanced knowledge of forest harvesting impacts on stream DOC variability under a range of hydroclimatic conditions and catchment settings, most forest harvesting studies are conducted < 10 years post-disturbance and there is a paucity of studies conducted at decadal-scales (> 10 years post-harvest) (Cawley et al., 2014; Lepistö et al., 2014; Yamashita et al., 2011). Additionally, many of the previous works have examined harvesting impacts on DOC concentrations, yields, and export but less is known about legacy harvesting impacts on DOC character. These knowledge gaps have implications for assessing whether forest harvesting may have long term effects on water treatability related to changes in stream DOC concentration, export, and/or character.

1.2 Research Purpose and Objectives

The goal of this thesis was to evaluate legacy (decadal-scale) impacts of clear-cut harvesting on the variability of stream DOC concentration, export, and character under varying flow conditions at the Turkey Lakes Watershed (TLW). The following research objectives were addressed:

1) Evaluate and relate inter- and intra-catchment variability in the concentration and export of stream DOC under varying flow conditions to intra-catchment variability in the concentrations, spatial distribution, and hydrologic connectivity of hillslope DOC pools in an unharvested reference catchment and a legacy clearcut catchment at Turkey Lakes Watershed (Chapter 2, manuscript in preparation)

2) Evaluate and relate event-scale variability in stream DOC concentration and stream DOC character, expressed in terms of the specific UV absorbance and fractional composition, to the concentrations and character of hillslope solute pool DOC in an unharvested reference catchment and a legacy clearcut catchment at Turkey Lakes Watershed (Chapter 3, manuscript in preparation)

1.3 Study Site

1.3.1 Turkey Lakes Watershed Background

The Turkey Lakes Watershed (47º 03´ N; 84º 25´ W, Figure 1.1) was established in 1979 as a platform for interdisciplinary, multi-agency research on the impacts of acid rain on the aquatic and terrestrial systems of undisturbed Precambrian Shield forested catchments (Foster et al., 2005; Jeffries et al., 1988; Morrison et al., 1999; Webster et al., 2021a). Original collaborating agencies included: the Canadian Forest Service, the Department of Fisheries and Oceans, the Ontario Ministry of Natural Resources, the Inland Waters Directorate, and Environment and Climate Change Canada (Webster et al., 2021a; Morrison et al., 1999). In 1997, the scope of research at TLW expanded to include a Forest Harvesting Impacts Program, in alignment with widespread calls for research on the links between forest harvesting and water supply (Morrison et al., 1999). Accordingly, a before-after control-impact (BACI) design was established and headwater study catchments were identified for an intensity gradient of forest harvesting practices (clearcut, shelterwood, and selection cut) (Webster et al., 2022). The Forest Harvesting Impacts Program at TLW is discussed in detail in Section 1.3.3. TLW is one of the longest-running experimental watersheds in Canada and a cornerstone of Canadian and international watershed-based ecosystem science resulting in over 400 research publications, multiple cross-site comparison studies, and significant scientific and forest management contributions to Canadian and international policy development (Webster et al., 2021a).

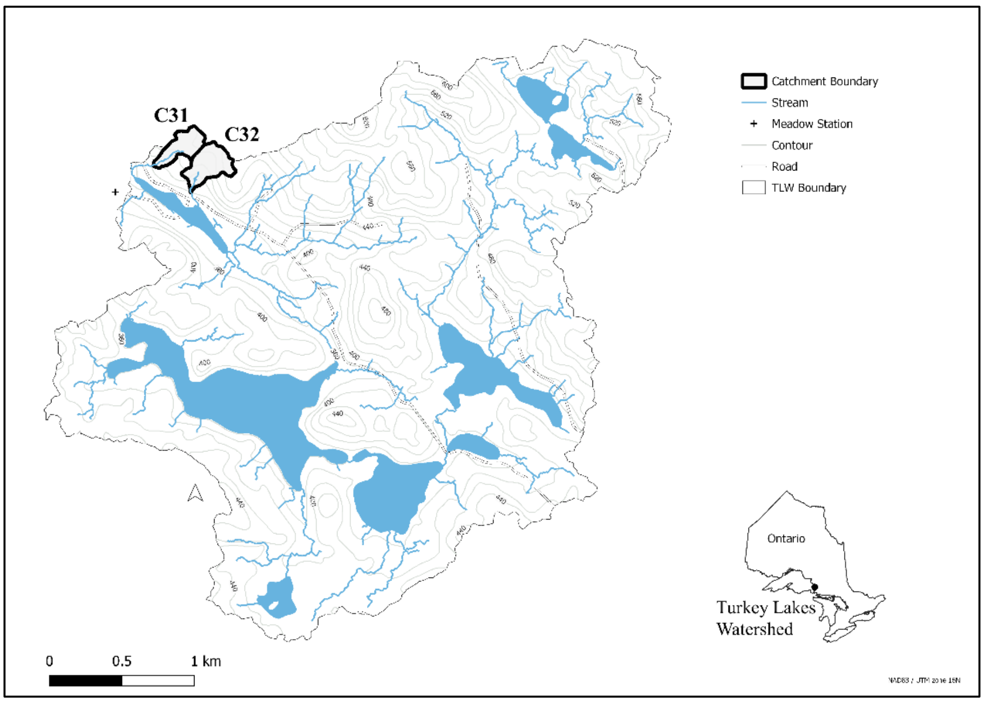

Figure 1.1 Map of Turkey Lakes Watershed

1.3.2 TLW Characteristics

Turkey Lakes Watershed drains an area of approximately 10.5 km^2 within Central Ontario's Boreal Shield Ecozone and has a total relief of ~300 m (Webster et al., 2021a, 2022). The regional geology is characterized by a Precambrian basement composed of silicate greenstone with occasional granitic outcrops (Foster et al., 2005) overlain by a compacted sandy loam basal till and silt-loam ablation till (Hazlett et al., 2001). Soils are predominantly orthic humo-ferric podzols characterized by ~5 cm-thick

LFH horizon composed of well-defined L and F layers (Hazlett et al., 2001) and by spatially dispersed, highly humified organic soils present in depressions, wetlands, and riparian areas (Creed et al., 2008). Characteristic of the Eastern Temperate Mixed Forest (Baldwin et al., 2018), forest cover at TLW is hardwood-dominated with approximately 90% uneven-aged, mature to over mature shade-tolerant sugar maple (*Acer saccharum*), 9% yellow birch (*Betula alleghaniensis*), and 1% conifers (Jeffries et al., 1988). Mean annual air temperature and precipitation at TLW from 1982 – 2021 were 4.5 °C and 1210 mm, respectively (Webster et al., 2022). Snow cover contributes approximately 35% of the annual precipitation (Buttle et al., 2018). Snow typically accumulates in October and melts during the March-May freshet period (Leach et al., 2020).

1.3.3 Forest Harvesting Impacts Program

The Forest Harvesting Impacts Program at TLW was initiated in the late summer and fall of 1997. The program purported to evaluate the impacts of a gradient of forest harvesting practices (clearcut, shelterwood cut, and selection cut) on a variety of forest ecohydrological variables including stand recovery, biodiversity, soil productivity, and the quantity and quality of surface waters (Buttle et al., 2018; Morrison et al., 1999; Webster et al., 2022). Although four reference catchments and three treatment catchments were included in the Forest Harvesting Impacts program (Morrison et al., 1999), the scope of this thesis extends only to one unharvested reference catchment (C32) and one treatment catchment (C31) (Figure 1.1). Catchments C32 and C31 have similar areas, relief, slope, aspect, and wetland coverage (Table 1.1). A notable inter-catchment difference is the location of the main wetlands in each catchment. In C31 the wetland is situated upland at the initiation point of the stream, whereas in C32 the wetland is located lower in the catchment near the stream outlet.

The harvesting procedure applied in C31 was a diameter-limited clearcut which entailed the felling, on-site de-limbing, and removal of trees with a diameter at breast height (DBH) >20 cm and the felling of trees with 10 cm ≥ DBH ≤ 20 cm. A Timberjack 2618 feller-buncher and cable skidders were used, for tree felling and transport of tree length stems, respectively (Webster et al., 2022).

Equipment operators followed the Riparian Code of Practice for Ontario, which prohibits the use of harvesting machinery within three meters of stream edges except for designated crossings. In addition to the provisions of the Riparian Code of Practice for Ontario, care was taken to keep treetops and limbs out of the stream channel, to avoid, whenever possible, upland wet areas, and to avoid causing downslope-oriented skidder trails (Webster et al., 2022). Notably, clearcutting is not a common silvicultural practice in the region (OMNRF, 2015) but may be used under certain conditions (Webster et al., 2022). Clearcutting was used as a high biomass-removal treatment (Morrison et al., 1999) to maximize harvesting impacts on hydrologic and biogeochemical processes in C31 (Buttle et al., 2001). Harvesting in C31 reduced basal area by 78% and stocking by 76% (Buttle et al., 2019).

Table 1.1 Study catchment physiographic characteristics

Catchment Characteristic	**C32**	**C31**
Harvest history	Unharvested reference	Diameter-limited clearcut (1997)
Area (ha)	6.74	4.62
Relief (m)	107	59
Weir Elevation (m.a.s.l.)	352	359
Average Slope (°)	17.49	14.61
Aspect	SW	SW
Wetland Area (%)	1.00	2.88

Adapted from Buttle et al. (2019)

Chapter 2. Legacy Harvesting Effects and Wetland Position Impact Stream DOC Concentrations and Export in two Northern Hardwood-dominated Headwater Catchments

2.1 Abstract

Forested landscapes are critical source regions of high-quality drinking water supplies for downstream communities. Natural and anthropogenic landscape disturbances of varying degrees and types can alter the quality of source waters with potential long-term impacts. In this study inter- and intra-catchment variability in stream DOC concentration and export were evaluated in two northern hardwood-dominated headwater catchments of contrasting forest harvest history (unharvested reference and 24 years post-clearcut) over a six-month intensive sampling program encompassing a freshet sampling period, baseflow conditions, precipitation events, and a fall sampling period. Variability in stream DOC was related to the concentrations, spatial distribution, and hydrologic connectivity of hillslope DOC solute pools. Stream DOC concentrations in the legacy clearcut catchment exceeded and were significantly ($p \leq 0.05$) different from the unharvested reference catchment under all flow conditions. The mean inter-catchment difference in stream DOC concentration was 1.21 mg L^{-1}. Differences in stream DOC export between the catchments were attributed to the influence of a wetland near the outlet of the unharvested reference catchment. In contrast to stream DOC, no significant inter-catchment difference in DOC concentration was observed for any hillslope solute pool. Concentration-discharge regression analysis and the evaluation of the aqueous potassium silica molar ratio suggest a strong and similar groundwater influence on streamflow in both catchments along with a wetland impact on streamflow and stream DOC in the unharvested reference catchment. Overall, the data suggest that while clearcut harvesting practices can have decadal-scale impacts on stream DOC concentrations in northern hardwood-dominated headwater catchments, the effects may be limited relative to the inherent intra-catchment variability and likely do not pose a reasonable threat to downstream drinking water treatment operations.

2.2 Introduction

Approximately 30% of the Earth's terrestrial surface is covered by forests (Cai & Chang, 2020), which provide high-quality drinking water supplies (FAO, 2018; Neary et al., 2009; Statistics Canada, 2018). In the conterminous United States, approximately 60 million people rely on forested lands for more than half of their drinking water supply, despite forests only accounting for 38% of the total land area (Liu et al., 2021). In Canada, the drinking water for approximately two-thirds of the population is sourced from surface waters, much of which originates in forested landscapes (Natural Resources Canada, 2021). The quality of source water delivered downstream to drinking water treatment plants has strong links to the disturbance history of the contributing landscapes (Emelko et al., 2011; Gartner et al., 2014) and is thus vulnerable to the impacts of natural and anthropogenic landscape disturbances such as wildfires (Robinne et al., 2019) and forest harvesting practices (Kreutzweiser et al., 2008). Turbidity and dissolved organic carbon (DOC) are two key source water quality metrics of concern for drinking water treatment (Emelko et al., 2011). High source water DOC concentrations can challenge drinking water treatment operations, through higher coagulant and disinfection demands, reactions with disinfectants to create disinfection by-products, and the potential for consumer-side taste and odour problems (Emelko et al., 2011).

The amount and timing of DOC transferred from forested hillslopes to receiving streams is governed by the interplay between catchment properties such as soil type and vegetation, soil biogeochemical processes that regulate soil solute concentrations, and catchment moisture conditions that influence the flux of hillslope solute pools to receiving waters (Christ & David, 1996; Hope et al., 1994; Kalbitz et al., 2000; Wen et al., 2020). Litterfall, root exudates, plant litter, microbial biomass, and soil organic matter are considered the main sources of DOC in soils (Kalbitz et al., 2000). DOC concentrations in forested soils typically decrease with depth in the soil profile (Kaiser & Kalbitz, 2012). The vertical gradient is attributed primarily to the adsorption of DOC to, or the co-precipitation of DOC with, mineral soils (McDowell & Likens, 1988) further complicated by mechanisms of organic matter retention, transformation, and degradation (Kalbitz et al., 2005; Mikutta et al., 2007). Due to ecological and hydrological linkages between streams and contributing forests, particularly for headwater streams where hydrology strongly influences stream solute concentrations and export (Casas-Ruiz et al., 2020), the spring freshet (where applicable) and precipitation events are key drivers of DOC in forested systems (Hinton et al., 1997; Morison et al., 2022). Under high-flow conditions in forested catchments, rising water tables can intersect with organic-rich, upper riparian and hillslope soil horizons of relatively high DOC concentrations, hydrologically connecting hillslope DOC pools and promoting the lateral transport of DOC pools into receiving surface waters (Vidon et al., 2008). Thus, stream DOC variability is intrinsically linked to the concentrations, spatial distribution, and hydrologic connectivity of hillslope solute pool DOC (Inamdar et al., 2004; McGlynn & McDonnell, 2003).

Forest harvesting is an important stand-replacing agent of disturbance in Canada's boreal forests (Kreutzweiser et al., 2008) with known implications for forest biogeochemical and hydrological cycles (Kreutzweiser et al., 2008). In post-harvest landscapes, the mechanisms of DOC mobilization and transport that govern pre-harvest variability in fluvial DOC typically respond to harvest-induced changes to hydro-climatic variables and soil characteristics (Kreutzweiser et al., 2008; Schelker et al., 2013), potentially impacting the ability of forests to provide high-quality source water for downstream consumption. Although there is considerable spatial variability in the response of forested catchments to harvesting practices, soils in harvested watersheds typically experience reductions in rates of interception and soil evapotranspiration due to the removal of canopy cover and vegetation (Oda et al., 2021), which leads to increases in soil moisture content and water table elevations (Hotta et al., 2010). In addition to the effects of canopy removal, the use of heavy machinery during harvesting operations can cause soil compaction, decrease soil porosity, reduce soil hydraulic conductivity (Cambi et al., 2015), and route water via surface and shallow subsurface flowpaths (Buttle et al., 2018; Kreutzweiser et al., 2008; Monteith et al., 2006b). Post-harvest increases in the magnitude and frequency of peak flows and total streamflow have been reported (Wei et al., 2022; Wei & Zhang, 2010) although some contradictory results have been observed (Goeking & Tarboton, 2020; Goodbrand et al., 2022). Notably, results from paired watersheds in Canada and Sweden have highlighted post-harvest increases in spring freshet streamflow (Macdonald et al., 2003; Monteith et al., 2006b) with potential implications for the transport of DOC from hillslopes to receiving streams.

The response of fluvial DOC concentrations and export to forest harvesting practices has been widely studied but the results of these studies are often contradictory. For example, in some cases stream DOC concentrations increase post-harvest (Laudon et al., 2009; Pinel-Alloul et al., 2002; Schelker et al., 2012; Webster et al., 2022) whereas in other cases stream DOC concentrations decrease post-harvest (Meyer & Tate, 1983) or do not respond to harvesting (Knoepp & Clinton, 2009; Lepistö et al., 2014). Although these studies provide important context regarding the influence of forest harvesting on the variability of stream DOC concentrations under a range of climatic conditions and catchment settings, most studies occur <10 years post-harvest. Notably, very few longer- term studies have been conducted (Cawley et al., 2014; Lepistö et al., 2014; Yamashita et al., 2011); accordingly, the legacy (decadal scale) impacts of forest harvesting on the variability of stream DOC concentrations and export is not well understood. Additionally, few studies have directly examined stream DOC dynamics to the concentrations, spatial distribution, and hydrologic connectivity of DOC in hillslope solute pools (Hood et al., 2006; Singh et al., 2015).

Multiple analytical methods have been used to relate in-stream solute dynamics to the concentration, spatial distribution, and hydrologic connectivity of hillslope solute pools. Examples include concentration-discharge regression analysis (Ducharme et al., 2021; Godsey et al., 2009; McPhail et al., 2023) and the use of geochemical tracers (Buttle et al., 2018; Monteith et al., 2006b). Variations in concentration-discharge relationships have been linked to catchment characteristics such as the spatial distribution of solute source pools, slope, size, vegetation, land-use history, and the relative location and size of wetlands (Butturini et al., 2008; Ducharme et al., 2021; McPhail et al., 2023; Rose et al., 2018). Geochemical tracers such as potassium (K^+) and silica (SiO_2) have been used in streams to track flowpath changes, necessarily integrating catchment-specific properties such as solute pool distribution and connectivity (Buttle et al., 2018; Monteith et al., 2006b; Musolff et al., 2015; Tetzlaff et al., 2015; Zimmer & McGlynn, 2018). Such analytical methods hold some promise in relating stream DOC dynamics to the concentration, spatial distribution, and hydrologic connectivity of hillslope solute pools DOC in a paired catchment setting.

To respond to the knowledge gaps above, this chapter presents the results from an intensive ecohydrological study to examine variability in stream and hillslope solute pool DOC in an unharvested control catchment and a legacy (24 years post-harvest) clearcut catchment in hardwood dominated forests of the Canadian Shield. Specific objectives of the study are to 1) evaluate inter- and intra-catchment variability in stream DOC concentrations and export and DOC concentrations in hillslope solute pools during a range of flow conditions, 2) investigate the spatial distribution and contribution to stream DOC of hillslope solute pool DOC using concentration-discharge regression analysis, and 3) evaluate and contrast changing hydrologic connectivity in the study catchments during a range of flow conditions using the potassium-silica molar ratio as a proxy for flowpath depth.

2.3 Methods

2.3.1 Study Site and Experimental Design

Please see Chapter 1, sections 1.3.2 and 1.3.3. for details on the study site and experimental design.

2.3.2 Field Methods

2.3.2.1 Hydrometeorological Monitoring

Streamflow was continuously monitored at the outlets of C32 and C31 using 90° V-notch weirs with stilling basins and Steven's Smart PT SDI-12™ pressure and temperature transducers. Stage data were converted to instantaneous discharge (ten-minute intervals). Ten-minute precipitation data were recorded approximately 0.4 km southeast of the study basins at a Natural Resources Canada monitoring station (“Meadow Station”, Figure 2.1) using an OTT Pluvio tipping bucket gauge (Jason Leach, personal communication, 2021).

2.3.2.2 Stream Sampling

Stream water samples were collected between 2021-03-25 and 2021-10-30 at the basin outlets. This study encompassed a range of hydrological conditions including a freshet sampling period, a post-freshet (hereafter “intermediate”) sampling period, and the fall wet-up (hereafter the fall sampling period). Freshet sampling began on 2021-03-25 and ended on 2021-05-09 as determined by on-site observations of stream discharge and snowpack. The intermediate sampling period from 2021-05-10 to 2021-10-08 included baseflow conditions and four precipitation events sampled at sub-daily frequencies (hereafter precipitation events A to D). The fall sampling period occurred between 2021-10-09 and 2021-10-30. During the freshet and the fall sampling periods, daily composite stream samples (250 mL sub-samples every six hours) were collected using automated ISCO 6700 samplers in acid-washed, triple-rinsed 1 L polypropylene sample bottles. During the precipitation events, ISCO samples were collected at pre-set frequencies between 30 minutes and 2 hours. Sampling frequency was constant within each event based on the intensity, timing, and duration of precipitation as predicted by local weather forecasts. Manual grab samples were collected weekly under baseflow conditions during the intermediate sampling period in acid-washed, triple-rinsed, triple sample rinsed 500 mL HDPE field bottles.

2.3.2.3 Groundwater Sampling

Basal till and ablation till groundwater were sampled from 2 cm i.d. drive-point piezometers (Solinst Canada Ltd) positioned along hillslope transects established perpendicular to the stream in each study catchment (Monteith et al., 2006a; Monteith et al., 2006b, Figure 2.1). Three piezometer nests were situated on both sides of the stream, positioned along a hillslope continuum (topslope-midslope-toeslope). At each nest, one piezometer was screened in each of the basal till and the ablation till. In C32, basal and ablation till piezometer installation depths were (mean ± SD) 0.93 ± 0.09 m and 0.40 ±

0.03 m, respectively. The corresponding piezometer installation depths in C31 were 1.09 ± 0.19 m and 0.45 ± 0.05 m. Although most piezometers had 10 cm screens, some were outfitted with 25 cm screens (Monteith et al., 2006b). In addition to the hillslope piezometer transects, groundwater was collected from a transect of piezometers deployed in wetlands in both catchments (Figure 2.1). Wetland piezometers were installed in C32 and C31 at depths of 0.37 ± 0.03 m and 0.39 ± 0.03 m, respectively.

Groundwater sampling occurred approximately weekly during the freshet and fall wet-up sampling periods and approximately monthly under baseflow conditions during the intermediate sampling period. Additionally, groundwater samples were collected during each of the four sampled precipitation events. A peristaltic pump was used to purge each piezometer 24 hours prior to sampling to allow the piezometer sufficient recharge time and to ensure that samples were representative of the conditions of the respective sampling times (Monteith et al., 2006b). Purging continued until either a) the piezometer was dry or b) 5 minutes had elapsed, whichever came first. Tubing of the sample lines was triple-rinsed with DI water between each purge or sample. Samples were collected in acid-washed, triple-rinsed 500 mL HDPE field bottles then triple-rinsed with sample water.

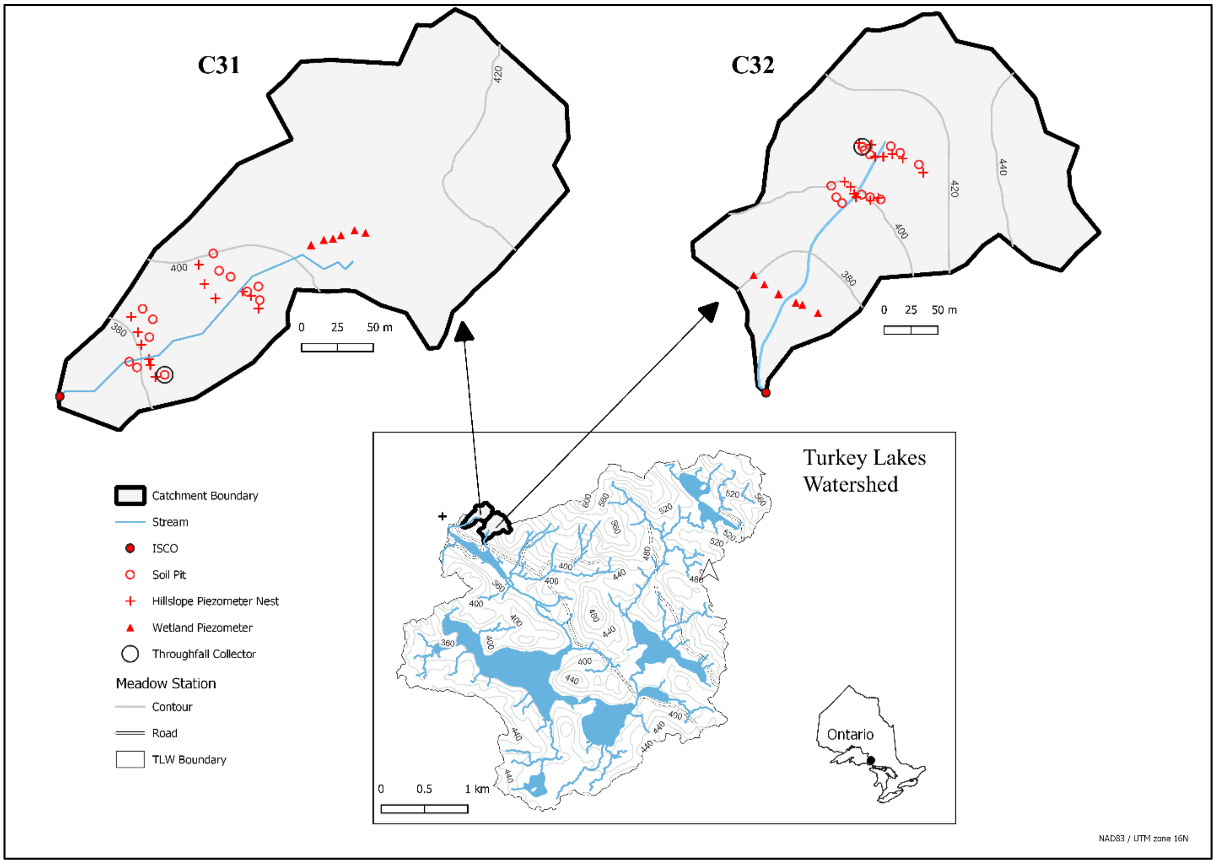

Figure 2.1 Field Instrumentation

2.3.2.4 Mineral Soil Water and LFH Percolate Sampling

To evaluate spatial and temporal variability of the soil water chemistry in the shallow subsurface hillslope profile, soil pits were dug by hand adjacent to the hillslope piezometer nests in each catchment. Soil pits depths were (mean ± SD) 0.64 ± 0.10 m and 0.65 ± 0.10 m in C32 and C31, respectively (Fines, 2023). Each soil pit was instrumented with two zero-tension lysimeters. Lysimeters were installed laterally into the upslope cut-face 6 months prior to the start of sample collection to allow the surrounding soil to equilibrate. The first lysimeter was placed directly below the leaf litter layer in each pit to capture water percolating through the organic-rich forest floor (hereafter “LFH percolate”). The second lysimeter was situated in the mineral soil horizon approximately 20 cm below the contact with the LFH layer to capture water traveling laterally through the mineral soil horizon (hereafter “mineral soil water”). Each lysimeter was constructed from PVC pipe, PVC sheeting, and topped with a plastic screen mesh. To facilitate the contact between the screen mesh and the overlying soil matrix (LFH or mineral soil), glass wool, topped with a mixture of local soil (taken from the area excavated to make room for the respective lysimeters) and saturated with DI water, was placed on top of the screen mesh. Each lysimeter drained into 1 L acid-washed, triple-rinsed HDPE sample bottles housed in protective plastic totes within each soil pit. Sample bottles were checked weekly during the freshet and fall sampling periods and collected when a minimum of 500 mL had accumulated. Although it is widely recognized that prolonged hold times can alter DOC concentration and character (Peacock et al., 2015), sample bottle collection was impacted by time constraints and potential lab capacity concerns due to COVID-19. Throughout the intermediate sampling period, lysimeters were checked approximately monthly and within 24 hours of the groundwater sampling as described above. Additionally, in advance of each sampled precipitation event, lysimeter bottles were collected and replaced with clean bottles to ensure an accurate representation of the respective precipitation events.

2.3.2.5 Throughfall Sampling

A throughfall collector was installed adjacent to one soil pit in each basin. In C32 it was deployed next to the "top" pit in the upper west transect and in C31 the throughfall collector was located adjacent to the "top" pit of the lower east transect (Figure 2.1). Throughfall collectors consisted of a plastic funnel, protected from the accumulation of leaf litter by a mesh, attached to a steel post driven securely into the ground (Fines, 2023). The proximity to the respective soil pits allowed the throughfall collectors to empty into 1 L acid-washed, triple-rinsed HDPE bottles in protective plastic pit liners. The collection of the throughfall sample bottles was coincidental with the collection of the lysimeter sample bottles.

2.3.3 Analytical Methods

2.3.3.1 Laboratory Analysis

Samples were transported on ice from the field and generally frozen within one week, but some samples were refrigerated at -4 °C (typically < 4 months) prior to freezing due to COVID-19-related shutdowns and limited lab access. It is recognized that freeze-thaw can impact DOC concentrations and character and is not recommended as a method of preservation (Peacock et al., 2015). After thawing, all samples were filtered using pre-soaked 0.45 µm mixed cellulose ester filters (GN-6 Metricel, VWR) pre-rinsed with 100 mL DI water. All samples were analyzed at the accredited Water Chemistry Laboratory at the Great Lakes Forestry Centre in Sault Ste Marie, ON, using standard methods and quality control practices (Webster et al., 2021b).

2.3.3.2 Data Analysis

Data processing, statistical analysis, and graphic visualization were conducted in R Studio version 4.0.2 (R Core Team, 2020). Differences were considered statistically significant at $p \leq 0.05$.

2.3.3.2.1 Analytical methods related to Objective 1: Evaluate inter- and intra-catchment variability in stream DOC concentrations, stream DOC export, and hillslope solute pool DOC concentrations under a range of flow conditions.

