Forest harvesting impacts on dissolved organic carbon in Alberta's southern Rocky Mountains: implications on shallow subsurface fate and transport

by

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Abstract

Dissolved organic carbon (DOC) is an important constituent of source water quality from forested headwaters regions that can have implications on downstream drinking water treatment. Landscape disturbances such forest harvesting are known to alter biotic and abiotic controls regulating subsurface DOC fate and transport in some forested regions. The objective of this thesis was to evaluate potential harvest-associated impacts on the magnitude, seasonal timing, and chemical character of hillslope DOC in Alberta's southern Rocky Mountains. This study explored the influences of harvesting, hillslope position (lowland vs upland) and depth in the soil profile on the transport and fate of shallow subsurface DOC. These potential impacts were assessed by comparing soil pore water, shallow groundwater and stream water DOC as well as mineral soil-DOC adsorption parameters from a reference and harvested catchment. Harvesting resulted in elevated DOC concentrations in soil pore water ($p < 0.01$) and, to a lesser extent, in shallow groundwater compared to the reference catchment. Additionally, soil pore water DOC from harvested plots was more aromatic ($p = 0.01$). Temporal trends were investigated over the snowmelt period showing the magnitude of DOC was consistent during snowmelt periods, while the DOC chemical composition was temporally variable among catchments. No difference in DOC concentration or aromaticity was observed between reference and harvested streams, providing evidence that hillslope scale impacts were muted at the catchment scale. Vertical transport of DOC in the soil profile can also be affected by adsorption to mineral soil as water percolates through the soil profile. While DOC adsorption to soils was not influenced by harvesting, adsorption of DOC was strongly influenced by variation in soil properties (pH, soil organic carbon, extractable iron and aluminum) that control mineral soil - DOC exchange among B- and C-horizons. B-horizon soils had a 33% lower sorption affinity and had a 65% greater desorption term than C-horizon soils. This study provides valuable insight into DOC dynamics in this region and helps to evaluate forest harvesting as a potential source water protection strategy.

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Table of Contents

List of Tables

List of Figures

Chapter 1: Background and research objectives

Forested headwaters of the eastern slopes of the Rocky Mountains provide the majority of high quality drinking water supplies to downstream communities (Emelko et al., 2011). High quality source water areas like these are highly susceptible to degradation from environmental and anthropogenic stressors such as climate change, forest harvesting and wildfire (Laudon et al., 2009; Silins et al., 2009; Stednick, 1996). Disturbances in headwater catchments can have a drastic impact on the frequency and magnitude of high streamflow events, especially at the regional scale (Moody and Martin, 2001; Jones and Perkins, 2010). In turn, these increases in extreme events can challenge drinking water treatment via increased sediment production and changes in dissolved organic carbon (DOC) magnitude and chemical character (Kunze and Stednick, 2006; Hood et al., 2006; Emelko et al., 2011). Disturbances coupled with climate change have the potential to degrade source water quality. Implementing source water protection strategies as the first point of water quality management is key to mitigating these impacts.

Forest harvesting is one the more extensive human caused disturbances in the eastern slopes of the Rocky Mountains (ABMI, 2017) with approximately 97% of harvested areas being clear-cut in Alberta (Alberta Agriculture and Forestry, 2017). Clear-cut harvesting has been documented to alter biotic and abiotic processes of DOC transport and fate (Cronan et al., 1992; Boyer et al., 1997). While Best Management Practices (BMPs) are commonly employed during forest harvesting, alterations to the forest functions (canopy removal, decreased organic matter inputs, decreased transpiration) often amplify mechanisms of DOC mobilization and transport (Schelker et al., 2013a). Forest harvesting is not commonly conducted with the protection of drinking water supplies as a top priority. However, with increasing pressures on forests and drinking water supplies due to expanding populations and climate change, source water protection strategies through forest management are becoming increasingly important.

Dissolved organic carbon (DOC) plays a vital role in a myriad of biogeochemical processes in soil and water (Kalbitz et al., 2000; Thurman, 1985). DOC affects the solubility and mobility of metals (Driscoll et al., 1988), it is also a precursor to the formation of potentially harmful, regulated compounds during chlorination for drinking water treatment (Nokes et al., 1999; Siddiqui et al., 1997) and is a source of carbon and energy for aquatic ecosystems (Webster and Meyer, 1997; Kreutzweiser and Capell, 2003). Dissolved organic carbon is operationally defined as organic carbon that pass through a 0.45μm filter (Zsolnay, 2003), compounds too large to pass through the filter is referred to as particulate organic carbon. DOC is comprised of a variety compounds and molecules ranging in size and complexity. In forested systems, the dominant sources of DOC are plant litter, humus, root exudates and microbial biomass (Kalbitz et al., 2000). Fate and transport of DOC is determined by processes such as adsorption, leaching, microbial decomposition and export (Figure 1-1). These processes are influenced by biotic and abiotic factors and alterations to these factors will influence the processes governing DOC dynamics.

DOC production and transformations through forested systems has been extensively studied (Agren et al., 2008; Burns et al., 2016, Wickland et al., 2007). However, much of this research focuses solely on streams and lakes. Hillslope DOC processes have been studied, though in much less detail. Process-based research on DOC dynamics moving from the hillslope, both laterally and vertically, is vital to determining the magnitude and character of carbon reaching receiving water bodies. It is widely known that processes such as adsorption to mineral soil, microbial decomposition and organic matter inputs govern subsurface DOC dynamics in forested systems. These processes cause DOC concentrations to decrease with depth in the soil profile. Groundwater levels, especially in the riparian or near-stream areas, have been reported to increase DOC mobilization to streams and influence the character of DOC reaching receiving streams (Bishop et al., 2008; Seibert et al., 2009). This mechanism of “transmissivity feedback” where elevated groundwater levels promote lateral flow through riparian soils has been shown to regulate stream DOC (Bishop et al., 2004; Seibert et al., 2009). Thus, groundwater levels in these soils during high flows can impact stream DOC. Temporal trends in DOC export have also been researched, comparing snowmelt, baseflow and stormflow. Hydrologic flushing of DOC has been reported in a number of catchments where patterns of snow accumulation and melt can regulate DOC movement (Boyer et al., 1997; Pacific et al., 2010; Schelker et al., 2013b). Wetland abundance and location in catchments have been shown to exert significant control on DOC concentration and character, more specifically aromaticity and molecular weight (Agren et al., 2008; Singh et al., 2015; Inamdar et al., 2012; Fellman et al., 2009). Sources of water, such as groundwater, overland flow and soil pore water, can have pronounced differences in DOC composition and concentration (Inamdar et al., 2012), though these unique carbon signatures become muted with mixing of these sources at larger spatial scales (Fellman et al., 2009).

In snow-dominated, mountainous catchments, shallow subsurface flow paths contribute greater proportions of water to streams during snowmelt compared to baseflow (Boyer et al., 1997). Adsorption of DOC to mineral soils can play a vital role in determining the magnitude and chemical character of DOC pulses during this time (Nelson et al., 1993). DOC concentrations decline greatly as water percolates down the soil profile, likely attributed to adsorption and microbial degradation (McDowell and Wood, 1984; Moore, 1989; Michalzik et al., 2001). Preferential adsorption of hydrophobic compounds has also been widely reported in the literature (Tipping, 1981; Jardine et al., 1989). This preferential adsorption influences chemical character of bulk DOC as water moves down the soil profile, becoming proportionally more hydrophilic. Hydrophobic compounds can even cause desorption of bound indigenous hydrophilic DOC thus further altering DOC character (Kalbitz et al., 2004). Adsorption of DOC has been largely attributed to physical and chemical characteristics of soils including iron and aluminum oxide/hydroxide content, clay content, total organic carbon and pH (Gu et al., 1994; Moore et al., 1992; Nelson et al., 1993; Vance and David, 1992). Adsorption processes likely lead to low groundwater DOC concentrations seen in numerous studies and, in turn, dictate the character and concentration of DOC reaching the stream from shallow subsurface sources.

Research on forest harvesting impacts to DOC has produced highly variable and conflicting results, suggesting watershed characteristics and local conditions are likely the first order controls on how DOC moves through watersheds. Overall, harvesting is thought to increase DOC exports from a watershed by increasing discharge, promoting rising water tables and increasing microbial activity (Laudon et al., 2009; Kalbitz et al., 2004). However, generalizing harvesting impacts to soil carbon is difficult with studies showing both decreases in soil carbon (Covington, 1981) and others showing increases (Yanai et al., 2003). A review of 73 studies on a variety of forest types showed changes in soil carbon after harvest are most often be <10% (Johnson and Curtis, 2001). A review by Kreutzweiser et al. (2008) further substantiated this conclusion for the boreal region. Harvesting impacts to soil carbon have been extensively linked to changes in stream or lake DOC. Laudon et al. (2009) found increased stream DOC concentrations and exports from a harvested catchment in the European boreal. Studies have also shown increased DOC concentrations in boreal lakes following harvesting (Carignan et al., 2000; France et al., 2000; Lamontagne et al., 2000; O'Driscoll et al., 2006). Other studies focused on soil pore water concentrations also report initial increases in DOC ~2-5 years post-harvest, followed by decreases (Plamondon, 1982; Hinton et al., 1997). The increases in DOC have been attributed to rising groundwater tables after harvesting intersecting with surficial soil horizons rich in DOC (Laudon et al., 2009; Schelker et al., 2013a) as well as potentially increased microbial decomposition due to increased soil moisture and temperature (Londo et al., 1999). Changes in water fluxes, soil moisture, soil temperature, microbial communities, and substrate quantity and quality all impact carbon movement down the soil profile (Kalbitz et al., 2000). Thus while it is quite clear DOC can be impacted by forest harvesting, the magnitude of impact depends on location and watershed characteristics.

DOC chemical character is an important determinant of bioavailability, it can influence the production of regulated and unregulated disinfection by-products during drinking water treatment (Siddiqui et al., 1997) and is a common measure of aqueous natural organic matter which can govern coagulant demand (Emelko et al., 2011). Two chemical character properties widely used to assess bulk properties of DOC include aromaticity and molecular weight, which can be determined by ultraviolet (UV) absorbance. Specific Ultraviolet Absorbance (SUVA) is the absorbance of a water sample at a given wavelength normalized by DOC concentration. SUVA is commonly calculated for wavelength 254 nm and is positively related to aromaticity (Weishaar et al., 2003). Aromatic compounds are generally more stable and less bioavailable than aliphatic compounds (Perdue, 1998). Organic aromatic compounds are widely accepted to be precursor material to the formation of trihalomethanes, haloacetic acids and other disinfection by-products which are of potential human health concern (Reckhow et al., 1990). Bulk molecular weight of carbon can also indicate bioavailability of compounds. The ratio of UV_{254}:UV_{365} can indicate the bulk molecular weight of water samples, and has an inverse relationship to molecular weight (Agren et al., 2008). DOC with a greater molecular weight is generally more recalcitrant than lower molecular weight compounds (Tranvik and Jorgensen, 1995). Aromaticity and molecular weight can also provide an indication of hydrophobicity of carbon in a sample where higher $SUVA_{254}$ values correspond to greater concentration of hydrophobic, high molecular weight compounds (Hua et al., 2015).

Research which focused on the chemical characteristics of DOC after harvesting has shown surprisingly consistent results, showing an enrichment of aromatic compounds in the forest floor following forest harvesting (Hannam et al., 2005; Kalbitz et al., 2004). Changes in the DOC composition was further reported in soil solutions, likely due to continued microbial processing coupled with decreased fresh organic matter inputs (Dai et al., 2001). While the forgoing has established a solid foundation of understanding on how forest disturbance may affect DOC dynamics in forested watersheds, several key questions remain uncertain. 1) The issue of how forest harvesting affects soil water, groundwater, and stream DOC remains highly uncertain. This is particularly true in Rocky Mountain settings where few, if any studies have been done. 2) Furthermore, the extent to which DOC may be modified by adsorption/desorption processes during transport from the forest floor to receiving streams remains unclear. This is key information needed to assess how disturbance signatures on DOC may be muted or amplified by flow paths at larger watershed scales.

Temporal and spatial dynamics of DOC production and chemical character have been studied in great detail across boreal and peatland settings, however literature coupling forest harvesting and DOC hillslope transport in a montane setting are few. This is an important barrier to developing and evaluating source water protection of drinking water supplies through forest management because DOC is a key water parameter affecting drinking water treatment. Linking harvesting impacts to vertical and lateral hillslope DOC transport towards receiving streams will allow for a greater understanding of disturbance influences on source water quality. The vast majority of studies on harvesting impacts to DOC have been conducted in boreal forests, tropical regions and peatlands, while exceedingly few studies document these effects in the Rocky Mountain region. This is particularly important in Alberta where the eastern slopes of the Rocky Mountains serve as a critical water supply region for the province.

Accordingly, the high-level objectives of this thesis were to evaluate the effects of clear-cut harvesting on DOC production and subsurface transport in Rocky Mountain watersheds. A direct comparison between a clear-cut and a reference catchment was used to assess how harvesting altered DOC. To determine the impacts of harvesting two studies were conducted with the following objectives.

Research outlined in Chapter 2 focused on investigating and quantifying differences in soil pore water and shallow groundwater DOC concentrations and chemical character following clear-cut harvesting. Specific research objectives were:

- Evaluate clear-cut harvesting impacts on the spatial (hillslope position and depth in soil profile) and temporal distribution of DOC in soil pore water and shallow groundwater.

- Investigate potential linkages between soil pore water and shallow groundwater, and stream water DOC concentration and chemical character

Research described in Chapter 3 focused on assessing changes in DOC adsorption/desorption behaviors in soils. Specific research objectives were:

- Assess the impact of harvesting on DOC adsorption behavior (sorption affinity, desorption capacity and null point concentrations).
- Assess potential physiographic controls on DOC adsorption behavior (sorption affinity, desorption capacity and null point concentrations) in a steep, mountainous catchment in the Montane Cordillera.
- Determine if harvesting and physiographic controls impact the chemical character (aromaticity and molecular weight) of DOC desorbed from mineral soils.

Finally, Chapter 4 synthesizes the results from Chapter 2 and 3 and outlines the broader implications of the findings for forest management-based source water protection efforts. This chapter details the scientific contributions of these studies and the importance of the research to forest managers and water utility operators, alike. Additionally, recommendations for future research are addressed in this chapter.

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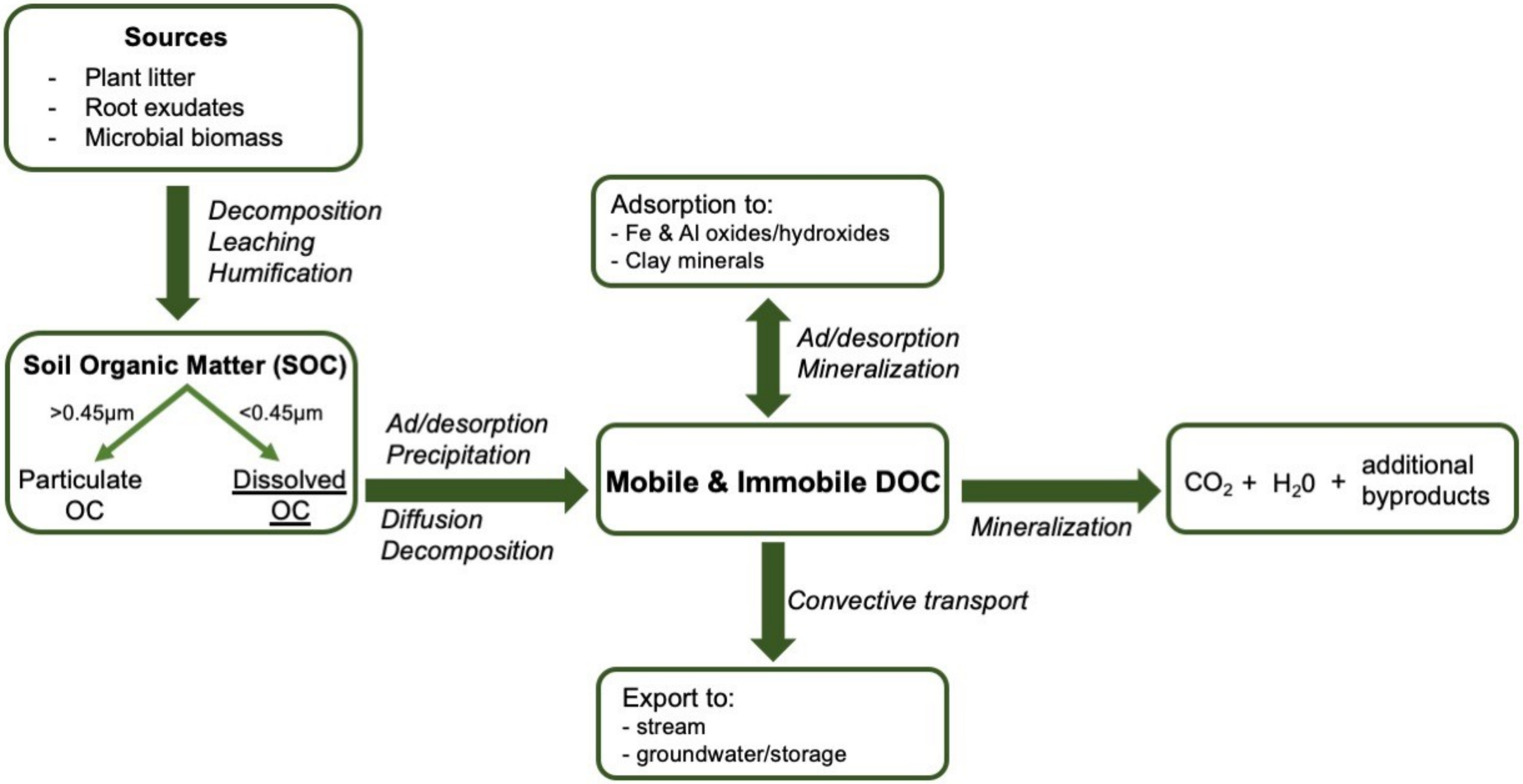
Figure 1-1: Conceptual model of dissolved organic carbon in a forested system. Adapted from Kalbitz et al. (2000).



Chapter 2: Impact of clear-cut harvesting on spatial and temporal trends of soil pore water and shallow groundwater DOC magnitude and chemical character

2.1. Introduction

Dissolved organic carbon (DOC) is an important constituent of source water quality from forested headwaters regions which has potential implications to downstream drinking water treatment (Emelko et al., 2011). Landscape disturbances such forest harvesting can affect DOC production and watershed export by altering biotic and abiotic controls regulating DOC in some forested regions (Kalbitz et al., 2000; Kreutzweiser et al., 2008). However, while many studies have been conducted on effects of land disturbance on DOC in forested watersheds, critical knowledge gaps remain on how these impacts vary in different forest regions under varying environmental conditions (Kalbitz et al., 2000; Laudon et al., 2009). One of the most extensive anthropogenic disturbances in Alberta's forests is timber harvesting (ABMI, 2017). In 2016, an estimated 767,000 ha of forested land was harvested in Canada, with approximately 12% occurring in Alberta (NRCan, 2017). Timber harvesting affects important hillslope processes governing water fluxes and nutrient transport (Londo et al., 1999; Yano et al., 2000; Judd and Kling, 2002; Kalbitz et al., 2004). Thus, while disturbance from forest harvesting could potentially degrade stream water quality and alter streamflow regimes in these important headwater regions (Laudon et al., 2009), comparatively little research has examined these effects in key Alberta water supply regions such as the Rocky Mountain eastern slopes.

In snow-dominated watersheds, the spring freshet is one of the most important hydrologic periods due to rapid increases in streamflow and hydrologic flushing of the landscape (Boyer at al., 1997). Snowmelt has been shown to initially increase DOC concentrations in forest floor leachates and upper soil horizons, which subsequently decline as snowmelt progresses and snowpacks eventually disappear (Boyer et al., 1997; Yavitt and Fahey, 1985). Temporal patterns in DOC during snowmelt are likely a result of heterotrophic activity occurring under the snowpack throughout the winter, slowly releasing water soluble organic matter (Fahey, 1983). The quantity of DOC accumulated overwinter is largely a function of water percolation dynamics and antecedent soil moisture content prior to freezing (DeLuca et al., 1992; Currie et al., 1996). Stream DOC is also affected by snowmelt when rising groundwater levels intersect surficial soil horizons (Boyer et al., 1997). Rising groundwater tables and associated increased DOC concentrations in receiving streams have also been observed following harvesting in boreal catchments (Schelker et al., 2013).

Forest harvesting affects DOC dynamics by removing the tree canopy, which can impact environmental factors regulating DOC production and transport. Forest canopy removal often decreases precipitation losses associated with canopy interception which increases net precipitation inputs, increases solar radiation to soil surfaces, and may reduce inputs of fresh organic matter to the soil (Olchev et al., 2009; Schelker et al., 2012; James and Harrison, 2016; Williams et al., 2019). In Rocky Mountain regions, reducing snow interception losses increases snow accumulation in open areas (Golding and Swanson, 1986; Hubbart et al., 2015) thereby increasing water fluxes through surface soil horizons during snowmelt (Bosch and Hewlett, 1982) which is considered a first-order control regulating hillslope DOC production (Schelker et al., 2013). Increases in solar radiation results in greater temperatures in the forest floor and surface soil horizons, which, in turn, increases microbial activity (Liechty et al., 1995). Greater water fluxes and microbial activity are both linked to increased DOC concentrations in soil pore water following harvesting. Forest cover removal also reduces water losses from transpiration (Gebhardt et al., 2014; Karpyshin, 2019) which can also contribute to greater soil water fluxes, potentially resulting in rising groundwater tables. Elevated post-harvest water table positions can also incrementally drive increased DOC concentrations in pore water and groundwater following harvesting where a rise in groundwater levels can increase water table contact with DOC rich surface soil horizons (Pacific et al., 2010; Schelker et al., 2012).

Clear-cut harvesting can also change forest floor organic matter composition (Kalbitz et al., 2004; Hannam et al., 2005). Harvesting impacts the rate, and the quality and quantity of organic matter inputs to the forest floor, with these effects potentially lasting for years (Keenan et al., 1993; Ballard, 2000). Aromaticity and molecular weight of carbon compounds are important determinants of bacterial activity and bioavailability (Berggren et al., 2007; Perdue, 1998). Both Hannam et al. (2005) and Kalbitz et al. (2004) reported enrichment of aromatic carbon in the forest floor after harvesting. Microbial communities are important to DOC cycling because they are both a source of labile carbon and a primary decomposer of organic matter (Lundquist et al., 1999). DOC fluxes should be controlled by biotic factors with responses to temperature-dependent fluctuations. However, abiotic factors associated with hydrological conditions such as water fluxes can largely mask biotic controls (Kalbitz et al., 2000). Changes to bulk properties of DOC can provide valuable information about carbon character (aromaticity and molecular weight), bioavailability, drinking water treatability and source pools (McKnight et al., 1997; Weishaar et al., 2003)

Increased attention has been focused on forest harvesting impacts on DOC because studies have observed clear-cutting can increase the concentration and export of DOC from boreal systems (Nieminen, 2004; Carignan et al., 2000). Understanding the fate and transport of DOC along vertical and lateral flow pathways will enable forest managers to mitigate impacts on source water quality. Further, forest harvesting studies on subsurface DOC dynamics are few. Laudon et al. (2009) recommended more disturbance-associated DOC studies be conducted in different locations with varying hydro-climatic conditions. Currently, disturbance-associated DOC studies have been conducted predominantly in boreal and peatland settings, with a clear lack in a mountainous montane setting. As previously mentioned, these areas are important sources of high-quality water and with drinking water supplies identified as one of the top strategic priorities from water professionals (Runge and Mann, 2008), it is imperative to understand how prolific disturbances affect Canadian forested headwaters.