Descriptive statistics and boxplots were used to evaluate inter- and intra-catchment variability in stream DOC concentrations, stream DOC export, and hillslope DOC concentrations. For the freshet and fall sampling periods, stream DOC export (mg s^{-1} ha^{-1}) was evaluated for each catchment by multiplying the average daily water yield (L s^{-1} ha^{-1}) by the daily composite stream DOC concentration (mg L^{-1}). For samples collected under baseflow conditions, instantaneous water yield (L s^{-1} ha^{-1}) was multiplied by stream DOC concentration for each sampling time. For samples collected during precipitation events A to D, the frequency of discharge sampling differed from the frequency of stream chemistry sampling. Accordingly, stream DOC concentrations (mg L^{-1}) were interpolated using linear regression and were multiplied by instantaneous water yield (L s^{-1} ha^{-1}) to determine DOC export (mg s^{-1} ha^{-1}). This approach has been previously used to interpolate event-scale stream DOC concentrations in forested headwater catchment of the Canadian Shield (Hinton et al., 1997; Schiff et al., 1998). In this study, linear regression intervals were defined as intervals between sequential local maxima and minima, determined from visual examination of the respective hydrographs. In cases where a local maximum or a local minimum occurred between two samples and a linear regression could not be determined for at least one adjacent limb, then the regression interval was extended to include the next local maximum or minimum and linear extrapolation was used (Hinton & Schiff, 1997).

The non-parametric Mann-Whitney U test was used to evaluate inter-catchment differences in stream DOC concentrations, stream DOC export, and hillslope solute pool DOC concentrations as normality assumptions were not met and sample sizes were often <30. To reduce bias in the inter-catchment comparisons of stream DOC concentration, samples from either catchment which did not have a temporal partner in the other catchment (same day under freshet, baseflow, and fall conditions, or same date and time during precipitation events) were excluded from inter-catchment Mann-Whitney U tests. Similarly, inter-catchment Mann-Whitney U tests for DOC export included only DOC export values from each catchment with a temporal partner in the other catchment. Intra-catchment differences in stream and hillslope DOC concentrations and stream DOC export were evaluated using the non-parametric Kruskall-Wallis test.

2.3.3.2.2 Analytical methods related to Objective 2: Investigate the distribution and contribution to streamflow of hypothesized hillslope DOC source pools using concentration-discharge regression analysis

Concentration-discharge (C – Q) regression relationships are widely used to investigate solute hillslope-stream transport dynamics and to characterize stream solute export regimes (e.g. transport-limited vs. source-limited) under varying seasonal and hydrologic conditions. Musolff et al. (2015) combined two metrics: the slope of the ln(C) – ln(Q) regression line (Godsey et al., 2009) and the ratio of the coefficient of variations (Thompson et al., 2011) to provide a conceptual framework for C – Q analysis which has since been applied in multiple studies (Ducharme et al., 2021; McPhail et al., 2023; Rose et al., 2018). In the present study, DOC C – Q relationships were evaluated for multiple flow conditions using the analytical framework presented in Musolff et al. (2015) and recently applied by McPhail et al. (2023) for undisturbed headwater catchments at Turkey Lakes Watershed. Briefly, the slope of the regression line between ln-transformed DOC concentration and ln-transformed discharge (hereafter ln

(DOC) – ln(Q)) was calculated for each catchment and flow condition (the freshet sampling period, baseflow, precipitation events A-D, and the fall sampling period). The ratio of the coefficients of variation (CV) of DOC concentration and discharge was also calculated (CV_{DOC}/CV_{Q}). The slopes and CV ratios were then interpreted with respect to four general categories of C – Q behavior described in Ducharme et al. (2021) and Moatar et al. (2017) (Table 2.1). As noted by Cartwright et al. (2020) and McPhail et al. (2023), the use of these categories is intended only to complement and to facilitate interpretation of the concept of a continuum of solute behavior, rather than as a strict set of operational definitions. Following McPhail et al. (2023), slope values of ln (DOC) – ln(Q) > 0.1 were considered indicative of flushing behavior and slope values of < -0.1 were considered indicative of dilution behaviour. Although other slope thresholds have been used (e.g. |0.2| in Cartwright et al. (2020)), |0.1| was selected for best alignment with McPhail et al. (2023) which was undertaken, like this study, at TLW. Where the ln (DOC) – ln(Q) regression relationship was not statistically significant (Spearman, $p > 0.05$), a CV_{C}/CV_{Q} value of 0.5 was considered as the threshold between chemostatic and chemodynamic behaviour in this study (McPhail et al., 2023) and predicated on the work of Thompson et al. (2011) which suggest values <0.5 (chemostatic behavior) may be indicative of a conservative tracer.

Table 2.1 C-Q analytical framework (adapted from Moatar et al. (2017), Ducharme et al. (2021), and McPhail et al. (2023))

ln (DOC) – ln(Q) Slope	CV_{DOC} / CV_{Q}	Interpretation
0 < slope < |0.1| or p > 0.05	≥ 0.5	Chemodynamic DOC behavior whereby DOC varies independently of Q
0 < slope < |0.1| or p > 0.05	< 0.5	Chemostatic DOC behavior, indicative of a relatively homogenous or uniform source distribution whereby changes in hydrologic connectivity and flowpaths do not impact DOC concentration
Slope > 0.1	-----	Flushing DOC behavior indicative of a transport-limited export regime
Slope < -0.1	-----	Dilution DOC behavior indicative of a source-limited export regime

2.3.3.2.3 Analytical methods related to Objective 3: Evaluate and contrast flowpath dynamics during a range of flow conditions

To evaluate catchment flowpath changes with potential implications for stream DOC variability, the aqueous molar ratio of potassium (K^+) and silica (SiO_2) ($K:SiO_2$) was evaluated for each stream and hillslope solute pool sample for which both K^+ and SiO_2 concentrations were above their respective detection limits. Larger $K:SiO_2$ ratios are associated with relatively rapid surface flowpaths whereas smaller ratios are indicative of slower subsurface pathways (Elsenbeer et al., 1995; Monteith et al., 2006b). The use of $K:SiO_2$ as a proxy for flowpaths assumes vertical gradients of both K^+ concentrations and SiO_2 concentrations, such that K^+ decreases with depth in the soil profile and SiO_2 increases with depth in the soil profile (Monteith et al., 2006b). $K:SiO_2$ has been previously used at TLW to examine the impact of forest harvesting practices on flowpath dynamics during the spring freshet (Monteith et al., 2006b) and across a long-term sampling program (Buttle et al., 2018). The present study presents detailed stream and hillslope solute pool $K:SiO_2$, K^+ concentrations, and SiO_2

concentrations for a range of flow conditions (freshet, baseflow, precipitation events, and fall). Inter- and intra-catchment variability in stream and hillslope K:SiO_2, K^+ concentrations, and SiO_2 concentrations are presented in boxplots and evaluated using descriptive statistics and contrasted via Mann-Whitney U tests (inter-catchment) or Kruskal-Wallis tests (intra-catchment). Following the approach of section 2.4.2.1, stream samples from either catchment without a temporal partner in the other catchment (same day under freshet, baseflow, and fall conditions, or same datetime during precipitation events) were excluded from inter-catchment Mann-Whitney U tests to reduce bias in the inter-catchment comparisons of stream K:SiO_2 ratios, K^+ concentrations, and SiO_2 concentrations.

2.4 Results

2.4.1 Precipitation and Streamflow

In 2021 the total precipitation was 1183.9 mm. The annual stream discharge was 424.2 mm and 320.3 mm in C32 and C31, respectively. Temporal changes in precipitation and streamflow for the two study catchments are presented in Figure 2.2 and Table 2.2. C32 had continuous streamflow throughout the study period whereas C31 had intermittent flow with 48 zero flow days.

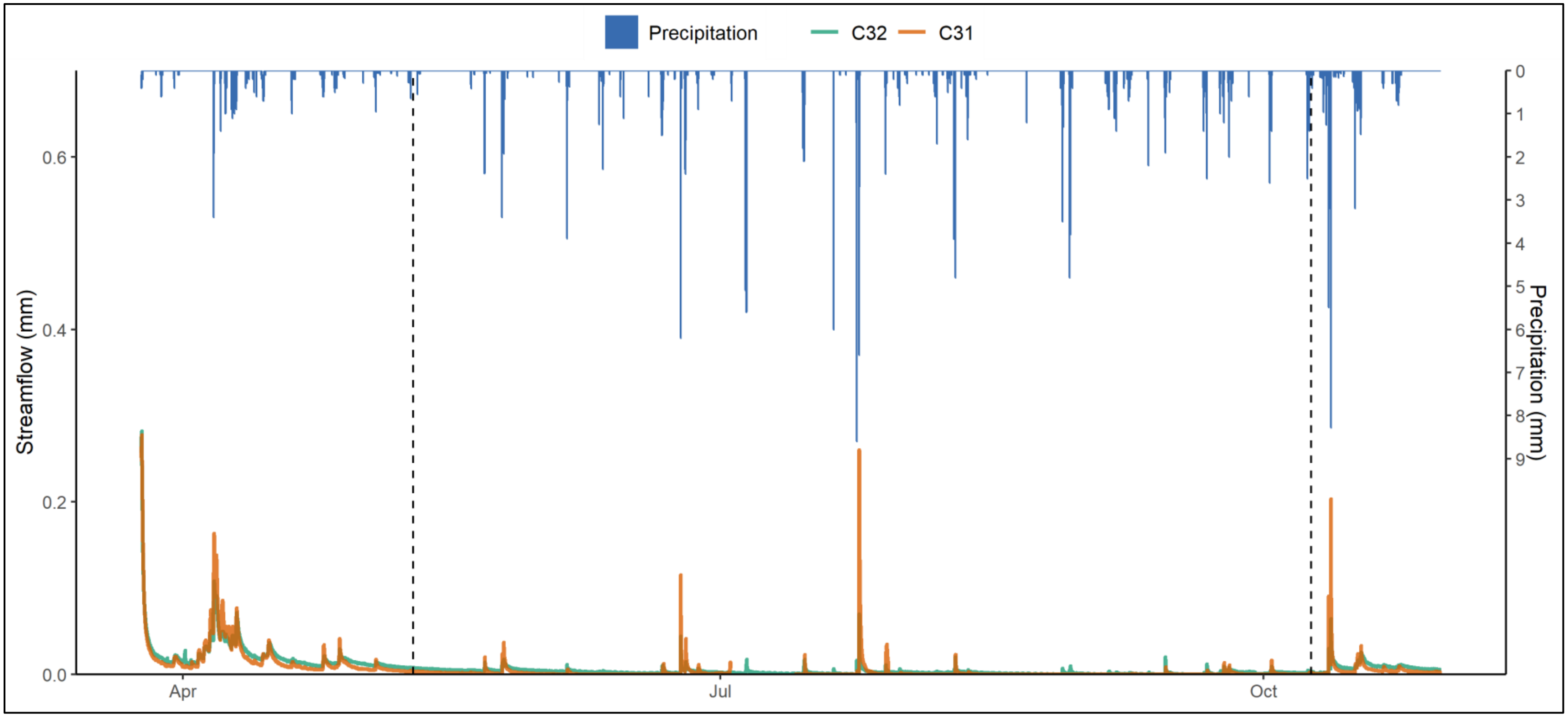

Figure 2.2 Study period streamflow (mm) and precipitation (mm). Dashed vertical lines delineate the end of the freshet sampling period (leftmost) and the start of the fall sampling period (rightmost). Gaps in the streamflow record for C31 are due to instrument malfunction.

Table 2.2 Precipitation and streamflow by flow condition

Flow Condition	Date Range	Total Precipitation (mm)	Total Streamflow (C32) (mm)	Total Streamflow (C31) (mm)
2021 Calendar Year	----	1183.9	424.2	320.3
Freshet	2021-03-25 to 2021-05-09	116.2	150.0	132.9
Precipitation Event A	2021-05-24 to 2021-05-25	25.4	1.6	2.0
Precipitation Event B	2021-06-21 to 2021-06-22	18.9	0.6	0.5
Precipitation Event C	2021-06-24 to 2021-06-26	13.7	1.8	2.5
Precipitation Event D	2021-07-14 to 2021-07-15	17.2	0.7	0.4
Fall	2021-10-09 to 2021-10-30	97.9	27.4	18.5

2.4.2 Results related to Objective 1: Evaluate inter- and intra-catchment variability in stream DOC concentrations, stream DOC export, and hillslope solute pool DOC concentrations

2.4.2.1 Stream DOC Concentrations

Stream DOC concentrations ranged from 0.93 mg L^{-1} to 5.13 mg L^{-1} and 1.41 mg L^{-1} to 6.32 mg L^{-1} in the unharvested reference catchment C32 (n = 179) and the legacy clearcut catchment C31 (n = 158), respectively. DOC concentrations for C32 and C31 were (mean ± SD) 2.42 ± 0.69 mg L^{-1} and 3.56 ± 1.02 mg L^{-1}, respectively. Additional descriptive statistics are listed in Appendix A, Table A2. Inter- and intra-catchment variability in stream DOC concentrations are presented respectively by Figures 2.3a and 2.3b. Notably, 26 stream samples from C32 and 2 stream samples from C31 were excluded from inter-catchment Mann-Whitney U tests as they could not be matched temporally with a sample in the other catchment.

Under all sampled flow conditions, the data show that stream DOC concentrations were higher in C31 than in C32 and statistically significant inter-catchment differences were observed (Mann-Whitney U Test, $p \leq 0.05$, Figure 2.3a). Absolute values of the mean inter-catchment (C32 – C31) difference in stream DOC concentration exceeded the detection limit for DOC concentration in this study (0.400 mg L^{-1}) and were, respectively, 0.53 mg L^{-1}, 0.84 mg L^{-1}, 2.01 mg L^{-1}, 1.66 mg L^{-1}, 0.89 mg L^{-1}, 1.48 mg L^{-1}, and 1.06 mg L^{-1} for the freshet sampling period, baseflow, event A, event B, event C, event D, and the fall sampling period.

Intra-catchment stream DOC concentrations differed significantly (Kruskal-Wallis, $p \leq 0.05$) between the sampled flow conditions. DOC concentrations during high-flow conditions (freshet, precipitation events A-D, and fall) were elevated relative to baseflow conditions (Figure 2.3b). Notably, the range of DOC concentrations observed during precipitation events A-D were comparable to those of the freshet and fall sampling periods. For both catchments, the maximum and minimum observed DOC concentrations occurred during the fall and freshet sampling period, respectively (Figure 2.3b).

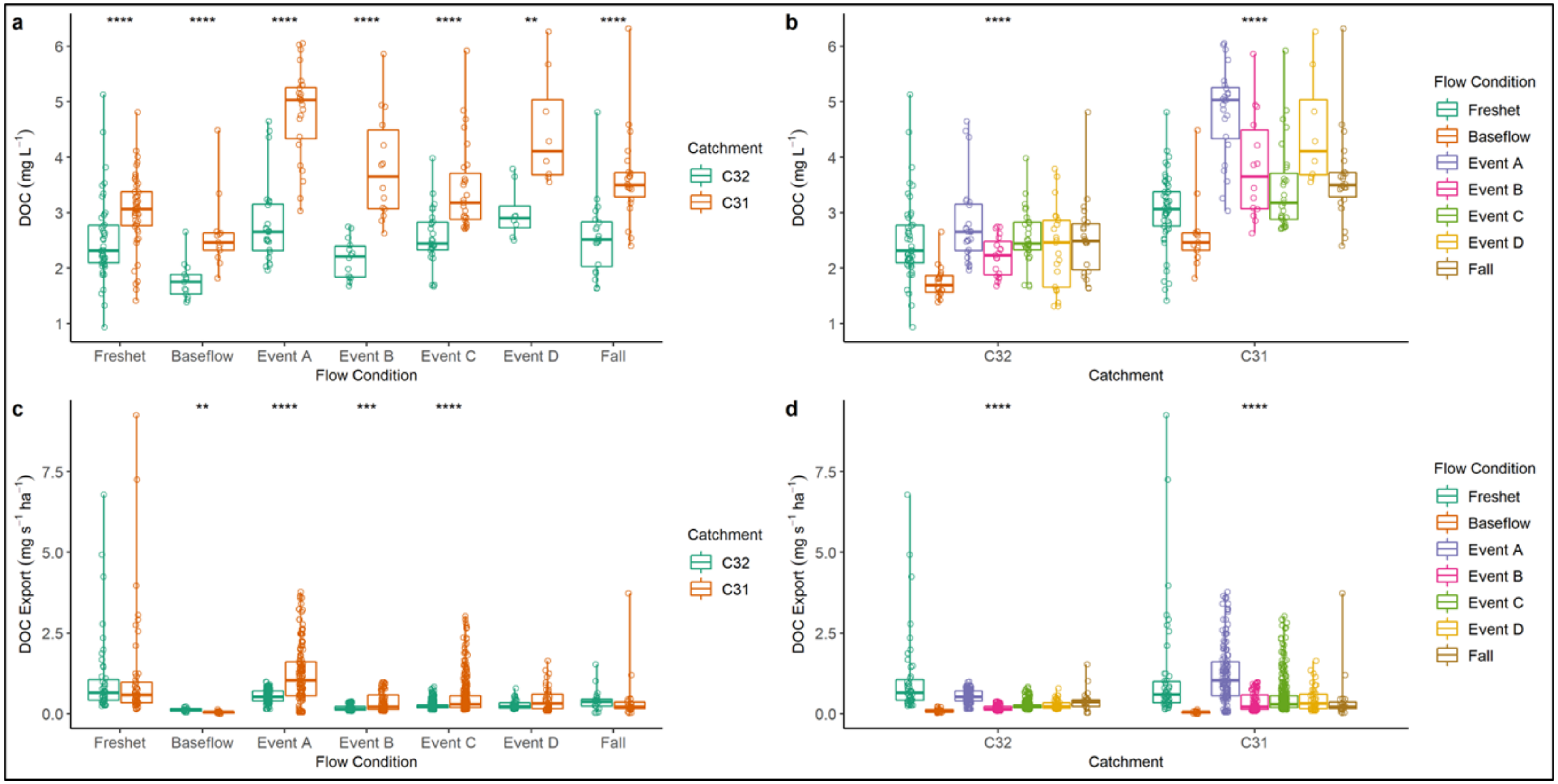

Figure 2.3 Inter- and intra- catchment variability in stream DOC concentrations and export under varying hydrologic conditions. 25th, 50th, and 75th percentiles are shown by horizontal lines. Whiskers indicate maximum and minimum values. Open circles represent individual data points. Asterisks represent the level of statistical significance for the Mann-Whitney U test (a and c) and Kruskal-Wallis test (b and d). *: $p \leq 0.05$, **: $p \leq 0.01$, ***: $p \leq 0.001$, ****: $p \leq 0.0001$.

2.4.2.2 Stream DOC Export

Stream DOC export in C32 ranged from 2.09×10^{-2} mg s^{-1} ha^{-1} to 6.79 mg s^{-1} ha^{-1} (n = 757). In the legacy clearcut catchment C31, stream DOC export from 1.61×10^{-7} mg s^{-1} ha^{-1} to 9.25 mg s^{-1} ha^{-1} was observed (n = 648). Average DOC export (± SD) from C32 was 0.36 ± 0.42 mg s^{-1} ha^{-1}, whereas average DOC export (± SD) from C31 was 0.69 ± 0.84 mg s^{-1} ha^{-1}. Inter- and intra-catchment variability in stream DOC export are presented in Figures 2.3c and 2.3d.

Inter-catchment comparisons of stream DOC export revealed significant differences (Mann-Whitney U test, $p \leq 0.05$) under baseflow conditions and during precipitation events A-C. Under baseflow conditions, stream DOC export from C32 exceeded that of C31, whereas during precipitation events A-C DOC export from C31 exceeded C32 (Figure 2.3c). In contrast, DOC export did not differ significantly between the catchments for the freshet sampling period, event D, and the fall sampling period (Figure 2.3c). Intra-catchment stream DOC export was lowest under baseflow conditions and peaked during the freshet sampling period in both C32 and C31 (Figure 2.3d). Of the four sampled precipitation events, the highest DOC export for both catchments occurred during event A.

2.4.2.3 Hillslope Solute Pool DOC Concentrations

Dissolved organic carbon concentrations were evaluated for hillslope solute pools hypothesized to contribute to stream DOC: basal till groundwater, ablation till groundwater, wetland groundwater, mineral soil water, LFH percolate, and throughfall. Figures 2.4a and 2.4b present inter- and intra-catchment variability in hillslope DOC concentrations by sampling period (freshet, intermediate, and fall) with stream samples included for reference. Descriptive statistics for the hillslope DOC pools are provided in Appendix A, Table A3. No significant inter-catchment differences in DOC concentration were observed for any hillslope solute pool (Figure 2.4a).

Intra-catchment hillslope DOC concentrations generally followed a vertical gradient, decreasing with depth from the upper soil horizon DOC pools (LFH percolate and mineral soil water) to the basal and ablation till groundwater DOC pools (Figure 2.4b). Vertical stratification was most apparent during the intermediate and fall sampling periods, corresponding with the highest observed DOC concentrations in the LFH percolate and mineral soil water solute pools (Figure 2.4b). Dissolved organic carbon concentrations observed in the LFH percolate and mineral soil water solute pools of each catchment significantly exceeded their respective stream DOC concentrations in all sampling periods (Mann-Whitney U test, $p \leq 0.05$, Figure 2.4b). In contrast, basal and ablation till groundwater DOC concentrations in C32 were not significantly different from the stream samples collected across all sampling periods (Figure 2.4b). Notably, only one sample was collected from both the basal till groundwater and ablation till groundwater solute pools in C32 during the intermediate sampling period (Appendix A, Table A3), as the water table was below the depth of most piezometers at sampling times. Accordingly, adequate characterization of DOC concentrations in either ablation till groundwater or basal till groundwater in C32 during the intermediate sampling period and robust comparison to stream DOC concentrations were not possible. In C31, basal till groundwater did not differ significantly from stream DOC concentrations under freshet, intermediate baseflow, and fall conditions (Figure 2.4b) but was significantly lower than stream event samples (Mann-Whitney U test, $p \leq 0.05$, Figure 2.4b). Ablation till groundwater DOC concentrations in C31 were significantly lower than stream DOC concentrations (Mann-Whitney U test, $p \leq 0.05$, Figure 2.4b) during the freshet and fall sampling periods. During the intermediate sampling period, ablation till groundwater DOC in C31 significantly exceeded baseflow stream DOC concentrations but was significantly less than stream DOC concentrations under precipitation event conditions.

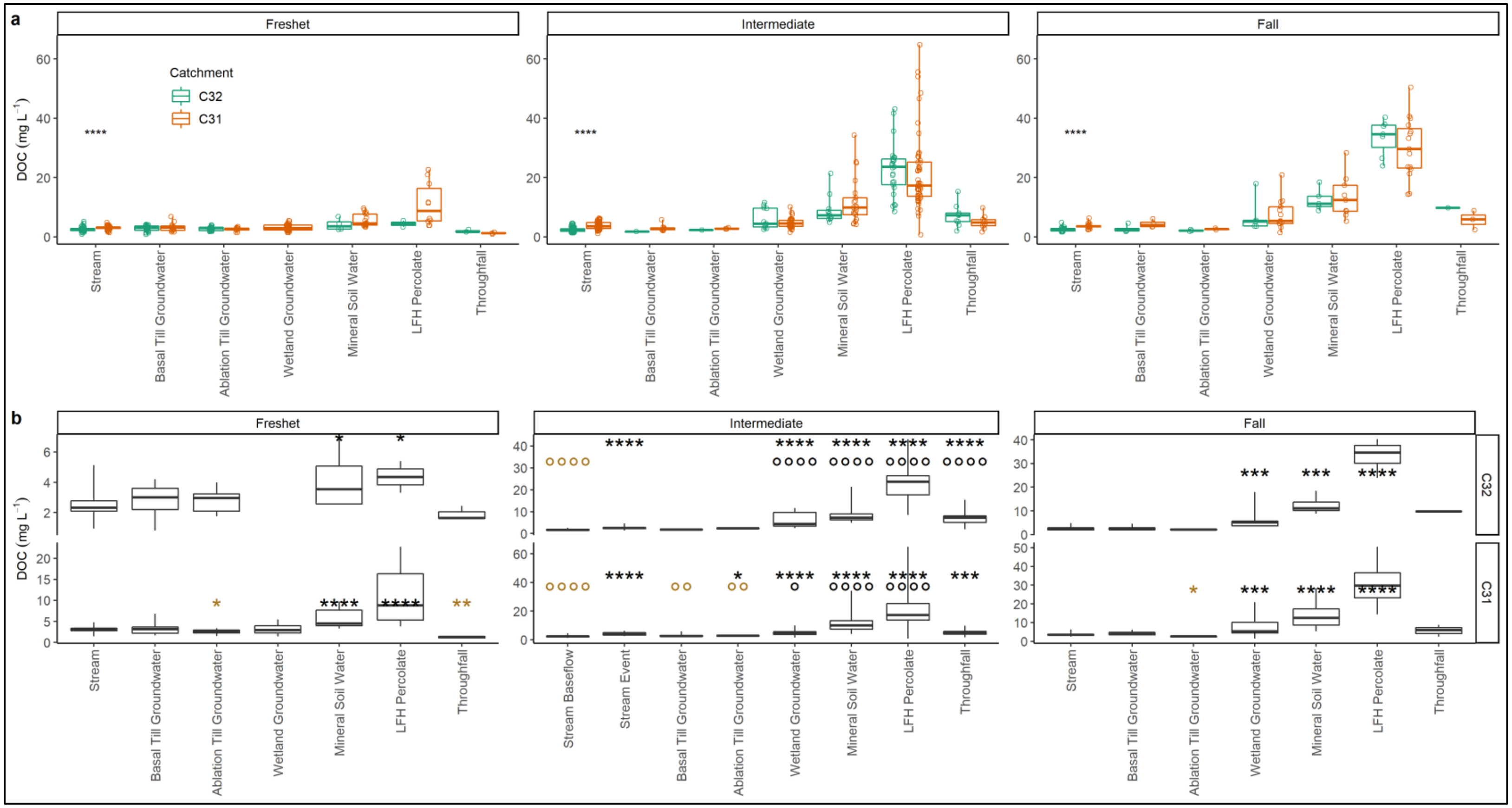

Figure 2.4 a) Inter- and b) intra-catchment stream and hillslope pool DOC concentrations by sampling period. 25th, 50th, and 75th percentiles are shown by horizontal lines. Whiskers indicate range. The reader is encouraged to note the differences in the y-axis. For all asterisks, *: p ≤ 0.05, **: p ≤ 0.01, ***: p ≤ 0.001, ****: p ≤ 0.0001 (Mann-Whitney U test). For b: asterisks in the freshet and fall sampling periods denote statistically significant differences relative to stream samples (black = "greater than", brown = "less than"); asterisks in the intermediate sampling period denote statistically significant differences relative to baseflow stream samples (black = "greater than", brown = "less than"); circles in the intermediate sampling period denote statistically significant differences relative to event (A-D) stream samples (°: p ≤ 0.05, °°: p ≤ 0.01, °°°: p ≤ 0.001, °°°°: p ≤ 0.0001; black = "greater than", brown = "less than").

2.4.3 Results related to Objective 2: Investigate the spatial distribution and contribution to stream DOC of hillslope solute pool DOC using concentration-discharge regression analysis

Regression relationships between streamflow and stream DOC concentrations were examined at seasonal- and event-scales to investigate the spatial distribution and contribution to stream DOC of hillslope solute pool DOC in C32 and C31. Log-transformed DOC concentration – discharge (ln (DOC) – ln(Q)) regression relationships are presented in Figure 2.5a for each sampled flow condition (freshet, baseflow, precipitation Events A-D, and the fall). The ln (DOC) – ln(Q) relationships were statistically significant ($p \leq 0.05$) in both catchments for all flow conditions with the following exceptions: baseflow (C32 only) and the fall sampling period.

Freshet, baseflow, and fall Spearman rank-order correlation coefficients were 0.80, 0.33, and 0.87 in C32 and 0.57, 0.20, and 0.66 in C31, respectively. During precipitation events A-D the Spearman rank-order correlation coefficient ranged from 0.70 to 0.90 for C32 and from 0.55 to 1 for C31 (Figure 2.5a). Slope values of the ln (DOC) – ln(Q) regression relationships in C32 were higher than those in C31 for all conditions except for precipitation Event B (Figure 2.5a). Slope values for all catchments and conditions were <0.5. The CV_{DOC} / CV_Q ratios for the study catchments are plotted in Figure 2.5b. The relatively lower CV_{DOC} / CV_Q ratios for C31 were grouped in the left of the graph whereas in C32 they were relatively higher and plotted more to the right of the graph (Figure 2.5b). Inter-catchment differences were most apparent for Event A and the fall sampling period, whereas CV_{DOC} / CV_Q ratios were most similar for baseflow and Event B (Figure 2.5b).

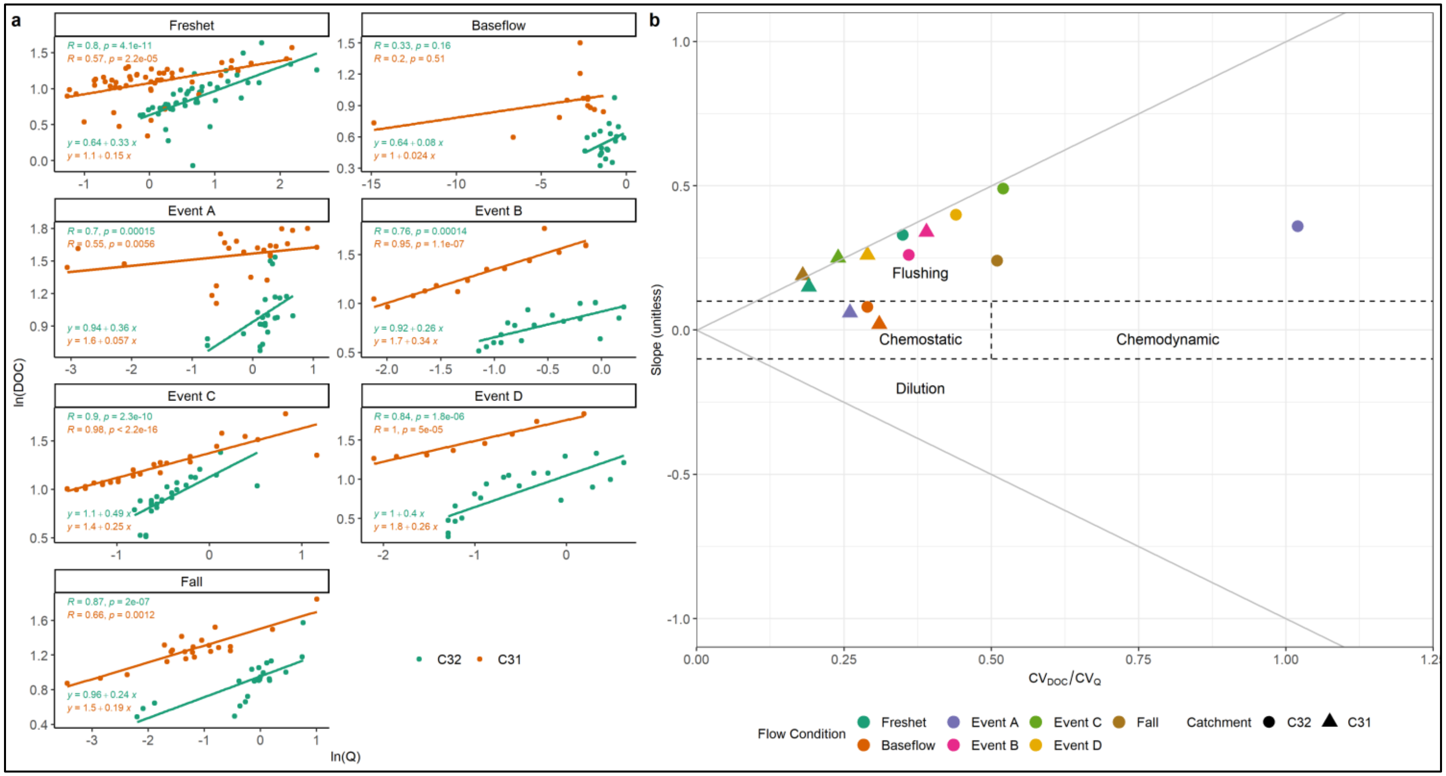

Figure 2.5 Concentration- discharge regression analysis by flow condition and catchment. a: ln (DOC) – ln(Q) regression relationships by flow condition. For daily composite samples collected during the freshet and fall sampling periods, Q refers to mean discharge for the sample collection date (L s^{-1}). For samples collected during baseflow and precipitation events A-D, Q refers to instantaneous discharge (L s^{-1}). DOC concentrations are given in mg L^{-1}. b: Slope of ln (DOC)-ln(Q) relationships vs. the ratio of the coefficient of variation of DOC concentration to the coefficient of variation of discharge by catchment and flow condition. The solid grey lines represent theoretical bounds described by Musolff et al. (2015). Dotted lines and text annotations illustrate the conceptual categories as described in Section 2.3.3.2.2.

2.4.4 Results related to Objective 3: Evaluate and contrast flowpath dynamics in the study catchments during a range of flow conditions

2.4.4.1 Stream K:SiO_2 Molar Ratios

Inter- and intra-catchment variability in stream K:SiO_2 ratios, K^+ concentrations, and SiO_2 concentrations in the study catchments are presented in Figure 2.6. In C31 stream K:SiO_2 ratios exceeded and differed significantly (Mann-Whitney U test, $p \leq 0.05$) from those in C32 across all sampled flow conditions except for the fall sampling period (Figure 2.6a). Similarly, stream K^+ concentrations were higher in C31 and significantly different (Mann-Whitney U test, $p \leq 0.05$) from those in C32 under all flow conditions except the fall sampling period. Stream SiO_2 concentrations did not differ significantly between the catchments during the freshet sampling period, under baseflow conditions, during precipitation event D, or during the fall sampling period. In contrast, during precipitation events A-C, stream SiO_2 concentrations in C31 exceeded and differed significantly from C32 (Mann-Whitney U test, $p \leq 0.05$, Figure 2.6a).

Within both C32 and C31, the lowest observed stream K:SiO_2 ratios occurred during the freshet sampling period (Figure 2.6b). In C32, the maximum observed stream K:SiO_2 ratios occurred during the fall sampling period, whereas the maximum observed stream K:SiO_2 value in C31 occurred during the freshet sampling period. During baseflow stream K:SiO_2 ratios were generally lower than all other flow conditions in both catchments (Figure 2.6b). The maximum observed stream K^+ concentrations occurred during the fall sampling period in both catchments. A notable contrast between the intra-catchment trends for stream K^+ is shown in Figure 2.6b such that, in C32, stream K^+ concentrations during the freshet sampling period generally exceeded those observed under baseflow conditions, whereas the opposite was observed in C31. Considering intra-catchment trends in stream SiO_2, stream SiO_2 concentrations were markedly lower during the freshet sampling period, relative to other flow conditions, for both C32 and C31. In C32, a general increase in stream SiO_2 concentrations was observed across precipitation events A-D (Figure 2.6b). A similar trend was not observed in C31 –

events B and D showed slightly elevated stream SiO_2 concentrations, like baseflow SiO_2 concentrations, relative to events A, C, and the fall sampling period (Figure 2.6b).

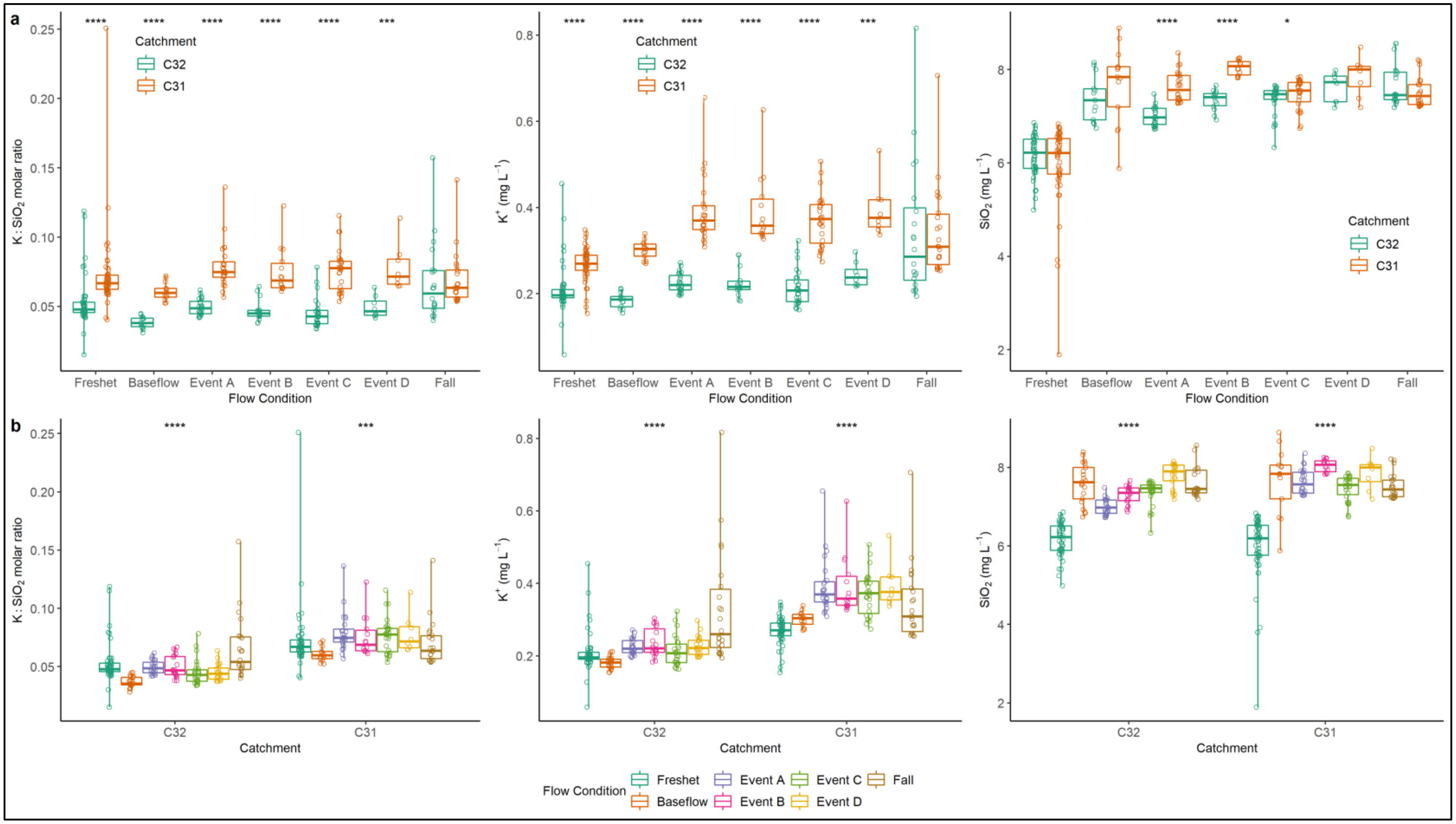

Figure 2.6 a) Inter- and b) intra- catchment variability in stream K:SiO$_2$ molar ratios, K$^+$ concentrations, and SiO$_2$ concentrations under freshet, intermediate baseflow, intermediate precipitation event (A-D), and fall sampling period flow conditions. 25th, 50th, and 75th percentiles are shown by horizontal lines. Whiskers indicate maximum and minimum values. Open circles represent individual data points. Asterisks represent the level of statistical significance for a) Mann-Whitney U test and b) Kruskal-Wallis tests. *: $p \leq 0.05$, **: $p \leq 0.01$, ***: $p \leq 0.001$, ****: $p \leq 0.0001$.

2.4.4.2 Hillslope Solute Pool K:SiO_2 Molar Ratios

Inter- and intra-catchment variability in hillslope solute pool K:SiO_2 ratios by sampling period are presented with stream data in Figure 2.7. Corresponding figures for K^+ concentrations and SiO_2 concentrations are provided in Appendix A (Figures A2 and A3). Notably, no significant inter-catchment differences in the K:SiO_2 ratio were observed for any hillslope solute pool during any sampling period with the following exceptions: basal till groundwater during the freshet sampling period, wetland groundwater during the intermediate and fall sampling periods, and LFH percolate during the fall sampling period (Mann-Whitney U test, $p \leq 0.05$, Figure 2.7a). With respect to freshet basal till groundwater, K:SiO_2 ratios in C31 exceeded those in C32. With respect to the wetland groundwater K:SiO_2 during the intermediate and fall sampling periods, K:SiO_2 ratios in C31 exceeded those in C32 (Figure 2.7a). For LFH percolate in the fall sampling period, K:SiO_2 ratios were higher in C31 than in C32. Intra-catchment variability in K:SiO_2 ratios for hillslope solute pool for both C32 and C31 followed an approximately vertical gradient with ratios highest in the throughfall, LFH percolate, and mineral soil water solute pools and relatively lower in the basal and ablation till groundwater solute pools (Figure 2.7b).

During the freshet sampling period, stream K:SiO_2 ratios in C32 were significantly (Mann-Whitney U test, $p \leq 0.05$) exceeded by the K:SiO_2 ratios observed in the ablation till groundwater and mineral soil water solute pools. In C31, stream K:SiO_2 ratios during the freshet sampling period were significantly lower than the basal till groundwater, mineral soil water, and LFH percolate solute pools (Mann-Whitney U test, $p \leq 0.05$, Figure 2.7b).

The K:SiO_2 ratios for basal till groundwater, wetland groundwater, mineral soil water, LFH percolate and throughfall solute pools during the intermediate sampling period were significantly greater than in the stream under both baseflow and event conditions in C32 (Mann-Whitney U test, $p \leq 0.05$, Figure 2.7b), whereas ablation till groundwater K:SiO_2 ratios were significantly lower (Mann-Whitney U test, $p \leq 0.05$, Figure 2.7b). In C31, the throughfall, mineral soil water, and LFH percolate solute pools were significantly greater than the stream K:SiO_2 ratios under both baseflow and event conditions. K:SiO_2 ratios for the basal till groundwater and wetland groundwater solute pools in C31 were significantly lower (Mann-Whitney U test, $p \leq 0.05$) than stream K:SiO_2 ratios collected during Events A-D (Figure 2.7b).

During the fall sampling period, stream K:SiO_2 ratios in C32 were significantly less (Mann-Whitney U test, $p \leq 0.05$) than the wetland groundwater, mineral soil water, LFH percolate, and throughfall solute pools and significantly higher (Mann-Whitney U test, $p \leq 0.05$) than the basal and ablation till groundwater K:SiO_2 ratios (Figure 2.7b). In C31, stream K:SiO_2 ratios did not differ significantly from, respectively, the basal till groundwater and wetland groundwater solute pools but were significantly less (Mann-Whitney U test, $p \leq 0.05$) than the respective K:SiO_2 ratios of the mineral soil water and LFH percolate solute pools (Figure 2.7b).

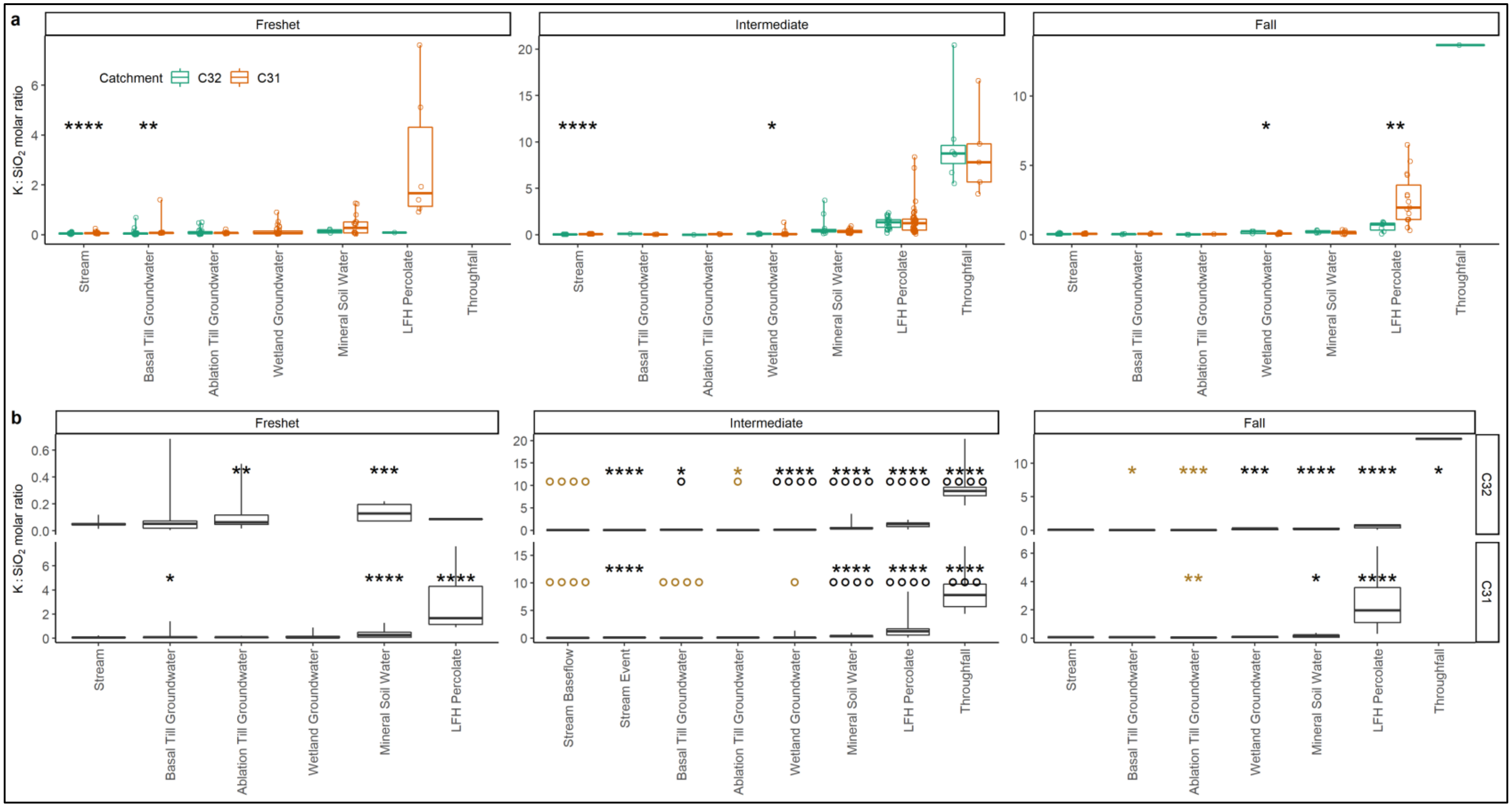

Figure 2.7 a) Inter- and b) intra-catchment stream and hillslope solute pool K:SiO$_2$ ratios by sampling period. 25th, 50th, and 75th percentiles are shown by horizontal lines. Whiskers indicate range. The reader is encouraged to note the differences in the y-axis. For all asterisks, *: p ≤ 0.05, **: p ≤ 0.01, ***: p ≤ 0.001, ****: p ≤ 0.0001 (Mann-Whitney U test). For b: asterisks in the freshet and fall sampling periods denote statistically significant differences relative to stream samples (black = "greater than", brown = "less than"); asterisks in the intermediate sampling period denote statistically significant differences relative to baseflow stream samples (black = "greater than", brown = "less than"); circles in the intermediate sampling period denote statistically significant differences relative to event (A-D) stream samples (°: p ≤ 0.05, °°: p ≤ 0.01, °°°: p ≤ 0.001, °°°°: p ≤ 0.0001; black = "greater than", brown = "less than").

2.4.5 Intra-Catchment Synchronicity of DOC Concentrations and K:SiO_2 Ratios

Intra-catchment fluctuations in stream and hillslope solute pool DOC concentrations, K:SiO_2 ratios, K^+ concentrations, and SiO_2 concentrations are shown in Figure 2.8 for the freshet sampling period, in Figure 2.9 for the intermediate sampling period, and in Figure 2.10 for the fall sampling period. Individual graphs for precipitation events A-D are presented in Appendix A (Figures A3 to A6).

Stream DOC concentrations, K:SiO_2 ratios, and K^+ concentrations were generally synchronous, with higher values observed during relatively high streamflow. In contrast, SiO_2 concentrations were typically lowest under relatively high streamflow conditions. Under all sampled flow conditions, stream DOC concentrations and stream K:SiO_2 ratios for each catchment plotted closely to the basal till, ablation till, and wetland groundwater solute pools. Wetland groundwater samples had similar K:SiO_2 ratios to the mineral soil water solute pool, particularly during the freshet and fall sampling periods (Figures 2.8 and 2.10).

Stream DOC concentrations and K:SiO_2 ratios in both C32 and C31 decreased across the freshet sampling period although the trend was more visually apparent for C32 relative to C31 (Figure 2.8). Stream K^+ concentrations did not show a clear visual trend across the freshet sampling period whereas stream SiO_2 concentrations increased in both catchments (Figure 2.8). Notably, stream SiO_2 concentrations in C32 were higher than those observed in the hillslope solute pools of C32, whereas in C31 the highest SiO_2 concentrations were observed in the wetland groundwater (Figure 2.8).

Variability in stream DOC concentrations, K:SiO_2 ratios, K^+ concentrations, and SiO_2 concentrations during the intermediate sampling period was dominated by stream solute responses to precipitation events and by an overall increase in SiO_2 concentrations within both study catchments (Figure 2.9, Figures A3-A6). Stream SiO_2 concentrations in both catchments were higher than the SiO_2 concentrations observed in the hillslope solute pools during the intermediate sampling period apart from the wetland groundwater (Figure 2.9). Like the trends observed throughout the intermediate sampling period, event-scale, variability in stream $K:SiO_2$ ratios and K^+ concentrations in C32 and C31 was visually similar to the variability in stream DOC concentrations for both catchments (Appendix A, Figures A3-A6).

During the fall sampling period stream $K:SiO_2$, K^+ concentrations, and SiO_2 concentrations decreased slightly from start to end of sampling in both catchments (Figure 2.10). DOC concentrations remained relatively stable in C32 following a precipitation event at the start of the fall sampling period, whereas C31 showed a slight increase in stream DOC concentrations following the early precipitation event (Figure 2.10).

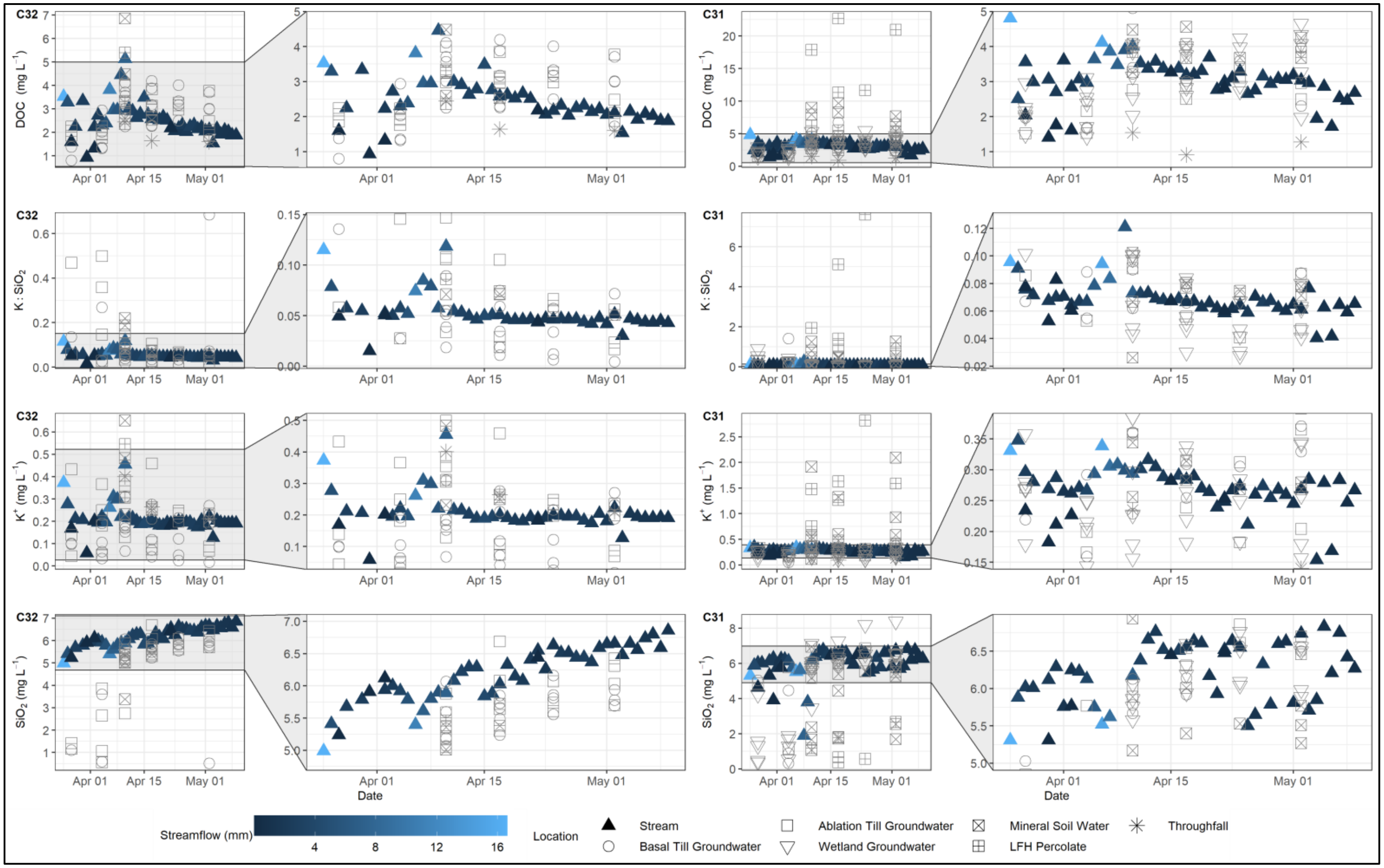

Figure 2.8 Freshet sampling period stream and hillslope solute pool DOC concentrations, K:SiO$_2$ ratios, K$^+$ concentrations, and SiO$_2$ concentrations for C32 (unharvested control) and C31 (legacy clear-cut). Zoomed facets (grey shading) highlight the range of stream values. Colour denotes total daily streamflow (mm).

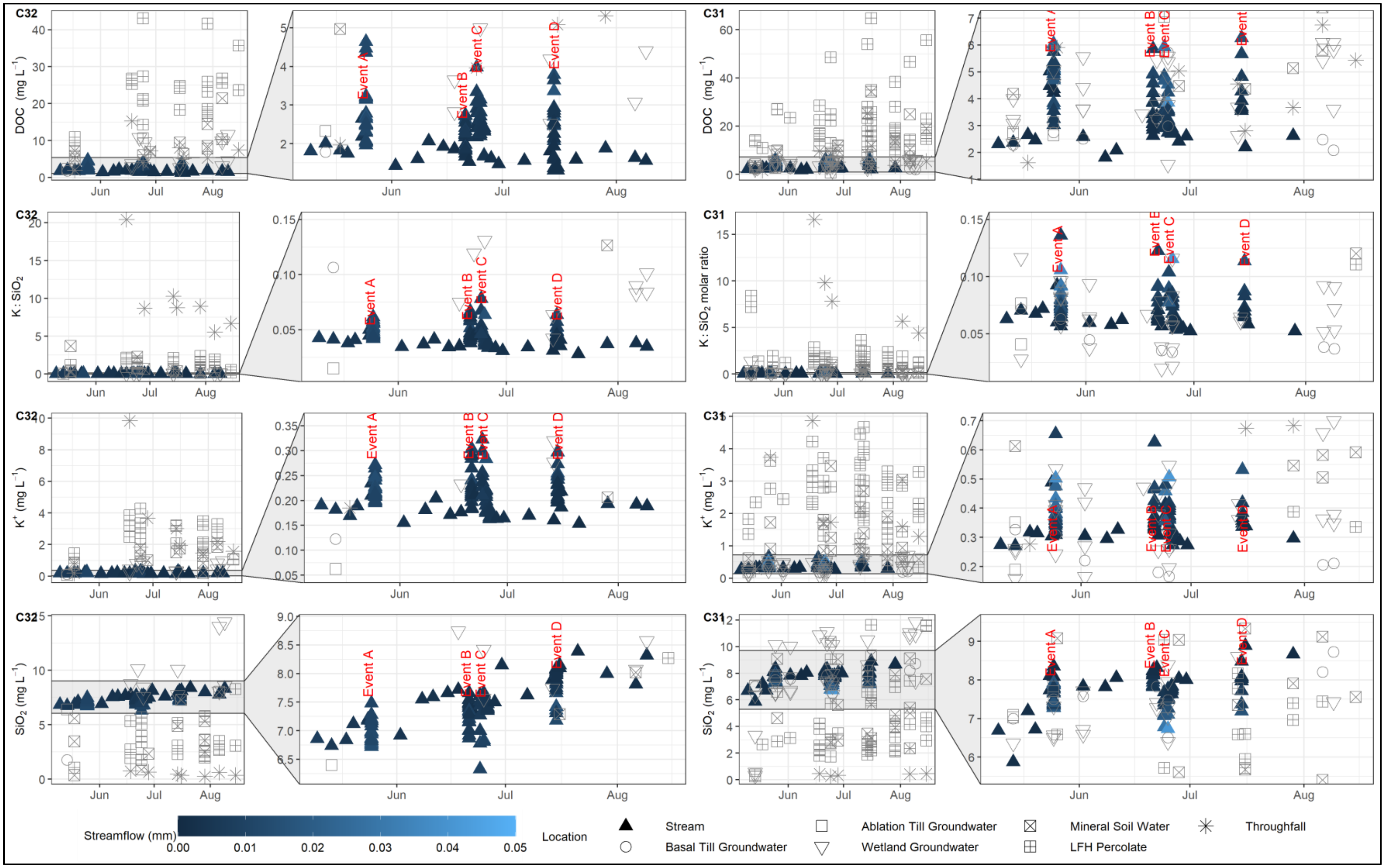

Figure 2.9 Intermediate sampling period stream and hillslope solute pool DOC concentrations, K:SiO$_2$ ratios, K$^+$ concentrations, and SiO$_2$ concentrations for C32 (unharvested control) and C31 (legacy clear-cut). ***Zoomed facets highlight stream weir values.*** **Colour denotes streamflow (mm). Precipitation events A-D indicated by red text.**

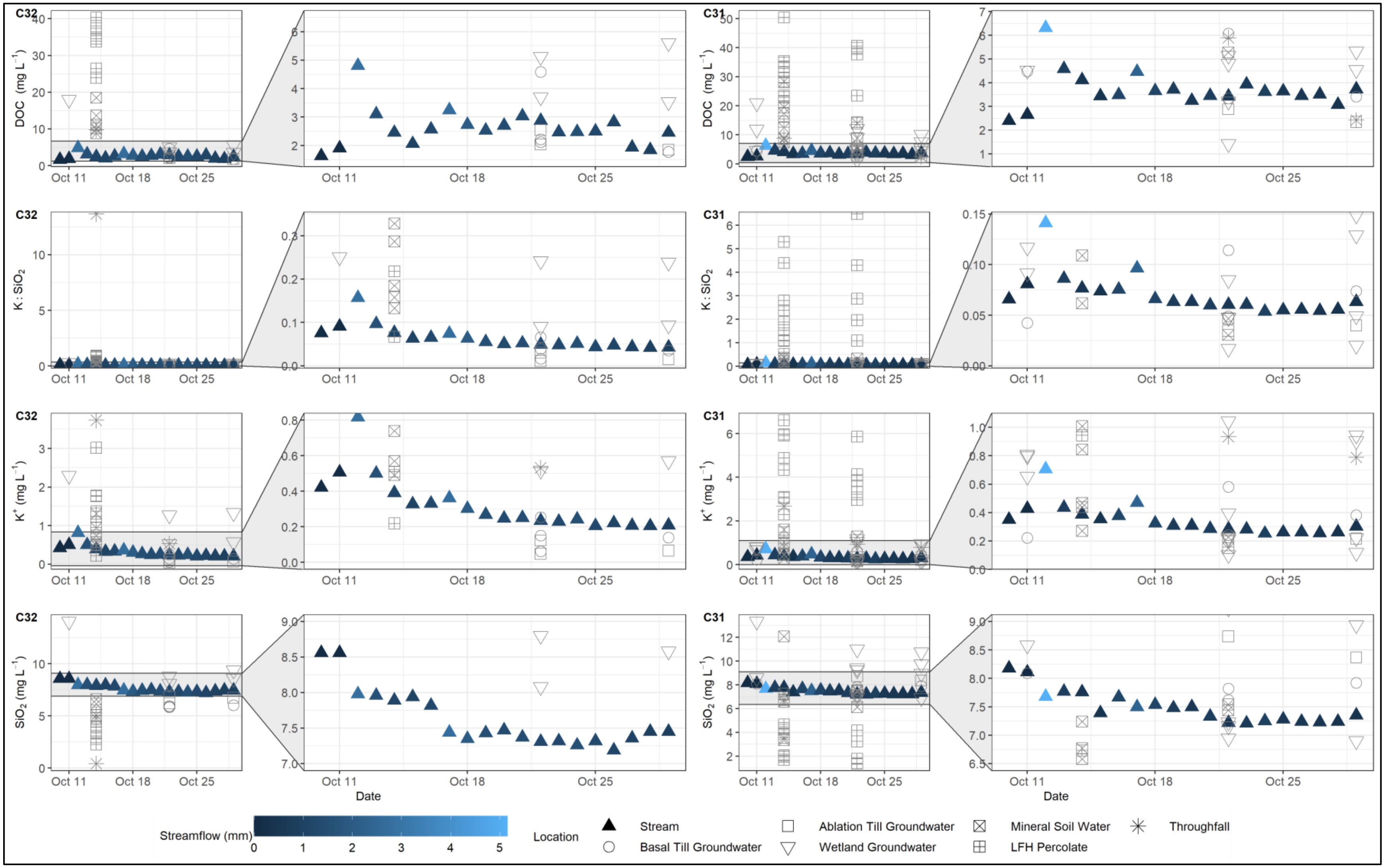

Figure 2.10 Fall sampling period stream and hillslope solute pool DOC concentrations, K:SiO_2 ratios, K^+ concentrations, and SiO_2 concentrations for C32 (unharvested control) and C31 (legacy clear-cut). Zoomed facets highlight streamvalues. Colour denotes total daily streamflow (mm).