Thus, the broad objective of the research summarized in this chapter was to evaluate the potential impact of clear-cut harvesting on DOC in soil pore water and shallow groundwater in a forested headwater system. In particular, key objectives were to explore the variation in seasonal patterns of shallow and deeper pore water and groundwater DOC concentrations during the key snowmelt period (April-June) along hillslopes (upper hillslope to lowland/riparian areas adjacent streams) to provide insight into potential DOC transport to receiving streams four years after harvesting. Specific study objectives set out to answer the questions: (1) how does clear-cut harvesting impact spatial and temporal patterns of DOC concentrations in soil pore water and shallow groundwater?; (2) how does DOC chemical character in subsurface waters change following harvesting?; (3) do these temporal and composition changes differ between upland and lowland hillslope positions?; and (4) how do trends in DOC concentrations and chemical character observed in shallow subsurface waters compare to receiving streams? This research will provide important insights into DOC hillslope transport pathways that potentially contribute altered DOC to receiving streams following harvesting.

2.2. Materials & Methods

2.2.1. *Study area*

The study was conducted in the Star Creek and North York Creek watersheds in the front-ranges of the Rocky Mountains near Coleman, Alberta (49°37’N, 114°40’W). Star Creek and North York Creek drain into the Crowsnest River, forming part of the Oldman River headwaters. The Oldman River basin is one the highest water-yielding regions in Alberta, however it is highly stressed because of high regional water demand (Silins et al., 2014). Both watersheds are part of a larger, long-term hydro-climatic monitoring network, known as the Southern Rockies Watershed Project (SRWP) (Silins et al., 2016). SRWP consists of 34 hydro-climatic stations across nine watersheds initially to study the impacts of the 2003 Lost Creek wildfire (Phase I). The project evolved to research the impact of three harvest strategies on a multitude of hydrometric and climatic parameters (Phase II).

North York Creek and Star Creek watersheds are adjacent to each other (Figure 2-1) and have mean elevations of 1931 m and 1851 m, respectively. Vegetation is comprised dominantly of lodgepole pine (*Pinus contorta* var. *latifolia*), Douglas fir (*Pseudotsuga menziesii* var. *glauca*), trembling aspen (*Populus tremuloides*) and white spruce (*Picea glauca*). Geologic deposits in the area are characterized by Cretaceous shale and sandstone with poorly developed, overlying Eutric Brunisol soils (Bladon et al., 2008). Runoff generation in Star and North York is influenced by snowmelt, groundwater contributions and periodic rainfall driven stormflows (Macdonald et al., 2014). The surface water hydrology is characteristic of snow-dominated watersheds, with an annual hydrograph dominated by a large seasonal snowmelt peak (typically April – June).

North York watershed drains 865 ha and is undisturbed, except for designated multi-use trails. The Star Creek watershed drains 1035 ha and has been further divided into three catchments. Three harvest strategies were applied to three catchments in 2015 with whole tree harvesting implemented in all treatments. The Star West catchment (463 ha) was clear-cut with green patch retention. The Star East catchment (389 ha) was strip-shelterwood harvested with strips running east-west in alternating 35 m strips of shelterwood and 35 m clear-cut strips. Finally, the McLaren catchment (95 ha) was partial cut by single-tree and group selection harvest, resulting in 28% stand retention in the harvested area. This study focuses exclusively on the Star West catchment where 68 ha of 463 ha (~15%) was clear-cut harvested and North York served as the reference catchment. Both watersheds represent typical headwaters found in the south-west eastern slopes of the Rocky Mountains and are valuable in terms of water yield and quality, fisheries and wildlife habitat, timber and recreation.

2.2.2. *Study design*

This study used a descriptive, post-hoc reference/impact design employing replicated distributed sampling within Star West and North York watersheds to produce insights on potential forest harvesting effects on DOC. A key assumption underlying this approach is that DOC dynamics evident on hillslopes and in the stream draining the North York reference catchment would be representative of DOC dynamics in the harvested Star West catchment in the absence of harvesting (i.e. serves as a “control” for the factor of harvesting). Star West and North York catchments each had three instrumented hillslopes. Each hillslope consisted of an upland and lowland sampling plot. Initial plot selection was conducted with ArcGIS (version 10.7, ESRI) using a 1 m Light Detection and Ranging (LiDAR) digital elevation model (DEM). Using ArcGIS, upslope accumulating area (UAA; Grabs et al., 2010) was determined in order to find hillslopes that were mostly likely to be hydrologically connected to the stream during snowmelt (Jencso et al., 2009). Additional variability among hillslopes was controlled by selecting hillslopes with similar aspect, slope and vegetation community. Final plot selection was completed by field reconnaissance to verify ArcGIS findings. Aspect of the hillslopes ranged from southeast to east and the slopes were limited from 2 to 8%. Lowland and upland plots ranged from 20-35 m and 50-130 m from the stream, respectively. Two soil suction lysimeters (Figure 2-2) were installed in each plot, at an approximate depth of 30 and 100 cm belowground, or until depth of refusal due to stones or cobbles – whichever occurred first (Table 2-1). A shallow groundwater monitoring well was also installed in each plot (Table 2-1; Figure 2-2). This study design enabled the characterization of vertical and lateral movement of DOC in soils and shallow groundwater. Star Creek and North York catchments have previously been selected as reference watersheds for Phase I of the SRWP because of similarities in physical characteristics and hydrologic/climatic regimes. The primary difference between the two watersheds is that Star Creek was harvested in 2015, while North York is remained relatively undisturbed.

2.2.3. *Plot instrumentation*

Suction lysimeters were constructed from 3.18 cm PVC tubing (schedule 40) attached to a porous ceramic cup (0.5 bar air-entry, SoilMoisture Equipment Corporation). The ceramic cup was sealed to the PVC tubing using a low-vaporizing epoxy and rinsed with deionized (DI) water once sealed. A 3.18 cm hole was hand-augered in each plot to the desired depth, or depth of refusal, and a slurry was made from the native soil with DI water to allow for a better seal between the soil and ceramic cup. The suction lysimeter was inserted into the cored hole, pressed into the slurry and the remaining native material was used as backfill, roughly recreating the soil profile. The shallow groundwater wells were constructed with 5.08 cm PVC tubing (schedule 40). The bottom 75 cm of the wells were perforated every 2.5 cm and wrapped in landscape fabric to prevent sediment intrusion into the wells. Wells were hand-augered to refusal or 195 cm, whichever came first, determined by the presence of stones and cobbles. Bentonite was placed around the surface of the well and lysimeters to prevent preferential flow from the surface along the outside of the PVC tubing.

The groundwater wells were instrumented with Odyssey capacitance water level loggers (Dataflow Systems Ltd., New Zealand). The water level was recorded in 10 minute intervals and a water level sounder (Heron Instruments Inc., Ont, Canada) was used to verify the water level during each site visit. Discrepancies between the capacitance loggers and the water level sounder were corrected for by adjusting the recorded water table to match the water sounder level.

2.2.4. *Sampling and analysis*

Soil pore water and shallow groundwater samples were collected during the snowmelt period, April to June 2019. Samples were collected every 2 to 13 days (weekly on average) between March 31, 2019 and June 27, 2019. Samples were collected until the soil was too dry, the water table dropped below the terminal depth of the well or until the end of the snowmelt season. Suction lysimeters were sampled by applying a vacuum of 75 kPa for 24 hours to allow water to percolate into the ceramic cup. A peristaltic pump was used to collect the sample from the lysimeter. Between samples the peristaltic tubing was triple rinsed with DI water. The shallow groundwater wells were “sounded” to verify the water level. The wells were then either purged dry or three times the volume of water within the well using a peristaltic pump. All samples were collected in acid-washed, amber-colored 240 mL glass bottles. The first sample from each lysimeter was discarded and all subsequent samples were analyzed. Samples were stored in the dark at 4°C and submitted to the University of Alberta's Biogeochemical Analytical Services Laboratory (BASL) for analysis within 4 days. Prior to analysis for DOC and UV-Vis absorbance the samples were filtered with 0.45 µm cellulose acetate filters. DOC concentrations were determined using a Shimazdu TOC-500A Total Organic Carbon Analyzer. UV-Vis absorbance analysis was completed using a Varian Cary 50 Probe UV-Visible Spectrophotometer. Total dissolved iron (TDI) was determined using an ICP-OES (Thermo ICAP-6300 Inductively Coupled Argon Plasma - Optical Emission Spectrometer). Sample pH was measured using electrometric method using a Mantech PC-Titration Plus System. Due to limited sample volumes, not all parameters could be measured for all samples. UV-Vis absorbance and DOC concentration took priority followed by pH and dissolved iron. Sample pH and total dissolved iron was measured to quantify potential interferences with UV absorbance measurements. A narrow range in pH values (Table 2-2) reinforced the assumption that pH effects on absorbance could be ignored (Jaffrain et al., 2007). Additionally, most samples yielded total iron below the detection limited to a maximum value of 0.34 mg L^{-1} which would have increased UV_{254} measurements by 2-4 % and therefore could also be ignored (Jaffrain et al., 2007).

DOC chemical character proxies using UV-Vis absorbance were used as indicators of DOC chemical composition (aromaticity and molecular weight). Absorption coefficients were determined for wavelengths 254 and 365 nm using Equation 2-1:

$$A_\lambda = a_\lambda/\mathrm{d} \qquad [2\text{-}1]$$

where A_λ is the absorbance coefficient (m^{-1}) at wavelength λ nm, a_λ is the absorbance (unitless) at wavelength λ nm and d is the path length (m). $SUVA_{254}$ was calculated for all samples using Equation 2-2:

$$SUVA_{254} = \frac{(A_\lambda)}{DOC} * 100 \qquad [2\text{-}2]$$

where A_λ is the absorbance coefficient (m^{-1}) at wavelength 254 nm and DOC is the concentration (mg L^{-1}). Weishaar et al., (2003) reported a positive relationship between $SUVA_{254}$ with the percent aromaticity of carbon in a sample determined by ^{13}C Nuclear Magnetic Resonance (NMR). Mean molecular weight of DOC was estimated using the absorbance ratio, A_{254}:A_{365} (herein referred to as UV_{254}:UV_{365}) after Agren et al. (2008). Higher UV_{254}:UV_{365} ratios indicates a lower molecular weight of DOC within a sample.

2.2.5. *Hydrometric and climatic data collection*

Streamflow and water quality data collected as part of the SRWP core hydrometric monitoring program was used here to explore the coupling of soil, groundwater and stream DOC dynamics. Streamflow measurements were conducted downstream of the bottom-most instrumented hillslope in each catchment at SRWP's long-term hydrometric gauging stations, "North York Main" and "Star West". Streamflow was measured using a SonTek velocity meter (SonTek/Xylem In., San Diego, CA, USA) approximately 10 times throughout the ice-free season. Stage data was collected in 10-minute intervals using HOBO pressure transducers (Onset Computer Corp., Bourne, MA, USA). Stage and streamflow data were used to develop stage-discharge relationships to estimate continuous discharge based on recorded stage. To normalize for catchment area the discharges were converted to daily unit area discharge (mm d^{-1}). Stream water samples were collected every 10-14 days during the ice-free season and every 30-40 days during winter. Stream samples were collected in acid-washed (10% HCl), triple rinsed polyethylene bottles. Samples were stored at 4°C in the dark before being transported BASL for analysis. DOC concentration and UV-Vis absorbance were measured using identical methods to the soil pore water and groundwater samples.

Precipitation for each catchment was measured at 10-minute intervals using Jarek tipping bucket gauges (Geoscientific, Vancouver, Canada), fitted with an antifreeze overflow system for winter collection. Precipitation was collected at the same locations as streamflow was gauged. Air temperature was collected from "North York Mid" and "Star Main" stations, though the elevations differ for these two stations air temperature was used to explain potential causes of variation seen in the stream hydrographs and groundwater tables.

2.2.6. *Statistical analysis*

A post-hoc, comparative analysis was conducted to determine the effect of harvesting and physiographic controls on subsurface DOC dynamics. Assumptions of normality and homogeneity of variances for water quality data were tested by Shapiro-Wilk's test and an F-test as well as visually by Q-Q plots. Minor deviations to the assumption of normality were allowed for soil pore water samples as parametric tests are robust to deviations. A factorial ANOVA was used to determine which factors, harvesting (catchment), depth (horizon) or hillslope position had an impact on DOC concentration or character. Temporal differences were tested with Tukey's honest significant difference test to determine difference groupings. Stream DOC data was not normally distributed, therefore, a Mann-Whitney *U* test was used to determine potential harvesting impacts. All statistical analyses were performed in R (R-Studio, version 1.1.423, 2017) with an alpha threshold of 0.05 for statistical significance.

2.3. Results

2.3.1. *Climate and streamflow*

Total annual precipitation in Star Creek for 2019 was 738.8 mm, slightly below the 2005 to 2019 historic average of 753.2 mm (range: 532.7 - 954.1 mm). Total annual precipitation in North York was 934.5 mm for 2019, also slightly below the 2005 to 2019 average of 948.1 mm (range: 695.7 - 1190 mm).Total annual streamflow for 2019 was 516 mm yr^{-1} for the Star West catchment compared to 620 mm yr^{-1} in North York. Streamflow for both catchments fell within the historical range of 379 to 995 mm yr^{-1} and 608 to 1280 mm yr^{-1} for Star Creek and North York, respectively. The 2019 streamflow in both watersheds was only slightly below average compared to the previous 14 years. The 2019 stream hydrographs for both catchments were characterized by two distinct peaks during snowmelt, the first occurring on May 16th and the second on June 2nd (Figure 2-3). The first peak was caused by a large rise in air temperature in the preceding days as well as a relatively large precipitation event on May 16th. Air temperatures then decreased to near 0°C causing streamflow to decrease between the two peaks. Mean daily air temperatures at 'North York Mid' station ranged from -28.5°C on February 4th to 18.7°C on July 23rd (daily average = 1.2°C) in 2019. 'Star Main' mean daily air temperatures ranged from -27.0°C on February 5th to 18.7°C on June 3rd in 2019 (daily average = 2.6°C), however due to equipment malfunction a data gap exists between December 17th to 31st.

2.3.2. *Spatial variability of DOC following harvesting*

Both DOC concentrations and character in soil pore water varied strongly between harvested and reference catchments four years after harvest (Table 2-3; Figure 2-4). Median DOC of pore water in the harvested catchment was 13.9 mg L^{-1}, compared to only 3.6 mg L^{-1} in the reference catchment ($p < 0.01$; Table 2-4). The harvested catchment had DOC concentrations 129% and 94% greater than in the reference catchment at both shallow and deep soil profile depths, respectively (Figure 2-4). There was a significant difference in DOC concentration between the two depths where median pore water concentrations in shallow lysimeters was 13.9 mg L^{-1} compared to 5.3 mg L^{-1} observed in deeper lysimeters ($p < 0.01$; Table 2-3; Table 2-4). Hillslope position did not meaningfully affect DOC concentrations ($p = 0.08$), however median lowland pore water DOC was slightly greater, 6.9 mg L^{-1}, than upland pore water, 5.3 mg L^{-1}. (Table 2-3).

The chemical character of pore water DOC also differed significantly between harvested and reference catchments. Aromaticity, $SUVA_{254}$, was generally greater in pore water of harvested sites compared to reference sites. Median $SUVA_{254}$ of pore water in the harvested catchment was 3.3 L mg-C^{-1} m^{-1} while reference $SUVA_{254}$ was lower at 2.9 L mg-C^{-1} m^{-1} ($p = 0.01$; Table 2-3; Table 2-4). However, unlike DOC concentration, no significant variation in aromaticity due to depth in the soil profile was evident ($p = 0.65$; Figure 2-5; Table 2-4). Median $SUVA_{254}$ of shallow pore water was 3.2 L mg-C^{-1} m^{-1}, while deep pore water was only marginally less at 3.1 L mg-C^{-1} m^{-1}. Similarly, weaker variation in $SUVA_{254}$ across hillslope positions was observed where median $SUVA_{254}$ of lowland pore water was 3.5 L mg-C^{-1} m^{-1} compared to 3.0 L mg-C^{-1} m^{-1} in pore water from upland plots ($p = 0.07$, Table 2-3; Table 2-4).

Similarly, UV_{254}:UV_{365} of pore water from plots in the harvested catchment had a greater median molecular weight ratio (2.4) than that from reference plots (2.0) indicating the bulk molecular weight of compounds comprising DOC were lighter in the pore water from the harvested plots ($p = 0.04$, Table 2-4). The molecular weight ratio did not vary between shallow and deep pore water ($p = 0.09$; Table 2-4). Hillslope position had the least impact on UV_{254}:UV_{365}. Lowland pore water had a ratio of 2.2 while pore water from upland plots was only slightly greater at 2.3 ($p = 0.74$; Table 2-3; Table 2-4).

2.3.3. *Temporal variability of DOC following harvesting*

Temporal trends in DOC concentrations and indicators of chemical character were examined during the spring period when soil pore water could be more consistently sampled from suction lysimeters. The snowmelt period was divided into two distinct periods, early melt and late melt. Early melt in the harvested catchment was from March 30th to May 10th (5 sampling events), while late melt was from May 17th to June 19th (4 sampling events). Early melt in the reference catchment was from May 8th to May 24th (3 sampling events) and late melt was from May 29th to June 27th (4 sampling events). While snowmelt generally occurred in both catchments near early May, the onset of melt began about 5-10 days earlier in the harvested catchment (Star West) because of greater solar exposure than in North York (reference watershed). While these two periods reflected general timing of early and latter periods of snowmelt on hillslopes, they did not correspond precisely with the timing of melt water delivery to streams as reflected in stream hydrographs. Harvested early to late melt separation corresponded with the apex of the first peak in the Star West hydrograph while reference early to late melt separation corresponded with rising limb of the second peak in the North York hydrograph (Figure 2-3).

Surprisingly, temporal trends in pore water DOC concentrations during snowmelt were not evident in either catchment ($p > 0.05$; Table 2-5) where DOC concentrations remained relatively stable between the early and late snowmelt periods. Median DOC concentrations in harvested catchment were 13.3 and 14.9 mg L^{-1} during the early and late melt periods, respectively ($p > 0.05$; Table 2-5). Similarly, no difference in DOC concentrations were observed between the early (3.6 mg L^{-1}) and late (3.2 mg L^{-1}) melt periods for the reference catchment ($p > 0.05$). Only slightly greater variation in DOC chemical character was observed between early- and late-melt periods (Table 2-5; Figure 2-6). While median $SUVA_{254}$ increased from 3.1 to 3.8 L mg-C^{-1} m^{-1} and molecular weight ratio decreased from 2.5 to 1.9 (molecular weight became heavier) between the early and late melt period in the harvested catchment, neither of these trends were significant ($p > 0.05$; Table 2-5; Figure 2-6). In contrast, the general pattern of variation during the melt season in the reference plots was opposite to that observed in harvested plots with a slight (non-significant) decrease in aromaticity and significant ($p < 0.05$) increase in the molecular weight ratio (molecular weight became lighter) between early and late snowmelt periods.

2.3.4. *Groundwater and stream DOC*

Water tables in the groundwater monitoring wells developed around April 20th in both catchments, with the exception of Star West Upland well #1 which developed in late March (Figure 2-7). April 20th corresponds to a large precipitation event, coupled with air temperatures rising above 0°C (Figure 2-3). A rise in water table levels was noted in the reference lowland wells, which matches the first peak of the North York hydrograph on May 16th. The wells then receded, with three of water tables dropping below the terminal depth of the wells. The remaining three wells (RL-#2 & #3, RU-#1) responded to a precipitation event on July 8th and water levels remained present in the wells beyond the end of snowmelt.

Despite strong seasonal variation of shallow groundwater elevations, DOC concentrations in groundwater were generally stable with little variation throughout the snowmelt period. However, DOC in North York Lowland well #3 increased by 200% towards the end of snowmelt as groundwater levels were receding (Figure 2-7). Median seasonal groundwater DOC concentrations were greater in the harvested catchment (4.7 mg L^{-1}) compared to the reference catchment (2.6 mg L^{-1}) however the strength of these differences could not be evaluated due to the limited number of samples/plots with groundwater present (2 wells in the harvested and 4 wells in the reference catchments). In contrast, aromaticity ($SUVA_{254}$, Figure 2-7) and molecular weight ratio (UV_{254}:UV_{365}) of groundwater displayed high variation amongst the different wells but were similar between harvested and reference catchments. Median $SUVA_{254}$ of groundwater DOC was 4.1 and 3.9 L mg-C^{-1} m^{-1}, while median UV_{254}:UV_{365} was 2.0 and 1.7 for harvested and reference catchments, respectively. Moderate temporal variation in the chemical composition of groundwater DOC indicated by these two parameters was evident during the snowmelt season.

Stream water DOC concentrations were notably lower than both soil pore water and groundwater where the pattern of DOC concentration was soil pore water DOC >> groundwater DOC >> stream water DOC in both watersheds. However, stream water DOC also showed much stronger temporal fluctuations compared to soil pore water and groundwater. Stream water DOC concentrations increased approximately twofold from overwinter baseflows to peak early summer flows. During baseflow conditions, both streams fluctuated between 0.2 and 0.7 mg L^{-1} and peaked at 1.1 mg L^{-1} during snowmelt. Concentrations then slowly subsided during the falling limb of the annual hydrograph (Table 2-6) and continued to decrease before plateauing during fall baseflows. Median DOC concentrations did not differ ($p = 0.47$) between the harvested (0.6 mg L^{-1}) and reference watersheds (0.5 mg L^{-1}) across the entire 2019 season, nor was any difference evident when DOC concentrations were greatest during the snowmelt period ($p = 0.85$; Table 2-6). Similarly, while the median annual $SUVA_{254}$ value was marginally lower in the harvested catchment, the ranges observed largely overlapped and did not differ over 2019 nor during the snowmelt freshet ($p > 0.05$). However, UV_{254}:UV_{365} was variable across catchments showing higher median DOC molecular weight ratio in the harvested catchment (*p* = 0.01) though this difference was not evident during higher melt freshet flows (*p* = 0.46, Table 2-6).