2.5 Discussion

2.5.1 Hillslope Solute Pool and Wetland Controls on Stream DOC Concentration and Export – Intra-catchment Insights from DOC Concentration-Discharge Regression Analysis and $K:SiO_2$

Hillslope solute pool DOC concentrations, stream DOC concentration-discharge regression relationships and the aqueous potassium silica molar ratio were used to determine inter- and intra-catchment patterns in the concentrations, spatial distribution, and hydrologic connectivity of hillslope solute pool DOC in C32 and C31. Intra-catchment vertical stratification of DOC concentrations was observed for the hillslope solute pools in both catchments. Relatively high DOC concentrations were observed in the organic-rich, upper soil horizon solute pools (LFH percolate and mineral soil water) whereas relatively low DOC concentrations were found in the basal and ablation till groundwater solute pools (Figure 2.4b). Decreases in DOC concentration with depth in the soil profile are well documented for forested watersheds (Hope et al., 1994; Kaiser & Kalbitz, 2012) and are commonly attributed to complex mechanisms of organic matter retention, transformation, and degradation including DOC adsorption to and/or co-precipitation with mineral soils (McDowell & Likens, 1988; Kalbitz et al., 2005; Mikutta et al., 2007).

Concentration-discharge regression analysis suggests that DOC export behaviour in both C32 and C31 is primarily transport-limited (flushing). DOC concentrations in both study catchments were positively correlated with discharge and peaked during high-flow events (freshet and precipitation). These results are consistent with a previously reported study in TLW (Semkin et al., 2002) and widely documented elsewhere for forested catchments (Ågren et al., 2010; Hagedorn et al., 2000; Kaiser & Guggenberger, 2005; Raymond & Saiers, 2010). Shifting flowpaths and rising water tables during high-flow conditions in forested catchments can saturate organic-rich riparian zones and upper soil horizons thus promoting lateral hillslope-stream DOC transport (Hood et al., 2006; Vidon et al., 2008). Notably, both flushing and chemostatic DOC – Q behaviour has been previously observed in C32 (McPhail et al., 2023). Despite the classification of the DOC dynamics in C32 and C31 as predominantly "flushing" in this study, the slopes of the ln(DOC) – ln(Q) regression relationships were consistently <0.5 in both basins. This result is consistent with observations from other small, boreal forested catchments which commonly report weak C – Q relationships (Ducharme et al., 2021; Oswald & Branfireun, 2014). For any given flow condition, C31 had lower CV_{DOC}/CV_{Q} ratios compared to C32, suggesting a relatively homogenous/uniform distribution of solute sources in C31 whereby shifts in hydrologic connectivity (flowpath changes) do not influence DOC concentrations (Musolff et al., 2015). Should harvest-induced flowpath changes still be impacting stream DOC in C31, it could be expected that changing flowpaths, such as the contribution of fast, near-surface flowpaths associated with clearcut harvesting in C31, would be reflected in the C-Q framework and result in relatively higher CV_{DOC}/CV_{Q} ratios for C31. However, this hypothesis is not supported by the data in the present study but suggest the presence of a wetland near the catchment outlet in the unharvested reference C32 may be influencing that catchment's relatively higher CV_{DOC}/CV_{Q} ratios and thereby masking harvesting impacts in C31. Wetland cover as a fraction of catchment area has been positively correlated with CV_{DOC}/CV_{Q} in undisturbed headwater catchments of TLW (McPhail et al., 2023). Notably, relative wetland extent in C32 (1%) was lower than C31 (3%), which seemingly contradicts the findings of McPhail et al. (2023). However, McPhail et al. (2023) also discussed the possibility that wetland position, in addition to relative wetland extent, may impact CV_{C}/CV_{Q}. The influence of wetland proximity on streamflow and chemistry, particularly in relation to variability in DOC concentrations and export is well documented. Wetland proportion (% area of watershed) is a good predictor of dissolved organic carbon concentrations in headwater catchments of southern Ontario (Casson et al., 2019). Lane et al. (2020) established that wetlands in small catchments of the southern Boreal Precambrian Shield can accelerate the movement of water during wet antecedent conditions or, conversely, delay water movement under dry conditions.

Variability in K:SiO_2 in stream samples was used as a proxy indicator of changing hydrologic connectivity and flowpaths at seasonal and event-scales, such that higher K:SiO_2 ratios are indicative of faster surface flowpaths and lower K:SiO_2 ratios denote slower, deeper flowpaths. Previous work on K:SiO_2 at TLW provided evidence for harvest-induced flowpath shifts in favour of faster, near-surface flowpaths (Monteith et al., 2006b; Buttle et al., 2018). In the present study, K:SiO_2 ratios in both catchments were most similar to the ablation till groundwater, basal till groundwater, and wetland groundwater across all sampling periods (freshet, intermediate, and fall), tending toward the upper range of the groundwater solute pools only under high flow conditions. Some limitation is placed on this interpretation due to the spatial variability inherent to each hillslope solute pool, even within the same sampling period. Previous, freshet-centric work on flowpaths at TLW highlights the importance of shallow soil water pathways, routed above the ablation till / basal till contact (Hazlett et al., 2001) by means of a perched water table over the basal till (Semkin et al., 2002). Perhaps most importantly, the insights offered through this study's K:SiO_2 analysis findings agree with the recent findings in Fines (2023) that evaluated end-member contributions to streamflow in C32 and C31 using end-member mixing analysis for the freshet sampling period, for two precipitation events, and for the fall sampling period. End-member mixing analysis revealed that stream chemistry in C32 and C31 is primarily driven by basal and ablation till groundwater, with wetland groundwater contributions in both catchments, especially C32. Accordingly, the agreement of this study with Fines (2023) provides some support for the continued use of K:SiO_2 as a proxy for changing flowpaths at TLW. Nonetheless, the future use of K:SiO_2 as a flowpath proxy in C32, and its insight in this study, may be hindered by the confounding influence of wetlands on SiO_2 (Leach et al., 2020). In summary, with respect to inter- and intra-catchment patterns in both DOC concentrations and K:SiO_2, catchment C31 demonstrated DOC concentration-discharge and flowpath patterns typical of forest-dominated headwater catchments, whereas the patterns observed in C32 likely point to a comingling influence of forest-dominated and wetland-dominated characteristics due to the presence of a wetland near the outlet of C32.

2.5.2 Legacy Clearcutting Implications for Stream DOC Variability

Dissolved organic carbon concentrations in surface waters are a critical metric for the design and operations of drinking water treatment plants (Emelko et al., 2011). In the present study, stream DOC concentrations and stream DOC export were evaluated in an unharvested control catchment (C32) and a legacy clearcut catchment (C31) in the Turkey Lakes experimental watershed across a range of flow conditions.

A statistically significant (Mann-Whitney U test, $p \leq 0.05$) inter-catchment difference in stream DOC concentrations was observed for each sampled flow condition, with C31 yielding higher stream DOC concentrations relative to C32. Absolute values of the mean inter-catchment differences in stream DOC concentration (0.53 – 2.01 mg L^{-1}) exceeded the reported detection limit for DOC in this study (0.400 mg L^{-1}). The overall mean inter-catchment difference in stream DOC concentration, 1.21 mg L^{-1}, aligns with previously reported increases in stream DOC attributed to forest harvesting: 1 mg L^{-1} (modelled, Oni et al., 2015), 1.02 mg L^{-1} (mean peak increase, Webster et al., 2022), and 3.0 mg L^{-1} (net increase, clearcut vs reference, Schelker et al., 2012). Accordingly, the data of this study suggest a legacy impact of clearcut harvesting on stream DOC concentrations. In notable contrast to the persistent elevations of stream DOC concentrations in C31 relative to C32, stream DOC export differed inconsistently between the study catchments. Stream DOC export from C32 exceeded that of C31 under baseflow conditions, whereas stream DOC export in C31 was higher for the precipitation events A-C (Figure 2.3c) and the freshet and fall sampling periods showed no significant inter-catchment difference in stream DOC export (Mann-Whitney U test, $p > 0.05$, Figure 2.3c). The inconsistent inter-catchment differences in stream DOC may be explained in part by inter-catchment differences in streamflow. Throughout the study period, C32 experienced 0 no-flow days in contrast to the 48 no-flow days observed in C31 (Section 2.4.1). Streamflow in C32 generally exceeded streamflow in C31 under low-flow conditions, consistent with observations of relatively higher DOC export in C32, whereas peak flows in C31 such as event-scale hydrograph responses often exceeded C32, consistent with the relatively higher event-scale DOC exports observed in C31 (Figure 2.3c). Thus, while this study suggests that post-harvesting increases in stream DOC concentration are persisting in the study catchment, decadal-scale harvesting impacts on stream DOC concentration in northern hardwood-dominated headwater catchments is relatively low (~ 1 mg L^{-1} DOC), especially when considered in the context of intra-catchment variability observed within and across flow conditions in this study, and may not result in concurrent increases in stream DOC export. Accordingly, the data suggest that clear-cut harvesting may not pose a reasonable threat to downstream drinking water treatment operations at decadal-scales in northern hardwood-dominated headwater catchments.

Forest harvesting-induced elevations of stream DOC concentrations have been previously found at TLW (Webster et al., 2022) and in other settings (Laudon et al., 2009; Löfgren et al., 2009; Moore, 1989; Nieminen, 2004; Schelker et al., 2012; Tetzlaff et al., 2007; Yamashita et al., 2011). Post-harvest DOC elevations are typically attributed to one or more of the following (Kreutzweiser et al., 2008; Schelker et al., 2012): harvest-induced increases in hillslope solute pool DOC concentrations, increased water fluxes leading to enhanced DOC transport, and/or flowpath shifts in favour of faster, near-surface flowpaths which can intersect organic-rich upper soil horizons. Some insight into the influence, or lack thereof, of each of these mechanisms was provided by section 2.5.1 and is discussed in turn below.

No significant inter-catchment differences were observed for any hillslope solute pool DOC concentrations (Mann-Whitney U test, $p > 0.05$). This suggests that any impact(s) of clearcut harvesting on hillslope solute pool DOC concentrations have not persisted 24 years post-clearcut. Accordingly, the data do not support post-harvest impacts on hillslope solute pool DOC concentrations as an explanation for the relatively higher DOC concentrations observed in C31. Previous studies have reported both increases (Johnson et al., 1995) and decreases (Meyer & Tate, 1983) of hillslope solute pool DOC concentrations < 10 years post-harvest. Mixed findings may be due to inter-study differences in factors such as soil conditions and the timing and type of forest harvest used, among other site-specific conditions (Kreutzweiser et al., 2008).

There was limited evidence for persistent increases in water flux in the legacy clearcut catchment – peak streamflow in the legacy clearcut catchment C31 tended to exceed that of the unharvested reference catchment C32 but was lower under lower flow conditions. No-flow days were observed in C31 but not in C32. The observed inter-catchment differences in streamflow may simply be related to different, catchment-inherent behaviours due to the presence of a wetland near the outlet of C32, rather than to legacy clearcut harvesting impacts. As a detailed hydrologic comparison of pre- vs. post-harvest streamflow dynamics in C31 is outside the scope of this study, the possibility of persistent, post-harvest impacts on streamflow in C31 may not be rejected but is not explicitly supported by this study.

With respect to flowpaths and hydrologic conductivity, as evaluated in this study by the aqueous potassium silica molar ratio, there is no evidence to suggest that harvest-induced flowpath changes are, 24 years post-clearcutting, impacting stream DOC concentrations in C31. While peak stream DOC concentrations and streamflow in C31 were higher than C32, this is not in itself conclusive evidence of harvesting impacts. Additionally, should flowpath changes be impacting DOC concentrations in C31, it might be expected that, in contrast to the results of the DOC concentration-discharge regression analysis, the CV_{DOC}/CV_{Q} ratios in C31 would exceed those of C32, representing the expected scenario where flowpath changes made a larger difference in the legacy clearcut catchment.

Data in this study do not support the mechanisms typically attributed to post-harvest increases in stream DOC concentrations, therefore other possible factors may be considered. In particular, the levels of stream DOC in C31 under baseflow conditions is of note and consistent with the pattern observed by Laudon et al. (2009) for harvested boreal catchments in Sweden who noted that, although harvesting impacts on stream DOC concentrations under high flow conditions may be explained by factors commonly associated with forest harvesting such as higher water tables and flowpath changes, the presence of persistently elevated DOC concentrations under groundwater-driven baseflow conditions may require further investigation. A possible explanation for elevated baseflow stream DOC concentrations observed in harvested catchments was discussed in Laudon et al. (2009) - the release of DOC from harvesting residues (e.g. stumps, branches, twigs) which may, over time, reach the deeper groundwater pools which typically contribute to baseflow in forested catchments. Although Laudon et al. (2009) deemed the explanation not applicable within the context of their investigation (1-year post-clearcut), the mechanism may have more merit in the present study (approximately 24 years post-clearcut). The suggestion of a missing “endmember” in Fines (2023) may provide some insight as to why stream DOC concentrations in C31 exceeded C32 under baseflow conditions in this study. It is possible that a groundwater endmember may be contributing to baseflow in C31 (Fines, 2023) with a DOC concentration influenced by the release and downward vertical transport of DOC from harvesting residues over time (Laudon et al., 2009). Yamashita et al. (2011) suggested that decadal-scale, harvest-induced differences in vegetation (e.g. leaf litter quality) and in processes of organic matter accumulation and deposition in organic horizons could result in long-term effects on stream DOC. This hypothesis is supported by observations of the water table being below the depth of most basal and ablation till piezometers in C31 during this study's intermediate sampling period (Section 3.2.2). It is also possible that inter-catchment differences in basal and/or ablation till groundwater DOC concentration which may be related to forest harvesting were obscured in this study simply due to low sample sizes (Chapter 2, Section 2.4.2.3). However, as noted by Lee & Lajtha (2016), post-harvest decreases in organic matter inputs via coarse woody debris may also impact stream DOC concentrations on decadal time scales. Another factor which may be influencing inter-catchment differences in streamflow and/or stream DOC is vegetation regrowth in C31, in favour of pioneer species such as yellow birth and cherry, with implications for transpiration and water availability (Buttle et al., 2018). The data of this study cannot distinguish among these potential factors. Additionally, the persistent inter-catchment differences in DOC concentrations observed in this study may not be related to forest harvesting but rather to inherent inter-catchment differences in the spatial distribution, DOC concentration, and hydrologic connectivity of landscape components known to impact stream DOC dynamics such as cryptic wetlands (Creed et al., 2003), characteristics of the riparian zone, discrete riparian inflow points, and subsurface geology (Ploum et al., 2020).

Overall, while the data of this study suggest a persistent, decadal-scale impact of clearcut harvesting on stream DOC concentrations of approximately 1 mg L^{-1}, the data did not provide evidence for the persistence of commonly cited post-harvest mechanisms of stream DOC. It is possible that, over time, the relevance of individual post-harvest mechanisms shifts from commonly cited, short-term impacts (flowpath changes, higher water tables, etc.) to other, less well-understood impacts. Further research is needed to better understand the factors influencing stream DOC in post-harvest headwater catchments at decadal timescales, especially with respect to groundwater-driven baseflow conditions. Additional research investigating decadal-scale impacts of clearcut harvesting on stream DOC in northern hardwood-dominated headwater catchments would benefit from the inclusion of inter-annual data, of

DOC character data, and of study sites which include common, harvest-associated linear features such as skid trails, roads and culverts.

2.6 Conclusions

Stream and hillslope solute pool DOC concentrations were evaluated in an unharvested reference catchment and a legacy clearcut catchment at the Turkey Lakes Watershed under a range of flow and seasonal conditions. The potassium-silica molar ratio and DOC concentration-discharge regression relationships were also evaluated to elucidate the influences of changing flowpaths and the spatial distribution of hillslope DOC on stream DOC. While stream DOC concentrations in the clearcut catchment were higher than (mean increase 1.21 mg L^{-1}) and significantly different (Mann-Whitney U test, $p \leq 0.05$) from those in the unharvested reference catchment, no significant inter-catchment differences were observed in the DOC concentrations of various hillslope solute pools. DOC export differed variably between the study catchments. Concentration-discharge regression analysis for DOC, coupled with the aqueous potassium silica molar ratio as a proxy for changing flowpaths and hydrologic connectivity, suggested similar and primarily groundwater-driven streamflow in both catchments across various seasonal and hydrologic conditions, albeit with a strong wetland influence in C32 likely due to the proximity of C32's wetland to the catchment outlet. Fluctuations in the $K:SiO_2$ molar ratio were generally synchronous with changes in DOC concentration at the weirs of both basins, with the latter exhibiting flushing (transport-limited) behaviour in both basins under almost all observed flow conditions. Although the results of this study support a persistent and decadal-scale impact of clearcut harvesting on stream dissolved organic carbon at Turkey Lakes Watershed, the effect was limited and likely does not represent a threat to downstream drinking water treatment operations. Further research is needed to understand how the impacts of forest harvesting, and the associated mechanisms, propagate over time. In particular, the data of this study raise questions about post-harvest factors influencing stream DOC under baseflow conditions. The results of this study also highlight that the relative location of wetlands can have a considerable impact on stream DOC variability in forested headwater catchments and may hinder the ability of a paired-catchment design to conclusively evaluate forest harvesting impacts on stream DOC. Complementary lines of inquiry to this study include an evaluation of stream and hillslope solute pool DOC character in post-harvest watersheds and the identification of additional DOC source pools on the landscape thus providing a more complete understanding of the long-term impacts of clearcut harvesting practices in forested headwater catchments of the Boreal Shield.

Chapter 3. Wetland Position and Legacy Harvesting Influence Event-Scale Dynamics of Stream DOC Concentration and Character in Northern Hardwood-Dominated Headwater Catchments

3.1 Abstract

Forested landscapes are critical source regions for the supply of high-quality drinking water to downstream communities. Landscape disturbances such as forest harvesting can degrade water quality and alter both the amount and character of dissolved organic carbon (DOC) with potential implications for downstream drinking water treatment operations. Liquid-chromatography organic carbon detection (LC-OCD) is used in this study to examine event-scale variability in the concentration, specific UV absorbance (SUVA), and fractional composition of DOC in streams and hillslope solute pools (basal and ablation till groundwater, wetland groundwater, mineral soil water, LFH percolate, throughfall) draining two northern hardwood-dominated headwater catchments with different forest harvest histories (unharvested reference and approximately 24 years post-clearcut). The DOC concentrations, SUVA, and DOC fractional composition of stream and hillslope solute pool samples were characterized during three precipitation events of varying magnitude, duration, and antecedent moisture condition. The humic substance fraction and the hydrophobic organic carbon fraction were the predominant contributors to stream DOC in both catchments. Concentrations of DOC and the relative proportion of the humic substances fraction were higher in the stream draining the legacy clearcut catchment, while the hydrophobic organic carbon fraction was relatively higher in the stream draining the unharvested reference catchment. The data suggest that streamflow in both catchments is derived primarily from groundwater, although inter-catchment, intra-event differences in the dynamics and fractional composition of stream DOC are strongly related to the proximity of a wetland to the outlet of the unharvested reference catchment with some evidence pointing to decadal-scale forest harvesting

impacts on stream DOC concentration and character. This study contributes to recent advances in the LC-OCD-based characterization of stream and hillslope solute pool DOC in forested watersheds, improves our understanding of event-scale DOC dynamics in northern hardwood-dominated watersheds, and inspires further research into the joint influences of forest harvest history and wetland position on DOC concentration and character in harvested and unharvested headwater catchments.

3.2 Introduction

Dissolved organic matter (DOM) is a complex, heterogenous mixture of soluble organic compounds found ubiquitously in natural waters (Hutchins et al., 2017). In fluvial systems, the amount and character of DOM can influence biogeochemical processes, food web stability, and the downstream transport of contaminants such as heavy metals (Aiken et al., 2011). Notably, the quantity and variability of DOM is a key design consideration for water treatment plant design and operations (Chow et al., 2008; Emelko et al., 2011; Parsons et al., 2004; Shi et al., 2021).

Changes in the concentration, yield, and/or character of stream DOM have been linked to natural and anthropogenic landscape disturbances such as urbanization (Zhang et al., 2022), agriculture (Pisani et al., 2020; Wilson & Xenopoulos, 2013), wildfire (Roebuck et al., 2022) and forest harvesting (Lee & Lajtha, 2016; Yamashita et al., 2011). Notably, these disturbances can increase the downstream propagation of DOM (Schelker et al., 2014) and challenge downstream drinking water treatment operations (Emelko et al., 2011; Shi et al., 2020). High concentrations of DOM in lower quality source waters have been associated with increased coagulant demands, decreased treatment efficiency, taste and odour problems, and the formation of potentially harmful disinfection by-products (Emelko et al., 2011; Ritson et al., 2014). Changes in DOM character can strongly influence coagulation and other treatment protocols required to process source water for safe consumption (Chow et al., 2008; Fabris et al., 2008; Krzeminski et al., 2019; Volk et al., 2005). Thus, increased knowledge of the mechanisms and factors driving temporal variability in stream DOM in relation to streamflow and watershed disturbance is necessary for the sustainable management of forested watersheds for the ecosystem service of source water provision.

Forest harvesting is a major stand-replacing disturbance agent in Canada's boreal forests with known impacts on forest biogeochemistry and hydrology (Kreutzweiser et al., 2008). Forest harvesting practices can alter biogeochemical and hydrologic processes which typically govern the development, mobilization, and export of dissolved organic matter into receiving waters through alterations to soil evapotranspiration, soil porosity, soil hydraulic conductivity, and runoff generation processes (Kreutzweiser et al., 2008) that result from the removal of canopy cover and vegetation (Oda et al., 2021). Multiple studies have investigated the impact of forest harvesting practices on the concentration and/or character of stream DOM, often expressed as DOC, with mixed results (Schelker et al., 2012; Laudon et al., 2009). Notably, focus is almost always given to the immediate (<10 year) impacts of harvesting on DOM concentration and/or character and few studies report the legacy impacts of forest harvesting. Lee & Lajtha (2016) investigated stream DOM quantity and quality 50-60 years post-harvest in watersheds of the H.J. Andrews Experimental Forest. They saw lower DOM concentrations and a higher proportion of protein-like DOM in legacy harvested watersheds compared to unharvested watersheds. In contrast, Yamashita et al. (2011) found higher DOM concentrations in a clear-cut watershed 30 years post-harvest. Lajtha & Jones (2018) found that harvest-induced impacts on stream DOC flux persisted 30-50 years post harvesting, while Lepistö et al. (2014) saw minimal harvesting impacts on short- and long-term total organic carbon fluxes. Such differing results point to the need for further research on the variability and drivers of DOM in watersheds affected by legacy forest harvesting. Notably, long-term impact studies are often hindered by necessarily low-frequency sampling regimes (e.g. monthly sample collection) which may not be sufficient to capture seasonal and sub-daily event variability in DOM concentration and character during precipitation events (Mistick & Johnson, 2020).

Precipitation is a key driver of DOM mobilization in forested watersheds as, during precipitation events, rising water tables can intersect organic-rich upper soil horizons, causing lateral hillslope-stream transport from DOM-rich riparian and hillslope source pools which may not have been hydrologically connected under dry conditions (Hood et al., 2006; Vidon et al., 2008). Multiple studies have reported event-scale changes in stream DOM concentration and character in response to precipitation events, often expressing DOM character using the specific UV absorbance at 254nm (SUVA) (Hood et al., 2006; Lee & Lajtha, 2016; Saraceno et al., 2009), considered a proxy for aromaticity. Specifically, stream DOM aromaticity has been shown to increase during precipitation events relative to baseflow conditions (Hood et al., 2006; van Verseveld et al., 2008) with the change often related to DOM contributions from aromatic, organic-rich riparian and surficial solute pools (Hood et al., 2006). Notably, the meaningful interpretation of event-scale changes in the amount and character of stream DOM can benefit from the concurrent characterization of hillslope solute pool DOM (Hood et al., 2006; Singh et al., 2015).

Liquid-chromatography organic carbon detection (LC-OCD) is a version of size-exclusion chromatography (SEC) coupled with organic carbon detection (OCD) often used for DOM characterization in the context of drinking water treatment operations (Baghoth et al., 2011; Chen et al., 2016; Krzeminski et al., 2019). In contrast to SUVA, LC-OCD considers both adsorbing and non-adsorbing DOM components (Aukes et al., 2021). This technique separates DOM into five method-defined, molecular-weight-based fractions and quantifies each fraction with respect to DOC (Huber et al., 2011). However, the use of LC-OCD to characterize surface and/or subsurface DOC in forested watersheds is limited. Studies to date focus primarily on single catchments (He et al., 2016), comparisons across ecozones or other geographical divisions (Aukes et al., 2021; Rutlidge et al., 2021), or comparisons along stream networks (Hutchins et al., 2017). To our knowledge, no study to date has yet applied high-frequency LC-OCD analysis to evaluate event-scale variability in the concentration and fractional composition of stream DOC in headwater catchments of contrasting forest harvest history, nor have the spatial patterns of hillslope DOC fractional composition in soil water been assessed in legacy (> 10 years) clearcut headwater catchments.

The goal of the present study is to investigate event-scale variability in DOC concentration and character in two forested Boreal headwater catchments with contrasting levels of landscape disturbance (unharvested reference and legacy (24 years) clearcut). Dissolved organic carbon character was evaluated using LC-OCD and expressed in terms of SUVA and in terms of fractional composition for stream samples and for hillslope solute pool samples hypothesized to contribute to streamflow (basal and ablation till groundwater, wetland groundwater, mineral soil water, LFH percolate, and throughfall). The SUVA value of water samples provides an assessment of potential water treatment impacts. Objectives of the study are to 1) evaluate and contrast variability in the concentration, SUVA, and fractional composition of stream DOC during three precipitation events of varying magnitudes, durations, and antecedent conditions ma in the study catchments, 2) evaluate inter- and intra-catchment variability in the concentration, SUVA, and fractional composition of hillslope solute pool DOC, and 3) assess spatial patterns in the concentration, SUVA, and fractional composition of stream and hillslope solute pool DOC in the study catchments using principal component analysis.

3.3 Methods

3.3.1 Study Site and Experimental Design

Please see Chapter 1, sections 1.3.2 and 1.3.3. for details on the study site and experimental design.

3.3.2 Field Methods

3.3.2.1 Hydrometeorological Monitoring

Streamflow was continuously monitored at the outlets of C32 and C31 using 90° V-notch weirs with stilling basins and Steven's Smart PT SDI-12™ pressure and temperature transducers. The resultant stage values were converted to instantaneous discharge. Ten-minute precipitation data were recorded approximately 0.4 km southeast of the study basins at a Natural Resources Canada monitoring station ("Meadow Station", Figure 1) using an OTT Pluvio tipping bucket gauge (Jason Leach, personal communication, 2021).

3.3.2.2 Stream Sampling

Stream sampling occurred during three high-flow events in 2021: two short-duration precipitation events in June (hereafter Events 1 and 2), and a period of multiple days of intermittent precipitation in October (hereafter Event 3). Stream samples were collected using automated ISCO 6700 samplers with acid-washed, triple-rinsed 1L polypropylene sampling bottles. Sample collection frequency for the two June precipitation events (hourly and every two hours for Events 1 and 2, respectively) were pre-set based on the forecasted intensity, timing, and duration of precipitation. During Event 3, daily composite samples made up of samples taken every 6 hours were collected.