2.4. Discussion

The major finding of this study was that while greater soil pore water and groundwater DOC concentrations were evident in the clear-cut harvested catchment compared to an adjacent reference catchment four years after logging, these differences did not correspond the meaningful differences in DOC concentration between harvested and reference streams. DOC production in soil pore water was most strongly influenced by differences in harvesting history among catchments and depth within the soil profile. Overall, the influence of harvesting (difference between harvested/reference catchments) on DOC dynamics was strongest in soil pore water, intermediate in shallow groundwater, and weakest (no effect) in stream water draining harvested and reference watersheds. This was likely due to either, or both, dilution of disturbance effects along the soil pore water - groundwater - stream transport pathway or may reflect pre-existing differences in DOC dynamics amongst adjacent watersheds, unrelated to harvesting impacts on DOC.

2.4.1. *Spatial variability of DOC following harvesting*

The greater soil pore water DOC concentrations and more aromatic DOC composition in the clear-cut harvested catchment is generally consistent with other studies, however the literature does not support consistent conclusions. Research on impacts of clear-cut harvesting on DOC shows highly variable results across the literature (Kalbitz et al., 2000). For example, Johnson et al. (1995) observed increased DOC concentrations in the forest floor and underlying soil horizons after harvesting, while Meyer and Tate (1983) report decreased DOC after logging. Furthermore, studies by McDowell and Likens (1988) and Moore and Jackson (1989) reported clear-cut harvesting had no impact on DOC concentrations. Changes in land management are understood to affect DOC dynamics by altering microbial decomposition, shifting organic matter inputs to soils and altering substrate quality for microbial communities (Kalbitz et al., 2000). Clear-cut harvesting has been shown to result in warmer, wetter soils, especially during the spring and summer months (Schelker et al., 2013 and Greenacre, 2019). A 2.1°C increase in soil temperatures has shown to increase DOC concentrations in forest floor solutions by 16% (Liechty et al., 1995). Soil moisture has also shown a positive relationship with DOC production with the cause likely being enhanced biological activity (Falkengren-Grerup and Tyler, 1993; Christ and David, 1996). Consistent with this understanding, the present study showed higher DOC concentrations in the harvested catchment compared to the reference suggesting short-term impacts on hillslope DOC production likely occurred during this period. Increased water fluxes due to a reduction in precipitation interception and increased microbial activity can result in greater carbon fluxes from the Oe and Oa layers (the fibric and humic layers, respectively, under the Canadian System of Soil Classification) up to 10 years following harvesting (Piirainen et al., 2002, Kalbitz et al., 2004; Bowering et al., 2020). Therefore, it would be reasonable to assume this increased carbon export leaches into the soil profile increasing DOC concentrations in pore water. Schelker et al. (2013) argued that mechanisms controlling DOC mobilization are not altered by harvesting but, rather are amplified following harvesting in a boreal setting. This appears to be the case in the watersheds studied here as well.

Aromaticity and molecular weight of DOC in soil pore water were significantly different between the two catchments. The harvested catchment had greater aromaticity. Enrichment in aromatic carbon following harvesting has been reported in the forest floor layer in the boreal forest (Kalbitz et al., 2004, Hannam et al., 2005). While aromaticity was greater in the harvested catchment, the molecular weight of the compounds were slightly lighter, contrary to the positive correlation between molecular weight and aromaticity typically observed (Agren et al., 2008). Kalbitz et al. (2004) postulated a stark reduction in organic matter inputs coupled with increased microbial activity leads to more aromatic carbon and greater complexity of carbon compounds in the forest floor. This finding was corroborated in the boreal mixedwood region in northern Alberta by Hannam et al. (2005). Due to changes in the dominant vegetation following harvesting, the quality of litter and subsequently DOC in soil solutions is likely affected (Kuiters and Mulder, 1993).

DOC concentrations in soil pore water were strongly variable by depth with shallow soil pore water having greater DOC concentrations in both catchments. This finding is consistent with the literature and widely attributed to adsorption of DOC to mineral soil and, to a lesser degree, decomposition (Kalbitz et al., 2000). However, DOC chemical character was not influenced by depth in these catchments. The surficial sources of DOC (throughfall, organic matter, soil water) tend to be more aromatic than deeper sources such as deep groundwater due to greater contact time with mineral soil coupled with preferential adsorption of hydrophobic compounds (Inamdar et al., 2012; Jardine et al., 1989). However, aromaticity and molecular weight were not meaningfully different between shallow and deep pore water. This result was unexpected because it is commonly reported that hydrophobic DOC is preferentially adsorbed to mineral soil (Jardine et al., 1989). In some cases, preferential adsorption is strong enough to displace indigenous (bound) hydrophilic DOC (Kaiser et al., 1996), resulting in surface soil horizons that are more humic and aromatic (Aitkenhead-Peterson et al., 2003). The unexpected result in this study could be due to the shallow pore water being from the B-horizon, while comparisons of shallow surface pore water (i.e. 5-10 cm belowground) to deep (100 cm or more) pore water would potentially yield a difference in DOC character. Adsorption influences on DOC character are more thoroughly explored in Chapter 3.

Hillslope position did not significantly impact DOC concentrations or DOC chemical character in these catchments. However, lowland DOC had slightly greater DOC concentration and aromaticity than upland sites, though these were minor and likely due to natural variability. Riparian soils tend to be flushed more often than upland soils leading to lower DOC concentrations (Boyer et al., 1997). The riparian areas for Star Creek and North York Creek are small and an abrupt, steep bank was present in Star West along the west edge of the stream where sampling plots were located. Sampling plots in Star West were likely more characteristic of lower hillslope position soils, rather than true riparian soils. Lowland soils were more aromatic than corresponding upland soils which could reflect poor decomposition in wetter, cooler environments.

2.4.2. *Temporal variability of DOC following harvesting*

Temporal variability in soil pore water DOC concentrations were not evident through early and late snowmelt periods. DOC concentrations remained stable through snowmelt indicating hydrologic flushing did not likely control DOC concentrations in soil pore water during this period. Boyer et al. (1997) reported rapid decreases in upper soil DOC during the rising limb of the hydrograph (early melt) and then as snowmelt ended many sites showed a subsequent increase in DOC concentrations. Pore water in this study did not display this trend, rather most sites had stable DOC concentrations. Burns et al. (2016) found DOC concentrations in pore water on south-facing slopes were initially low then became more variable throughout snowmelt while north-facing slopes showed an initial drop on DOC concentrations with melt water dilution and were stable thereafter as snowmelt progressed. Plots in this study were on south or southeast facing slopes and did not display these temporal trends. DOC is highly influenced by the groundwater table where seasonal rising and lowering of the water table intersecting with surficial soil horizons has been commonly found to result in temporal changes in soil pore water and stream water DOC concentrations. Due to no shallow groundwater tables developed in many study plots (especially in Star West) it is not surprising that DOC concentrations were stable. Increased water fluxes during snowmelt would conceivably alter DOC concentrations in pore water, however, it appears a buildup of DOC over winter along with continued microbial activity in spring may have promoted a steady, consistent source of DOC. However, late winter (pre-melt) pore water could not be collected because of frozen soils or soils too dry to enable lysimeter sampling.

Aromaticity and molecular weight of DOC were weakly and inconsistently variable during snowmelt. In the reference catchment, early melt was generally more aromatic, and compounds comprising DOC had a higher molecular weight than late melt. This contrasts with the harvested catchment where early melt was more aliphatic and of lighter molecular weight than late melt. It should be noted that early melt $SUVA_{254}$ values were similar between the two catchments. Soil conditions in the fall of 2018 had low antecedent soil moisture, therefore likely little microbial activity occurred over the winter. Initial flushing of soils during snowmelt flushes built up DOC from fall and winter heterotrophic activity and microbial biomass (Brooks et al., 1999). However, as snowmelt progressed, pore water in the reference catchment became marginally less aromatic while it became marginally more aromatic in the harvested catchment. While this pattern was not strong, this may have reflected differences in soil moisture promoting differential fluxes of organic matter constituents to become more prevalent. DOC chemical character has been used to trace temporal shifts in source water to receiving streams by investigating changes in hydrologic connectivity of catchment soils (Burns et al., 2016). In coastal, temperate rainforests aromaticity did not vary temporally from May to October and biodegradable DOC (BDOC) showed no seasonal patterns (Fellman et al., 2009) which is consistent with a hardwood forest study (Boyer and Groffman, 1996). Further, Fellman et al. (2009) found a poor predictive relationship of $SUVA_{254}$ with BDOC indicating $SUVA_{254}$ may not be the best predictor of DOC lability across different environments. However, these indicators of DOC chemical character were included in the present study more simply to explore if harvesting was associated with clear pattern in DOC chemical composition, rather than tracing hydrologic flow paths.

2.4.3. *Stream and groundwater linkages to soil pore water DOC*

DOC of shallow groundwater was marginally different between harvested and reference watersheds, however due to the lack of groundwater tables developing in wells within the harvested catchment, strong inferences on harvesting effects are not supported from this study. DOC concentrations in shallow groundwater were stable throughout the snowmelt period with the exception of North York Lowland well #3 which increased in concentration when groundwater elevations were declining during the falling limb of the stream hydrograph (Figure 2-7). Rising groundwater levels intersecting with surficial soil horizons has been shown to increase DOC concentrations (Boyer et al., 1997; Pacific et al., 2010). However, there was no evidence of this occurring in this study as groundwater DOC concentrations were unaffected by the groundwater level. In Vindeln Experimental Forests (Agren et al., 2008) and Jemez River Basin Critical Zone Observatory (Perdrial et al., 2014) the rise of water tables was shown to correspond with increases in stream DOC concentrations. Though stream water DOC increased during early spring in the present study, this was likely due to greater hydrologic connectivity with soils immediately adjacent to the streams and overland flow rather than longer distance hillslope transport of soil water or shallow groundwater. Pabich et al. (2001) found shallow groundwater DOC was stable at individual sites over time but highly variable spatially suggesting that local heterogeneity at hillslope scales rather than longer hillslope transport pathways are an important influence on DOC delivery to shallow groundwater. This assertion appears consistent with general findings from the present study.

Aromaticity of DOC in groundwater showed both high temporal and spatial variability. However, aromaticity of DOC in groundwater did not respond to changes in the water table which was expected to be a dominant control (Agren et al., 2008). Variation of aromaticity was high during snowmelt ranging from 2.0 to 7.5 L mg-C^{-1} m^{-1} for all samples. High aromaticity observed in a several wells was not expected because preferential adsorption of aromatic compounds occurs when water percolates down the soil profile leading to groundwater receiving aliphatic DOC. However, adsorption of DOC may not be the primary driver of DOC reductions in the subsurface environment in this area based on these results. This is also explored in more detail in Chapter 3. Heterotrophic activity in the soil and groundwater would target hydrophilic, aliphatic compounds and may lead to the loss of labile DOC as water percolates down the profile, resulting in highly aromatic DOC reaching shallow groundwater.

Despite differences in soil pore water and groundwater DOC, stream water DOC was similar in concentration and chemical character between the harvested and reference watersheds (with the minor exception of annual molecular weight ratio). This finding is in contrast to several previous studies. Laudon et al. (2009) found stream DOC concentrations increased one year following harvest due to increased runoff resulting in surficial horizons becoming connected to the stream through a mechanism of “transmissivity feedback” (Weiler et al., 2003). Though increases in pore water DOC were evident, a lack of connectivity demonstrated by undeveloped shallow water tables in the majority of wells in the harvested catchment was likely responsible for the lack of a strong response to harvesting in the stream. Where groundwater tables remained deep, groundwater DOC was stable as observed in the reference catchment. Watershed sources for Star Creek have been previously characterized as snow from the alpine during the rising limb of the hydrograph, soil and till storage during the receding limb and deeper storage (fractured bedrock) during baseflows (Spencer et al., 2019). Based on this information and the results of this study, it is likely that soil water and shallow groundwater account for a very small proportion of stream water. Groundwater in upland plots indicated almost no hydrologic connectivity to the stream through shallow, subsurface flow pathways. Due to the lack of hydrologic connectivity, water percolates vertically into deeper groundwater and till storage where dilution and adsorption may further decrease concentrations. Soil pore water and shallow groundwater that does connect to the stream is likely diluted by other sources and therefore disturbance signatures on DOC concentration or chemical character are not likely to be observed. Large differences in DOC concentrations between groundwater and surface water are reported in the literature and indicate the majority of DOC originating from the landscape may also be removed at or below the sediment-water boundary by detritivores (Ford and Naiman, 1989). Indeed, the three- to fourfold decreases in DOC concentration between the shallow groundwater and stream water suggests another process or source may be important in these catchments and likely masked the harvest effects on the linkage between soil pore water, shallow groundwater and catchment scale stream water.

2.5. Conclusion

Differences in pore water and groundwater DOC were observed between hillslopes in harvested and unharvested catchments in otherwise similar, adjacent watersheds. Soil pore water DOC concentrations were significantly elevated compared to the reference catchment. DOC concentrations in hillslope pore water were strongly variable by depth in the soil profile likely a result of microbial decomposition and, to a lesser extent, adsorption to mineral soils. Surprisingly, DOC concentrations showed little difference between lowland and upland sampling plots, indicating hillslope position within otherwise upland soil settings may have a smaller influence on pore water DOC.

Aromaticity and molecular weight of DOC were different between catchments. Difference in substrate quality and microbial decomposition processes likely resulted in altered DOC moving down the soil profile. The effects of harvesting (as evidenced by difference between harvested and reference watersheds) on DOC character were not as strong as those observed on DOC concentration. Other factors such as depth in soil profile and hillslope position had minor to no effect on DOC composition in soil pore water. Overall, DOC chemical character was more temporally than spatially variable.

Shallow groundwater DOC seemed to be elevated in the harvested watershed, however this difference could not be statistically tested due to a low number of samples (only two wells had a water table in the harvested watershed). Stream water DOC concentration and aromaticity were similar between the two catchments. However, differences in DOC concentration between soil pore water, shallow groundwater, and stream water likely reflected dilution during runoff generation processes in these catchments. Soil pore water and shallow groundwater likely contribute only a small proportion of water to the streams. Therefore changes in DOC at the catchment scale after land disturbance would likely be much smaller than impacts at the hillslope scale.

It is noteworthy to mention that the strength of the inferences regarding effects of harvesting from this study are predicated on the assumption that differences in DOC dynamics evident at plot, local hillslope (local groundwater), and catchment scales reflected the presence / absence of harvesting in these two otherwise similar, adjacent catchments. However, without pre-disturbance data on soil/groundwater DOC dynamics, the potential influence of pre-existing differences in DOC among harvested and reference watersheds cannot be discounted. While differences in DOC observed between reference and harvested catchments were consistent at both plot and local hillslope scales (i.e. groundwater footprint), the strength of the inferences on the effects harvesting should be interpreted with caution.

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Table 2-1: Summary of study factors on instrumented hillslopes and sampling plots.

Site ID	Land classification	Hillslope position	Shallow lysimeter depths	Deep lysimeter depths	Groundwater well depths	No. of replicates
HU	Harvested	Upland	30-32 cm	85-106 cm	104-136 cm	3
HL	Harvested	Lowland/Riparian Buffer	32-33 cm	83-98 cm	103-185 cm	3
RU	Reference	Upland	34-35 cm	100-107 cm	154-195 cm	3
RL	Reference	Lowland	32-34 cm	94-100 cm	133-139 cm	3

Table 2-2: Summary table of pH and dissolved iron (mg L^{-1}) in shallow soil pore water (PW), deep soil pore water, groundwater and streams separated by catchment. Mean, range and number of samples are shown in the table.

		pH			**Fe (mg L^{-1})**		
		Mean	*Range*	*n*	*Mean*	*Range*	*n*
Harvested	*Shallow PW*	7.0	5.9 - 8.1	18	0.13	<0.02 - 0.34	17
	Deep PW	7.6	7.0 - 8.3	32	0.03	<0.02 - 0.20	29
	Groundwater	7.6	7.1 - 8.1	14	<0.02	<0.02	17
	Star West Creek	8.2	7.5 - 8.4	16	<0.02	<0.02	14
Reference	*Shallow PW*	7.6	7.1 - 7.9	17	0.02	<0.02 - 0.04	12
	Deep PW	7.5	7.0 - 8.2	28	<0.02	<0.02	28
	Groundwater	7.3	7.1 - 8.0	21	<0.02	<0.02	18
	North York Creek	8.2	7.7 - 8.4	15	<0.02	<0.02	13

Table 2-3: Summary table of DOC concentration (mg L^{-1}), $SUVA_{254}$ (L mg-C^{-1} m^{-1}) [proxy for aromaticity] and UV_{254}:UV_{365} [proxy for molecular weight]. Values indicate the median ±(SD).

	Catchment		**Depth**		**Hillslope position**	
Parameter	*Harvested*	*Reference*	*Shallow*	*Deep*	*Lowland*	*Upland*
DOC concentration	13.9 (9.5)	3.6 (4.0)	13.9 (7.6)	5.3 (8.9)	6.9 (10.2)	5.7 (4.7)
$SUVA_{254}$	3.3 (0.9)	2.9 (0.9)	3.2 (0.9)	3.1 (0.9)	3.5 (0.9)	3.0 (0.8)
UV_{254}:UV_{365}	2.4 (0.6)	2.0 (0.8)	2.5 (0.7)	2.1 (0.7)	2.2 (0.8)	2.3 (0.7)

Table 2-4: Statistical significance (p values) of main and interaction effects from factorial ANOVAs of DOC concentration (mg L^{-1}), SUVA$_{254}$ (L mg-C^{-1} m^{-1}) [proxy for aromaticity] and UV$_{254}$:UV$_{365}$ [proxy for molecular weight]. Underlined values indicate significant differences at $\alpha = 0.05$.

Parameter	**Harvesting**	**Depth**	**Hillslope position**	**Harvesting:Depth**	**Harvesting:Hillslope**	**Depth:Hillslope**
DOC concentration	<0.01	<0.01	0.08	0.82	0.04	0.36
SUVA$_{254}$	0.01	0.65	0.07	0.94	0.16	0.08
UV$_{254}$:UV$_{365}$	0.04	0.09	0.74	0.49	0.75	0.66

Table 2-5: Variation of DOC concentration (mg L^{-1}) and DOC chemical character proxy parameters ($SUVA_{254}$ – L mg-C^{-1} m^{-1}) in harvested and reference catchments. Samples were separated by median date for each catchment. Groups were determined by a post-hoc Tukey's HSD test. Values indicate the median ±(SD).

		DOC concentration	**Group**	**$SUVA_{254}$**	**Group**	**UV_{254}:UV_{365}**	**Group**
Harvested	*Early melt*	13.3 (11.8)	a	3.1 (0.8)	ab	2.5 (0.4)	a
	Late melt	14.9 (6.3)	a	3.8 (0.9)	a	1.9 (0.8)	a
Reference	*Early melt*	3.6 (4.1)	b	3.1 (0.9)	ab	1.5 (0.5)	b
	Late melt	3.2 (4.0)	b	2.7 (0.8)	b	2.5 (0.9)	a

Table 2-6: Comparison of DOC concentration (mg L^{-1}) and DOC chemical character proxy parameters ($SUVA_{254}$ – L mg-C^{-1} m^{-1}) in North York (reference) and Star West (harvested) streams over 2019 and focused on snowmelt (April 5th to July 5th). Underlined values indicate significant differences at $\alpha = 0.05$ tested by a Mann-Whitney *U* test.

	Harvested		**Reference**		
Annual	**Median**	**Range**	**Median**	**Range**	**p-value**
DOC concentration	0.5	0.2-1.1	0.6	0.3-1.1	0.47
$SUVA_{254}$	3.0	1.2-6.8	2.6	1.4-4.8	0.19
$UV_{254}:UV_{365}$	6.0	1.7-8.9	7.0	5.3-9.0	<u>0.01</u>
Snowmelt					
DOC concentration	0.7	0.4-1.1	0.9	0.5-1.1	0.99
$SUVA_{254}$	3.8	3.0-6.8	2.7	1.8-4.8	0.25
$UV_{254}:UV_{365}$	7.2	1.7-8.9	7.0	6.1-9.0	0.79

Figure 2-1: Map of Star and North York watersheds showing instrumented sampling plots and hydrometric stations. Right inset shows watershed location in Alberta.

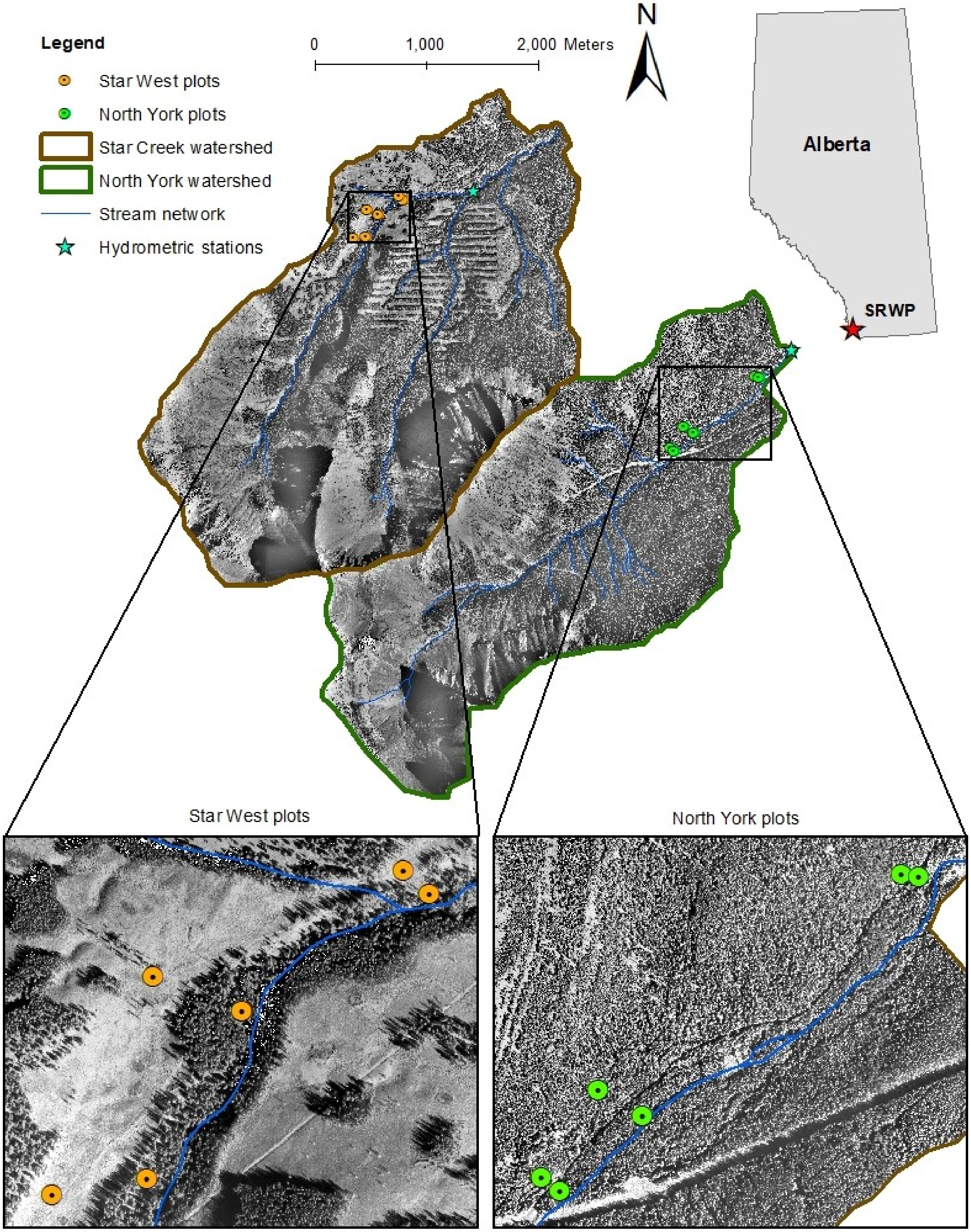


Figure 2-2: Photographs showing typical sampling plots in the upland hillslope position.

Harvested (upland)

Reference (upland)

Figure 2-3: Hydrometric and climatic variables for harvested (Star West) and reference (North York) catchments for 2019. Solid blue lines indicate area-weighted mean daily discharge, dashed gray lines indicate mean daily air temperature and gray bars denote daily precipitation.

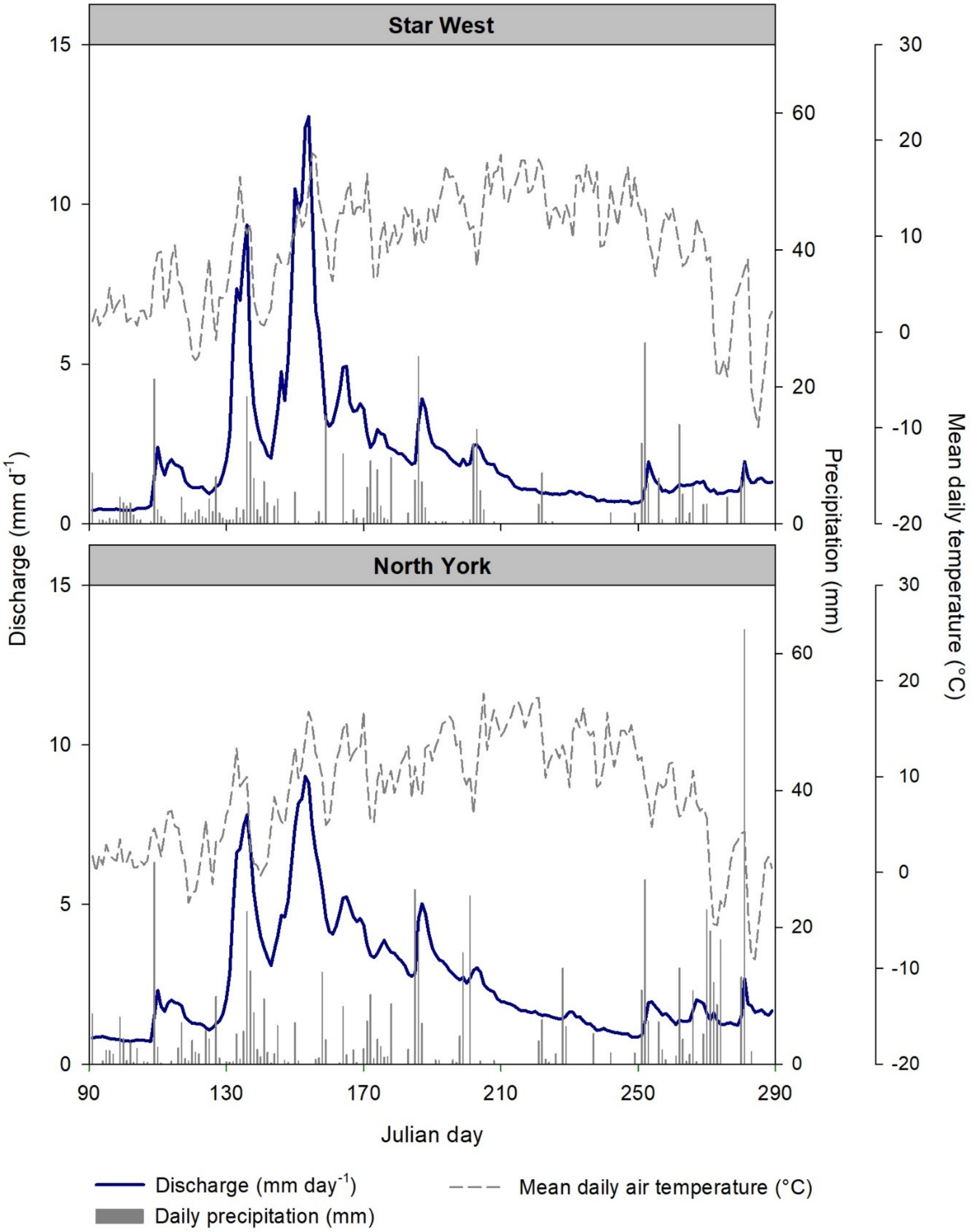


Figure 2-4: Distribution (boxplots) of soil pore water (PW) DOC concentrations during 2019 snowmelt for two soil depths in harvested and reference catchments. Upper and lower rectangle bounds denote 25th and 75th percentiles, the horizontal line indicates the median and “whiskers” denote 5th and 95th percentiles.

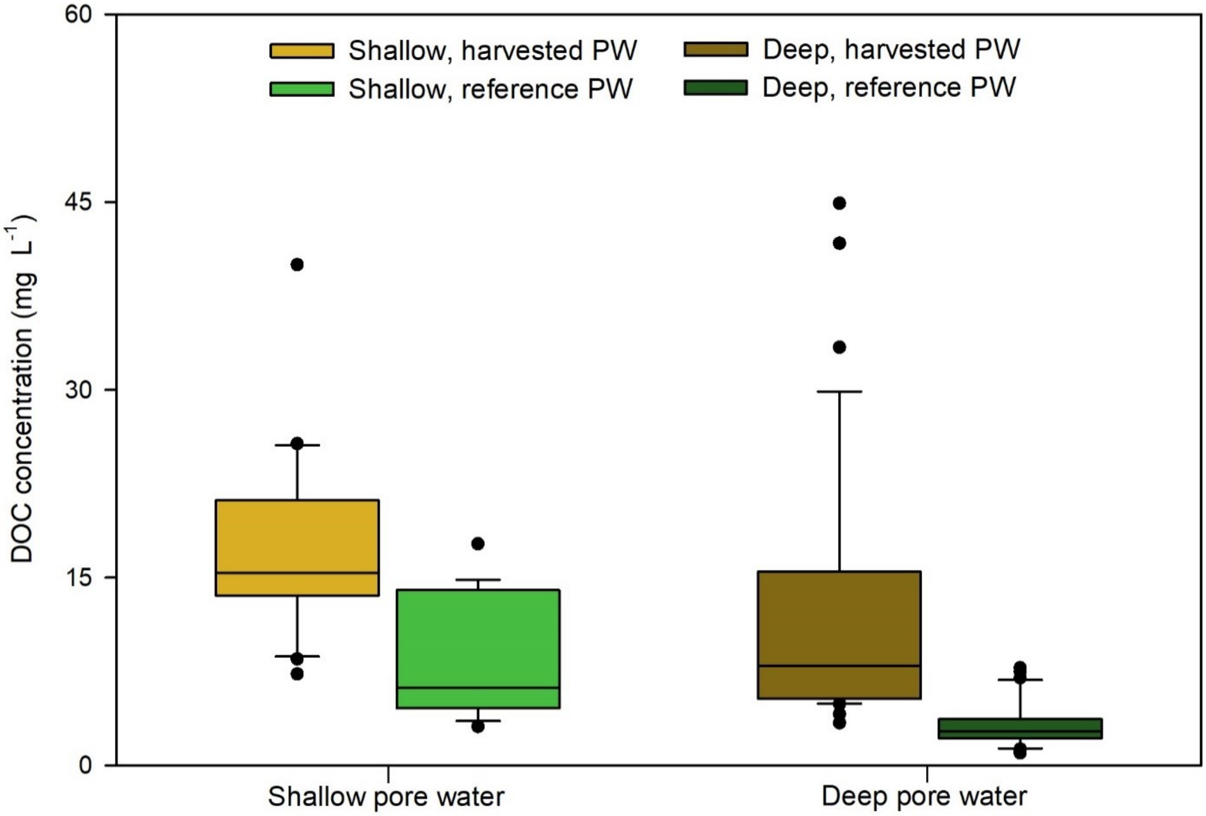


Figure 2-5: Distribution (boxplots) of soil pore water DOC chemical character proxy indicators during 2019 snowmelt for two soil depths in harvested and reference catchments. Upper and lower rectangle bounds denote 25th and 75th percentiles, the horizontal line indicates the median and “whiskers” denote 5th and 95th percentiles.

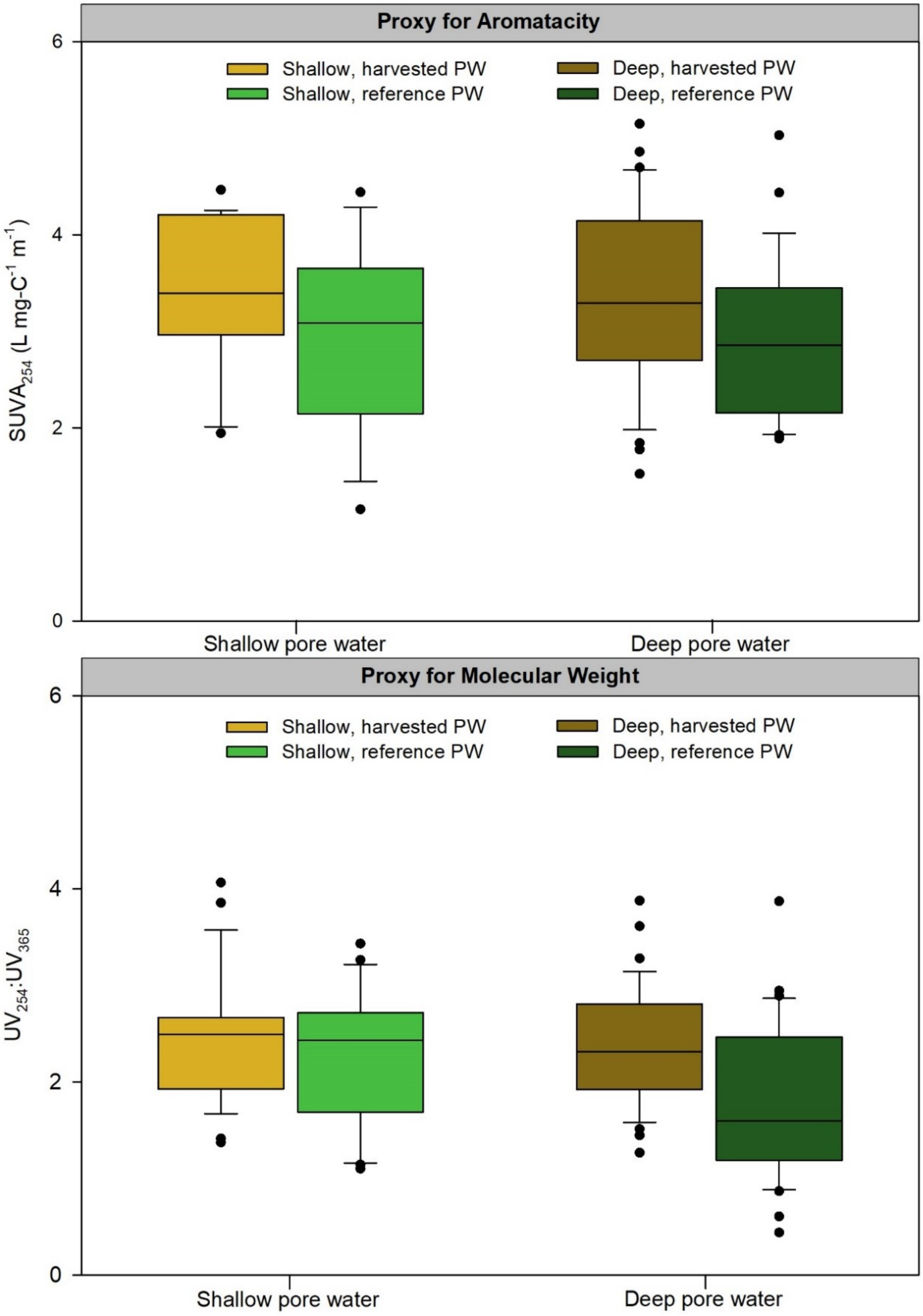


Figure 2-6: Distribution (boxplots) of soil pore water DOC concentrations and chemical character proxy indicators during 2019 snowmelt for two soil depths in harvested and refence catchments. Upper and lower rectangle bounds denote 25th and 75th percentiles, the horizontal line indicates the median and "whiskers" denote 5th and 95th percentiles.

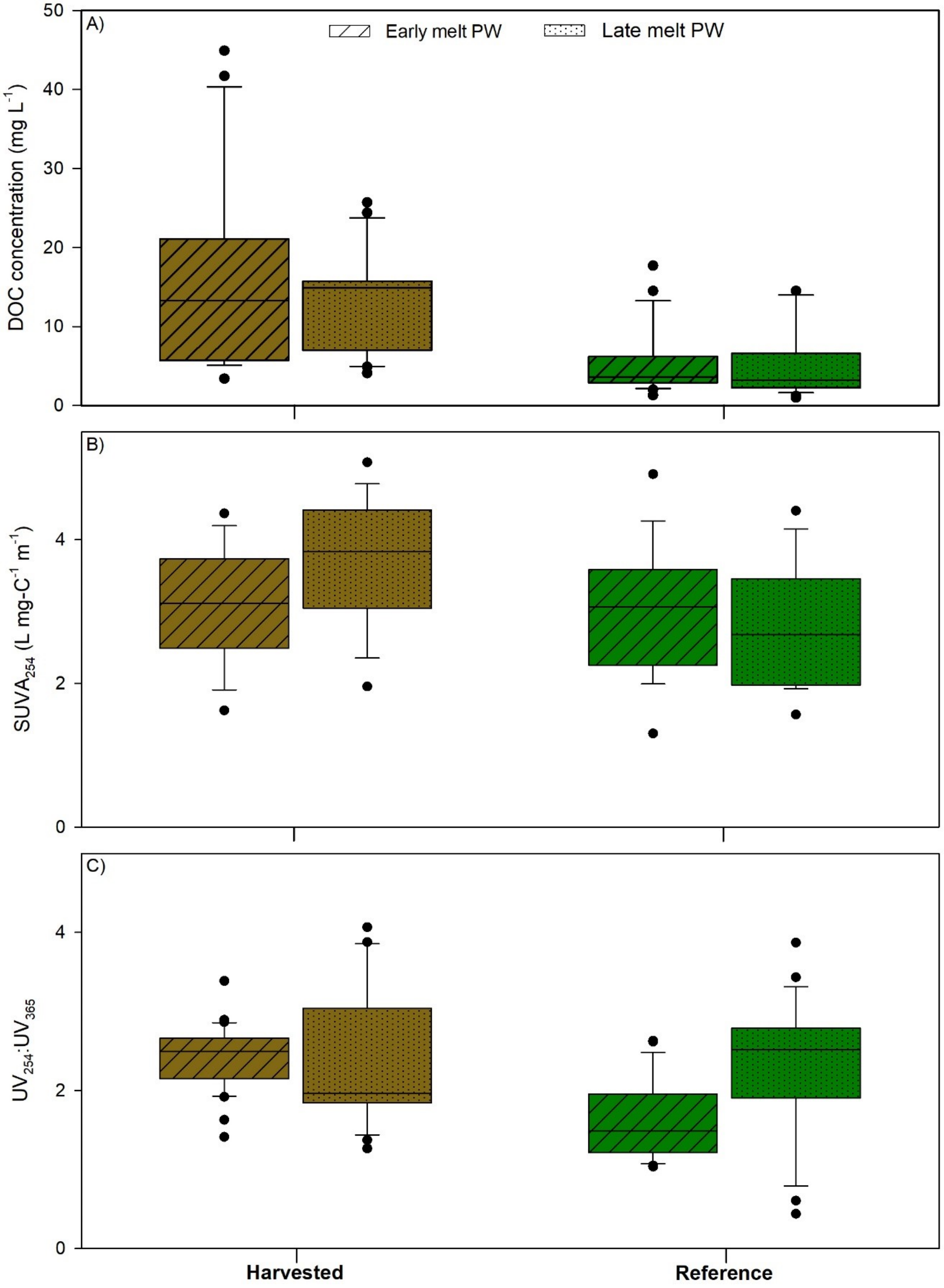
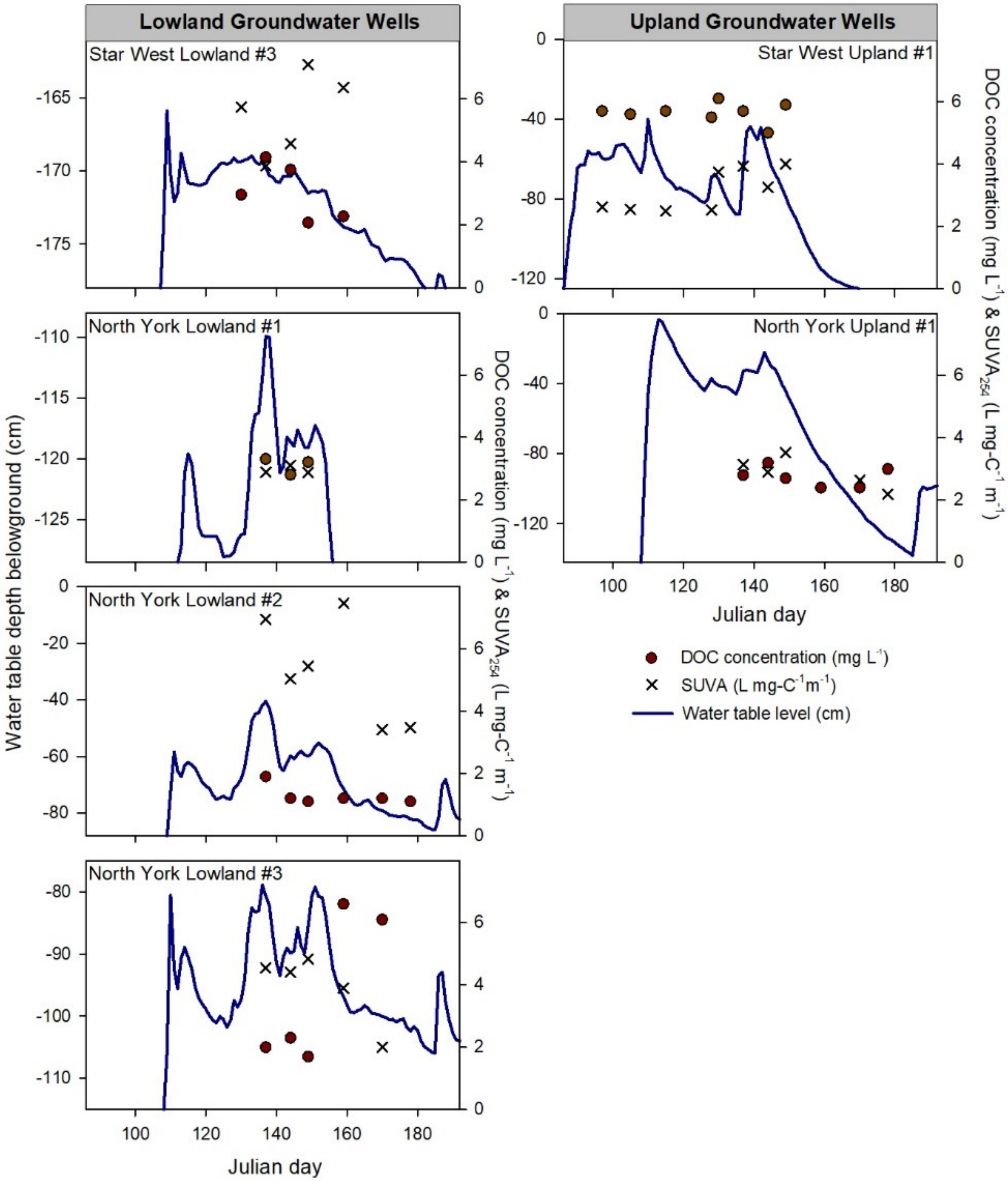


Figure 2-7: Groundwater level, DOC concentrations and SUVA254 (proxy for aromaticity) in monitoring wells that developed a groundwater table. Red dots indicate DOC concentration (mg L^{-1}) and the X symbol indicated SUVA254 (L mg-C^{-1} m^{-1}).



Chapter 3: Assessing dissolved organic carbon adsorption behavior in poorly developed soils following clear-cut harvesting

3.1. Introduction

Dissolved organic carbon (DOC) plays an important role in soil and water by influencing soil formation (Dawson et al., 1978), providing an energy source to soil and aquatic fauna (McDowell et al., 2006) and affecting the mobilization and transport of nutrients (Qualls and Haines, 1991). Forest harvesting has been known to increase DOC leaching from the forest floor to underlying mineral soils (Johnson et al., 1995) and subsequent export from harvested watersheds (Laudon et al., 2009). Increases in DOC loading after harvesting could potentially impact downstream drinking water "treatability", because dissolved organic carbon requires removal during water treatment leading to increased treatment costs and other challenges such as potential taste and odor issues (Emelko et al., 2011).

Forested watersheds provide a source of critical, high-quality drinking water to downstream communities (Emelko et al., 2011). These watersheds are sensitive to disturbances such as wildfire and forest harvesting, which can impact the quality and quantity of water in these streams (Silins et al., 2009; Stone et al., 2014; Murray and Buttle, 2003). Disturbances can impact local conditions and disrupt the natural biogeochemical processes regulating nutrient export to receiving streams (Kreutzweiser et al., 2008; Ballard, 2000). Removal of the forest canopy can increase solar radiation and precipitation reaching the forest floor leading to elevated soil temperature and soil moisture (Bosch and Hewlett, 1982; Gebhardt et al., 2014; Greenacre, 2019), both of which play a key role in organic matter mineralization. Subsequently, these changes increase microbial activity leading to elevated DOC leaching to underlying soil (Startsev et al., 1998).

However, the storage and transport of DOC through the subsurface can also play a key role in regulating watershed DOC export. Once DOC percolates from the forest floor organic matter into mineral soils, adsorption to soil surfaces occurs rapidly (Jardine et al., 1989; Dahlgren and Marrett, 1991) and DOC delivery may be further affected by microbial degradation along subsurface transport pathways (Qualls et al., 2002). Mechanisms controlling soil DOC exchange are still not widely understood though anion exchange, ligand exchange-surface complexation, cation bridging, hydrogen bonding, van der Waal forces or physical adsorption are considered as dominant processes (Kalbitz et al., 2000). Soil and aqueous DOC exchange processes also influence the chemical character of DOC in soil solution because hydrophobic compounds are preferentially adsorbed over hydrophilic compounds (Guggenberger and Zech, 1993a; Gu et al., 1995). In general, the fate of DOC in the soil profile is determined by the nature and extent of microbial-adsorption-organic carbon interactions (Bolan et al., 2011; Huang et al., 2005; Young et al., 2008).