3.3.2.3 Hillslope Solute Pool Sampling

The hillslopes of catchments C32 and C31 were extensively instrumented to evaluate spatial and temporal variability in the DOC concentrations, SUVA, and DOC fractional composition of hillslope solute pools: basal till groundwater, ablation till groundwater, wetland groundwater, mineral soil water, LFH percolate, and throughfall. Figure 3.1 illustrates the field instrumentation in C32 and C31. Details are described below for the hillslope solute pools. The samples used in this study represent a subset of samples collected in June and October 2021.

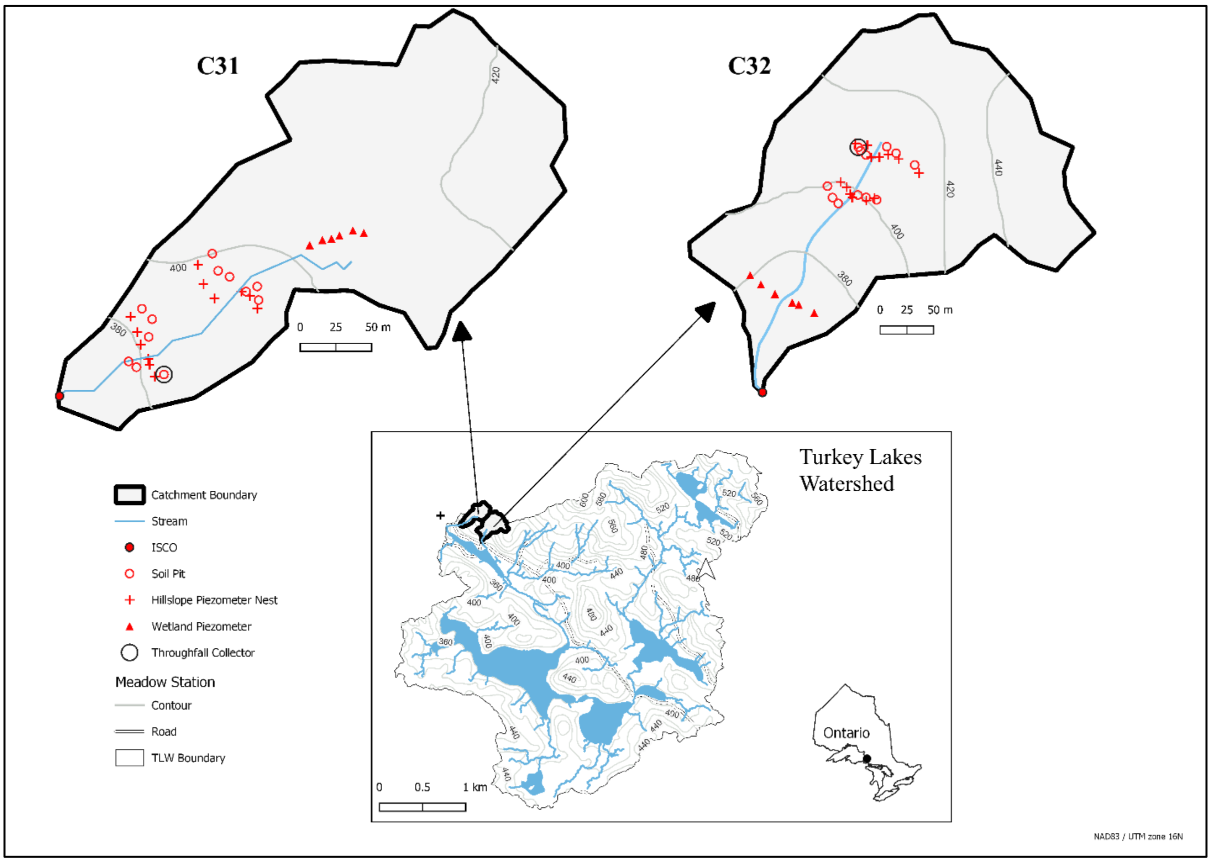

Figure 3.1 Field Instrumentation in C32 and C31.

3.3.2.3.1 Groundwater Sampling

Basal till and ablation till groundwater were sampled from 2 cm i.d. drive-point piezometers (Solinst Canada Ltd) positioned along hillslope transects (topslope-midslope-toeslope) perpendicular to, and on each side of both study catchment streams (Monteith et al., 2006a; Monteith et al., 2006b, Figure 3.1). At each piezometer nest, one piezometer was screened in both the basal till and the ablation till.

Ablation till piezometer installation depths were 0.40 ± 0.03 m in C32 and 0.45 ± 0.05 m in C32. Basal till piezometer installation depths were 0.93 ± 0.09 m in C32 and 1.09 ± 0.19 m in C31. Wetland groundwater was sampled from a transect of six piezometers in each catchment's wetland (Figure 3.1). Piezometer installation depths in the wetlands were (mean ± SD) 0.37 ± 0.03 m and 0.39 ± 0.03 m for C32 and C31, respectively.

Groundwater samples were collected once during each Event 1 and 2. During Event 3, groundwater samples were collected approximately weekly. Piezometers were purged 24 hours prior to sampling using a peristaltic pump (Monteith et al., 2006b). A piezometer was considered purged once a) it was dry, or b) 5 minutes had elapsed, whichever came first. Pump hose lines were triple-rinsed with DI water between samples to reduce cross-contamination between piezometers. Samples were collected in acid-washed, triple-rinsed 500 mL HDPE field bottles rinsed three times with sample water.

3.3.2.3.2 Mineral Soil Water and LFH Percolate Sampling

To evaluate the fractional composition of dissolved organic carbon in shallow subsurface soil, mineral soil water and LFH percolate samples were collected from zero-tension lysimeters installed laterally into the upslope-facing cut faces of soil pits manually excavated approximately next to each piezometer nest (Figure 3.1). Lysimeters were installed in October of 2020 to allow for an equilibration time of 8 months. The lysimeters discharged into 1 L acid-washed, triple-rinsed HDPE sampling bottles located in protective plastic totes. The lysimeter bottles were collected and replaced in advance of Event 1 and 2 to ensure an accurate representation of each event. During Event 3, the lysimeter bottles were checked approximately weekly and within 24 hours of groundwater sampling.

3.3.2.3.3 Throughfall Sampling

A throughfall collector was constructed in each basin (Figure 3.1), entailing a plastic funnel, protected from the accumulation of leaf litter by a mesh, attached to a steel post driven securely into the ground. The throughfall collectors discharged into 1 L acid-washed, triple-rinsed HDPE bottles in protective plastic pit liners. The collection of throughfall sample bottles was coincidental with the collection of the lysimeter sample bottles.

3.3.3 Analytical Methods

Samples were transported on ice from the field, refrigerated at 4°C, then frozen within approximately one week of collection. Refrigeration times and freezing were due to COVID-19-related lab closures and limited access. After thawing, all samples were filtered through 0.45 μm mixed cellulose ester filters (GN-6 Metricel, VWR) at the Great Lakes Forestry Centre in Sault Ste Marie, ON, Canada. DOC concentration, specific UV-absorbance, and fractional composition were evaluated using a Liquid-Chromatography Organic Carbon detection system (LC-OCD, DOC-Labor, Karlsruhe, Germany; Huber et al. 2011) at the University of Waterloo in Waterloo, Ontario, Canada. Detailed description of the LC-OCD procedure including materials and calibration standards is provided by Huber et al. (2011).

The LC-OCD system fractionates dissolved organic matter into 5 hydrophilic categories using a size-exclusion column (250 mm x 20 mm, TSK HW 50S, 3000 theoretical plates, Toso, Japan). The LC-OCD-defined fractions from highest to lowest molecular weight are 1) biopolymers (BP), 2) humic substances fraction (HS), 3) building blocks (BB), 4) low molecular-weight neutrals (LMWn) and 5) low molecular-weight acids (LMWa). A sixth DOC fraction includes the residue remaining in the chromatographic column, operationally designated as hydrophobic organic carbon (HOC). In addition to the fractionation, a part of each sample's volume bypasses the size exclusion column, is acidified, and is measured for DOC concentration using a Grantzel thin film UV-reactor (Huber et al., 2011). The

LC-OCD system also provides the DOC specific UV absorbance at 254 nm (SUVA) for each sample and for the HS fraction of each sample (hereafter SUVAhs). Table 3.1 provides further details on the LC-OCD-defined DOC fractions used in this study. The customized software ChromCalc (DOC-LABOR, Karlsruhe, Germany) was used to process LC-OCD chromatograms with all resultant data analyzed and visualized in R Studio (R Core Team, 2020). In cases where the DOC value for a given fraction was less than the applicable MDL (Table 3.1), the value for that fraction was set to 0.5* MDL (n = 3). This was done to minimize data loss.

A non-parametric statistical approach was taken for data analysis as normality assumptions were not met and sample sizes were often < 30. The non-parametric Mann-Whitney U test was employed to test for inter-catchment differences in the variables of interest. To prevent bias introduced by differences in stream sample sizes, tests for statistically significant differences included only those stream samples in either catchment for which a sample was collected at a corresponding time in the other catchment. Intra-catchment differences in the variables of interest were evaluated using the non-parametric Kruskall-Wallis test. Principal component analysis (PCA) was applied in R Studio to investigate spatial and temporal patterns in the variability of stream and hillslope solute pool DOC concentrations, SUVA, SUVAhs, and fractional composition (Aukes et al. 2021). The prcomp function in R Studio was used to scale and centre the variables prior to PCA analysis.

Table 3.1 Summary of LC-OCD-defined DOC fractions used in this study. Adapted from Huber et al., 2011. MDL values: Bill Anderson & Fariba Amiri, Email Communication (January 2022).

Metric	Abbreviation (this study)	Description	Approximate Molecular Weight (g/mol)	Method Detection Limit (ppb C)
Biopolymers Fraction	BP	Polysaccharides, proteins, amino sugars, polypeptides, TEPs, EPS	> 20,000	9
Humic Substances Fraction	HS	Humic and fulvic acids	~ 1000	9
Building Blocks Fraction	BB	Breakdown (weathering and oxidation) products of humic substances	300-500	26
Low Molecular Weight-Neutrals Fraction	LMWn	Includes mono-oligosaccharides, alcohols, aldehydes, ketones, amino acids	< 350	44
Low Molecular Weight-Acids Fraction	LMWa	Summaric value for monoprotic organic acids	< 350	7
Hydrophobic Organic Carbon Fraction	HOC	Compounds which do not elute from the chromatographic column	n/a, assumed to be high molecular weight	---

3.4 Results

3.4.1 Precipitation Event Characteristics and Hydrograph Responses

Hyetographs for the three precipitation events (10-minute intervals) are presented in Figure 3.2. Events 1 and 2 were relatively short-duration events in mid-summer with contrasting antecedent precipitation conditions. The 7-day total antecedent precipitation for Events 1 and 2 were, respectively, 12.4 mm and 56.4 mm. Of the 2021 total annual precipitation (1183.9 mm), Events 1-3 accounted respectively for 1.60 % (18.9 mm), 1.2 % (13.7 mm), and 8.27% (97.9 mm). Total streamflow in C32 was 0.6 mm, 1.8 mm, and 27.4 mm for Events 1-3 respectively. Total streamflow in C31 was 0.5 mm, 2.5 mm, and 18.5 mm for Events 1-3 respectively. Runoff ratios in both C32 and C31 were < 0.30 for all events. Event 2 was sampled on the falling limb of a previous peak but a secondary, albeit smaller, hydrograph response was measured. Notably, peak streamflows in C31 exceeded peak streamflows in C32 but then decreased to lower relative discharge on the recessional limbs of the hydrographs during each precipitation event (Figure 3.2).

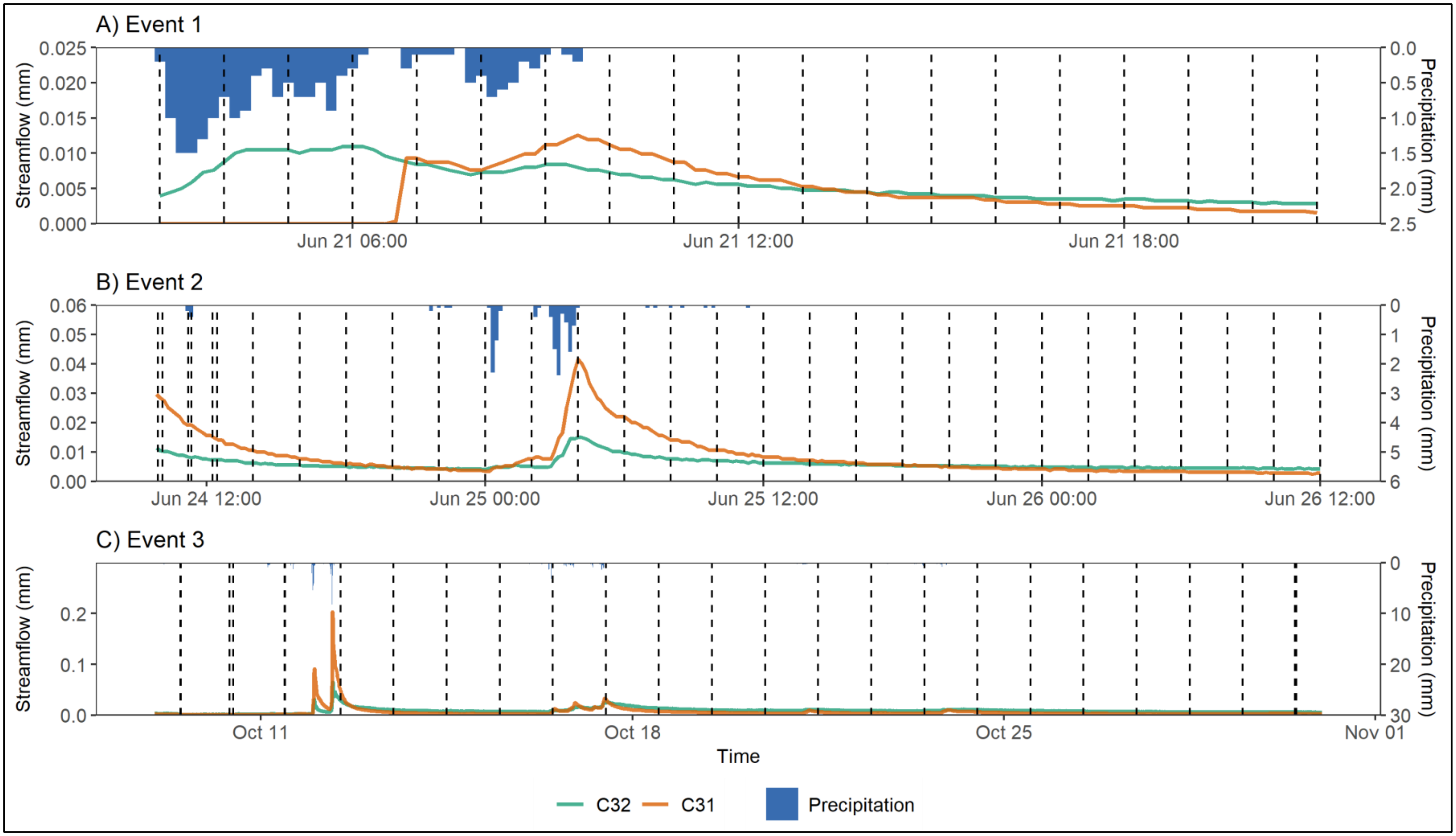

Figure 3.2 Precipitation and streamflow for Events 1 to 3. Dotted lines denote sampling times.

3.4.2 Event-scale Variability in Stream DOC Concentrations and Specific UV Absorbance

Event-scale variability in stream DOC concentrations, SUVA, and SUVAhs for catchments C32 and C31 is shown in Figure 3.3.

Dissolved organic carbon concentrations in C32 were (mean ± SD) 3 ± 1 mg L^{-1}, 4 ± 1 mg L^{-1}, and 3 ± 1 mg L^{-1} respectively for Events 1 ($n = 19$), 2 ($n = 27$), and 3 ($n = 22$). In C31, DOC concentrations were (mean ± SD) 5 ± 1 mg L^{-1}, 6 ± 1 mg L^{-1}, and 4 ± 1 mg L^{-1} for Events 1 ($n = 14$), 2 ($n = 27$), and 3 ($n = 20$), respectively. Additional descriptive statistics are given in Table 3.2. Significant inter-catchment differences in DOC concentration (Mann-Whitney U test, $p \leq 0.05$) were seen for the three precipitation events such that DOC concentrations were higher in C31 than C32 (Figure 3.3). DOC concentrations were visually synchronous with streamflow in both catchments (Figure 3.3).

With respect to SUVA, values in C32 were (mean ± SD) 3 ± 0 L mg^{-1} m^{-1} during Event 1, 3 ± 1 L mg^{-1} m^{-1} during event 2, and 3 ± 0 L mg^{-1} m^{-1} during Event 3. In C31, SUVA was (mean ± SD) 4 ± 1 L mg^{-1} m^{-1} during Event 1, 3 ± 0 L mg^{-1} m^{-1} during Event 2, and 3 ± 0 L mg^{-1} m^{-1} during Event 3. Additional descriptive statistics are given in Table 3.2. SUVA was significantly different between the catchments for Event 3 (Mann-Whitney U test, $p \leq 0.05$) with higher values seen in C31 (Figure 3.3). Specific UV absorbance values within C31 tended to follow changes in streamflow, while no visual trend was observed in C32 (Figure 3.3).

Values of SUVAhs (mean ± SD) for Events 1-3 in C32 were respectively 4 ± 1 L mg^{-1} m^{-1}, 3 ± 1 L mg^{-1} m^{-1}, and 4 ± 0 L mg^{-1} m^{-1}. The corresponding SUVAhs values in C31 were (mean ± SD) 4 ± 1 L mg^{-1} m^{-1}, 3 ± 0 L mg^{-1} m^{-1}, and 4 ± 0 L mg^{-1} m^{-1}. Additional descriptive statistics are given in Table 3.2. No significant inter-catchment differences in SUVAhs were seen for any event. During Events 1 and 2, SUVAhs variability in C31 resembled streamflow, while in C32 no visual trend was observed (Figure 3.3). An overall downward trend in SUVAhs was visible for both catchments during Event 3 (Figure 3.3).

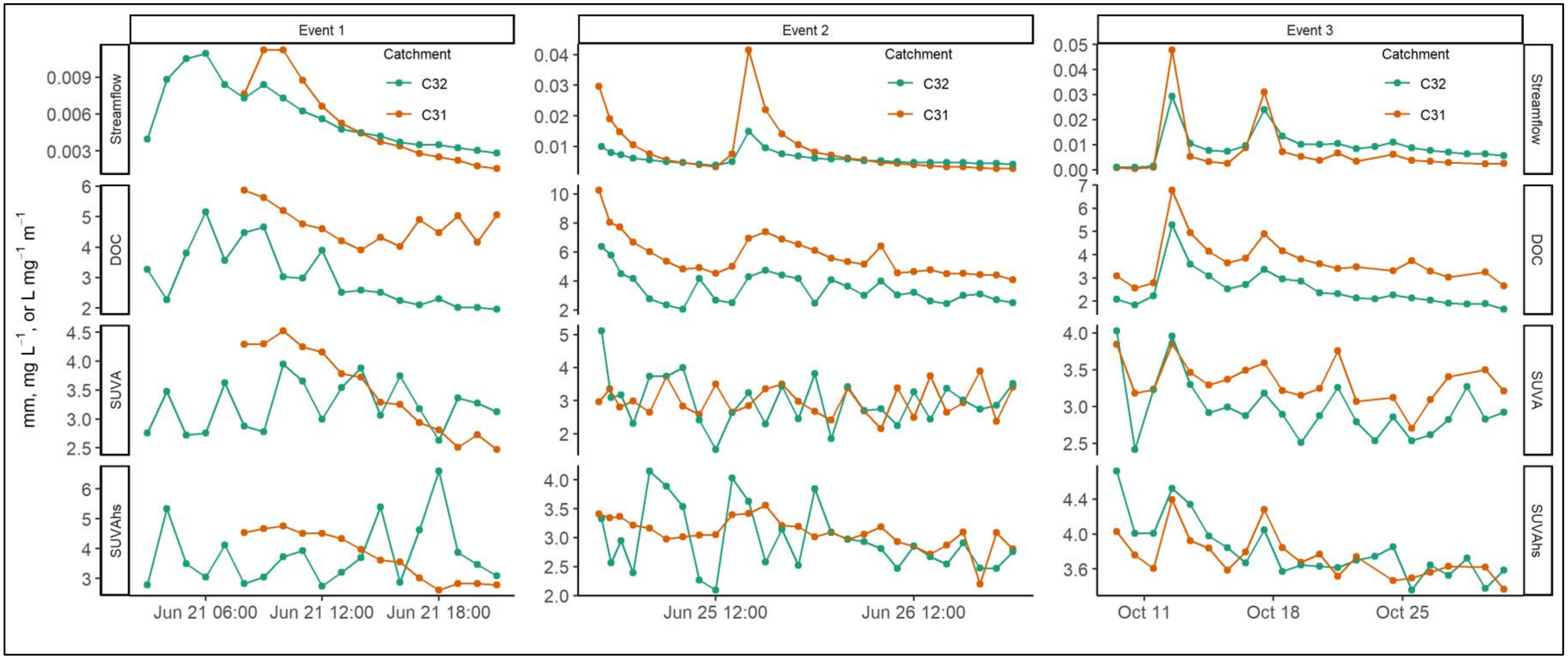

Figure 3.3 Event-scale variability in streamflow, stream DOC concentration, SUVA, and SUVAhs.

Table 3.2 Descriptive statistics of stream DOC concentration, SUVA, and SUVAhs. The reader is referred to Table 3.1 for abbreviation definitions.

Event	**Catchment**	**n**		**DOC** ($mg\ L^{-1}$)	**SUVA** ($L\ mg^{-1}\ m^{-1}$)	**SUVAhs** ($L\ mg^{-1}\ m^{-1}$)
1	C32	19	Range	2 – 5	3 – 4	3 – 7
			Mean ± SD	3 ± 1	3 ± 0	4 ± 1
	C31	14	Range	4 – 6	2 – 5	3 – 5
			Mean ± SD	5 ± 1	4 ± 1	4 ± 1
2	C32	27	Range	2 – 6	2 – 5	2 – 4
			Mean ± SD	4 ± 1	3 ± 1	3 ± 1
	C31	27	Range	4 – 10	2 – 4	2 – 4
			Mean ± SD	6 ± 1	3 ± 0	3 ± 0
3	C32	22	Range	2 – 5	2 – 4	3 – 5
			Mean ± SD	3 ± 1	3 ± 0	4 ± 0
	C31	20	Range	3 – 7	3 – 4	3 – 4
			Mean ± SD	4 ± 1	3 ± 0	4 ± 0
All	C32	68	Range	2 – 6	2 – 5	2 – 7
			Mean ± SD	3 ± 1	3 ± 1	3 ± 1
	C31	61	Range	3 – 10	2 – 5	2 – 5
			Mean ± SD	5 ± 1	3 ± 1	3 ± 1

3.4.3 Event-scale Variability in Stream DOC Fractional Composition

Figure 3.4 presents event-scale variability in stream DOC fractions expressed as % DOC and arranged in decreasing order of contribution. The data show an overall predominance of the HS fraction followed by the HOC fraction in both catchments. Across all events, the HS fraction accounted for (mean ± SD) 53% ± 6% of the stream DOC in C32 and 58 % ± 5% of the stream DOC in C31 (Table 3.3). The HOC fraction accounted for 21% ± 8% of the stream DOC in C32 and 17% ± 4% of the stream DOC in C31. The BB fraction, LMWn fraction, LMWa fraction, and the BP fraction contributed 12% ± 2%, 10% ± 4%, 3% ± 1%, and 1% ± 1% respectively of the stream DOC in C32 across the sampled events. In C31, the respective contributions were 12% ± 1%, 9% ± 3%, 3% ± 1%, and 1% ± 1% (Table 3.3). Of the LC-OCD-based DOC fractions, only the BP fraction in C31 showed a response with streamflow, although the contribution of the BP fraction to stream DOC was consistently $< 4\%$ (Figure 3.4, Table 3.3). Further descriptive statistics are provided in Table 3.3 by event and catchment.

Significant inter-catchment differences in the relative (% DOC) contributions of the HS and HOC fractions to stream DOC occurred across all sampled events (Mann-Whitney U test, $p \leq 0.05$) such that higher HS (% DOC) was observed in C31 whereas higher HOC (% DOC) was observed in C32. In contrast, there were no significant inter-catchment differences in the relative contribution of the BB fraction to stream DOC. Significant (Mann-Whitney U test, $p \leq 0.05$) inter-catchment differences were observed for the LMWn fraction (Event 3, C32 higher), for the LMWa fraction (Event 1, C31 higher), and for the BP fraction during Events 1 (C31 higher) and 3 (C32 higher).

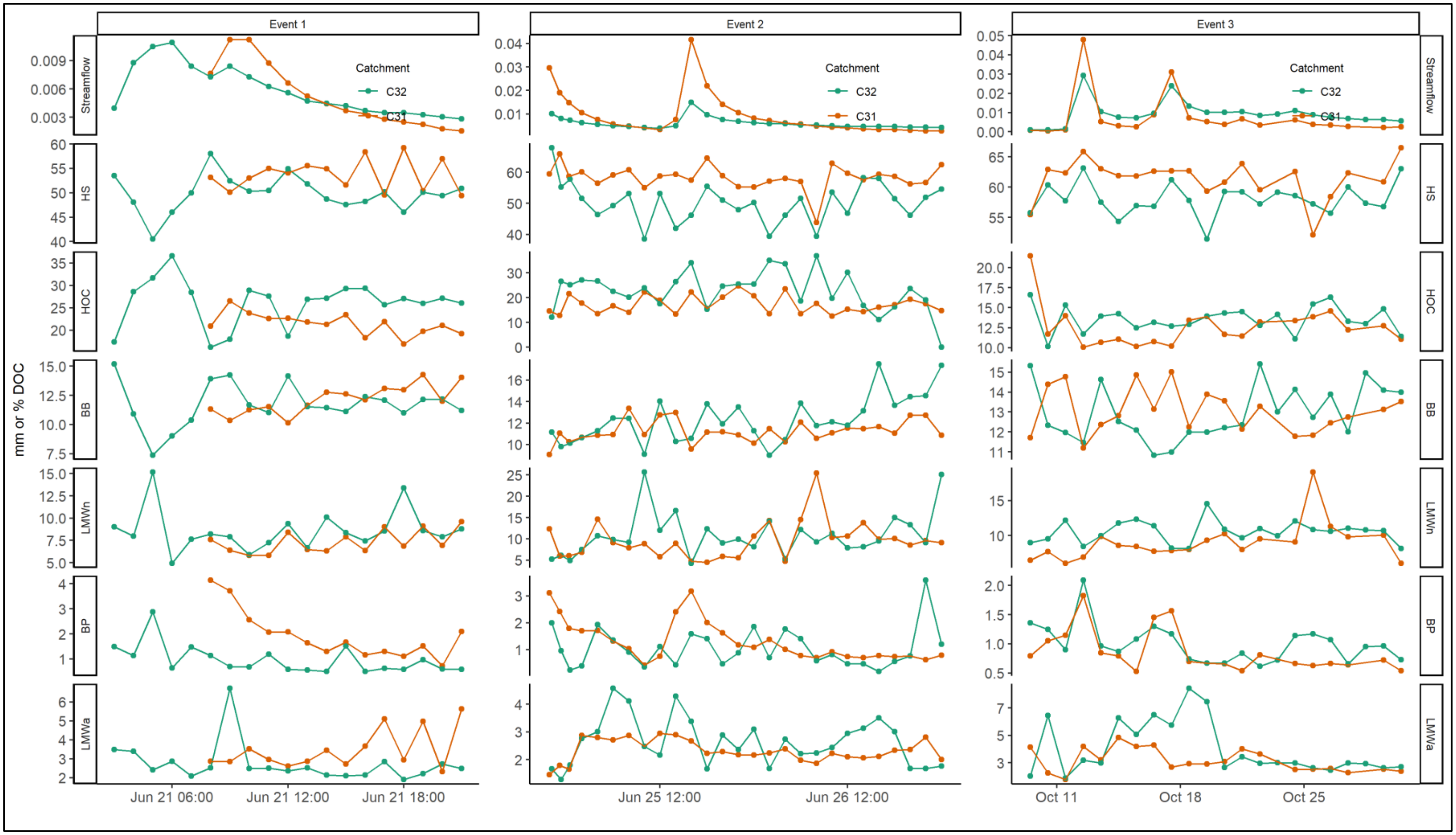

Figure 3.4 Event-scale variability in streamflow and stream DOC fractional composition.

Table 3.3 Descriptive statistics of stream DOC fractions. The reader is referred to Table 3.1 for abbreviation definitions.