The impact of forest harvesting on the chemical composition of organic matter has been the focus of several studies, mostly in boreal or boreal mixed-wood regions (Hannam et al., 2005; Kalbitz et al., 2004). Chemical changes in organic matter may lead to altered microbial communities, changes in the rate of decomposition and forest productivity (Park et al., 2002; Scott and Binkley, 1997; Dai et al., 2001). Shifts in chemical composition of organic matter constituents can be visible for decades after harvesting (Thiffault et al., 2008). Coupling these findings with the knowledge that indigenous soil carbon is the source of adsorbed DOC (Kaiser et al., 1996), it is conceivable that harvesting could have an impact the composition of DOC adsorbed and desorbed from soils.

Soil properties are known to be the primary control on DOC adsorption/desorption processes, but the chemical character of the DOC also plays a role (Kaiser et al., 1996; Kothawala et al., 2009) where sorption affinities differ for various carbon fractions comprising DOC. Iron and aluminum oxides/hydroxides have been reported as the dominant sites of DOC adsorption across a number of soil types (Moore et al., 1992). Some studies have also shown clay content can also impact adsorption (Jardine et al., 1989; Moore et al., 1992), however other studies have shown a weak influence of clay content compared with Fe and Al oxides (Kaiser and Zech et al., 2000). A negative correlation between soil organic carbon (SOC) content and DOC adsorption has been reported in the literature, and is likely due to binding sites being occupied (Kaiser et al., 1996; Bolan et al., 2011). The effect of soil pH on DOC dynamics is fragmented in the literature, often only focusing on laboratory studies (Kalbitz et al., 2000). At higher pH values in subsoils, DOC adsorption capacity is often diminished and therefore mobilization is enhanced (Kalbitz et al., 2000).

DOC dynamics in forested systems are affected by many complex processes. These processes are not well understood despite the apparent importance of DOC for ecological and human health. While previous DOC sorption studies focus on the soil properties influencing adsorption and the relative abundance of hydrophobic or hydrophilic DOC being adsorbed or immobilized (Moore et al., 1992;

McDowell and Wood, 1984; Kaiser et al., 1996), there has been little research into how land-use affects these processes.

Thus, the broad objectives of this study were to evaluate the impact of clear-cut harvesting and physiographic controls on DOC adsorption behavior and explore if carbon chemical character (aromaticity and molecular weight) is an important factor in DOC adsorption behavior. This study was conducted four years following harvesting and direct comparisons were made between soils from harvested and reference catchments. This study set out to achieve the following objectives: (1) Assess the impact of harvesting on DOC adsorption behavior (sorption affinity, desorption capacity and null point concentrations); (2) Assess potential physiographic controls on DOC sorption behavior in poorly developed soils from a steep, mountainous catchment; (3) Evaluate the influence of harvesting and physiographic controls on the character of DOC desorbed from mineral soils. This information is needed as to better understand and manage the potential impacts of forest harvesting to safe-guard drinking water supplies from forested headwater regions.

3.2. Materials and Methods

3.2.1. *Study area*

This study was conducted on soil samples collected from the Star Creek and North York Creek watersheds in the front-ranges of the Rocky Mountains near Coleman, Alberta (49°37’N, 114°40’W). Star Creek and North York Creek flow into the Crowsnest River, forming part of the Oldman River headwaters. A more detailed description of both watersheds can be found in Chapter 2. These watersheds share similar surficial geology, soil types, vegetation composition and hydrologic regimes. Both watersheds are part of a larger hydro-climatic monitoring network, known as the Southern Rockies Watershed Project (SRWP). SRWP consists of 34 hydro-climatic stations across nine watersheds initially set up to study the impacts of the 2003 Lost Creek wildfire (Phase I of SRWP). The project evolved to research the impact of three harvest strategies on a multitude of hydrometric and climatic parameters (Phase II). In Phase I of SRWP, North York and Star Creek watersheds served as reference, unburned watersheds. North York remains undisturbed with the exception of designated mixed-recreation trails. In the winter of 2015, Star Creek watershed was harvested using three different harvest strategies: clear-cut with green patch retention (Star

Creek West), strip-shelter wood cut (Star Creek East) and partial cutting (McLaren Creek). For the purposes of this study, Star Creek West and North York watersheds were the primary focus. North York served as the undisturbed reference and Star Creek West as the disturbed (clear-cut harvested with green patch retention) watershed (Figure 3-1).

3.2.2. *Study design*

A descriptive, post-hoc reference/impact study with a 2^3 factorial design was implemented for this study. Star Creek and North York have previously been selected as reference watersheds for Phase I of the SRWP because of similarities in physical characteristics and hydrologic/climatic regimes. The primary difference between the two watersheds is that Star Creek was harvested in 2015, while North York remained relatively undisturbed. Both watersheds represent typical headwaters found in the eastern slopes of the Rocky Mountains and are valuable in terms of water yield, timber and recreation. The 2^3 factorial design included the following factors: two "treatments" – reference and clear-cut with green patch retention; two hillslope positions – lowland and upland; two soil profile depths – ~20-40 cm, representative of the B-horizon and ~77-110 cm, representative of the BC- or C-horizon (Table 3-1). Soil samples were collected in September of 2018 to characterize mineral soil-DOC adsorption/desorption dynamics and the potential linkage to clear-cut harvesting with green patch retention impacts.

3.2.3. *Hillslope selection and description*

Plots were selected on multiple hillslopes to standardize sampling across aspect, slope, vegetation cover and soil types. Three similar (i.e., replicate) hillslopes were selected in Star Creek West (harvested) and North York (reference) watersheds. Each hillslope included both hillslope position factor levels where soil samples at two depths were collected. Lowland hillslope positions in Star Creek West were located in the ≥30m riparian buffer surrounding Star Creek. Hillslopes and plots were initially selected using ArcGIS (version 10.6, ESRI) based on the Alberta Vegetation Inventory (AVI), upslope accumulating area (Jensco et al., 2009) using a digital elevation model (1 m bare ground LiDAR) and aspect. Final selection of hillslopes and plots were based on field reconnaissance. Aspect of the hillslopes ranged from southeast to east and the slopes were limited from 2 to 8%. Lowland and upland plots ranged from 20-35 m and 50-130 m from the stream, respectively. Soils in this study are classified as poorly developed Eutric Brunisols with profile depths of 75-150 cm before reaching unmodified glacial till. Within each plot, discrete soil samples were taken from depth intervals of ~20-40 cm and ~90-110 cm, with the exception of one transect in Star West where glacial till was reached at 85 cm. Therefore, the sample was collected from 77 to 85 cm for both the lowland and upland plots. The depth of 20-40cm was representative of the B-horizon and the 90-110cm depth was representative of the C-horizon in this area (Figure 3-2). A total of 24 soil samples were collected, based on eight unique factorial combinations, each with three replicates.

3.2.4. *DOC adsorption experiment*

Dissolved organic carbon adsorption/desorption characteristics were determined for mineral soils by a four-point batch adsorption experiment. DOC adsorption experiments are used to describe the amount of DOC adsorbed or released from soils across a gradient of concentrations. At low stock solution concentrations, DOC tends to be released from the soil to solution ($RE < 0$, see Eq 3-1/Figure 3-3), while at greater concentrations DOC is typically adsorbed from solution to the soil ($RE > 0$). A linear relationship can be established by plotting DOC adsorbed/released as a function of the initial stock solution concentration (Figure 3-3).

DOC isotherms were determined for the 24 mineral soil samples collected from the reference and harvested hillslopes. The mineral soil samples were collected by hand-auger and stored in low-density polyethylene bags at 4°C. The samples were air-dried for 72 hours and sieved to <2mm within one week of collection. Forest floor (LFH) samples were concurrently sampled from the plots, sieved to <4mm, air-dried and ground as preparation for the DOC stock solution. DOC extraction for the stock solution occurred immediately before the adsorption experiment by adding 500g of dried, ground LFH to 5L of deionized water. The mixture was stirred vigorously in a milkshake blender for 10 minutes and allowed to soak for 24 hours. Next, the stock solution was centrifuged for 15 minutes at 4000g and filtered through a 0.45μm polyethersulfone filter (Millipore Express). The resulting filtrate was subsampled to determine to the DOC concentration by US EPA Method 415.1 (Shimadzu TOC-5000A Total Organic Carbon Analyzer), pH and ionic strength (electrical conductivity). The stock solution was diluted using deionized water to create four solutions with DOC concentrations of 1.6, 24.6, 61.2 and 122.3 mg L^{-1}, indicating batches #1 through #4 respectively. The pH and ionic strength of the new solutions were adjusted to match the initial full-strength stock solution with a pH of 6.4 and electrical conductivity of 115.7 μS cm^{-1}. The pH was adjusted by adding either 0.1M HCl or 0.1M NaOH and ionic strength (electrical conductivity) was adjusted by adding 0.1M $CaCl_2$.

Fifty mL of each solution was added to 5g of air-dried, sieved mineral soil and the mixtures were shaken on a platform shaker (100 rpm) at 4°C for 18 hours. Equilibrium of DOC adsorption/desorption was assumed to occur within 18 hours (Dahlgren and Marrett, 1991). After 18 hours, the samples were centrifuged for 15 minutes at 4000 g and filtered with 0.45 μm polyethersulfone syringe filters (Millipore Express). The experiment was completed in triplicate and all centrifuge tubes and glassware were acid-washed with 2.5% HCl solution. Three control samples (DOC solution with no soil added) and three method blanks (deionized water) accompanied each batch. Samples were submitted to the University of Alberta Biogeochemical Analytical Services Laboratory within 24 hours. DOC concentrations were analyzed using the method listed above and absorbance spectra was determined using a Varian Cary 50 Probe UV-Visible Spectrophotometer.

The initial mass (IM) isotherm approach (Nodvin et al., 1986) (Equation 3-1; Figure 3-3) was employed to explore DOC adsorption characteristics as it has been commonly used for DOC soil adsorption experiments because it accounts for indigenous adsorbed DOC. The IM equation is described as follows:

$$RE = m\,Xi - b \tag{3-1}$$

where *RE* is the net adsorption or release of DOC (mmol-DOC kg-soil^{-1}) following equilibrium, calculated by: *RE* = initial solution concentration – final solution concentration. Sorption affinity, denoted *m*, is obtained from the slope of the IM isotherm regression line and is the fraction of reactive DOC retained/adsorbed by the soil. The desorption term (mmol-DOC kg-soil^{-1}), denoted *b*, is equal to the amount of DOC released from mineral soil when the initial DOC stock solution concentration is 0 mg L^{-1} (y-intercept). The desorption term partially quantifies indigenous adsorbed carbon however, it should be noted that not all DOC will be desorbed. The initial concentration of the stock solution is represented by *Xi* (mmol-DOC kg-soil^{-1}). Finally, the null point concentration is the x-intercept of the regression line, where the net DOC adsorption/release (RE) is 0 mmol-DOC kg-soil^{-1} (note: this is also referred to as the equilibrium DOC concentration in the literature). The mean of the triplicate values from each sample were used to calculate the overall isotherm regression.

3.2.5. *DOC character analysis*

Proxy indicators of DOC chemical character (aromaticity, molecular weight) were determined using UV-Visible spectrum absorbance between 190 – 500 nm using a 2 cm quartz cuvette. Absorption coefficients were determined for wavelengths 254 and 365 nm using Equation 3-2:

$$A_\lambda = a_\lambda / \mathrm{d} \qquad [3\text{-}2]$$

where A_λ is the absorbance coefficient (m^{-1}) at wavelength λ nm, a_λ is the absorbance (unitless) at wavelength λ nm and d is the path length (m). $SUVA_{254}$ was calculated for all samples using Equation 3-3:

$$SUVA_{254} = \frac{(A_\lambda)}{DOC} * 100 \qquad [3\text{-}3]$$

where A_λ is the absorbance coefficient (m^{-1}) at wavelength 254 nm and DOC is the concentration (mg L^{-1}).

Weishaar et al. (2003) reported a positive relationship between $SUVA_{254}$ with the percent aromaticity of carbon in a sample determined by ^{13}C Nuclear Magnetic Resonance (NMR). Proxy molecular weight of DOC was estimated using the absorbance ratio, A_{254}:A_{365} (herein referred to as UV_{254}:UV_{365}). According to the approach of Agren et al. (2008), greater UV_{254}:UV_{365} ratios indicates a lower molecular weight of DOC. All samples were analyzed for UV-Vis absorbance and the mean of the triplicates was used for statistical analyses. Samples exceeding the range of the spectrophotometer (3 units of absorbance) were diluted to enable measurement. The resulting diluted absorbance measurement was multiplied by the dilution factor to determine the actual absorbance measurement of the sample.

3.2.6. *Soil properties*

Soil chemical properties of samples were measured to examine variation in DOC adsorption with variation in these properties across the soils in this study. The Natural Resources Analytical Laboratory (NRAL) completed all soil property analyses where total organic carbon was measured by dry combustion using a Costech Model EA 4010 Elemental Analyzer, and soil pH was analyzed using a standard 0.01M $CaCl_2$ solution with a soil:solution ratio of 1:2. Soil particle size analysis was completed using a Beckman Coulter Laser Diffraction Particle Size Analyzer. A spinning riffler was used to subsample soils for particle size. Aluminum and iron from amorphous oxides/hydroxides were extracted with a 0.2M acid ammonium oxalate solution using a modified Blume and Schwertmann (1969) method reported by Haluschak (2006). The extract was analyzed for Al and Fe by ICP-OES (Thermo iCAP6300 Duo inductively coupled plasma-optical emission spectrometer). Iron from amorphous and crystalline oxides/hydroxides were determined by a sodium dithionite-citrate-bicarbonate extraction using a modified Mehra and Jackson (1960) method also reported in Haluschak (1996). Iron extracts from this extraction were analyzed by atomic adsorption spectroscopy (SpectrAA 880 Atomic Absorption Spectrometer). Both extractions included one method blank and one duplicate sample for every 12 samples.

3.2.7. *Statistical analyses*

A post-hoc, comparative analysis was conducted to determine the effect of harvesting and physiographic controls on DOC adsorption behavior. Assumptions of normality and homogeneity of variances were tested by Shapiro-Wilk's test and an F-test as well as visually by Q-Q plots. Adsorption parameters and soil properties were log transformed to fit a Gaussian normal distribution, if necessary. A factorial ANOVA was used to determine which factors, harvesting (catchment), depth (horizon) or hillslope position were important in variation of DOC adsorption and chemical character. To identify soil properties related to DOC adsorption behavior Pearson's correlation coefficient matrices were calculated with adsorption parameters, *m* (sorption affinity), *b* (desorption term) and *np* (null point concentration) as well as character proxies, $SUVA_{254}$ and UV_{254}:UV_{365}. Unless otherwise indicated, DOC character proxies were calculated from Batch #1 (1.6 mg/L initial stock solution) values to fully characterize indigenous adsorbed DOC. Multiple linear regressions were formed to determine which combinations of soil properties were most closely associated with adsorption behavior. Variance inflation factor (VIF) was tested for the soil properties used in the regressions with a threshold of 5. Properties exceeding a VIF of 5 were removed or combined (ie. Al_{ox} and Fe_{ox} were combined to $(Al+Fe)_{ox}$). All statistical analyses were performed in R (R-Studio, version 1.1.423, 2017) with an alpha threshold of 0.05 for statistical significance.

3.3. Results

3.3.1. *DOC Initial Mass isotherm parameters*

Initial Mass (IM) isotherm regressions (Eq. 3-1) were developed for each sample base on three replicates which enabled comparisons of sorption affinity, the desorption term and null point concentrations among factors (Table 3-2). Mean sorption affinity (*m*) in the harvested catchment was 0.09 compared to 0.07 observed the reference catchment ($p = 0.23$; Table 3-2; Table 3-3). Hillslope position (lowland and upland) did not exert any meaningful physiographic influence on sorption affinity, in fact lowland and upland sorption affinities were nearly identical at $m = 0.08$ and 0.07, respectively ($p = 0.54$; Table 3-3). The dominant factor influencing sorption affinity was depth in the soil profile. B-horizon soils had a mean sorption affinity of 0.06, while the C-horizon was 50% greater with a mean of 0.09 ($p = 0.03$; Table 3-2; Table 3-3; Figure 3-4). It should be noted that soil sample RLS-2 was removed from the dataset because DOC adsorption behavior could not be confidently determined based on the IM isotherm approach used here ($m < 0$).

The desorption term (b) from the harvested catchment was greater than that from the reference catchment with soils from the harvested catchment releasing 14.4 mmol kg^{-1} of DOC, compared to only 9.2 mmol kg^{-1} from soils in the reference catchment ($p = 0.02$; Table 3-2; Table 3-3). As with sorption affinity, hillslope position had little effect on the desorption term. Lowland soils desorbed slightly more DOC than upland soils, however the difference between hillslope positions was only 1.7 mmol kg^{-1} and was not statistically meaningful ($p = 0.50$; Table 3-3). Once again, depth in the profile was the most influential factor on the amount of DOC desorbed ($p = 0.02$; Table 3-3). B-horizon soils released significantly more DOC with a mean of 15.0 mmol kg^{-1} of DOC whereas C-horizon soils released only 9.1 mmol kg^{-1} (Figure 3-4).

The mean null point concentration (log-transformed np), of reference soils was greater than those from the harvested catchment (514.1 compared to 227.2 mmol kg^{-1}, respectively, Table 3-2). Though this difference was large, the variation of null point concentrations was high (especially in the reference catchment) thus the difference between catchments was not significant ($p = 0.42$; Table 3-3). As observed with other adsorption parameters, hillslope position was not identified as an important factor influencing null point concentrations ($p = 0.49$; Table 3-3). The mean np for B-horizon soils was greater, 645.3 mmol kg^{-1}, compared to the C-horizon soils, 107.0 mmol kg^{-1} (Table 3-2). Again, soil depth exerted the greatest influence on null point concentrations, similar to results for sorption affinity and the desorption term ($p < 0.01$; Table 3-2; Figure 3-4).

3.3.2. *DOC chemical character analysis*

Character analysis was conducted on Batch #1 with the lowest initial stock DOC concentration (1.6 mg L^{-1}) to evaluate potential changes in DOC character when the greatest amount of indigenous carbon would be released. Harvesting impacts were negligible on aromaticity of indigenous carbon being released as both catchments had mean $SUVA_{254}$ values of 2.2 L mg-C^{-1} m^{-1} (p = 0.72; Table 3-2; Table 3-3). Aromaticity was marginally influenced by hillslope position, where lowland soils released more aromatic carbon than upland soils. Following equilibrium, $SUVA_{254}$ of lowland soils was 2.4 compared to 2.1 L mg-C^{-1} m^{-1} for upland soils (p = 0.03; Table 3-2; Table 3-3). Depth in the soil profile had a moderate effect on aromaticity with C-horizon soils releasing more aromatic DOC than B-horizon soils, though the difference was not strong (p = 0.08; Table 3-3). The aromatic content in all samples were lower than the control samples ($SUVA_{254}$ = 3.4 L mg-C^{-1} m^{-1}) indicating native, adsorbed aliphatic compounds were released or aromatic compounds in the stock solution replaced indigenous aliphatic compounds during the adsorption experiment.

The proxy indicator for mean molecular weight of DOC (UV_{254}:UV_{365}) was not significantly affected by harvesting (p = 0.13; Table 3-3) though this ratio was slightly lower in reference soils than from harvested samples indicating reference soils released heavier carbon compounds (Table 3-2). Hillslope position had the least effect on the molecular weight of compounds released or exchanged during adsorption/desorption (p = 0.39; Table 3-3) where soil solutions from upland soils had a UV_{254}:UV_{365} ratio of 4.2 compared 4.3 from lowland soils (Table 3-2). Similarly, while B-horizon soils had slightly greater UV_{254}:UV_{365} ratios (4.4 compared to 4.1 in C-horizon samples), soil depth did not have a meaningful effect on molecular weight ratio (p = 0.13, Table 3-2).

3.3.3. *Soil properties*

Variation of soil properties were examined using a factorial ANOVA to determine if variation of properties were important in regulating carbon adsorption between catchments, hillslope positions or soil depth. Soil texture fractions were similar in both catchments: mean reference clay and sand content was 33.1% and 23.7%, respectively, while in the harvested catchment clay and sand content was 31.6% and 22.7%, respectively. The differences between catchments for each soil fraction, including silt, were not significant (p = 0.08 – 0.79; Table 3-3). Further, soil texture did not vary by soil depth for any of the three size fractions (p = 0.35 – 0.61; Table 3-3; Figure 3-5). Hillslope position did appear to influence soil texture, with lowland soils having greater sand content (27.6% vs 19.7%) and lower clay content (28.6% vs 36.2%) compared to the upland hillslope position (p = 0.02 – 0.03; Table 3-3; Table 3-4). Soil organic carbon (SOC) was approximately 40% greater in the harvested catchment, though there was high variation within each catchment (*p* = 0.12; Table 3-3; Table 3-4). Overall, B- and C-horizons had high variability in SOC content, with a mean SOC of 26.3 g kg^{-1} in the B-horizon, compared to 31.6 g kg^{-1} in the C-horizon, (*p* = 0.39; Table 3-3; Table 3-4). Soil pH in the reference catchment was 6.9 which was similar to the harvested catchment where the pH was only slightly more acidic at 6.7 (*p* = 0.49; Table 3-2; Table 3-4). Hillslope position also did not meaningfully impact soil pH, though upland soils were slightly more acidic than lowland soils (*p* = 0.14; Table 3-3). Soil depth was the dominant factor influencing soil pH; B-horizon soils were significantly more acidic than the C-horizon (*p* < 0.01; Table 3-3). B-horizon soils had a pH of 6.4, compared to 7.2 observed in C-horizon soils (Table 3-4; Figure 3-5). While extractable forms of Fe and Al were only slightly greater in the harvested catchment, no pattern in variation of Fe_{ox} was evident amongst catchments (Table 3-4); none of these properties differed between catchments (*p* = 0.39 – 0.95; Table 3-3). Similarly, hillslope position had no effect on the quantity of extractable-Fe and -Al and minor weak trends were not consistent among the different forms (Table 3-3; Table 3-4). More consistent (but still weak) patterns in extractable forms of Fe and Al between soil depths where the B-horizon had marginally greater concentrations than the C-horizon (*p* = 0.07 – 0.40; Table 3-3; Figure 3-5). Overall, hillslope position influenced soil texture and SOC while variation of soil pH and extractable-Fe and -Al was mostly related soil horizons.