Event	**Catchment**	**n**		**HS (% DOC)**	**HOC (% DOC)**	**BB (% DOC)**	**LMWn (% DOC)**	**BP (% DOC)**	**LMWa (% DOC)**
1	C32	19	Range	41 – 58	16 – 37	7 – 15	5 – 15	1 – 3	2 – 7
			Mean ± SD	50 ± 4	26 ± 5	12 ± 2	9 ± 2	1 ± 1	3 ± 1
	C31	14	Range	49 – 59	17 – 27	10 – 14	6 – 10	1 – 4	2 – 6
			Mean ± SD	54 ± 3	21 ± 2	12 ± 1	7 ± 1	2 ± 1	3 ± 1
2	C32	27	Range	39 – 68	0 – 37	9 – 17	4 – 26	0 – 4	1 – 5
			Mean ± SD	50 ± 7	23 ± 8	12 ± 2	11 ± 5	1 ± 1	3 ± 1
	C31	27	Range	44 – 66	12 – 25	9 – 13	4 – 25	0 – 3	1 – 3
			Mean ± SD	58 ± 4	17 ± 4	11 ± 1	10 ± 4	1 ± 1	2 ± 0
3	C32	22	Range	51 – 63	10 -17	11 – 15	8 – 15	1 – 2	2 – 8
			Mean ± SD	58 ± 3	14 ± 2	13 ± 1	10 ± 2	1 ± 0	4 ± 2
	C31	20	Range	52 – 66	10 – 21	11 – 15	6 – 19	1 – 2	2 – 5
			Mean ± SD	61 ± 3	13 ± 3	13 ± 1	9 ± 3	1 ± 0	3 ± 1
All	C32	68	Range	39 – 68	0 – 37	7 – 17	4 – 26	0 – 4	1 – 8
			Mean ± SD	53 ± 6	21 ± 8	12 ± 2	10 ± 4	1 ± 1	3 ± 1
	C31	61	Range	44 – 66	10 - 27	9 – 15	4 – 25	0 – 4	1 – 6
			Mean ± SD	58 ± 5	17 ± 4	12 ± 1	9 ± 3	1 ± 1	3 ± 1

3.4.4 Inter- and Intra- Catchment Variability in the Concentrations, Specific UV Absorbance, and Fractional Composition of Hillslope Solute Pool DOC

The concentrations, SUVA, SUVAhs, and fractional composition of hillslope solute pool DOC (basal and ablation till groundwater, wetland groundwater, mineral soil water, LFH percolate, and throughfall) are described in in Table 3.4. Inter- and intra-catchment variability are presented respectively in Figures 3.5 and 3.6. Stream samples (Events 1, 2, and 3) are included in Figures 3.5 and 3.6 for comparison.

There were no significant inter-catchment differences in DOC concentration, the SUVA variables, or the relative contribution of LC-OCD-defined DOC fractions (Mann-Whitney U test, $p > 0.05$) for any hillslope solute pool in June (Figure 3.5). However, for samples collected in October there were statistically significant inter-catchment differences (Mann-Whitney U test, $p \leq 0.05$) in the relative contributions (% DOC) of the HOC fraction and the LMWa fraction of the LFH percolate solute pool, as well as for the LMWa fraction of the mineral soil water solute pool (Figure 3.5).

Considerable intra-catchment spatial variability was observed for both catchments and for all hillslope solute pools (Figure 3.6). In both catchments, DOC concentrations, SUVA values, and SUVAhs were generally highest in the LFH percolate solute pool and lowest in the basal and ablation till groundwater solute pools (Figure 3.6). With respect to DOC fractional composition as defined through LC-OCD, the HS fraction accounted for > 45% of the DOC and the HOC fraction accounted for < 30% of the DOC in all sampled solute pools in both catchments with the exception of throughfall (Table 3.4). The respective ranges of the DOC fractions overlapped considerably in both catchments and in both sampling months (June and October) (Figure 3.6). Overall, no distinct intra-catchment visual trends in the fractional composition of hillslope solute pool DOC were found.

Table 3.4 Descriptive statistics of hillslope solute pool DOC (June and October).

Hillslope Solute Pool	Catchment	n		DOC (mg L^{-1})	SUVA (L mg^{-1} m^{-1})	SUVAhs (L mg^{-1} m^{-1})	HS (% DOC)	HOC (% DOC)	BB (% DOC)	LMWn (% DOC)	BP (% DOC)	LMWa (% DOC)
Basal Till Groundwater	C32	4	Range	2 – 4	2 - 3	3 – 4	60 – 74	0 – 3	15 – 22	7 – 12	0 – 2	2 – 4
			Mean ± SD	3 ± 1	3 ± 1	3 ± 0	68 ± 7	1 ± 1	17 ± 3	9 ± 2	1 ± 1	3 ± 1
	C31	3	Range	3 – 9	3 – 4	3 – 4	52 – 74	0 – 26	11 – 15	5 – 7	----	1 – 3
			Mean ± SD	5 ± 4	4 ± 1	4 ± 1	63 ± 11	15 ± 13	13 ± 2	6 ± 1	1 ± 0	2 ± 1
Ablation Till Groundwater	C32	1	Range	-----	-----	-----	-----	-----	-----	-----	-----	-----
			Mean ± SD	-----	-----	-----	-----	-----	-----	-----	-----	-----
	C31	2	Range	2 – 3	2 – 3	-----	60 – 63	0 – 3	20 – 23	10 – 11	----	----
			Mean ± SD	2 ± 0	3 ± 0	4 ± 0	61 ± 2	2 ± 2	21 ± 3	10 ± 1	1 ± 0	4 ± 0
Wetland Groundwater	C32	3	Range	3 – 8	3 – 5	3 – 5	68 – 77	0 – 9	11 – 14	5 – 7	3 – 5	1 – 3
			Mean ± SD	5 ± 2	4 ± 1	4 ± 1	72 ± 5	3 ± 5	13 ± 1	6 ± 1	4 ± 1	2 ± 1
	C31	14	Range	2 – 15	3 – 5	2 – 5	48 – 81	0 – 26	9 – 17	3 – 15	0 – 5	1 – 3
			Mean ± SD	8 ± 4	4 ± 1	4 ± 1	66 ± 11	12 ± 11	12 ± 2	6 ± 3	2 ± 1	2 ± 1
Mineral Soil Water	C32	6	Range	7 – 20	2 – 5	3 – 5	53 – 71	0 – 24	8 – 13	4 – 18	3 – 13	1 – 11
			Mean ± SD	12 ± 4	4 ± 1	4 ± 1	62 ± 7	7 ± 10	11 ± 2	7 ± 5	6 ± 3	7 ± 4
	C31	11	Range	6 – 33	3 – 5	3 – 5	45 – 78	0 – 27	9 – 14	4 – 13	2 – 18	1 – 10
			Mean ± SD	15 ± 8	4 ± 1	4 ± 1	64 ± 10	9 ± 9	11 ± 2	7 ± 2	5 ± 4	5 ± 3
LFH Percolate	C32	13	Range	12 – 61	5 – 7	5 – 6	56 – 81	0 – 27	7 – 11	3 – 7	2 – 9	1 – 3
			Mean ± SD	31 ± 13	5 ± 1	5 ± 0	70 ± 9	11 ± 12	9 ± 1	5 ± 1	3 ± 2	2 ± 1
	C31	16	Range	8 – 51	4 – 6	5 – 7	51 – 80	1 – 28	7 – 14	3 – 9	2 – 8	1 – 10
			Mean ± SD	28 ± 14	5 ± 1	6 ± 1	66 ± 9	11 ± 11	10 ± 2	6 ± 2	3 ± 2	4 ± 3
Throughfall	C32	1	Range	-----	-----	-----	-----	-----	-----	-----	-----	-----
			Mean ± SD	-----	-----	-----	-----	-----	-----	-----	-----	-----
	C31	2	Range	6 – 7	3 – 4	3 – 5	32 – 62	3 – 33	11 – 13	12 – 15	-----	3 – 4
			Mean ± SD	6 ± 1	3 ± 1	4 ± 1	47 ± 21	18 ± 21	12 ± 2	14 ± 2	5 ± 0	4 ± 1

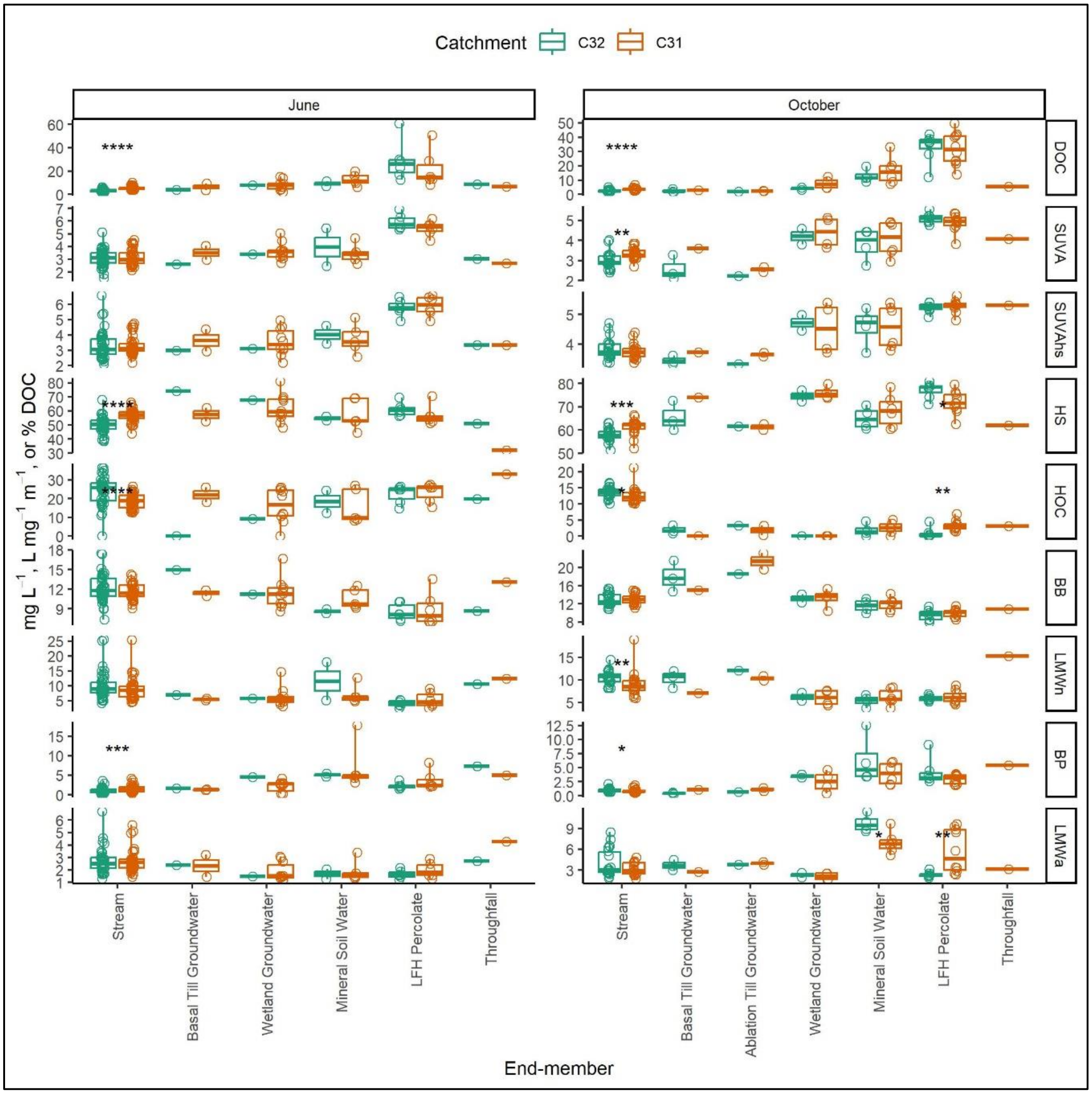

Figure 3.5 Inter-catchment concentrations, UV absorbance, and fractional composition for stream and hillslope solute pool DOC samples by month of sample collection. DOC concentrations are given in mg L^{-1}. SUVA and SUVAhs values are given in L mg^{-1} m^{-1}. LC-OCD-defined DOC fractions are given in % DOC. The reader is encouraged to note the changes in the y axis. Stream samples correspond to Events 1 and 2 for June and Event 3 for October. Open circles represent individual samples. Boxplots show the 25th, 50th, and 75th percentiles. Whiskers extend to the maximum and minimum values. Asterisks indicate statistical significance (Mann-Whitney U test): *: $p \leq 0.05$, **: $p \leq 0.01$, ***: $p \leq 0.001$, ****: $p \leq 0.0001$.

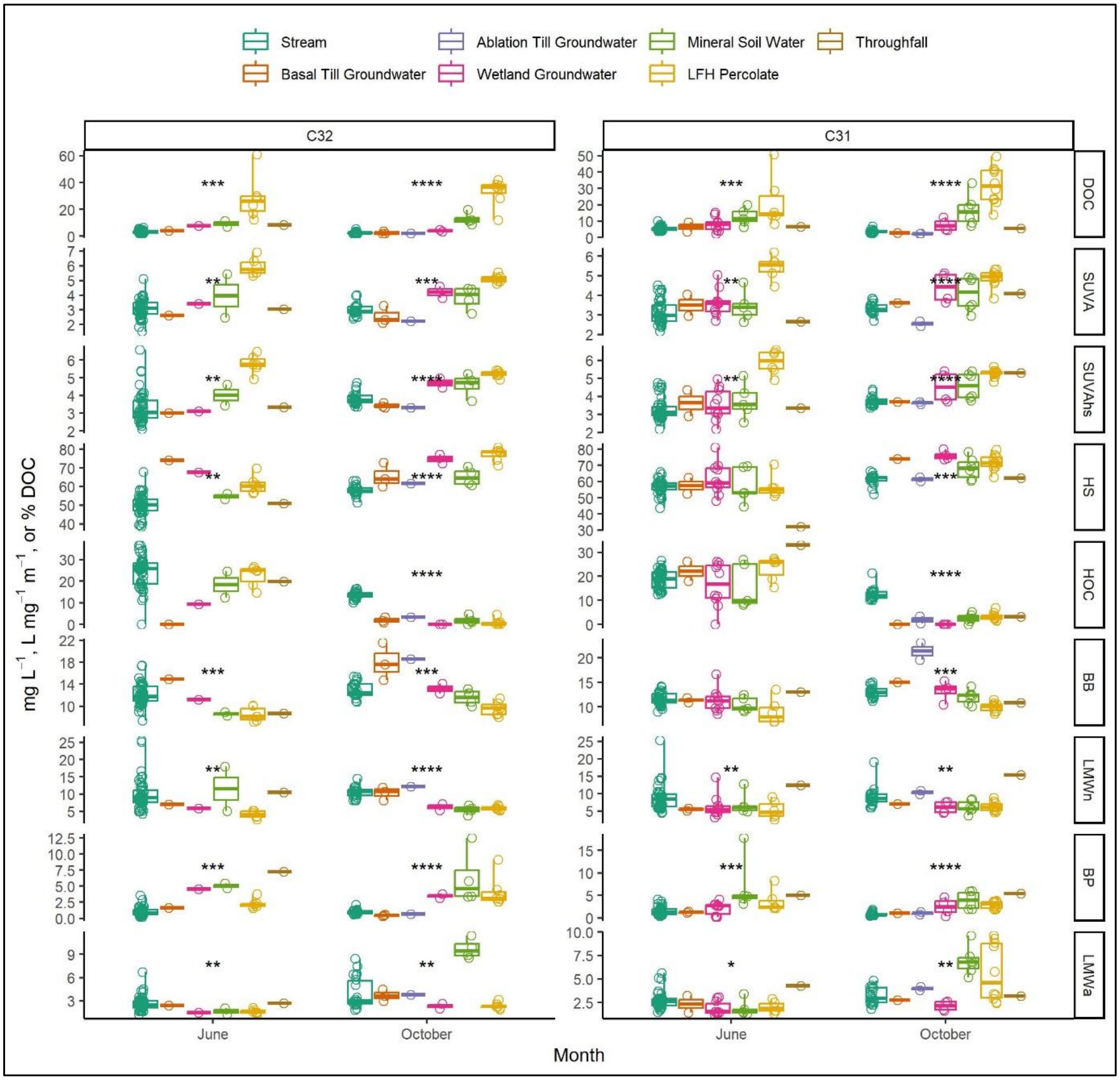

Figure 3.6 Intra-catchment concentrations, UV absorbance, and fractional composition for stream and hillslope solute pool DOC samples by month of sample collection. DOC concentrations are given in mg L^{-1}. SUVA and SUVAhs values are given in L mg^{-1} m^{-1}. LC-OCD-defined DOC fractions are given in % DOC. The reader is encouraged to note the changes in the y axis. Stream samples correspond to Events 1 and 2 for June and Event 3 for October. Open circles represent individual samples. Boxplots show the 25th, 50th, and 75th percentiles. Whiskers extend to the maximum and minimum values. Asterisks indicate statistical significance (Kruskall-Wallis test): *: $p \leq 0.05$, **: $p \leq 0.01$, ***: $p \leq 0.001$, ****: $p \leq 0.0001$.

3.4.5 Spatial Patterns of Stream and Hillslope Solute Pool DOC

Principal component analysis (PCA) was used to elucidate spatial patterns in the concentration, UV-absorbance, and fractional composition of stream and hillslope DOC. The months of June and October were considered separately as they correspond to different precipitation events (Events 1 and 2 in June, Event 3 in October). For samples collected in June, the two principal axes accounted for 60% of the variability (Figure 3.7a). The first principal component axis shows a transition from the variables representing UV- absorbance (SUVA and SUVAhs) to lower molecular-weight DOC fractions such as BB, LMWn, and LMWa. The second principal component axis represents a continuum from the hydrophobic organic carbon fraction to the humic substances fraction. In contrast, the first two principal axes for samples collected in October accounted for 71% of the variability (Figure 3.7b). The first principal component axis shows a similar pattern to that seen in June – a transition from HS to lower molecular-weight contributions and products of HS breakdown. The second principal component axis was related to variability in the LMWa fraction.

Figure 3.8 illustrates intra-event, intra-catchment variability in stream DOC concentrations, UV absorbance, and LC-OCD fractional composition in relation to streamflow. In C32, the first two principal components accounted for only 47% (June, Figure 3.7a) and 58% (October, Figure 3.8c) of the variance. The first two principal components of the corresponding C31 PCA plots (Figure 3.8b for June and Figure 3.8d for October) accounted for 59% and 61% of the variance, respectively.

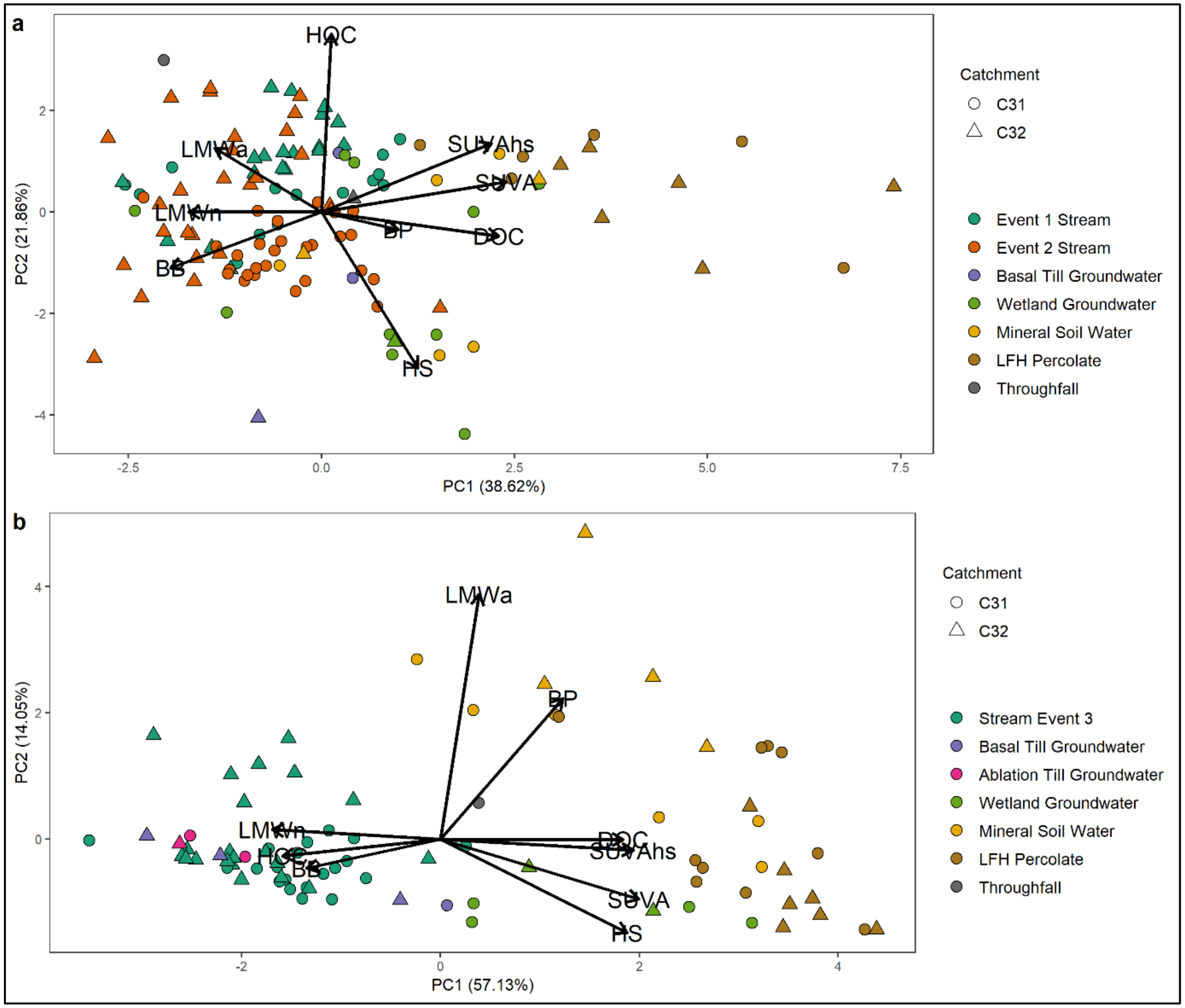

Figure 3.7 Principal component analysis of a) June and b) October concentrations, UV absorbance, and fractional composition of stream and hillslope solute pool DOC.

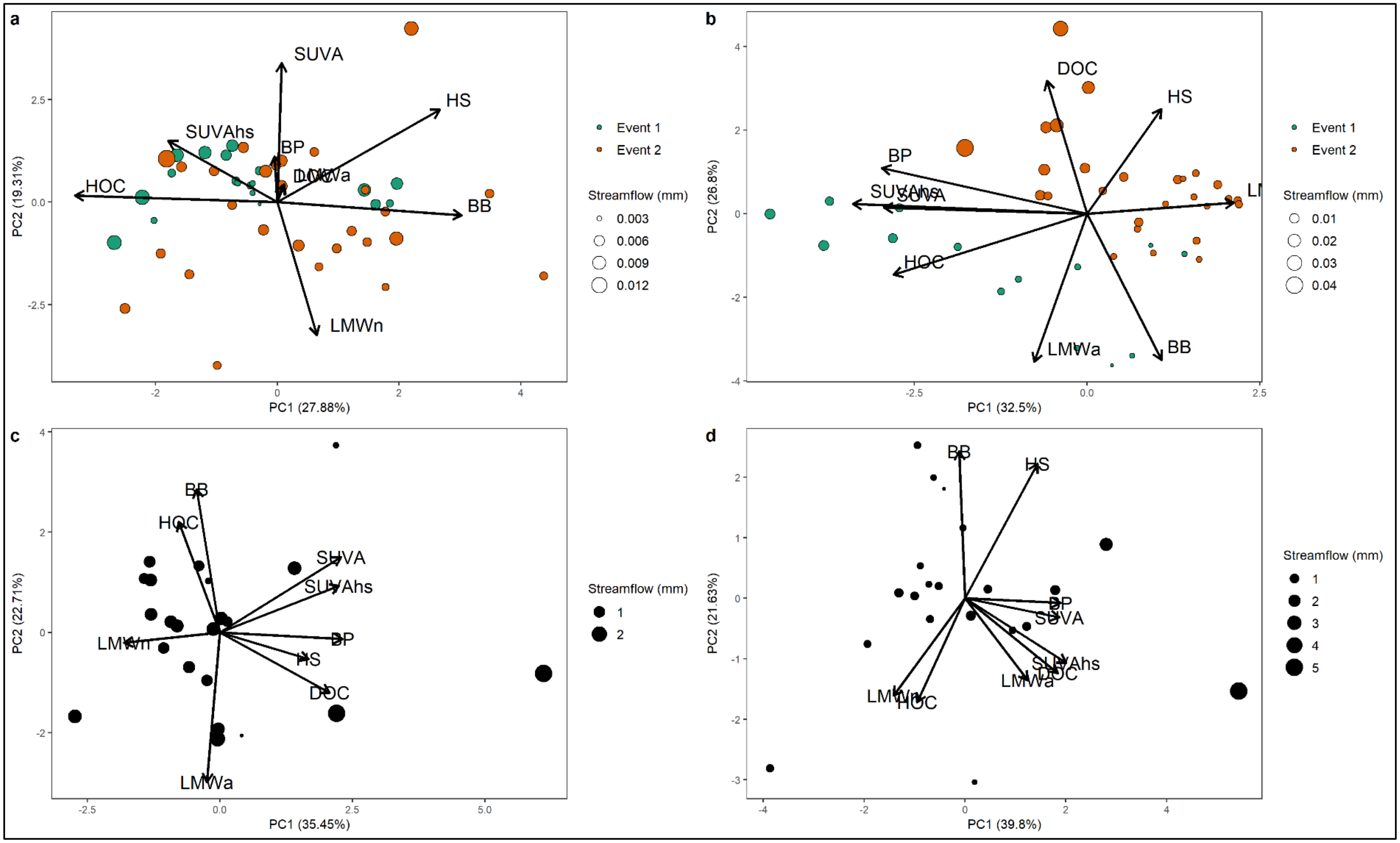

Figure 3.8 Principal component analysis of June (a and b, C32 and C31 respectively) and October (c and d, C32 and C31 respectively) stream DOC concentrations, UV absorbance, and DOC fractional composition.

3.5 Discussion

3.5.1 Inter- and Intra-catchment Variability of Stream DOC Concentrations, Specific UV Absorbance, and Fractional Composition

In this study event-scale variability in the concentration, specific UV-absorbance, and fractional composition of stream dissolved organic carbon was evaluated in two headwater catchments of contrasting forest harvest history (unharvested reference vs. legacy clearcut). Across all sampled events, the humic substances fraction and the hydrophobic organic carbon fraction accounted for the majority of stream DOC as defined through LC-OCD analysis, while the relative contribution of the LMWa and BP fractions were small (generally < 10% stream DOC). The pattern of stream DOC fractionation in this study agrees with previously published, LC-OCD-based characterizations of surface water DOC conducted globally (Table 3.5). Across several landscapes the HS fraction accounted for ≥ 50% of the DOC (Table 3.5). In contrast, the LMWa and BP fractions accounted respectively for < 3% and < 20% (all but one location were < 9%) of the DOC reported in Table 3.5.

Table 3.5 Inter-study comparisons of LC-OCD-based DOC character in surface waters. All values given, where applicable, in mean ± SD.

Location	HS (% DOC)	HOC (% DOC)	BB (% DOC)	LMWn (% DOC)	BP (% DOC)	LMWa (% DOC)	Reference
Australia	50 ± 12	9 ± 10	12 ± 5	19 ± 7	9 ± 4	1 ± 2	Rutlidge et al. (2021)
Turkey Lakes Watershed (Boreal Shield)	80.7 ± 2.85	n/a	9.40 ± 3.40	7.27 ± 1.62	2.50 ± 2.66	0.17 ± 0.27	*Aukes et al. (2021)
Yellowknife (Taiga Shield)	55.4	n/a	15.8	8.67	19.5	0.64	*Aukes et al. (2021)
Québec (Boreal region)	74 ± 5	0	11 ± 2	8 ± 2	6 ± 3	0	Hutchins et al. (2017)
Turkey Lakes Watershed C32 (Boreal Shield)	53 ± 6	21 ± 8	12 ± 2	10 ± 4	1 ± 1	3 ± 1	**This Study**
Turkey Lakes Watershed C31 (Boreal Shield)	58 ± 5	17 ± 4	12 ± 1	9 ± 3	1 ± 1	3 ± 1	**This Study**

*Values for Aukes et al. (2021) represent % hydrophilic DOC

Previous studies report that hydrophobic DOC components may be preferentially removed from solution as the DOC is transported vertically through soils (Kaiser & Zech, 1997) which suggests that groundwater in forested landscapes may contain elevated levels of hydrophilic DOC. Aukes & Schiff (2021) reported that the contribution of the HS fraction (% DOC) was relatively highest in groundwater samples. Accordingly, the predominance of LC-OCD-defined hydrophilic fractional components (HS, BP, BB, LMWn, and LMWa, generally > 70% DOC cumulatively) relative to the HOC fraction (generally < 30% DOC) observed in the streams of both C32 and C31 may suggest that groundwater is an important source of streamflow in both catchments. This observation is consistent with previous work in C32 and C31 which highlighted the importance of streamflow generation during spring freshets by shallow soil water pathways, routed above the ablation till / basal till contact (Hazlett et al., 2001) by means of a perched water table over the basal till (Semkin et al., 2002). Furthermore, a recent application of end-member mixing analysis (EMMA) to streamflow chemistry in C32 and C31, conducted concurrently with this study, provides further evidence for the groundwater-driven nature of streamflow in C32 and C31 (Fines, 2023) and was also supported by the evaluation of the aqueous potassium silica molar ratio as a proxy for flowpath depth (Chapter 2). Fines (2023) also demonstrated that a wetland near the outlet of C32 influences event-scale, intra-catchment streamflow and stream chemistry including DOC. Notably, the coupling of wetland and groundwater solute pools in C32 may be contributing to the statistically significant inter-catchment differences observed in the relative contributions of the HS fraction (higher in C31) and the HOC fraction (higher in C32) to stream DOC in this study. This difference may be related to legacy clearcut harvesting in C31, to the wetland in C32, or to some combination of both factors and agrees with the conceptual "swapping" relationship between HS and HOC noted by Krzeminski et al. (2019) whereby increases in the relative contribution of HOC fraction typically entailed a decrease in the hydrophilic HS fraction and vice versa.