3.3.4. *Partitioning of samples by soil pH*

While the relationships of DOC adsorption behavior (3.3.1 above) with soil properties were explored, Pearson's correlation coefficients and multiple linear regressions failed to identify important relationships with soil properties. However, differing patterns of carbon adsorption among B and C soil horizons were more strongly associated with variation of soil pH among these two soil depths and, to a much lesser degree, extractable-Fe and -Al. Samples were partitioned into pH classes to more clearly explore if carbon adsorption was associated with soil pH, a threshold of pH = 7.15 was used (median soil pH value). In general, partitioning samples in this way yielded two distinct populations (Figure 3-6). More acidic samples (pH < 7.15) were dominantly from the B-horizon, herein referred to as Population A, while more basic samples (pH > 7.15) were from C-horizon samples, herein referred to as Population B. There was one B-horizon sample, HLS-3, with a pH > 7.15 and a C-horizon sample, HUD-2, with a pH < 7.15, these samples were partitioned by pH but were an exception to the depth classification. The two exceptions were possibly due to differences in sand content, with HLS-3 having 43% sand and HUD-2 having 3% sand which were the extremes seen in this study. Overall, Population A (lower pH) had a lower sorption affinity, and a greater desorption term as well as null point concentration compared to Population B with pH > 7.15 (Figure 3-6).

In general, Population A (lower pH) displayed poor correlations between DOC adsorption parameters and soil properties (Pearson's correlation coefficients, Table 3-5). Oxalate-extractable Al had a significant positive correlation with sorption affinity for Population A ($p < 0.05$; Table 3-5). Dithionite-bicarbonate extractable Fe displayed a positive 0.50 correlation with sorption affinity, though this was not significant (Table 3-5). The desorption term of Population A only had one significant correlation with SOC at 0.71 ($p < 0.05$; Table 3-5). All other soil properties were poorly correlated with $r < 0.34$. No soil properties were significantly correlated with null point concentrations where the strongest correlation was with SOC ($r = 0.43$, $p > 0.05$; Table 3-5). Multiple linear regressions with soil properties did not identify any significant models associated with log-transformed sorption affinity or null point concentration (Table 3-6). The log-transformed desorption term found all soil parameters were important to the model and explained 76% of the variation ($p = 0.02$; Table 3-6). The dominant drivers in this model were SOC and Fe_{DCB} as determined by the standardized coefficients.

In contrast, sorption affinity of Population B soils (greater pH) were significantly correlated with all extractable forms of Fe and Al, Fe_{DCB}: $r = 0.66$, Fe_{ox}: $r = 0.71$, Al_{ox}: $r = 0.67$ ($p < 0.05$; Table 3-5) where variation of soil pH within this group was negatively correlated with sorption affinity ($r = -0.68$, Table 3-5). The desorption term in Population B soils was not significantly correlated to any soil property, however similar to findings for Population A, a weaker correlation was found with SOC ($r = 0.55$, $p > 0.05$). Finally, the null point concentration was most strongly (and negatively) correlated with percent clay ($r = -0.74$; $p < 0.05$; Table 3-5). No other individual soil properties were meaningfully correlated ($r > 0.50$) with the null point concentration for Population B samples. However, generally stronger correlations between carbon adsorption and some soil properties evident for Population B led to significant relationships between multiple soil properties and adsorption parameters. Oxalate-extractable Fe and Al, and percent clay explained 59% of the variation observed in the log-transformed m ($p < 0.01$; Table 3-6). Similar to Population A, SOC was dominant factor associated with variation of b among soils, however for Population

B it was the only property correlated with *b* and accounted for 42% of the variation ($p = 0.01$; Table 3-6). SOC was also identified as most closely associated with the null point concentrations, along with oxalate-extractable Fe and Al explaining 44% of the variation ($p = 0.03$; Table 3-6).

Relationships between absorbance indicators for DOC chemical character with soil properties were also explored. Similar to findings for DOC adsorption (above), correlations between soil properties and DOC character proxies for Population A samples were generally poor. Aromaticity was moderately (but not significantly) associated with Fe_{ox} (r = 0.52, $p > 0.05$; Table 3-5). All other soil parameters had exceptionally poor correlations with aromaticity (r ≤ 0.31). Minimal correlations were also found for molecular weight, with the exception of soil pH (r = -0.66; $p < 0.05$; Table 3-6). Consequently, no relationships between indicators of aromaticity with multiple soil properties were evident. No model could be found for Batch #1, and Batch #2 yielded a poor model which could only explain 33% of the variation using SOC and Fe_{DCB} ($p > 0.05$; Table 3-7). In contrast, meaningful relationships between molecular weight and soil properties were evident for both batches. Batch #1 was related to all extractable forms of Fe and Al, and soil pH accounting for 77% of the variation in $UV_{254}:UV_{365}$ ($p < 0.01$; Table 3-7). Soil pH remained an important variable for Batch #2 with SOC, but the relationship was not as strong (adjusted $R^2 = 0.43$; $p = 0.04$; Table 3-7).

Similar to findings for DOC adsorption parameters, variation of indicators of DOC chemical character were more strongly associated with soil properties for Population B. Aromaticity was strongly correlated with SOC, yielding the highest correlation observed in the study (r = 0.89). Additionally, percent clay showed a strong negative relationship with aromaticity ($p < 0.05$; Table 3-5). Molecular weight was also negatively correlated with SOC and positively with percent clay with r = -0.77 and r = 0.71, respectively ($p < 0.05$; Table 3-5). Dithionite-extractable Fe was strongly associated with molecular weight of DOC (r = 0.73; Table 3-5). Multiple regression showed aromaticity was best explained by SOC across both batches. For Batch #1, percent clay was also a factor and could account for 76% of the variation ($p < 0.01$; Table 3-7). The relationship between SOC and aromaticity of Batch #2 was not significant ($p > 0.05$). Variation of molecular weight of Batch #1 was explained by variation of all soil properties, though SOC and Fe_{DCB} were the most influential ($R^2 = 0.90$; $p < 0.01$; Table 3-7). However, at greater stock solution concentrations (Batch #2) these relationships were less evident and were marginally significant to insignificant ($p = 0.04$ - 0.10).

3.4. Discussion

The impact of harvesting on DOC adsorption behavior was negligible. Inherent soil characteristics associated with soil weathering and soil formation influenced the variation in DOC adsorption characteristics across catchments, hillslope position and soil depth. This finding is consistent with other studies from a variety of soils and ecozones such boreal forests and permafrost affected regions (Kaiser et al., 1996; Kawahigashi et al., 2006). Overall, of the physiographic controls studied, depth within the soil profile exerted the greatest influence on DOC adsorption behavior potentially due to variation in soil pH and extractable forms of Fe and Al among soils of varying depth.

3.4.1. *Physiographic controls on DOC adsorption behavior*

Sorption affinity of DOC was not affected by clear-cut harvesting. Adsorption of DOC in mineral soils has been widely attributed to various soil properties, including extractable-Fe and -Al, SOC, clay content and soil pH (Kalbitz et al., 2000). Kaiser et al. (1996) found sorption affinity to be highly related to SOC, Fe_{DCB} and Al_{ox}. Further, *m* in these soils appears to be most closely related to oxalate-extractable Fe and Al, with the relationship being most clear for Population B soils. Results from this study show there was no significant difference in the soil properties measured between the two catchments that would produce differences in sorption affinity. Hillslope position also did not impact DOC adsorption behavior, in fact the influence of hillslope position had the least impact on DOC sorption affinity of the factors studied. This result was surprising because soil particle size fractions were significantly different between hillslope positions as was SOC content. The greater clay content of upland soils in this study would have been expected to produce higher sorption affinities compared to lowland soils (Nelson et al., 1993), however other studies have also shown the relationship between clay content and *m* to be weak (Kaiser and Zech, 2000; Pengerud et al., 2014). Additionally, higher clay content in upland soils coupled with significantly lower SOC suggests while there may have been more adsorption sites for DOC exchange, the lower quantity of DOC may have masked potential differences that might have otherwise been evident.

Depth in the soil profile exerted the strongest control on sorption affinity, which has also been reported in numerous studies (Kothawala et al., 2009, Moore et al., 1992). The B-horizon had a lower sorption affinity compared to the C-horizon indicating a smaller fraction of reactive DOC was retained by surface soil horizons. The values of sorption affinity in this study were at the extreme low-end (*m* = 0.03 - 0.15) of those found in the literature. Low *m* values suggest these soils have poor DOC adsorption potential at field soil solution concentrations. Only one study (Kaiser et al. 1996) reported *m* values less than 0.10 (0.01 to 0.86) describing surface soils with little retention of DOC overlying strongly adsorbing subsoils. Kaiser et al. (1996) concluded the minimal adsorption of DOC in surface A- and Bh2-horizon of an Oxyaquic Haplumbrept likely resulted from hydrophobic DOC outcompeting and hindering the adsorption of hydrophilic DOC resulting in net zero release of DOC. Comparing to values found in other Canadian soils, Moore et al., (1992) reported *m* values ranging from 0.15 to 0.78. Kindler et al. (2011) and Pengerud et al. (2014) reported a saturation index of SOC:$\Sigma(Fe+Al)_{ox}$, where the quantity of soil carbon was related to the quantity of adsorption sites. Although this index implies the soils in this study may have been saturated with DOC, the correlation between this index and the observed sorption affinity was quite poor compared to the relationships observed in the two aforementioned studies. The mean saturation index in this study was 7.8 compared to 1.5 reported in Pengerud et al. (2014). The lack of a relationship between the index and *m* in the present study may have resulted because soils in this study are all near saturation resulting in a narrow range of extremely low *m* values.

Soil pH in the shallower B-horizon was significantly more acidic than the C-horizon, however reports on the effects of pH on DOC adsorption remains unclear in the literature. Solubility of DOC has been shown to be associated with pH where Tipping and Hurley (1988) showed lower solubility due to a high degree of protonation as a result of low pH. Adsorption of DOC has also been found to increase with decreasing pH as observed with iron oxides (Tipping, 1981; Gu et al., 1994), aluminum hydroxides (Parfitt et al., 1977; Davis, 1982) and bulk soil (Jardine et al., 1989; Kennedy et al., 1996). In contrast, David and Zech (1990) found decreasing DOC adsorption with decreasing equilibrium pH in the B-horizon of an acidic forest soil. Kalbitz et al. (2000) argued that observed differences in adsorption due to pH in the laboratory experiments equate to seemingly small differences observed in the field as the soil solutions have been equilibrated to the soil pH.

Strong correlations between sorption affinity (*m*) and Al_{ox} were observed across soil pH categories indicating the quantity of active adsorption sites related well with sorption affinity in these soils. While it was difficult to characterize the soil properties influencing sorption affinity in soils with lower pH, sorption affinity of Population B soils was related to oxalate-extractable Fe and, to lesser degree, percent clay explaining ~ 60% of the variation in *m*. This finding is similar to Kawahigashi et al. (2006) who report extractable Fe was a primary driver of DOC adsorption to mineral soils in the Siberian forest tundra. Kaiser et al. (1996) found SOC and *m* to be negatively correlated supporting their conclusion that high indigenous SOC hinders the adsorption of DOC by occupying adsorption sites. In the present study, SOC and *m* were only weakly (not significantly) correlated (Table 3-5). However, *m* was highly correlated with Fe and Al oxides/hydroxides, especially in Population B samples, showing that adsorption of DOC in this study was highly correlated with the quantity of adsorption sites rather than if these sites were occupied. Anions such as PO_4^{3-} outcompete DOC for adsorption sites and therefore can hinder adsorption (Gu et al., 1994; David and Zech, 1990). Multiple studies have shown PO_4^{3-} can displace DOC at adsorption sites even when phosphate concentrations are an order of magnitude lower (Tipping, 1981; Kaiser and Zech, 1997; Beck et al., 1999). Although phosphate was not measured for this study, it could provide insight into why there was low DOC adsorption in these soils.

There was a clear difference between catchments in the DOC desorption term of mineral soils, with Star West (harvested) releasing more DOC than North York (reference). This difference was likely, in part, due to differing SOC between the two catchments. Harvesting could impact SOC in the short-term (<5 years) as reported by Kreutzweiser et al. (2008), however no change in SOC content was observed in 76% of studies reviewed. Results from this study show a marginal difference in SOC content existed between catchments, with the harvest catchment having a greater SOC ($p = 0.12$). However, this is at least equally likely due to natural variation in stand and soil factors regulating SOC among adjacent watersheds than a reflection of harvesting impacts. The reference watershed (North York) has both slightly greater mean elevation and historic precipitation than Star (harvested) which could lead to greater SOC independent of land disturbance. The remaining soil properties were similar amongst the two catchments and explain why adsorption behavior did not vary between them. Hillslope position also did not affect the desorption term, which was unexpected as lowland soils tended to have greater SOC. While SOC was significantly greater in lowland soils, this did not result is a meaningful difference in desorption terms. Across both populations SOC was identified as the main soil property affecting DOC desorption consistent with many studies (Kalbitz et al., 2000). As the desorption term was not significantly different between hillslope positions, other soil properties must also be influencing the desorption of DOC. While previous studies report variable associations of DOC adsorption with SOC, Fe_{ox} and Al_{ox}. (Kaiser et al. 1996; Moore et al. 1992), results from this study suggest regulation of DOC desorption by Fe_{DCB} and $(Fe+Al)_{ox}$ can mask the commonly reported effect of SOC on DOC desorption.

Soil depth was the strongest study factor influencing DOC adsorption affinity in this study ($p < 0.05$), however soil pH (correlated with depth) and SOC were the most influential soil properties; these findings are generally consistent with other studies across a range of soil types and land uses (Moore et al., 1992; Kaiser et al., 1996; Kothawala et al., 2009; Pengerud et al., 2014). Kaiser et al. (1996) noted a close relationship between *b* and log-transformed SOC further indicating the source of adsorbed DOC originated from indigenous SOC. This relationship was found to be less pronounced for soils in this study ($R^2 = 0.23$; Figure 3-7). Analysis based on soil pH categories showed the amount of DOC released was a reflection of SOC, explaining 42% of the variation for Population B samples ($p < 0.05$; Table 3-6). Population A samples showed SOC was still the most influential soil property, but all soil properties were identified to explain variation in DOC adsorption (adjusted $R^2 = 0.76$, $p < 0.05$). It appears that other soil properties such as soil pH and percent clay influenced the quantity of DOC desorbed. Tipping and Woof (1990) reported an increase in soil pH would lead to ta 50% increase in the amount of organic matter mobilized therefore, indicating the solubility of DOC is dependent on the pH (Tipping and Hurley, 1988).

Harvesting and hillslope position did not meaningfully affect the null point concentration for these soils. This result was due to lack of harvesting or hillslope position effects on sorption affinities and desorption terms, which directly relate to the null point concentrations. However, as soil depth was an important factor affecting both *m* and *b* it was likely that *np* would also show a significant impact. B-horizon null point concentrations were significantly greater than the C-horizon. While the desorption terms were within the range reported in the literature, the sorption affinities observed were extremely low, resulting in much greater null point or equilibrium DOC concentrations than typically reported. The null point concentrations of B- and C- horizon soils observed in this study this area (mean = 182.8 excluding 1 potential outlier, RLS-3, range = 20.2 – 4359.6 mmol kg^{-1}) were considerably greater than typically reported (5.6 – 81.0 mmol kg^{-1}: Moore et al., 1992; Pengerud et al., 2014). Null point concentrations observed in this study were closer to A-horizon soils reported for Quebec podzols or Siberian Cryolsols (Moore et al., 1992;

Kawahigashi et al., 2009). There were no strong correlations between soil properties and *np* across both populations. Multiple linear regression analysis identified SOC and oxalate-extractable Fe and Al as weak controls on null point concentrations. SOC was identified as the dominant driver of null point concentrations for both soil pH populations in this study, though there was only a moderate linear correlation with *np*. In general, null point concentrations were difficult to explain. Pengerud et al. (2014) also had difficulty explaining high null point concentrations for poorly adsorbing soils, where the only correlation soil properties was with SOC:$\Sigma(Fe+Al)_{ox}$. While variation in pH, SOC and Fe and Al oxides were important properties governing DOC adsorption, explaining the high *np* or equilibrium DOC concentrations observed in this study remains an outstanding challenge.

3.4.2. *DOC character following adsorption experiment*

Sorption of DOC to mineral soil is known to alter the bulk chemical character of DOC through the soil profile by preferentially adsorbing high molecular weight, hydrophobic compounds that comprise DOC (Guggenberger and Zech, 1993a,b).

$SUVA_{254}$ has been recognized as a proxy measure for the proportion of DOC aromaticity (Weishaar et al., 2003). Most studies use adsorption column chromatography with Amberlite XAD-8 resin to determine the percent fractions of hydrophobic and hydrophilic DOC (Leenheer, 1981; Kaiser et al., 1996). The desorbed DOC from field-relevant concentrations, 1.6 and 24.6 mg/L, yielded $SUVA_{254}$ values from 1.69 to 3.07 L mg-C^{-1}m^{-1} after equilibrium, indicating the DOC is likely a mixture of hydrophobics and hydrophilic compounds but with generally lower bulk hydrophobicity (Edzwald and Tobiason, 1999). The results of this study show all samples had decreased aromaticity when compared to the control samples (no soil added). There were negligible differences observed between $SUVA_{254}$ values for harvested and reference samples. The same trend held true for the molecular weight of desorbed components. Hannam et al., (2005) and Kaiser et al., (2004) reported clear-cut harvesting can enrich aromatic carbon compounds in the forest floor, leading to altered character of DOC being leached from the LFH layer. It was hypothesized that harvested soils would be more aromatic than reference soils due to the enrichment of high molecular weight, aromatic DOC leaching from the organic matter layer following harvesting. Reference soils would undergo more exchange of heavy, aromatic compounds from the stock solution with native, adsorbed aliphatic compounds. Results show that harvesting did not impact the aromaticity or molecular weight of carbon adsorbed to mineral soils. Kothawala et al., (2012) reported only small changes in aromaticity following adsorption experiments, even across different soil horizons. Coupling this with the fact that depth (horizon) exerts the greatest control on DOC adsorption, it is conceivable that a slight change from harvesting would not be detected by $SUVA_{254}$. A more in-depth investigation examining adsorption of specific carbon fractions may provide a better understanding of the processes governing DOC adsorption. Aromaticity was most correlated with SOC for Population B soils. This is in agreement with Kaiser et al. (1996) who found SOC was the primary determinant of the quantity of DOC released across hydrophobic and hydrophilic DOC fractions. However, linear regression equations to explain the aromaticity of DOC desorbed were poor therefore making it difficult to understand the processes governing the character of released DOC in these soils.

$SUVA_{254}$ was lower in upland compared lowland soils though molecular weight of DOC in the equilibrium solution showed a minimal difference between hillslope positions. This finding is in agreement with Ledesma et al. (2018) where soil pore water in riparian zones had greater $SUVA_{254}$ values than upland zones in the Swedish boreal forest. Greater exchange of stock solution aromatic compounds replacing and releasing native aliphatic compounds occurred in upland soils, indicating adsorbed DOC in lowland soils was more aromatic.

The effect of soil depth on adsorption of DOC chemical fractions was minor. C-horizon soils released more aromatic carbon than B-horizon soils. The molecular weight of B-horizon soils was less than the C-horizon soils which coincides with their lower aromaticity. It should also be noted that B-horizon soils released a greater amount of DOC compared to the C-horizon as indicated by the desorption term. It was expected that B-horizon soils would be more aromatic as preferential adsorption is commonly reported in adsorption studies (Kaiser et al., 1996). While this was not observed in the present study; it was unclear if B-horizon soils had greater exchange with indigenous DOC than from the C-horizon.

3.4.3. *Relevance to field conditions and limitations*

The results from this study suggest low retention of DOC at B- and C-horizons within the soil profile. Indigenous DOC already adsorbed to mineral soil was strongly retained as suggested by the low *b* values. This is similar to the findings in Pengerud et al. (2014) for poorly podzolized high-latitude soils. Further, laboratory adsorption studies may not reflect DOC adsorption under field conditions. Kalbitz et al. (2000)

noted high adsorption of DOC to clay minerals and oxides may not control the transport of DOC under natural conditions if macropore fluxes dominate in undisturbed soil. These authors argued DOC in micropores may be largely immobile and only transported by diffusion to the mobile fraction in meso- and macropores. With a high proportion of clay within the soils in this study, micropores may be particularly important and may immobilize DOC until the soil is disturbed. In the case of Star West and likely North York, the lack of tighter coupling between the release of DOC in pore water at lower, field concentrations (~1-25 mg/L) and stream water concentrations (~0.2 – 1.1 mg/L) suggests subsurface pore water or groundwater from shallow pathways may not directly impact the concentration of DOC in receiving streams. This notion is consistent with other results from Star Ck. (Spencer et al., 2019) showing alpine snowmelt contributions and complex groundwater flow pathways generate a large proportion seasonal streamflow during and after the snowmelt freshet when soils are most likely hydrologically connected to streams. This hydrologic forcing would act to mute the concentration signal of soil pore water contributions to stream water for much of the active flow season.

3.5. Conclusion

Harvesting did not impact the DOC adsorption behavior determined by sorption affinities, desorption terms and null point (equilibrium) concentrations. Rather these parameters were influenced by inherent soil properties which were unaffected by harvesting in the short-term. Depth in the soil profile strongly influenced DOC behavior with B-horizon soils having lower sorption affinities, and greater desorption terms and null point concentrations. Soil pH was associated with the difference in behavior amongst the two depths and led to the partitioning of samples based on the soil pH. Population A (lower pH) samples generally had poor relationships between adsorption parameters and DOC chemical characteristics with soil properties, while Population B showed better relationships.

Preferential adsorption of hydrophobic (aromatic and high molecular weight) compounds was not clearly evident in this study. Harvesting did not impact the chemical character of the adsorbed DOC as was hypothesized. Depth in the soil profile also did not have a significant influence on DOC chemical character. Lowland soils were more aromatic than upland soils, likely a result of slow, poor decomposition in a wet environment. Molecular weight of DOC was not influenced by harvesting, depth or hillslope position in this study. An impact from harvesting of DOC chemical character was not detected potentially due to UV-Vis absorbance being a bulk proxy indictor and due to the complexity of the processes involved. An impact may be observed if more in-depth analyses were performed on the equilibrium solutions such as ^{13}C NMR or Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS).

Although laboratory experiments have their limitations, they do allow for a better understanding of natural processes. In this case, the knowledge that these soils poorly adsorb carbon provides insight into DOC dynamics in subsurface environments. Understanding this mechanism allows conclusions to be made about the fate and transport of DOC that otherwise would not have been made. With the knowledge that these soils poorly adsorb DOC but a decrease in DOC concentrations are observed moving down the soil profile indicates decomposition processes may be more important than initially thought.

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Table 3-1: Factors and levels of the experimental design.

Site Identification	Catchment	Land Classification	Hillslope Position	Soil Profile Depth	No. of Replicates
HUS	Star West	Harvested	Upland	20-40 cm	3
HUD	Star West	Harvested	Upland	90-110 cm	3
HLS	Star West	Harvested	Lowland/Riparian buffer	20-40 cm	3
HLD	Star West	Harvested	Lowland/Riparian buffer	75-110 cm	3
RUS	North York	Reference	Upland	20-40 cm	3
RUD	North York	Reference	Upland	90-110 cm	3
RLS	North York	Reference	Lowland	20-40 cm	3
RLD	North York	Reference	Lowland	90-110 cm	3

Table 3-2: Summary of adsorption parameters (*m*: sorption affinity; *b*: desorption term; *np*: null point concentration) and DOC chemical character proxies. Values indicate the mean ±(SE).