Support for a wetland influence on stream DOC in C32 comes from the statistically significant inter-catchment difference observed in the relative contribution of the LMWn fraction to stream DOC during Event 3, such that the LMWn fraction was higher in C32. Aukes et al. (2021) found that groundwater samples in wetlands of the Boreal Shield ecozone, which also included samples collected at TLW, contributed higher proportions of LMWns to hydrophilic DOC than all other sources, which suggests a causal relationship between wetland processes of biodegradation and accumulation. Thus, the relative abundance of the LMWn fraction in C32 for one of the three sampled events may be limited evidence of a wetland influence on stream chemistry in C32. Further evidence for wetland control on streamflow and stream chemistry in C32 is provided by Fines (2023). Notably, in contrast to the observation of Aukes et al. (2021), the relative contribution of the LMWn fraction to wetland groundwater DOC in this study was not higher than its contribution to the DOC of other solute pools. It is possible that higher sample sizes in this study would reveal the abundance of the LMWn in wetland groundwater observed by Aukes et al. (2021) or that LMWn in the present study was affected by increased laboratory hold times and freeze-thaw due to COVID-19. Aukes et al. (2021) further noted that groundwater environments with relatively low HS levels had relatively higher proportions of LMWn. This could suggest that the relatively higher contribution of the LMWn fraction to DOC in C31 may not be related to the wetland, but rather to the relative lack of HS.

In contrast, support for an assumption of legacy clearcut harvesting impacts on stream DOC character in C31 comes from the persistently higher DOC concentrations in C31 in this study, which are comparable to previous studies on harvesting-induced increases in stream DOC concentrations at TLW (Webster et al., 2022; Chapter 2). Additionally, SUVA differed significantly between the catchments during Event 3 with corresponding differences in the LMWn and BP fractional components. Presently, there is insufficient evidence to elucidate the mechanisms responsible for the inter-catchment differences identified herein. Further insight can be derived by examining event-scale intra-catchment DOC variability.

At the event-scale, stream DOC concentrations were generally synchronous with discharge – typically increasing on the rising limbs then decreasing in conjunction with the respective falling limbs of hydrographs. In forested systems, the event-scale increase in stream DOC concentrations with streamflow is typically associated with rising water tables and the flushing of nearer-surface DOC pools (Vidon et al., 2008). In C31, SUVA and SUVAhs were increased at high flow and decreased under low flow conditions, while in C32 this pattern was not always observed (Figure 3.3). Relatively high SUVA at high flows, commonly interpreted as elevated DOM aromaticity, has been observed in many studies (Hood et al., 2006; Nguyen et al., 2010; Vidon et al., 2008). In C31, this suggests not only a change in the overall aromaticity of stream DOC exported during precipitation events, but more specifically a change in the aromatic character of the humic substances DOC fractions. Notably, while event-scale changes in SUVA and SUVAhs observed in C31 were generally synchronous with streamflow, the HS fraction was not (Figure 3.4).

The HS fraction is a continuum of both humic and fulvic acids and subsequent changes in SUVAhs may be related to changes in the molecular size of compounds classified within the HS fraction (e.g. humic and fulvic acids, Table 3.1). A transition from DOC compounds with relatively "fulvic-like" fluorescence characteristics, often observed in groundwater, to relatively more "humic-like" fluorescence characteristics has been associated with increases in DOC concentration and in aromaticity as evaluated by SUVA during precipitation events in forested watersheds (Hood et al., 2006; Lee & Lajtha, 2016). This gradient is based on observations of increasing "fulvic-like" and decreasing "humic-like" DOM characteristics with depth in the soil profile of forested systems, including northern hardwood-dominated catchments (Fellman et al., 2009; Ussiri & Johnson, 2003). In the present study, relatively high SUVA and SUVAhs values were observed in the upper soil horizon hillslope solute pools (LFH percolate and mineral soil water) and the lowest values were observed in the basal and ablation till groundwater solute pools, potentially supporting the event-scale transition previously discussed. Other evidence comes from event-scale PCA analysis of stream samples in C31 (Figure 3.7b) that show the character of the stream DOC trended toward increased aromaticity (SUVA and SUVAhs) and relatively higher molecular weight compounds (HS and BP) and at higher flows during Events 1 and 2. Relative to streams, the BP fraction of DOC has been associated with shallow groundwater (soil) DOC that can become hydrologically connected via the soil-stream interface during precipitation events (Hood et al., 2006; Hutchins et al., 2017). Similarly, the data from this study show an overall decline in the relative contribution of the BP fraction to DOC with depth, with generally higher BP (% DOC) in the mineral soil water and LFH percolate relative to the stream and groundwater samples (Figure 3.5). An alternative interpretation of the BP fraction in C31 is evidence of in-situ/microbial processing, as the microbial processing of DOM has been linked to the presence of microbially-derived and protein-like DOM components (Aukes et al., 2021). Microbially-derived, protein-like DOM components may be a marker of landscape disturbance (Cawley et al., 2014) in C31. It is possible that changes in vegetation in C31, for instance the post-harvest establishment of pioneer species (Buttle et al., 2018), could be influencing soil moisture conditions and processes of organic matter cycling. Seasonally-driven factors such as the fall flushing of DOC built up due to decomposition throughout the summer (Wen et al., 2020; Wilson et al., 2013), and leaf litter inputs (Meyer & Wallace, 1998) may also be influencing certain inter-catchment differences in DOC character, for instance the inter-catchment differences in SUVA and in the LMWn faction (% DOC) observed only for Event 3 in October. Fines (2023) highlighted the importance of wetland groundwater and mineral soil water contributions to streamflow during the fall in C32, whereas basal and ablation till groundwater contributions were observed in C31 during the same period.

Overall, the event-scale stream data suggests that precipitation events and high discharge are associated with the contributions of near-surface DOC pools in both catchments but that the association is clearer in C31 compared to C32. Notably, the position of the wetland in C32 and its control on intra-catchment stream DOC concentrations and character, may be masking the legacy impacts of forest harvesting on stream DOC in C31.

3.5.2 Hillslope Solute Pool DOC and Catchment-Scale Spatial Trends

No significant inter-catchment differences in DOC concentration, SUVA, or SUVAhs were observed for any hillslope solute pool. This suggests that legacy clearcut harvesting is not affecting hillslope solute pool DOC concentration and specific UV absorbance in C31 relative to the conditions in C32. In contrast, significant inter-catchment differences in the fractional composition of DOC were observed for select hillslope solute pools and DOC fractional components, suggesting that LC-OCD-based DOC characterization may detect differences in the character of hillslope solute pool DOC which are not captured by the specific UV absorbance (Aukes et al., 2021).

In October, significant inter-catchment differences in the relative contributions (% DOC) of the HS fraction, the HOC and LMWa fractions were seen for the LFH percolate solute pool (Mann-Whitney U test, $p \leq 0.05$). The HS fraction was higher in C32 while the HOC fraction and the LMWa fraction were higher in C31. The mineral soil water solute pool sampled in October also showed a significant inter-catchment difference (Mann-Whitney U test, $p \leq 0.05$) in LMWa (% DOC, higher in C32). These results may suggest a legacy clearcut harvesting impact on character of hillslope solute pool DOC in the upper soil horizons. However, PCA analysis revealed a preferential grouping by solute pool rather than by catchment, albeit with considerable visual overlap between hillslope solute pools and catchments. This agrees with the PCA-based findings of Aukes et al. (2021) such that landscape compartment, not ecozone, was reflected in PCA groupings of DOC character. Overall, evidence supports a legacy impact of clearcut harvesting on the character of hillslope solute pool DOC, but the low sample sizes of hillslope solute pool DOC prevent a definitive statement with respect to harvesting and require further investigation.

3.5.3 Forest Harvesting Impacts on Source Water Quality

Data presented in this study suggest a persistent, decadal-scale impact on the concentration and character of stream DOC in the study catchments. Specifically, clearcut harvesting may have increased DOC concentrations and the relative contribution (% DOC) of the humic substances (HS) fraction in stream samples draining C31. However, the presence of a wetland near the outlet of C32 may also account for the discrepancy in DOC character.

Dissolved organic carbon concentrations and character are relevant to the operation of drinking water treatment plants (Chen et al., 2016; Chow et al., 2008; Emelko et al., 2011; Volk et al., 2005). In particular, SUVA is commonly used to predict the reactivity and behavior of source waters in a drinking water treatment context (Hua et al., 2015; Kitis et al., 2001). Relatively higher values of SUVA (e.g., > 4) are typically associated with hydrophobic compounds amenable to coagulation techniques, although hydrophilic compounds can also have high SUVA values (MWH, 2012). In this study, the relative contribution of the HS fraction, considered a part of the hydrophilic DOC pool as defined through LC-OCD analysis (Huber et al., 2011), to stream DOC in the legacy clearcut catchment C31 consistently exceeded and differed significantly ($p \leq 0.05$) from that of the unharvested reference catchment whereas SUVA values in C31 were higher, and differed significantly ($p \leq 0.05$) from C32 during Event 3. Accordingly, the data may suggest mixed impacts of forest harvesting on source water treatability. Higher SUVA in the legacy clearcut catchment under certain conditions may suggest relatively greater amenability to standard treatment operations, whereas the relative enrichment of the humic substances fraction could be more problematic and challenge water treatment.

Previous research into landscape disturbance-induced changes to stream DOC character has identified protein-like, microbially derived compounds as a marker of landscape disturbance (Yamashita et al., 2011; Cawley et al., 2014) and these protein-like components have been associated with the BP fraction defined through LC-OCD analysis (Hutchins et al., 2017). Notably, the significant inter-catchment difference in the relative contribution of the BP fraction for Events 1 and 3, with higher values in C31, may be connected to harvesting impacts. Event 3 also showed significant inter-catchment differences in the LMWn fraction ($p \leq 0.05$, higher in C32) and in SUVA. It is possible that the BP fraction, defined through LC-OCD as hydrophilic, could be affecting the higher SUVA in C31.

Overall, while forest harvesting practices may degrade surface water quality in terms of DOC concentrations, post-harvest changes to DOC character may not always be a challenge to drinking water treatment operations, due to the inherent complexity of, and overlap between, metrics and methods of characterizing stream DOC. Further research is needed to elucidate potential harvest-associated, inter-catchment differences in stream DOC character, especially under varying flow conditions.

3.6 Conclusions

Humic substances and hydrophobic organic carbon fractions, as defined through LC-OCD analysis, were the predominant contributors to event-scale stream DOC in two northern hardwood dominated headwater catchments of contrasting forest harvest history. Stream sampling during three precipitation events of differing durations, magnitudes, and seasonal conditions revealed consistent and statistically significant inter-catchment differences in DOC concentration and in the relative contributions of the humic substances fractional component and the hydrophobic organic carbon component to DOC. Stream DOC concentrations and the relative contribution of the HS fraction were higher in the legacy clear-cut catchment, whereas the relative contribution of HOC to DOC was higher in the undisturbed reference catchment, with the discrepancy likely related to the presence of a wetland near the outlet of

C32. Few inter-catchment differences were observed in the DOC character of hillslope solute pool samples. The data suggest that clear-cut harvesting may have long-term impacts on the concentration and fractional composition of stream DOC in northern hardwood-dominated headwater catchments, although further research is required to characterize and understand the influence of wetlands on the variability of LC-OCD-defined DOC fractional composition, and DOC character in general, in the study systems.

Chapter 4. Summary, Future Research, and Implications

4.1 Research Summary

The sustainable management of forested watersheds for the ecosystem service of drinking water provision requires careful consideration of the impacts of natural and anthropogenic landscape disturbance such as forest harvesting over long timescales, particularly with respect to water quality parameters of operational relevance to the drinking water treatment industry (Emelko et al., 2011). One such parameter is DOC, a ubiquitous and ecologically significant component of aquatic ecosystems. Dissolved organic carbon can challenge drinking water treatment operations through increases in concentration and/or through changes in character. Forest harvesting-induced increase in source water DOC concentration (Laudon et al., 2009; Schelker et al., 2012) can result in increased treatment costs, higher coagulant and disinfectant demands, and potential degradation of the aesthetic quality of drinking water delivered to consumers (Emelko et al., 2011). Additionally, post-disturbance changes in stream DOC character (Yamashita et al., 2011) can alter the procedures and materials required to safely treat source water for eventual consumption (Chow et al., 2008).

Whereas most DOC-centric harvesting impact studies focus solely on sub-decadal timescales, less is known about the legacy (decadal-scale) impacts of harvesting practices on the concentrations, export, and character of stream and hillslope solute pool DOC in key water bearing areas. Further research is needed to elucidate the potential magnitude and duration of harvesting impacts on stream DOC concentration and character.

This thesis presents the results from an intensive, field-based ecohydrological investigation into the impacts of legacy clearcut harvesting on inter- and intra-catchment variability of stream and hillslope solute pool DOC concentrations (Chapter 2), export (Chapter 2), and character (Chapter 3). This thesis contributes jointly to the ongoing debate over the extent and duration of forest harvesting impacts on stream DOC, to knowledge of DOC hillslope-stream transport processes in northern hardwood-dominated headwater catchments, and to the recent efforts toward the characterization of stream and hillslope solute pool DOC using liquid-chromatography organic carbon detection analysis.

Chapter 1 addresses inter- and intra-catchment variability of stream DOC concentrations and stream DOC export in the context of the concentrations, spatial distribution, and hydrologic connectivity of hillslope solute pool DOC under a range of flow conditions. Stream DOC concentration results reveal a mean inter-catchment difference of 1.21 mg L^{-1} likely attributable to decadal-scale clearcut harvesting impacts, as this value agrees with previously published increases in stream DOC attributed to forest harvesting (Oni et al., 2015; Schelker et al., 2012; Webster et al., 2022). In contrast, inter-catchment differences in streamflow related to the position of a wetland near the outlet of the unharvested catchment resulted in inconsistent inter-catchment differences in stream DOC export. Under baseflow conditions, higher streamflow in the unharvested catchment resulted in higher DOC export relative to the legacy clearcut catchment. Mixed results were observed for the high flow conditions (freshet sampling period, precipitation events, fall sampling period). In contrast to stream DOC concentrations and stream DOC export under certain flow conditions, no inter-catchment differences in DOC concentration were observed for the hillslope solute pools, implying that the observed decadal-scale impact of clearcut harvesting on stream DOC concentrations was not the result of inter-catchment differences in hillslope solute pool DOC concentrations. Wetland position impacted intra-catchment DOC concentration-discharge regression analysis and flowpath evaluation (via the potassium silica molar ratio) in the unharvested catchment, potentially limiting the ability of the paired-catchment approach to adequately characterize clearcut harvesting impacts on stream DOC. The overall results support the persistence of a clearcut harvest-induced impact on stream DOC dynamics, albeit one which may not represent a reasonable threat to drinking water treatment operations at decadal-scales. However, uncertainties remain as to the mechanism(s) responsible for this persistence, particularly under baseflow conditions during which organic-rich, upper soil horizon solute pools are not contributing substantially to streamflow in the clearcut catchment. Further research into the decadal-scale impacts of clearcut harvesting on shallow and deeper groundwater pools, which typically sustain baseflow in forested catchments, is encouraged.

To provide further context for the results of Chapter 2, Chapter 3 used liquid-chromatography organic carbon detection analysis to characterize event-scale variability in DOC concentration, specific UV absorbance, and DOC fractional composition from a subset of samples collected in Chapter 2. Stream DOC was characterized during three high-flow events of differing magnitudes, durations, and antecedent precipitation conditions in June and October. Hillslope solute pool DOC was characterized for samples collected during high-flow events. Dissolved organic carbon characterization via LC-OCD revealed that humic substances fraction and the hydrophobic organic carbon fraction accounted for the majority of stream DOC. A significant (Mann-Whitney U test, $p \leq 0.05$) inter-catchment difference in stream DOC concentrations and the relative contributions of the humic substances and hydrophobic organic carbon fraction was observed, such that DOC concentrations and HS (% DOC) were higher in C31 relative to C32, whereas the contribution to stream DOC of HOC was relatively higher in C32. The relatively higher HS contribution in the harvested catchment can not be directly attributed to, but may suggest a decadal-scale influence of, clearcut harvesting. Further LC-OCD-based characterization of stream DOC headwater catchments with varying wetland extents and positions is needed. On the hillslopes, low sample sizes precluded the ability of this study to conclusively determine inter-catchment differences in DOC fractional composition in hillslope solute pools.

4.2 Limitations and Future Research

Several factors limit the extent to which this thesis can conclude that clearcut harvesting has a decadal-scale impact on stream DOC concentrations and character in northern hardwood dominated headwater catchments. For instance, this study was limited to a single calendar year. Differing years, with differing antecedent and precipitation conditions, may further highlight or decrease the observed impact of clearcut harvesting on stream DOC concentration and character at TLW. Future research might also include DOC characterization under freshet conditions, as the freshet is recognized as a major contributor to stream DOC export in northern headwater catchments (Morison et al., 2022). Additionally, stream DOC characterization under baseflow conditions would provide a frame of reference for higher-flow conditions such as this study's precipitation events and the freshet, while potentially providing insight into the processes maintaining relatively higher stream DOC concentrations in C31 under baseflow conditions (Chapter 2).

To address a more general scope of forest harvesting, the spatial scope of future research could be extended to include catchments impacted by different harvesting strategies such as shelterwood and selection cut (both commonly used practices in Ontario) (OMNRF, 2015), especially those with infrastructure typically associated with forest harvesting practices such as roads and culverts (Macdonald et al., 2003). Additionally, this study was limited to a single clearcut catchment – harvesting impacts in multiple catchments may become cumulative and increase downstream DOC concentrations (Öhman et al., 2009).

A further drawback of this study's experimental design was the exclusion of dedicated riparian zone sampling, despite the inclusion of soil pits along topslope-midslope-toeslope transects. Although clearcut harvesting in C31 avoided riparian zones, pursuant to the Riparian Code of Practice for Ontario (Chapter 1), the riparian zone is a known hotspot of biogeochemical cycling and an important control on both stream DOC concentration and character (Ledesma et al., 2018; Lidman et al., 2017). Thus, future inclusion of the riparian zone could inform the connection between stream and hillslope solute pool DOC in both harvested and unharvested catchments, potentially offering further insight into how clearcut harvesting can impact stream DOC concentrations and character at decadal scales.

Evidence in Chapter 2 suggests that the mechanisms which are understood to govern post-harvest increases in stream DOC concentrations at sub-decadal scales, for instance flowpath changes and alterations to soil properties with implications for hillslope solute pool DOC concentrations, may not be the same as those that govern decadal-scale harvesting impacts. In the context of the long-term management of forest resources for the ecosystem service of source water protection, it is essential to investigate additional post-harvesting factors which may be influencing stream DOC concentrations at decadal scales. Potentially relevant factors which were not directly investigated in this study include the variability of DOC concentrations in deeper groundwater solute pools, the impact of vegetation regrowth, for instance the prevalence of pioneer species such as red cherry and yellow birch observed in C31 (Buttle et al., 2018), on hillslope solute pool DOC concentrations, and soil properties such as DOC adsorption parameters and organic carbon stocks.

Finally, while this thesis provides a detailed accounting of inter- and intra-catchment patterns in the concentration and character of stream DOC in northern hardwood-dominated headwater catchments impacted by legacy clearcut harvesting, the true impact of forest harvesting practices on stream DOC in such catchments will likely vary from location to location and from year to year and will require additional investigations, particularly in light of the knowledge gaps identified above. Thus, this thesis serves as a baseline investigation of post-harvest fluctuations in stream DOC concentrations, export, and character, providing recommendations for the spatial and temporal scopes of DOC-centric investigations into forest harvesting impacts.

4.3 Implications for Forest Management Practices and Drinking Water Treatment

Results of the two studies presented in this thesis provide evidence for decadal-scale impacts of forest harvesting on the concentration and character of stream dissolved organic carbon. Mean inter-catchment differences in stream DOC concentration consistently exceeded the detection limit for DOC concentration, adding confidence to the finding. Furthermore, the evaluated mean inter-catchment difference, 1.21 mg L^{-1}, aligns well with previously reported, post-harvest increases in stream DOC concentrations. However, the results also show that inherent catchment properties such as streamflow and the relative position of wetlands may mask, and in some cases overwrite, the impacts of forest harvesting on stream DOC concentrations. For instance, despite the persistent harvest-induced excess of stream DOC concentrations in the legacy clearcut catchment, inter-catchment differences in stream DOC export were inconsistent. This suggests that, at a decadal scale, the legacy effects of clearcut harvesting practices in northern hardwood-dominated headwater catchments may not pose a reasonable threat to downstream drinking water treatment operations, at least with respect to stream DOC concentrations. However, further research into the magnitude and nature of the downstream propagation of harvesting impacts on stream DOC is required, as some evidence has shown that post-harvest increases in stream DOC can propagate and impact downstream sites (Schelker et al., 2014). Additionally, as DOC is not the only parameter relevant to drinking water treatment operations, future evaluations of decadal-scale (and shorter) harvesting impacts should include water quality parameters such as turbidity, nitrogen, and phosphorous (Emelko et al., 2011).

One of the overarching themes of this thesis was the control exerted by wetlands on streamflow, stream DOC concentrations, and stream DOC character. Accordingly, future paired catchment designs focusing on stream DOC, especially in the context of evaluating the impacts of landscape disturbances, should consider the potential confounding influence of wetlands near catchment outlets, even if other physiographic properties are similar. Furthermore, due to their control on streamflow and stream DOC concentrations and character, wetlands may be especially vulnerable to forest harvesting practices (Webster et al., 2015) but may also represent a mitigating influence, potentially buffering flowpath changes and travel time reductions in harvested catchments (Leach et al., 2020).

In conclusion, the results of the two studies presented in this thesis indicate that, while clearcut harvesting-induced increases to stream DOC concentrations and, to a lesser extent, changes to stream DOC character may persist for extended periods of time in northern, hardwood-dominated headwater catchments, the effects may be limited (mean increase 1.21 mg/L in this study) relative to inherent, intra-catchment DOC variability and therefore likely do not represent a reasonable threat to downstream drinking water treatment operations at decadal-scales. Accordingly, forest harvesting for source water protection may represent a viable strategy in similar watersheds, at least with respect to stream DOC concentrations. The ongoing evaluation of this strategy, and the results of this study, would benefit from additional context potentially provided by larger catchments, robust comparisons to differing harvesting strategies, and a combined focus on both the short- and long-term implications of forest harvesting for stream DOC variability in northern hardwood-dominated headwater catchments, especially in the contexts of cumulative downstream effects and changing climatic conditions.

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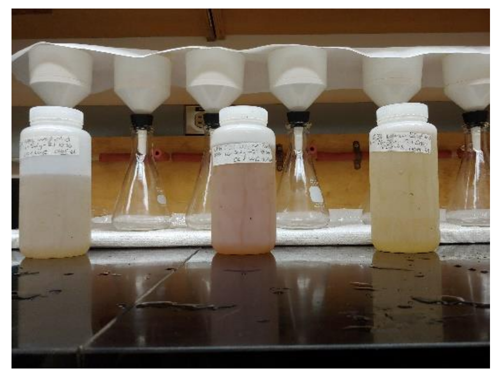
Appendix A Supplementary Material for Chapter 2

Table A1. Photos related to field and laboratory methods including stream sampling, hillslope solute pool sampling, and laboratory analysis.

Stream Sampling	Hillslope Solute Pool Sampling	Laboratory Analysis
 C32 Weir, March 2021	 C32 Hillslope Transect, April 2021	 Stream samples at the Great Lakes Forestry Centre, July 2021
		

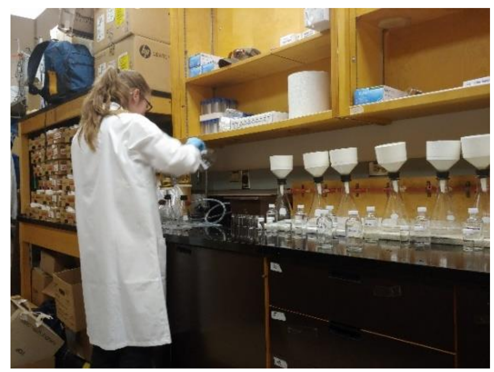
C31 Weir, October 2018 (Credit: Mike Stone)	Groundwater sampling equipment in C32, April 2021	Lysimeter samples ready for filtering at the Great Lakes Forestry Centre, July 2021
 Checking the ISCO at C32 Weir, October 2021 (Credit: Will Fines)	 Checking lysimeters in C32, October 2021 (Credit: Will Fines)	 Sampling splitting and filtration setup at the Great Lakes Forestry Center, July 2021 (Credit: Will Fines)
 Successful ISCO collection of a set of event-scale stream samples	 Throughfall collector in C32, March 2021	 Filtering samples at the Great Lakes Forestry Centre, October 2021 (Credit: Shelby Robertson)

Table A2. Stream DOC concentrations (mg L^{-1}) by flow condition and catchment

	Total	Freshet	Baseflow	Event A	Event B	Event C	Event D	Fall
n	C32: 179 C31: 158	C32: 46 C31: 50	C32: 20 C31: 13	C32: 24 C31: 24	C32: 19 C31: 14	C32: 27 C31: 27	C32: 21 C31: 8	C32: 22 C31: 22
minimum	C32: 0.93 C31: 1.41	C32: 0.93 C31: 1.41	C32: 1.38 C31: 1.82	C32: 1.96 C31: 3.03	C32: 1.67 C31: 2.63	C32: 1.67 C31: 2.70	C32: 1.31 C31: 3.55	C32: 1.63 C31: 2.40
maximum	C32: 5.13 C31: 6.32	C32: 5.13 C31: 4.81	C32: 2.65 C31: 4.48	C32: 4.64 C31: 6.05	C32: 2.74 C31: 5.86	C32: 3.98 C31: 5.92	C32: 3.79 C31: 6.26	C32: 4.81 C31: 6.32
mean	C32: 2.42 C31: 3.56	C32: 2.50 C31: 3.04	C32: 1.75 C31: 2.61	C32: 2.81 C31: 4.81	C32: 2.22 C31: 3.82	C32: 2.56 C31: 3.44	C32: 2.37 C31: 4.48	C32: 2.53 C31: 3.62
median	C32: 2.36 C31: 3.38	C32: 2.31 C31: 3.06	C32: 1.69 C31: 2.46	C32: 2.66 C31: 5.03	C32: 2.23 C31: 3.65	C32: 2.44 C31: 3.18	C32: 2.46 C31: 4.10	C32: 2.49 C31: 3.50
SD	C32: 0.69 C31: 1.02	C32: 0.76 C31: 0.66	C32: 0.29 C31: 0.67	C32: 0.75 C31: 0.84	C32: 0.35 C31: 0.96	C32: 0.51 C31: 0.80	C32: 0.75 C31: 1.02	C32: 0.70 C31: 0.81

Table A3. Descriptive Statistics for Hillslope Solute Pool DOC Concentrations (mg L^{-1})

Sampling Period	Catchment		Basal Till Groundwater	Ablation Till Groundwater	Wetland Groundwater	Mineral Soil Water	LFH Percolate	Throughfall
Freshet	C32	*n*	24	26	0	4	2	3
		range	0.80 – 4.20	1.76 – 3.99		2.52 – 6.85	3.30 – 5.40	1.60 – 2.44
		mean	2.78	2.73		4.11	4.35	1.90
		median	3.00	2.96		3.54	4.35	1.64
		SD	0.98	0.68		2.04	1.48	0.47
	C31	*n*	12	10	34	17	10	3
		range	1.67 – 6.77	1.53 – 3.41	1.42 – 5.43	3.27 – 9.69	3.84 – 22.69	0.91 – 1.54
		mean	3.26	2.53	3.10	5.54	10.92	1.24
		median	3.12	2.63	2.92	4.48	8.77	1.27
		SD	1.50	0.64	1.05	2.15	7.24	0.32
Intermediate	C32	*n*	1	1	11	11	25	9
		range			2.52 – 11.57	4.97 - 21.40	8.49 – 43.14	1.97 – 15.30
		mean	1.78	2.33	6.11	9.00	22.72	7.17
		median	1.78	2.33	4.40	7.20	23.65	7.21
		SD			3.51	4.85	8.81	3.90
	C31	*n*	8	4	30	21	53	10
		range	2.09 – 5.73	2.64 – 3.13	1.55 – 10.05	4.18 - 34.24	0.75 – 64.76	1.62 - 9.78
		mean	3.01	2.80	4.71	11.89	21.43	4.96
		median	2.63	2.71	4.49	9.88	17.30	4.80
		SD	1.16	0.22	1.80	7.90	12.82	2.26
Fall	C32	*n*	4	3	5	5	7	1
		range	1.77 – 4.58	1.85 – 2.54	3.53 – 17.96	8.83 – 18.49	23.92 – 40.33	
		mean	2.67	2.14	7.18	12.45	33.48	9.78
		median	2.17	2.04	5.12	11.12	34.55	9.78
		SD	1.29	0.36	6.09	3.81	6.11	
	C31	*n*	4	2	13	9	15	3
		range	3.35 – 6.08	2.34 – 2.88	1.42 – 20.89	5.28 – 28.41	14.37 – 50.40	2.42 – 8.88
		mean	4.33	2.61	7.73	13.52	29.99	5.73
		median	3.95	2.61	5.33	12.41	29.66	5.90
		SD	1.27	0.38	5.15	7.28	10.16	3.23

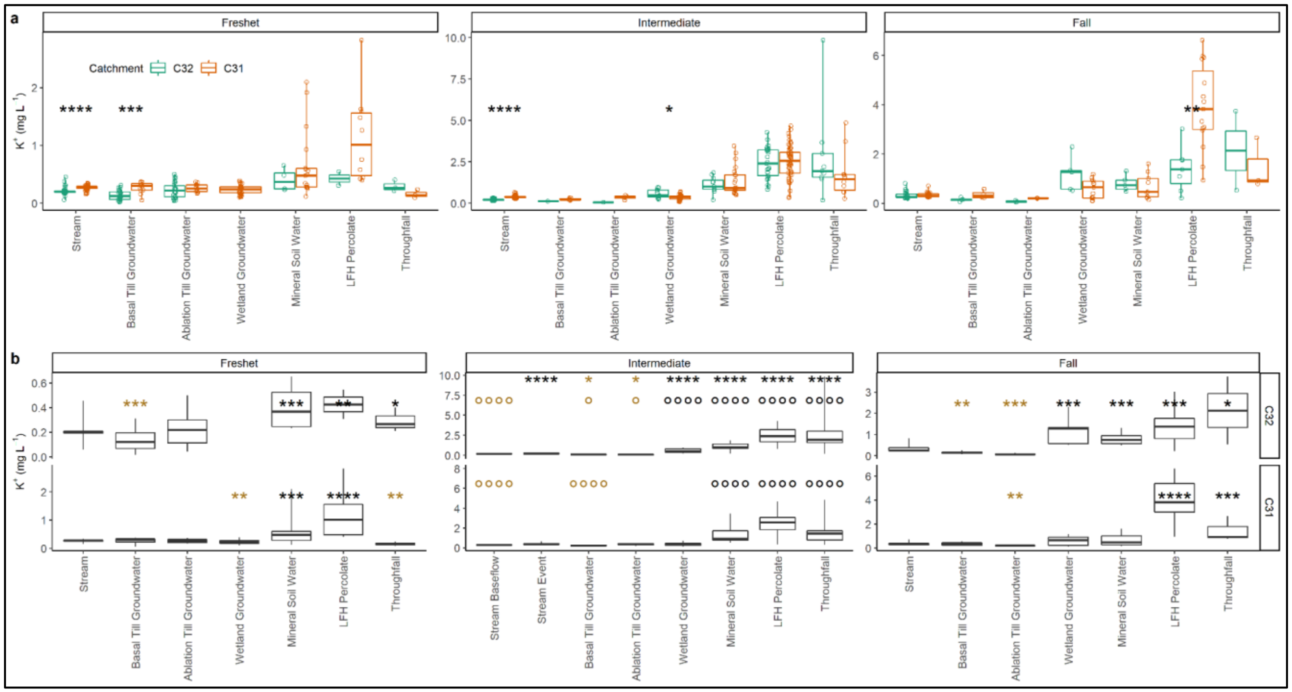


Figure A1. a) Inter- and b) Intra- catchment variability in stream and hillslope solute pool K^+ concentrations by catchment and sampling period. 25^{th}, 50^{th}, and 75^{th} percentiles are shown by horizontal lines. Whiskers indicate range. The reader is encouraged to note the differences in the y-axis. For all asterisks, *: $p \leq 0.05$, **: $p \leq 0.01$, ***: $p \leq 0.001$, ****: $p \leq 0.0001$ (Mann-Whitney U test). For b: asterisks in the freshet and fall sampling periods denote statistically significant differences relative to stream samples (black = "greater than", brown = "less than"); asterisks in the intermediate sampling period denote statistically significant differences relative to baseflow stream samples (black = "greater than", brown = "less than"); circles in the intermediate sampling period denote statistically significant differences relative to event (A-D) stream samples (°: $p \leq 0.05$, °°: $p \leq 0.01$, °°°: $p \leq 0.001$, °°°°: $p \leq 0.0001$; black = "greater than", brown = "less than").

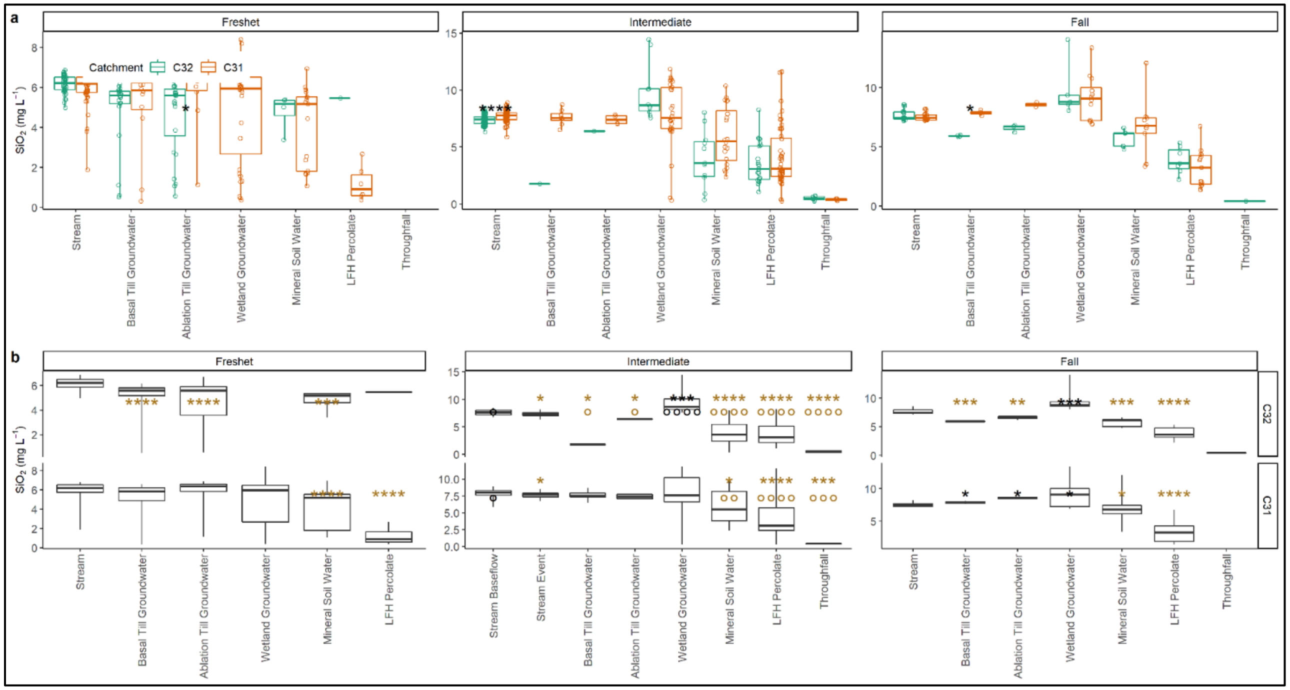


Figure A2. a) Inter- and b) Intra- catchment variability in stream and hillslope solute pool SiO_2 concentrations by catchment and sampling period. 25th, 50th, and 75th percentiles are shown by horizontal lines. Whiskers indicate range. The reader is encouraged to note the differences in the y-axis. For all asterisks, *: p ≤ 0.05, **: p ≤ 0.01, ***: p ≤ 0.001, ****: p ≤ 0.0001 (Mann-Whitney U test). For b: asterisks in the freshet and fall sampling periods denote statistically significant differences relative to stream samples (black = "greater than", brown = "less than"); asterisks in the intermediate sampling period denote statistically significant differences relative to baseflow stream samples (black = "greater than", brown = "less than"); circles in the intermediate sampling period denote statistically significant differences relative to event (A-D) stream samples (°: p ≤ 0.05, °°: p ≤ 0.01, °°°: p ≤ 0.001, °°°°: p ≤ 0.0001; black = "greater than", brown = "less than").

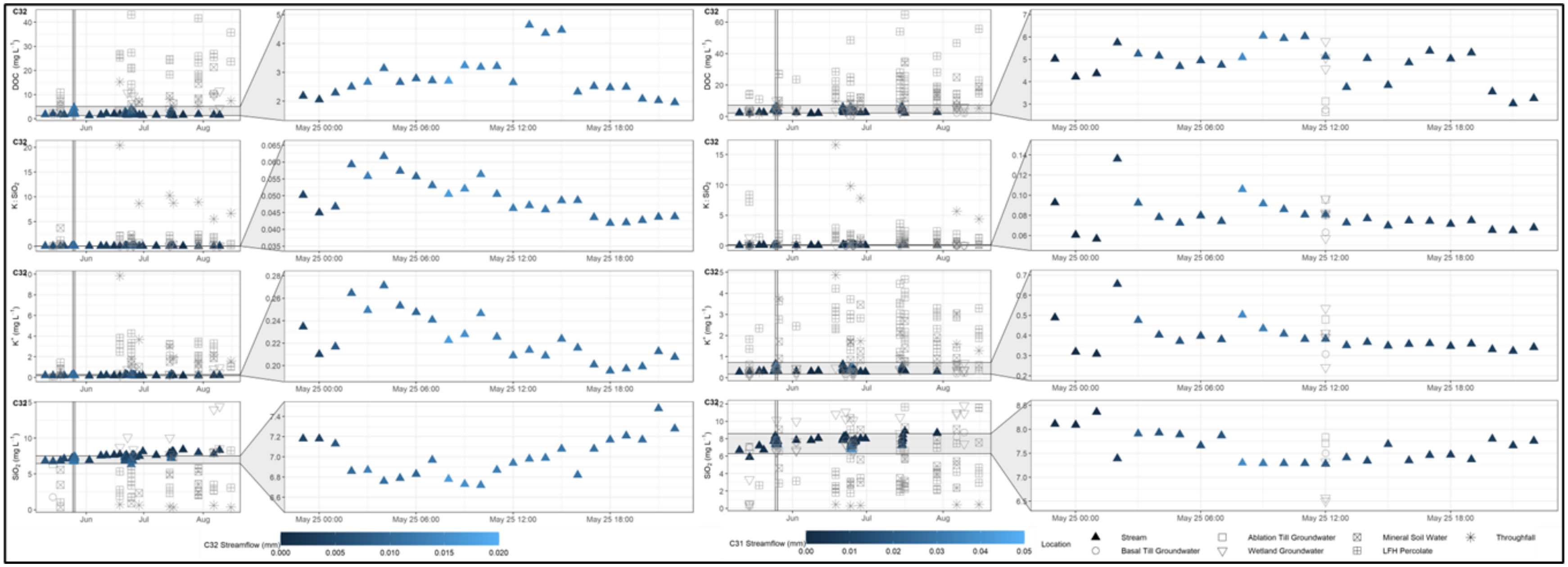


Figure A3. Stream and hillslope solute pool DOC concentrations, K:SiO_2, K^+ concentrations, and SiO_2 concentrations for precipitation event A.

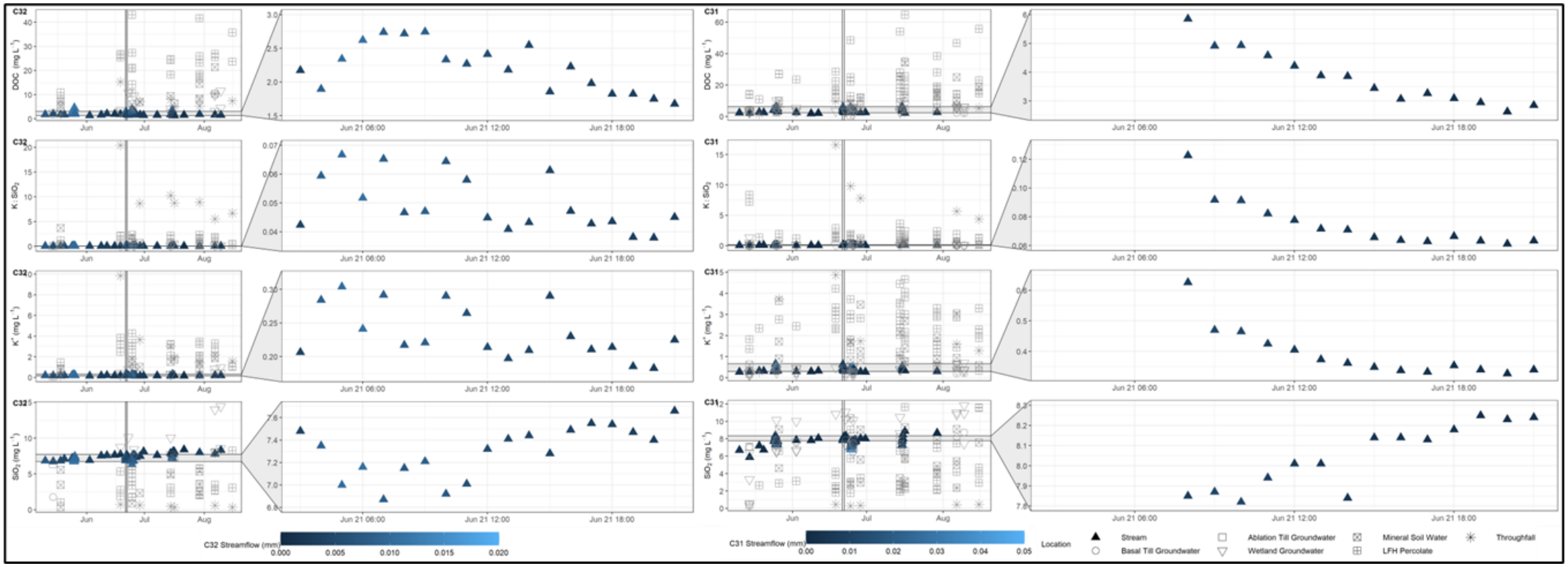


Figure A4. Stream and hillslope solute pool DOC concentrations, K:SiO_2, K^+ concentrations, and SiO_2 concentrations for precipitation event B.

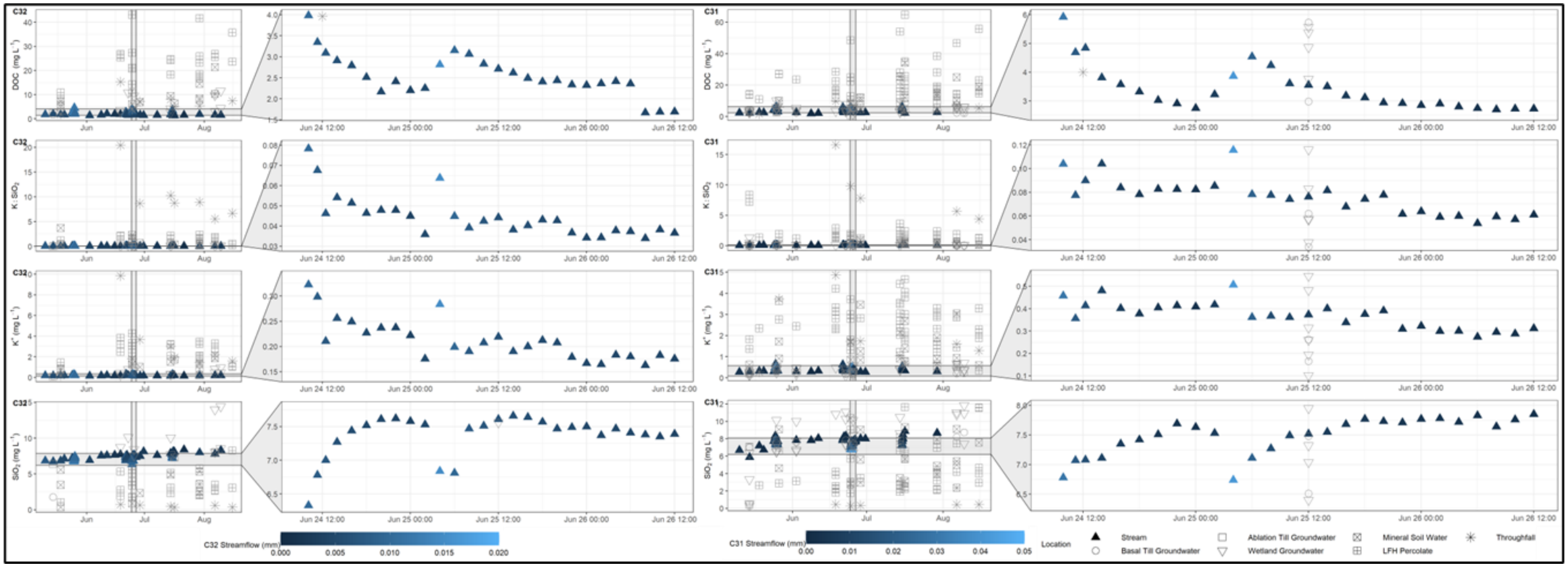


Figure A5. Stream and hillslope solute pool DOC concentrations, K:SiO_2, K^+ concentrations, and SiO_2 concentrations for precipitation event C.

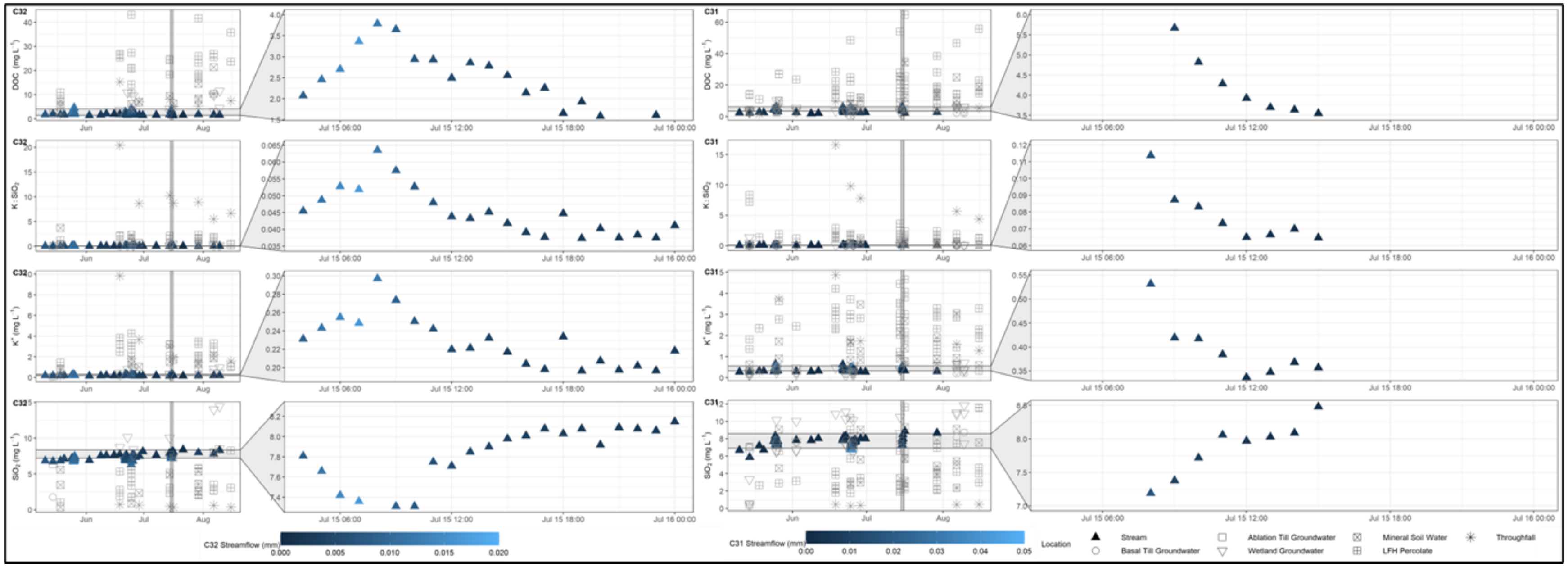


Figure A6. Stream and hillslope solute pool DOC concentrations, K:SiO$_2$, K$^+$ concentrations, and SiO$_2$ concentrations for precipitation event D.

Appendix B Supplementary Material for Chapter 3

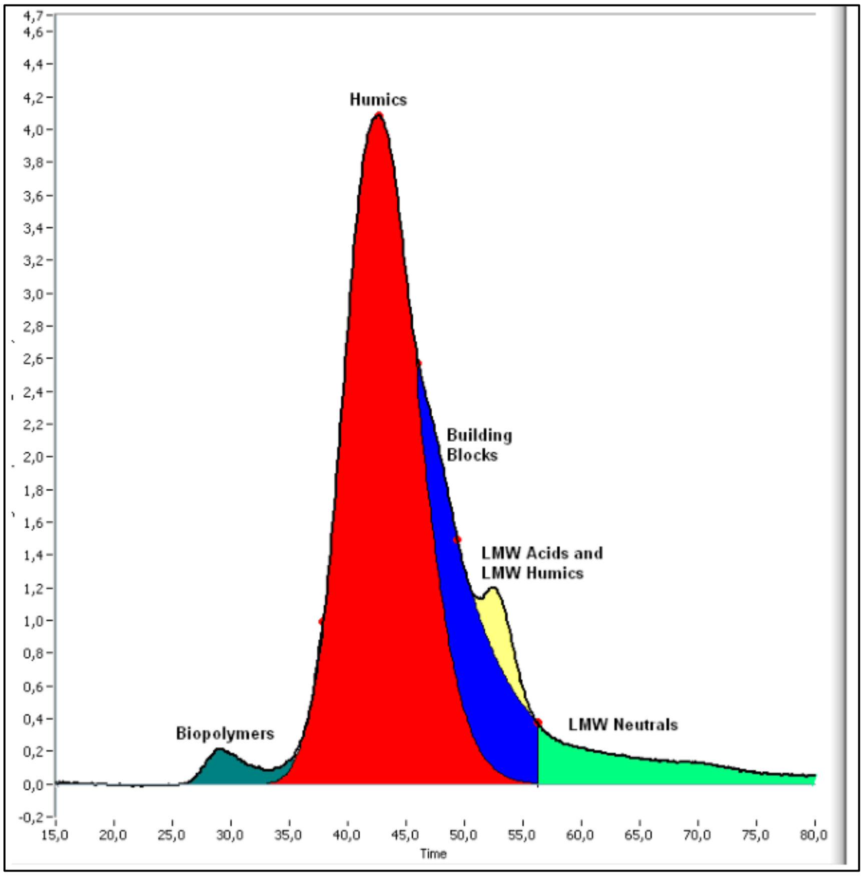


Figure B1. LC-OCD chromatograph illustrating method-defined fractional components (Ngo & Amiri, 2022).

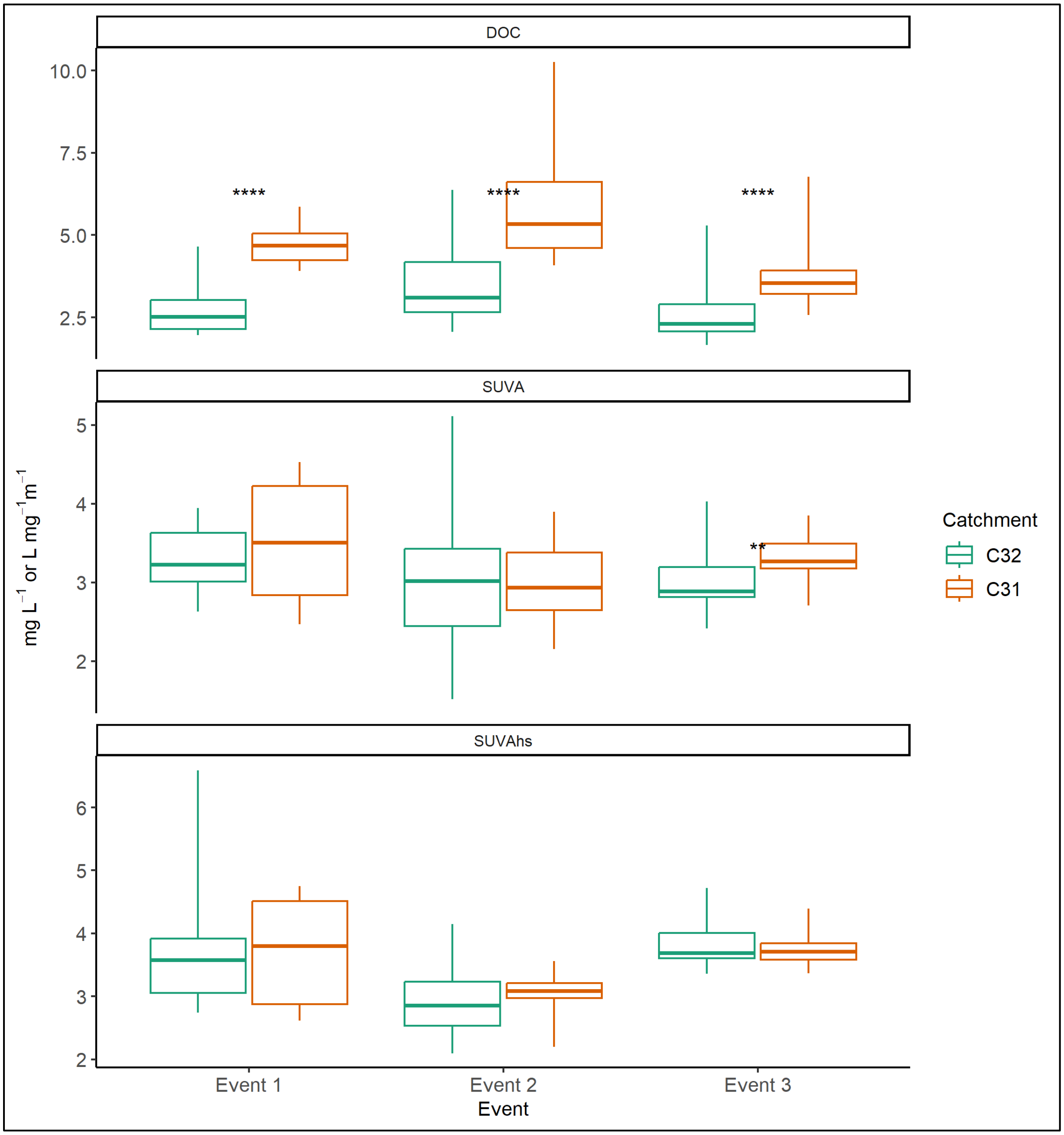


Figure B3. Inter-catchment variability in stream DOC concentrations, SUVA, and SUVAhs. Asterisks denote statistically significant differences (Mann-Whitney U test) as follows: *: p ≤ 0.05, **: p ≤ 0.01, ***: p ≤ 0.001, ****: p ≤ 0.0001.

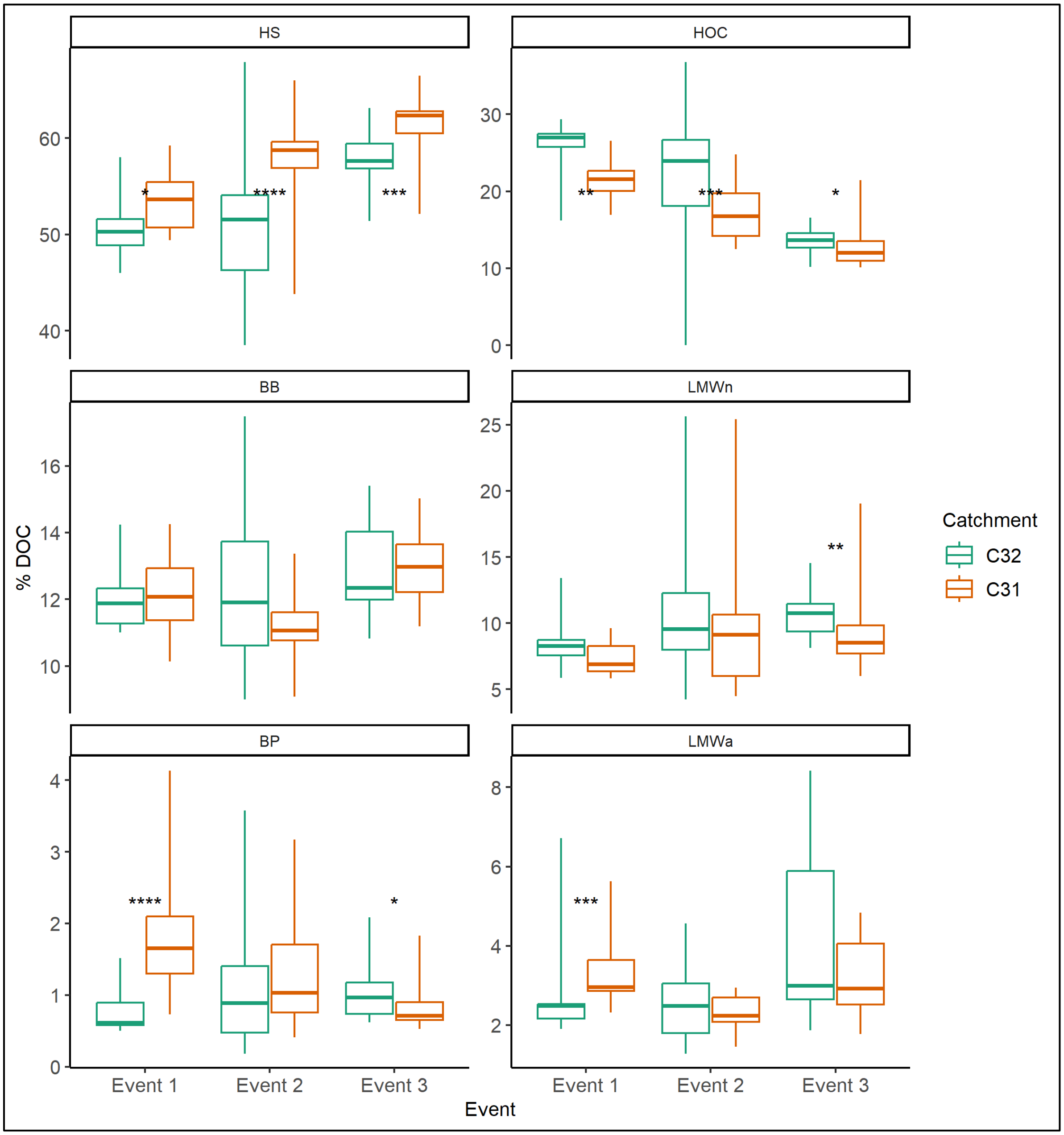


Figure B4. Inter-catchment variability in stream DOC fractional composition. Asterisks denote statistically significant differences (Mann-Whitney U test) as follows: *: p ≤ 0.05, **: p ≤ 0.01, ***: p ≤ 0.001, ****: p ≤ 0.0001.