	Hillslope position		**Depth**		**Catchment**	
Parameter	*Lowland*	*Upland*	*B-horizon*	*C-horizon*	*Reference*	*Harvested*
m	0.08 (0.02)	0.07 (0.01)	0.06 (0.01)	0.09 (0.01)	0.07 (0.01)	0.09 (0.01)
b (mmol kg^{-1})	12.8 (1.9)	11.1 (1.9)	15.0 (1.7)	9.1 (1.6)	9.2 (1.7)	14.4 (1.7)
np (mmol kg^{-1})	549.2 (382.3)	195.0 (47.2)	645.3 (374.0)	107.0 (17.6)	514.1 (385.6)	227.2 (44.9)
$SUVA_{254}$ (L mg-C^{-1} m^{-1})	2.4 (0.1)	2.1 (0.1)	2.1 (0.1)	2.3 (0.1)	2.2 (0.1)	2.2 (0.1)
UV_{254}:UV_{365}	4.3 (0.03)	4.2 (0.2)	4.4 (0.1)	4.1 (0.1)	4.1 (0.1)	4.4 (0.1)

Table 3-3: Probabilities (p-values) from F-tests from factorial ANOVA for Initial Mass (IM) adsorption parameters, DOC chemical character proxies, and soil properties. Underlined values indicate significant differences at $\alpha = 0.05$. Values for DOC chemical character analyses were from Batch #1, with an initial stock solution concentration of 1.6 mg/L. Null point concentrations (*np*) were log-transformed to meet the assumption of normality.

Parameter	**Catchment**	**Depth**	**Hillslope position**	**Catchment:Depth**	**Catchment:Hillslope**	**Depth:Hillslope**
m	0.23	0.03	0.54	0.50	0.71	0.31
b	0.03	0.02	0.50	0.27	0.51	0.92
np	0.42	<0.01	0.49	0.20	0.20	0.45
SUVA$_{254}$	0.72	0.08	0.03	0.83	0.59	0.80
UV$_{254}$:UV$_{365}$	0.13	0.13	0.39	0.83	0.18	0.50
Clay (%)	0.62	0.35	0.02	0.70	0.36	0.60
Silt (%)	0.08	0.61	0.32	0.64	0.48	0.19
Sand (%)	0.79	0.57	0.03	0.90	0.34	0.39
pH	0.49	<0.01	0.14	0.97	0.59	0.26
SOC	0.12	0.39	<0.01	0.30	0.83	0.28
Fe$_{DCB}$	0.39	0.40	0.50	0.41	0.39	0.71
Fe$_{ox}$	0.95	0.07	0.22	0.17	0.06	0.35
Al$_{ox}$	0.62	0.14	0.93	0.45	0.22	0.36

Table 3-4: Summary of soil properties across land use classification, depth in the soil profile and hillslope positions. Values indicate the mean ±(SE).

	Catchment		**Depth**		**Hillslope position**	
Soil Property	*Harvested*	*Reference*	*B-horizon*	*C-horizon*	*Lowland*	*Upland*
Clay (%)	31.6 (2.6)	33.1 (1.9)	31.0 (2.1)	33.8 (2.4)	28.6 (1.9)	36.2 (2.0)
Silt (%)	45.7 (1.1)	43.2 (0.7)	44.8 (1.1)	44.1 (0.8)	43.8 (0.9)	45.1 (1.0)
Sand (%)	22.7 (3.4)	23.7 (2.0)	24.3 (2.8)	22.1 (2.8)	27.6 (2.2)	18.7 (2.7)
pH	6.7 (0.2)	6.9 (0.2)	6.4 (0.2)	7.2 (0.1)	7.0 (0.1)	6.6 (0.3)
SOC (g kg^{-1})	33.9 (6.2)	24.0 (4.3)	26.3 (3.8)	31.6 (6.7)	40.0 (5.6)	17.9 (2.6)
Fe_{DCB} (g kg^{-1})	14.4 (1.6)	12.7 (1.0)	14.4 (1.2)	12.7 (1.4)	12.9 (1.2)	14.2 (1.5)
Fe_{ox} (g kg^{-1})	2.9 (0.3)	2.9 (0.5)	3.4 (0.4)	2.5 (0.3)	3.2 (0.4)	2.6 (0.3)
Al_{ox} (g kg^{-1})	1.7 (0.2)	1.5 (0.2)	1.9 (0.2)	1.4 (0.2)	1.6 (0.3)	1.6 (0.2)

Table 3-5: Pearson's correlation coefficients (r) between selected soil properties, DOC chemical character proxies and DOC adsorption parameters. Soil samples were partitioned by soil pH classes with a threhold of 7.15. Underlined values indicate statistical significance at α = 0.05.

Population A Samples - Soil pH < 7.15

	SOC	pH	$\mathrm{Fe_{DCB}}$	$\mathrm{Fe_{ox}}$	$\mathrm{Al_{ox}}$	% clay	$\mathrm{SUVA_{254}}$	$\mathrm{UV_{254}:UV_{365}}$	*m*	*b*	*np*
SOC	1.00										
pH	0.46	1.00									
$\mathrm{Fe_{DCB}}$	-0.37	-0.25	1.00								
$\mathrm{Fe_{ox}}$	0.00	-0.18	0.57	1.00							
$\mathrm{Al_{ox}}$	-0.30	-0.07	0.72	0.69	1.00						
% clay	-0.60	-0.47	0.66	0.19	0.23	1.00					
$\mathrm{SUVA_{254}}$	0.13	-0.31	0.09	0.52	-0.05	0.06	1.00				
$\mathrm{UV_{254}:UV_{365}}$	-0.02	-0.66	-0.11	0.36	0.13	0.02	0.35	1.00			
m	-0.22	0.33	0.50	0.21	0.61	0.33	-0.56	-0.38	1.00		
b	0.71	0.13	-0.01	-0.05	-0.16	-0.34	-0.01	0.05	-0.18	1.00	
np	0.43	0.27	-0.20	-0.09	-0.32	-0.36	0.40	-0.11	-0.61	0.47	1.00

Population B Samples - Soil pH > 7.15

	SOC	pH	$\mathrm{Fe_{DCB}}$	$\mathrm{Fe_{ox}}$	$\mathrm{Al_{ox}}$	% clay	$\mathrm{SUVA_{254}}$	$\mathrm{UV_{254}:UV_{365}}$	*m*	*b*	*np*
SOC	1.00										
pH	0.19	1.00									
$\mathrm{Fe_{DCB}}$	-0.32	-0.57	1.00								
$\mathrm{Fe_{ox}}$	-0.01	-0.70	0.55	1.00							
$\mathrm{Al_{ox}}$	-0.31	-0.77	0.50	0.86	1.00						
% clay	-0.69	-0.42	0.63	0.26	0.46	1.00					
$\mathrm{SUVA_{254}}$	0.89	0.23	-0.35	0.08	-0.34	-0.76	1.00				
$\mathrm{UV_{254}:UV_{365}}$	-0.77	-0.30	0.73	0.43	0.49	0.71	-0.65	1.00			
m	-0.07	-0.68	0.66	0.71	0.67	0.43	-0.09	0.34	1.00		
b	0.55	-0.30	0.18	0.31	0.09	-0.31	0.58	-0.38	0.41	1.00	
np	0.49	0.18	-0.42	-0.30	-0.49	-0.74	0.60	-0.60	-0.54	0.40	1.00

Table 3-6: Multiple linear regressions using AIC selection criteria for log-transformed DOC adsorption parameters with independent variables including log-transformed SOC, percent clay, dithionite-citrate-bicarbonate extractable iron, oxalate extractable iron and aluminium and pH (pH was not log-transformed). Coefficients reported were standardized using standard deviations. Underlined values indicate significance at $\alpha = 0.05$.

Population	Independent Variables Identified	Adjusted R^2	p-value
	log *m*		
A	No quality model found	NA	NA
B	0.63 $(Al+Fe)_{ox}$ | 0.33 % clay	0.59	<0.01
	log *b*		
A	0.97 SOC | 0.85 Fe_{DCB} | -0.58 $(Al+Fe)_{ox}$ | -0.27 pH | -0.33 % clay	0.76	0.02
B	0.69 SOC	0.42	0.01
	log *np*		
A	0.49 SOC	0.16	0.13
B	0.63 SOC | -0.39 $(Al+Fe)_{ox}$	0.44	0.03

Table 3-7: Multiple linear regressions using AIC selection criteria for DOC chemical character proxies with independent variables including log-transformed SOC, percent clay, dithionite-citrate-bicarbonate extractable iron, oxalate extractable iron and aluminium and pH (pH was not log-transformed). Coefficients reported were standardized using standard deviations. Samples were partitioned by soil pH and regressions were generated for batches with initial stock solution DOC concentrations of 1.6 mg/L and 24.6 mg/L. Underlined values indicate significance at $\alpha = 0.05$.

Population	Independent Variables Identified	Adjusted R^2	p-value
	SUVA$_{254}$ / Batch 1: Stock solution = 1.6 mg/L		
A	No quality model found	NA	NA
B	0.65 SOC | -0.33 % clay	0.76	<0.01
	SUVA$_{254}$ / Batch 2: Stock solution = 24 mg/L		
A	0.50 SOC | -0.36 Fe$_{DCB}$	0.33	0.08
B	0.56 SOC	0.24	0.06

Population	Independent Variables Identified	Adjusted R^2	p-value
	UV$_{254}$:UV$_{365}$ / Batch 1: Stock solution = 1.6 mg/L		
A	-0.82 Fe$_{DCB}$ | 0.75 (Al+Fe)$_{ox}$ | -0.78 pH	0.77	<0.01
B	-0.75 SOC | 0.68 Fe$_{DCB}$ | 0.52 (Al+Fe)$_{ox}$ | 0.51 pH | -0.21 % clay	0.90	<0.01
	UV$_{254}$:UV$_{365}$ / Batch 2: Stock solution = 24 mg/L		
A	-0.39 SOC | -0.47 pH	0.43	0.04
B	0.49 Fe$_{DCB}$	0.17	0.10

Figure 3-1: Map of Star and North York watersheds showing soil sampling plots. Right inset shows watershed location in Alberta.

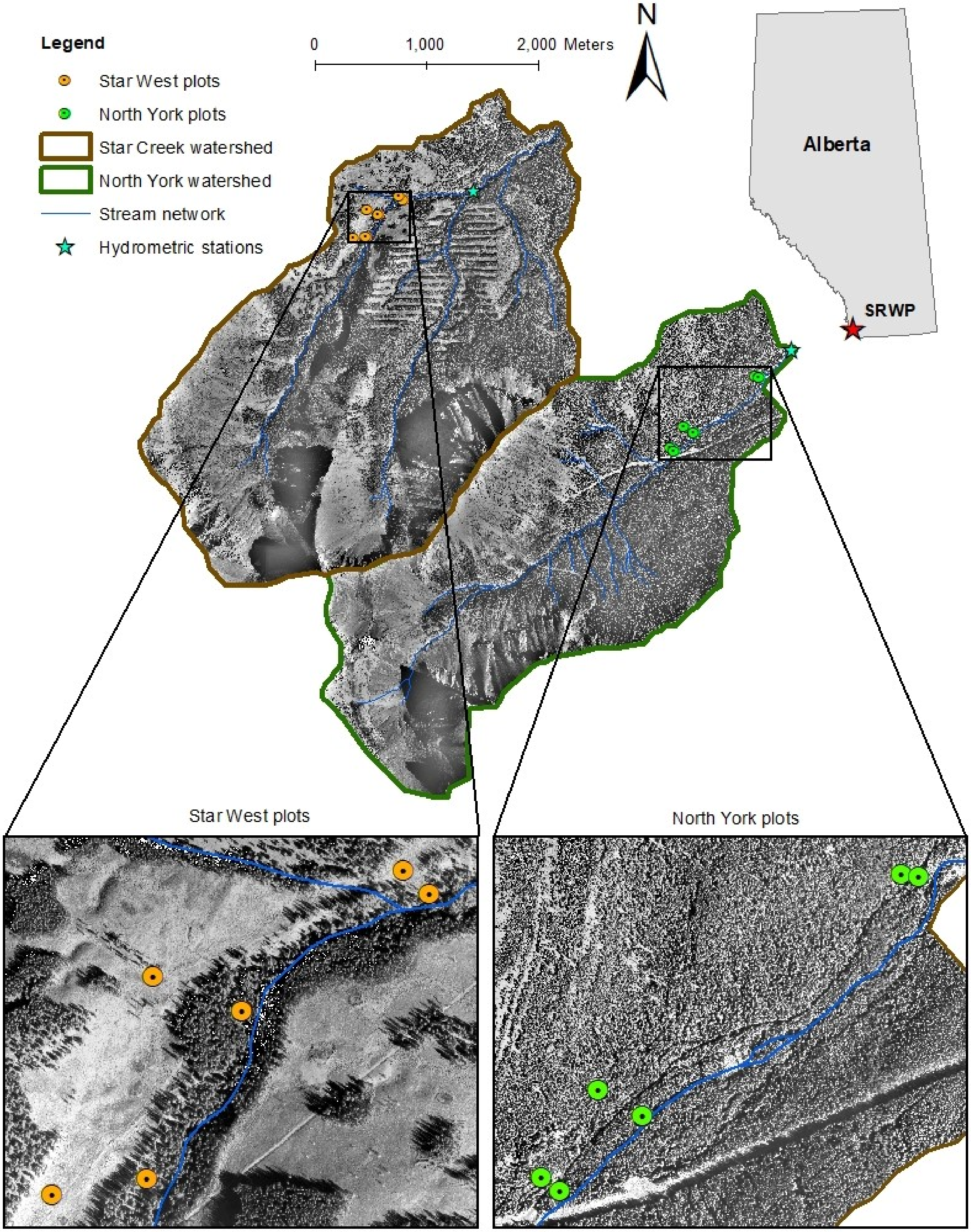


Figure 3-2: Photographs of representative air-dried soil from reference and harvested hillslope #3. Labels indicate the following: R/H: reference vs harvested; L/U: lowland vs upland; S/D: shallow (B-horizon) vs deep (C-horizon).

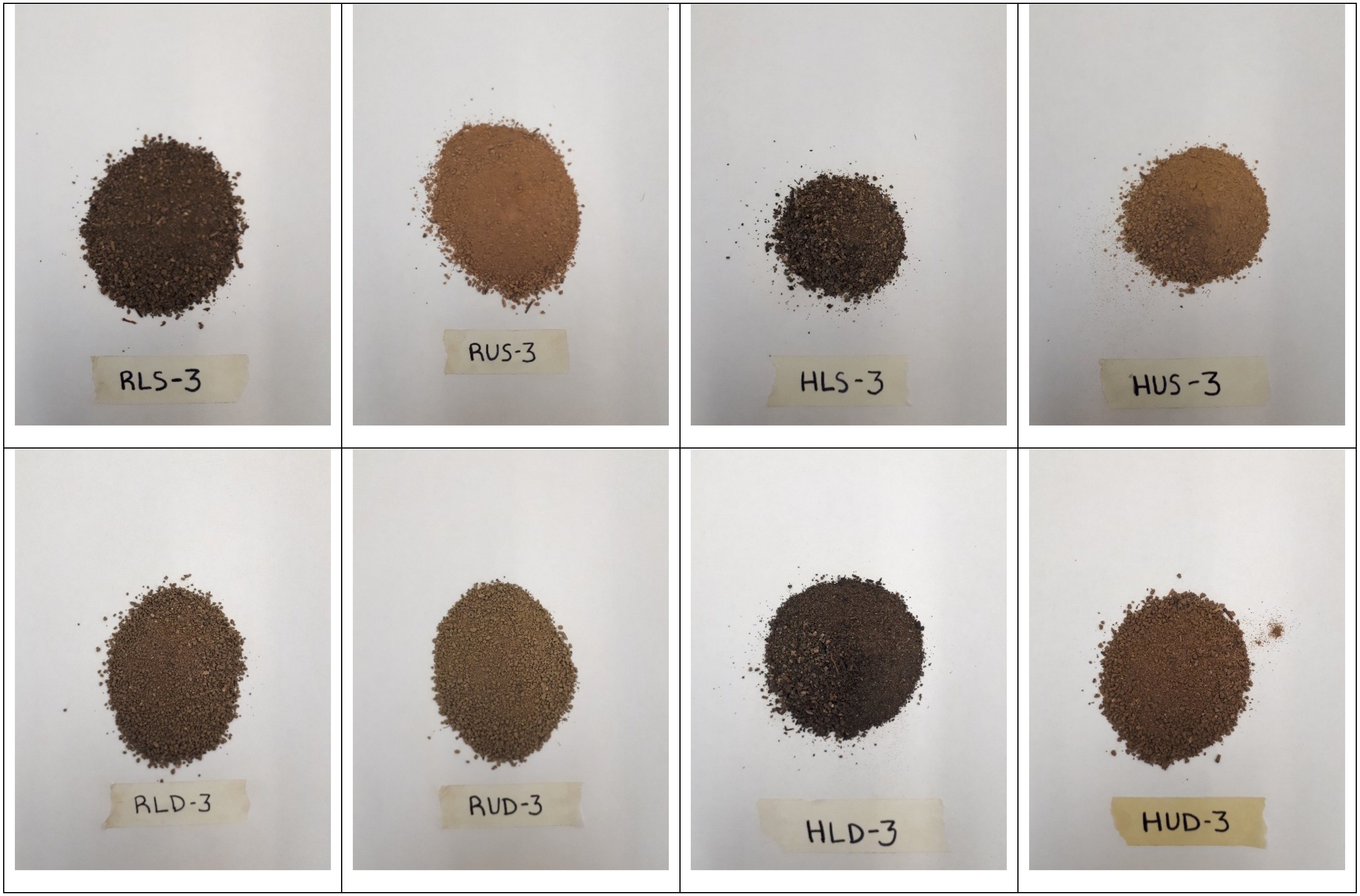


Figure 3-3: Conceptual relationship between DOC aqueous solution concentration and soil desorption/adsorption using the Initial Mass (IM) isotherm. Red circles identify the null point or equilibrium DOC concentrations (mmol kg^{-1}) and the blue circles indicate the desorption term (mmol kg^{-1}). Sorption affinity (*m*) is identified as the slope of the regression line (unitless). Negative values on y-axis indicate DOC desorption from soil to solution, while positive values indicate DOC adsorption from solution to soil.

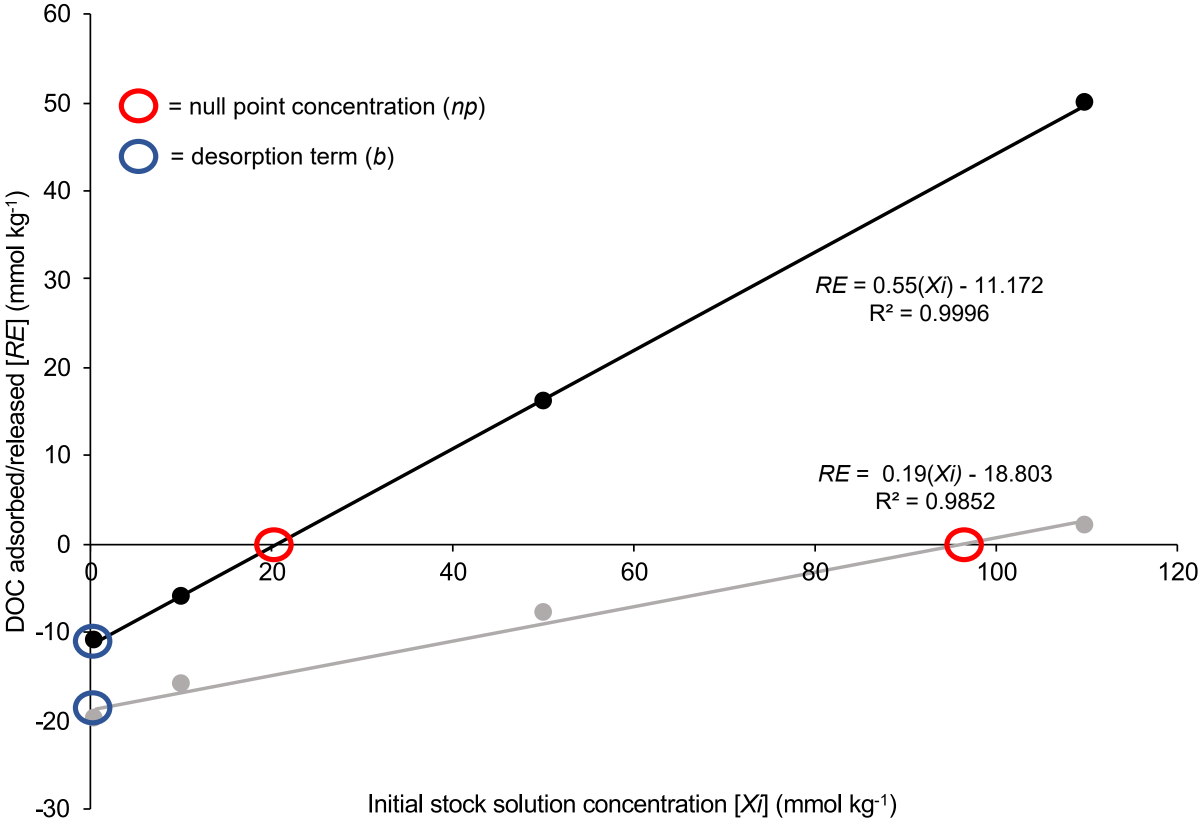


Figure 3-4: Distribution of DOC adsorption parameters including A) sorption affinity, B) desorption term and C) null point concentrations for B-, and C- horizon samples. Upper and lower rectangle bounds denote 25th and 75th percentiles, the horizontal line indicates the median and “whiskers” denote 5th and 95th percentiles.

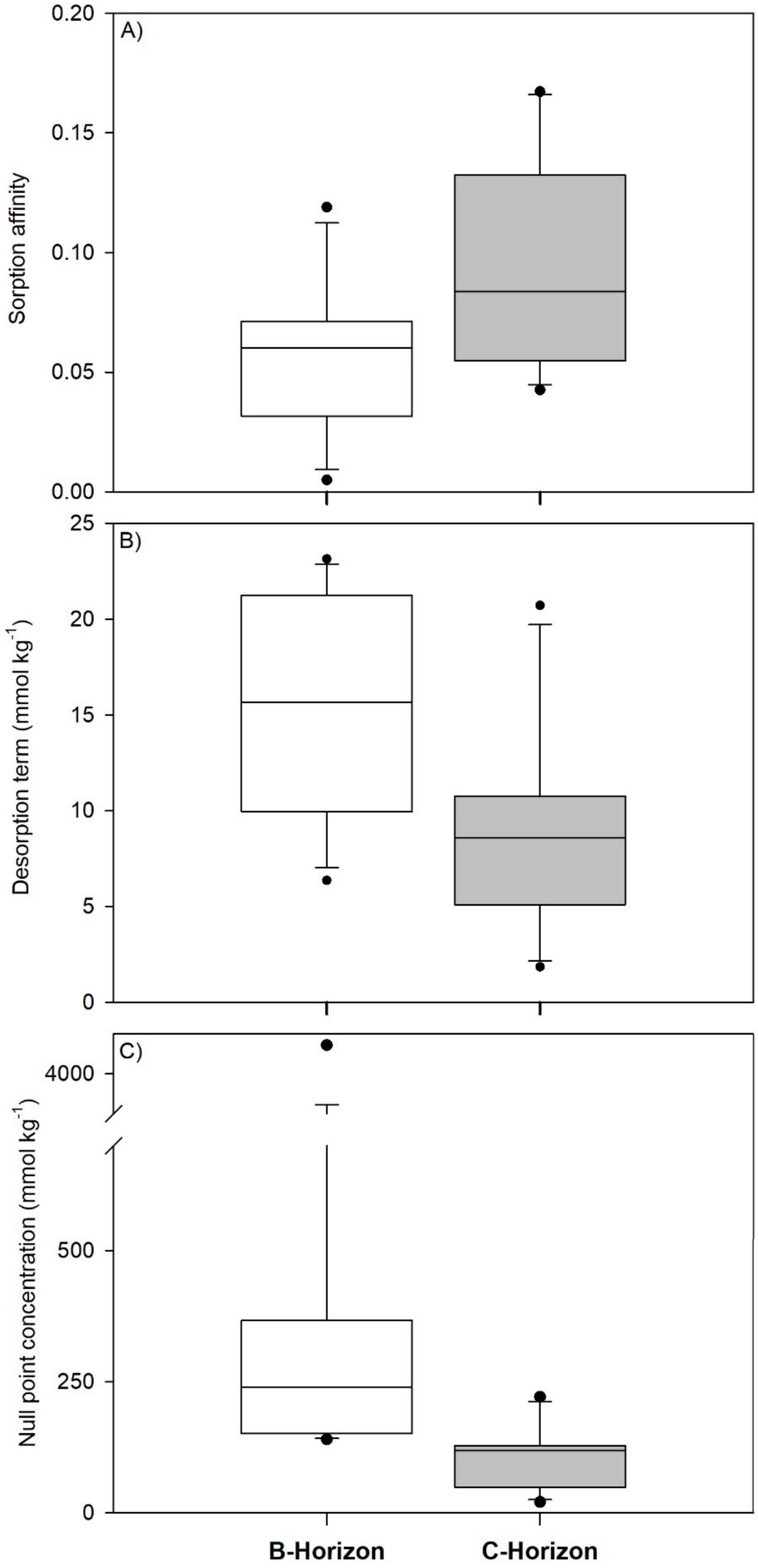


Figure 3-5: Distribution of A) soil pH, B) oxalate-extractable iron, C) oxalate-extractable aluminum and D) clay content of B-, and C- horizon samples. Upper and lower rectangle bounds denote 25th and 75th percentiles, the horizontal line indicates the median and “whiskers” denote 5th and 95th percentiles.

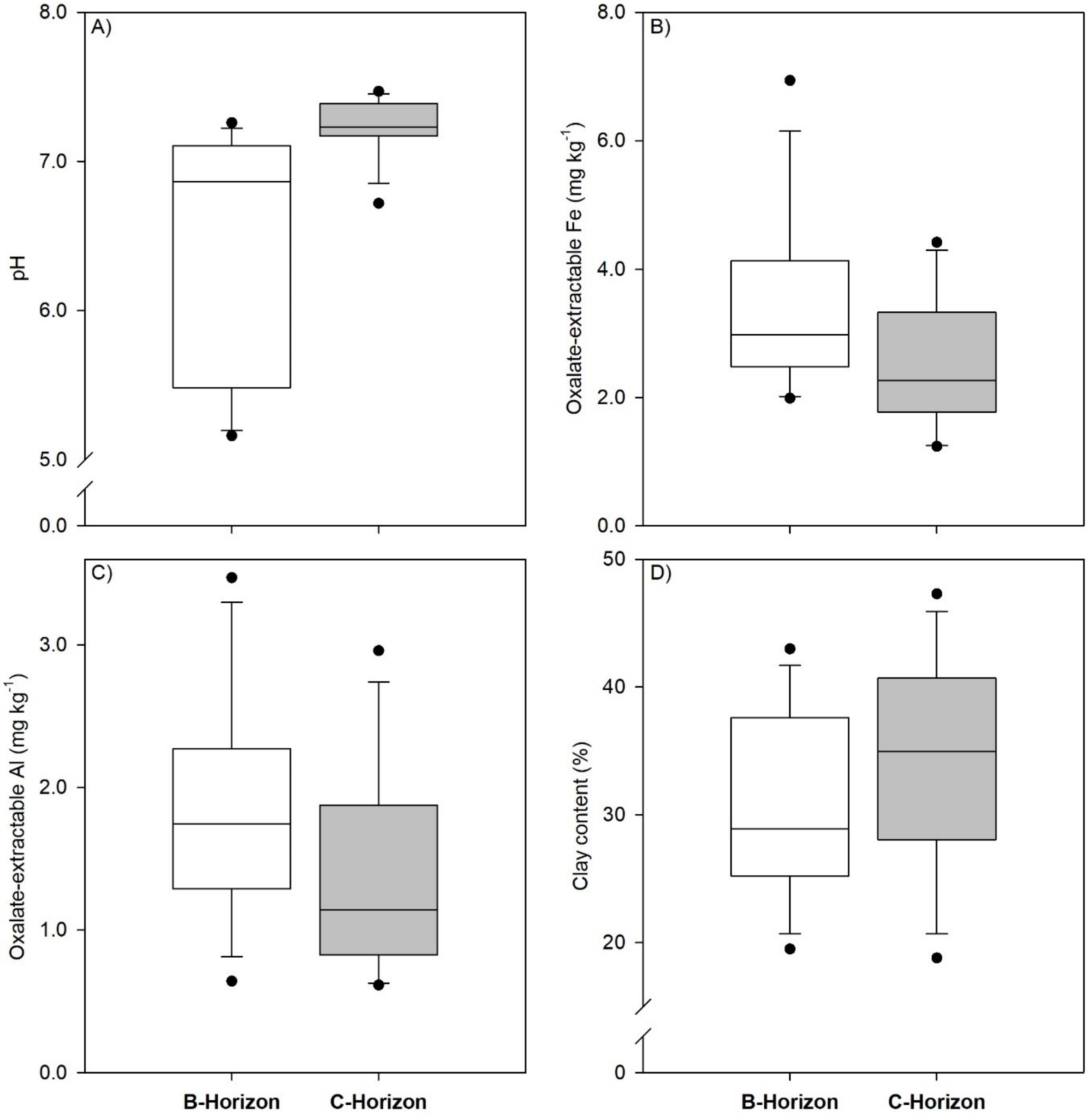


Figure 3-6: Combined DOC adsorption regressions comparing pH effects on adsorption behavior. Dashed gray lines indicates regression line for Population A samples (pH < 7.15) and the solid gray line indicates the regression lone for Population B samples (pH > 7.15).

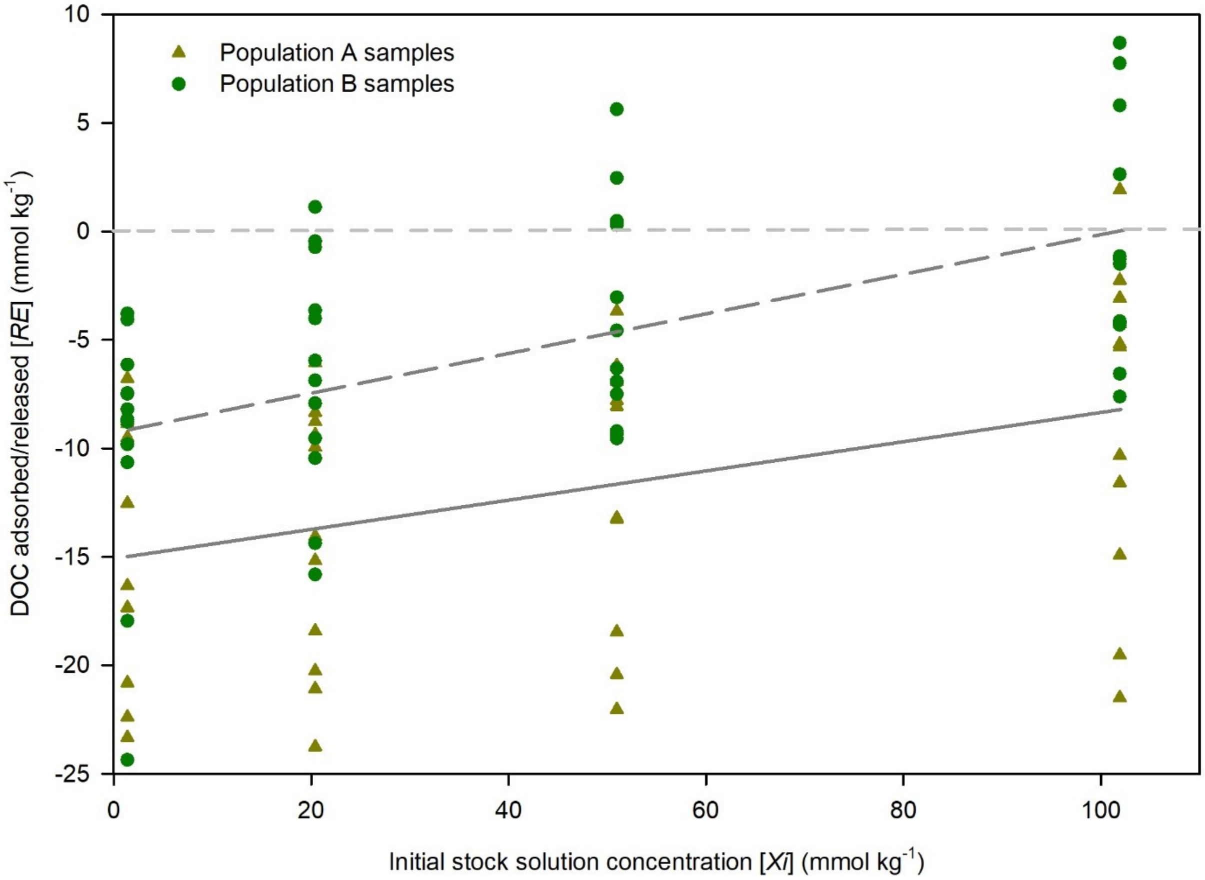
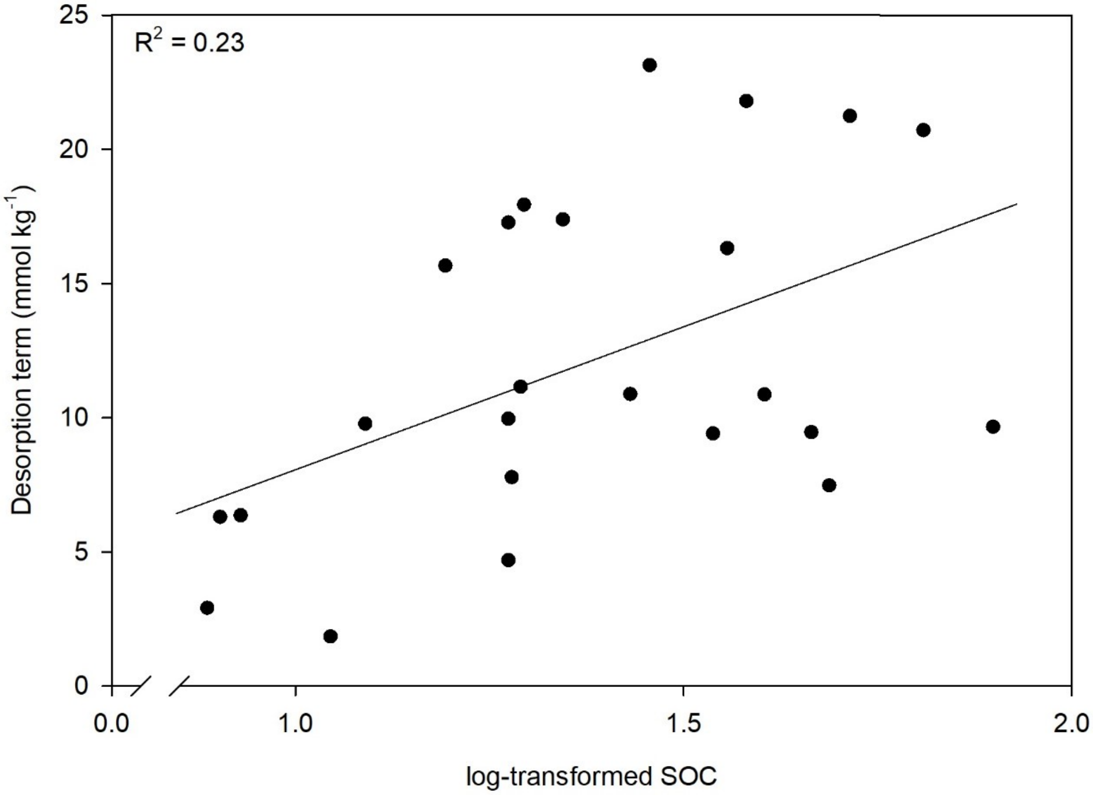


Figure 3-7: Relationship between the log-transformed SOC and the desorption term (n=23).



Chapter 4: Synthesis

The broad objective of this study was to determine the impact of clear-cut harvesting on subsurface DOC fate and transport in Alberta's southern Rocky Mountains. This study was focused on DOC in soil pore water and groundwater (Chapter 2) and on DOC-mineral soil adsorption/desorption processes (Chapter 3). Forested headwaters such as these are valuable as habitat for threatened fish species (Westslope cutthroat trout) and as a source of high quality drinking water. Providing an understanding of disturbance impacts on DOC will allow forest managers to limit degradation of water quality and aquatic habitat.

The first data chapter (Chapter 2) focused on quantifying the impact of forest harvesting on DOC magnitude and chemical character in shallow subsurface waters. This chapter also investigated the potential physiographic controls on DOC transport such as hillslope position (lowland vs upland) and depth in the soil profile (shallow vs deep pore water). Further, this chapter examined linkages of soil pore water and shallow groundwater to receiving streams. The effects of harvesting were significant for DOC concentrations and chemical character in soil pore water. Elevated DOC concentrations were observed in the harvested catchment compared to the reference catchment. This result was likely due to changes in environmental factors which influence DOC mobilization and transport in forested systems. The finding of greater DOC in soil pore water following harvesting is consistent with the literature, although only a limited number of studies have been conducted on pore water (Johnson et al., 1995). Pore water DOC in the harvested catchment was more aromatic, however it also had a lower molecular weight compared to the reference catchment. Differences in DOC chemical composition were likely caused by changes in substrate quality in the forest floor. Depth in the soil profile also influenced DOC concentrations, with shallow pore water having greater concentrations. This difference was possibly due to microbial decomposition as pore water moved down the soil profile. Adsorption processes and microbial decomposition usually considered as the dominant controls on DOC concentrations in mineral soil (Kalbitz et al., 2000). However, results from Chapter 3 indicate soils in these catchments had a low ability to adsorb carbon and, in fact, likely release carbon to pore water. B-horizon soils released more carbon than C-horizon soils at field relevant concentrations, likely a result of background SOC content and extractable Fe and Al. Additionally, B-horizon soils typically had lower sorption affinities than C-horizon soils. The difference in the sorption affinities and desorption terms between the two horizons likely contributes to some of the variation in pore water DOC concentrations. Given the notion that a) both adsorption and decomposition mechanisms influence subsoil DOC concentrations and b) that soils in this area do not adsorb carbon readily supports the conclusion that decomposition dynamics are likely more important in this region than initially thought. Shallow groundwater also appeared to be influenced by harvesting, however due to a small number of samples this could not be clearly substantiated. Groundwater samples from the harvested catchment had greater DOC concentrations than from the reference catchment, while the DOC composition was variable from well to well rather than across other study factors.

Temporal trends in DOC were evident in soil pore water chemical character but not in magnitude. DOC concentrations were spatially variable but did not exhibit strong temporal variation. Concentrations were stable across the snowmelt period suggesting greater potential influence of a continuous source of DOC leaching from the forest floor rather than a strong control by hydrology and water table interactions as a key regulator of DOC dynamics as other studies have suggested. This finding is contrary to other studies where variation in DOC concentrations was found throughout snowmelt (Boyer et al., 1997; Burns et al., 2016). However, DOC chemical character was influenced temporally and trends were different across catchments indicating harvesting has the potential to alter DOC carbon composition in soil pore water. Harvested pore water became more aromatic and heavier as snowmelt progressed, while reference pore water became more aliphatic and lighter. This difference may be attributed to differences in substrate quality and water fluxes between the two catchments. The organic matter in the harvested catchment was likely more degraded and therefore more aromatic than from the reference catchment. However, it should be noted the temporal differences in soil pore water chemical composition were relatively small and would be muted when scaled up to the catchment level.

A lack of strong correspondence between stream water and soil pore water was noted in this study. DOC concentrations decreased along the soil pore water – groundwater – stream water continuum. Studies in the literature have shown harvesting impacts stream water concentrations, especially during snowmelt (Laudon et al, 2009). In this study, the stream DOC was similar during both snowmelt and annually between the two catchments, Catchments that display impacts of harvesting usually have shallow soils and impermeable bedrock promoting stronger lateral movement of subsurface water towards a receiving water body. These characteristics are also associated with more dynamic seasonal water table fluctuations which likely promotes greater and more extensive interactions with DOC-rich surficial soil horizons than in the present study region. The ‘transmissivity feedback’ mechanism likely plays a stronger role governing DOC concentrations and chemical composition reaching the streams in these regions. Alternatively, Star West and North York soils are underlain by glacial tills and fractured bedrock promoting vertical movement of water and complex subsurface runoff generation pathways (Spencer et al., 2019). Therefore, soil pore water and shallow groundwater make up a small proportion of streamflow contributions in this region. Potential changes to hillslope DOC may not have been observed in the stream because of transformations and dilution through the more complex flow pathways before entering the streams.

The second data chapter (Chapter 3) explored adsorption/desorption processes which can immobilize DOC in soil. This study focused on understanding potential land-use effects and physiographic controls (hillslope position and soil depth) on DOC adsorption. Overall, harvesting had a negligible impact on DOC adsorption and desorbed DOC chemical character. Hillslope position had a moderate influence on the aromaticity of carbon, likely due to potential limitations on decomposition processes in the lowland hillslope positions. Soil depth was the strongest influence on the adsorption of DOC in these soils. B-horizon soils had lower sorption affinities, and greater desorption terms and null point concentrations than C-horizons. The two horizons behaved differently, seemingly due to differences in soil pH as well as other inherent soil properties. Dominant soil properties influencing adsorption parameters included extractable forms of Fe and Al as well as SOC. Determining the chemical composition of DOC released from mineral soils was difficult and resulted in only a limited ability to explain the observed variation because of weak or moderate relationships with soil properties.

Chapter 2 described the variation of soil pore water, groundwater, stream DOC dynamics in reference and harvested watersheds while Chapter 3 examined potentially key processes that would influence DOC storage and transport in the subsurface environment. Together these two chapters provided an understanding of how DOC is likely moving through the watersheds in this region. Shallow, B-horizon soils had greater DOC concentrations in pore water, which coincides with poor adsorption (additional storage) potential and a greater release of DOC. In contrast, C-horizon soils had lower concentrations, while they adsorb DOC slightly better. The combined field and laboratory studies herein produced unique insights into how DOC is transported from the hillslope to the stream, and how harvesting likely influences these processes. Notably, there are few studies in the literature combining field and laboratory components, especially adsorption experiments on soil types other than Podzols. This study approach supported the broader conclusion that microbial decomposition may be more important than hydrologically mediated processes (transport) in determining subsurface DOC dynamics than originally thought.

Evidence from this study indicates forest harvesting in these watersheds is a potentially effective source water protection strategy from a carbon standpoint. Although hillslope DOC may be impacted by harvesting, the complex flow pathways appeared to mask this change resulting in no meaningful apparent impact of harvesting on catchment scale DOC. One potential consequence of excluding forest management in these watersheds may include increased risk of wildfire which has shown to be particularly detrimental to source water quality, particularly DOC (Emelko et al., 2011). Forest management allows multiple landscape objectives to be met simultaneously. Objectives such as terrestrial and aquatic habitat conservation, source water protection, timber harvesting and fuel load management can be achieved if a forest management plan with Best Management Practices (BMPs) is in place. Overall, this research allows for a better understanding of landscape condition and forest disturbances on key source water quality parameters such as DOC that are key to provision of drinking water supplies. Previous research in these watersheds also support the notion that timber harvesting as a part of broader forest management is likely consistent with other source water protection objectives through the lens of sediment (Corrigan, 2017) and nitrogen water quality (Stewart, 2018). BMPs are vital to ensuring the protection of headwater streams for aquatic health and drinking water supplies.

4.1. Future Research

Results of this study also identify knowledge gaps that still exist in understanding DOC dynamics following harvesting. The following areas should be studied to provide a more complete understanding of harvesting impacts on DOC in high quality source water regions.

1. *Evaluate downstream propagation of multiple landscape disturbances on stream DOC and its relation to drinking water “treatability”.*

While this study provided knowledge on hillslope-scale processes on a first order stream, there should be further research on how impacts at plot scales are propagated at larger landscape scales to produce catchment scale effects. Scaling up to the watershed or basin scale would allow both forest managers and drinking water treatment engineers a more clear understanding of how multiple, small disturbances may interact to affect surface water quality at a regional scale. Cumulative impacts are particularly important to sensitive ecosystems such as high quality source water regions because they are vulnerable to degradation. Cumulative impacts of several small clear-cuts could alter runoff and DOC with the potential that these impacts could propagate downstream depending on the timing and extent of harvesting activities (Ohman et al., 2009).

2. *Evaluate the role of microbial decomposition in reducing DOC concentrations and altering DOC chemical character following clear-cut harvesting in the Rocky Mountains.*

This study showed that DOC adsorption to mineral soils accounts for small proportion of DOC concentration reductions moving down the soil profile and may even be a source of carbon in soil pore water. Microbial decomposition is widely considered the other dominant process mineralizing DOC. Experiments quantifying biodegradation of DOC moving through the soil profile would provide valuable insight into the fate of DOC and allow for a more complete understanding of DOC transport through the system. Additionally, investigating how DOC decomposition is impacted by forest harvesting would give a more complete understanding of carbon dynamics in this region.

3. *Evaluate long-term impacts of harvesting of DOC at the hillslope and catchment scales.*

Short-term impacts (<5 years) of harvesting on hillslope and stream DOC were investigated in this study. A recognized knowledge gap exists for long-term harvesting impacts (Laudon et al., 2009). Long-term (>10 years) impacts following harvesting should be evaluated to determine if hillslope DOC is still elevated and if this change has increased DOC export from receiving streams. The importance of studying long-term impacts is vital because they could provide vital empirical data and allow for predictive modelling of forest harvesting in comparison to other disturbances such as wildfire (Kreutzweiser et al., 2008).

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