FOREST HARVEST AND WATER TREATABILITY: ANALYSIS OF DISSOLVED ORGANIC CARBON IN HEADWATER STREAMS OF CONTRASTING FOREST HARVEST HISTORY DURING BASE FLOW AND STORM FLOW

by

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Abstract

Dissolved organic carbon (DOC) is important to ecosystem functioning and of interest to drinking water treatment as it is costly to remove from source water. The effects of land use change (e.g. forest harvest) on DOC are not fully understood. Past studies of the effects of forestry on DOC have found mixed results, and covariate effects complicate mechanistic understanding and may underlie regional differences. DOC is typically highest during storm events, and detailed time-resolved measurements of DOC over longer periods are just becoming feasible with advances in *in situ* sensors. In this thesis, I investigated DOC concentration and character for headwater streams of contrasting forest harvest history in the UBC Malcolm Knapp Research Forest near Maple Ridge, British Columbia, and discussed implications for water treatment through expert interviews with water treatment engineers at Metro Vancouver. I took a two-pronged approach to the field study by measuring not only temporally detailed DOC concentration at two contrasting sites, but also spatially broad DOC concentration and character at 24 sites for six time points during the same study period. From the temporal analysis, I found base flow DOC concentration to be lower in the clear-cut stream (Clear cut: 2.26 ± 0.43 mg/L; Forested: 4.30 ± 0.83 mg/L), but storm response to be stronger (mean increase DOC: Clear cut: 2.42 mg/L, Forested: 1.99 mg/L). Lower DOC concentration after cutting may be due to reductions in carbon inputs like leaf litter, though differences in drainage area and the presence of a bog lake may also account for some of the observed difference. Elevated storm responses may be due to changes in flow paths related to forest harvesting. From the broad sampling analysis, I found differences in DOC character between the two land use types: DOC in clear-cut sites was more protein-like whereas DOC in forested sites it was more humic-like, although once random factors were taken into account in generalized linear mixed models, the relationship was no longer significant. Using categorization and regression tree modeling, I found drainage area to be the most important covariate related to DOC followed by time of year (i.e. seasonality).

Lay Summary

Water from forested rivers and streams used for drinking must be disinfected to remove disease-causing bacteria. Before disinfection, dissolved organic carbon (DOC) must be removed, which is often the most difficult and expensive step in drinking water treatment. DOC is decaying plant or animal matter that seeps into water like tea and is too small to be removed with a filter. Watershed managers are interested in understanding how changes to forests will effect water quality including DOC content. In this thesis, I look at the effects of clear cutting on DOC for small streams in a research forest east of Vancouver, British Columbia, Canada. I found that clear cutting was not significantly related to the amount of DOC in streams, but it was related to the type of DOC and the way DOC responds to rain storms, which are also important to drinking water treatment processes.

Preface

This thesis is original, unpublished, independent work by the author, Emily Mistick. The framework for this thesis is based on the research objectives of the *for*Water NSERC Network for Forested Drinking Water Source Protection Technologies, a pan-Canadian, interdisciplinary strategic research network that contributes new knowledge and innovation to drinking water security in a changing climate. Mark Johnson and John Richardson contributed to the project design and suggested edits to the analysis and manuscript. Emily Mistick conducted all field work, laboratory testing, and data analysis. The method for interviews reported in Chapter 4 was approved by the UBC Behavioural Research Ethics Board under BREB H19-00946.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

Acronym	Definition
ANCOVA	Analysis of covariance
BIX	Biological index
C	Carbon
CART	Categorization and regression tree
DBP	Disinfection byproduct
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
FI	Fluorescence index
FLI	Flushing index
GLMM	Generalized linear mixed model
HAA	Haloacetic acid
HI	Hysteresis index
HIX	Hunification index
LRT	Likelihood ratio test
MKRF	Malcolm Knapp Research Forest
NOM	Natural organic matter
PARAFAC	Parallel factor analysis
PCA	Principle components analysis
SCD	Streaming current detector
SR	Slope ratio
THM	Trihalomethane

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On a more personal note, thank you so much to my family, friends, and Evan who encourage and support me always. Thanks and love to you all!

Chapter 1: Introduction

1.1 Context

Treating drinking water to prevent infectious disease has been one of the greatest achievements in the history of public health (Cutler and Miller, 2005). The primary goal in treating water is disinfection – the removal of disease causing pathogens. There are a variety of disinfection processes available, but the cheapest and most widespread is chlorination (Nikolaou et al., 1999). Beginning in the 1970s, it was observed that the interaction of chlorine with natural organic matter (NOM) in surface waters produces disinfection byproducts (DBPs) (Bellar et al., 1974; Rook, 1974), which were later found to be carcinogenic (Richardson et al., 2007; Villanueva et al., 2007). DBPs are regulated by Health Canada, which requires minimization of DBPs without compromising the effectiveness of disinfection and recommends removal of the precursor NOM material as the best DBP reduction strategy (Health Canada, 2019). Removal of NOM can be difficult and expensive for water treatment utilities (Matilainen et al., 2010), thus understanding the dynamics of NOM in source water from forested catchments, especially those undergoing land use change, has become increasingly important to water treatability (Emelko et al., 2011).

Drinking water utilities are primarily concerned with dissolved organic matter (DOM), the dissolved portion of NOM, as it requires more complex chemically assisted filtration to remove (Matilainen et al., 2010). Specifically, dissolved organic carbon (DOC), the carbon (C) content of DOM, is used as a proxy for DOM as the C content is typically consistent and DOC is more easily measured. DOC is derived from decaying material such as leaf litter, exudation from roots, or microbial byproducts, and undergoes biological and photolytic decomposition over time. The majority of DOC in rivers is terrestrially derived and transported from soils to streams, and a smaller portion is microbially derived via in-stream biological processes (Lambert et al., 2014; Laudon et al., 2011). DOC includes a diversity of large complex molecules that are characterized by whether they are generally more humic-like, which generally corresponds with terrestrial sources, or more protein-like, corresponding with microbial sources (Kathleen R. Murphy et al., 2011). Both DOC concentration and character affect water treatment processes (Liu et al., 2010; Zhao et al., 2009), and both are considered in the present study.

As the majority of the world's accessible freshwater is located in forested catchments and over a third of world cities rely on forested watersheds for drinking water (Dudley and Stolton, 2003), understanding the impact of forest change on DOC concentration and character is critically important for managing drinking water supplies. Land use change has been shown to variably affect DOC. Agricultural and urban uses have been found to influence the character of DOC and may or may not affect the concentration (Kolka et al., 2008; Parr et al., 2015; Sickman et al., 2007; Wilson and Xenopoulos, 2009). The effects of forest harvesting on DOC are not as well understood; there are many case studies in the literature, but they have yielded mixed results. Some studies have observed an increase in DOC after cutting 12/23/19 12:45 PM or no significant difference (Knoepp and Clinton, 2009; Lepistö et al., 2014; Startsev et al., 1998). Others that compared forested to clear cut sites after cutting have found DOC in clear cut streams to be higher (O'Driscoll et al., 2006), lower (Judy L. Meyer and Tate, 1983a), or not significantly different (Plamondon et al., 1982).

In this study, we consider the effects of recent forest harvest on DOC concentration and characterization during base flow as well as during storm events. It is understood that DOC concentration is usually discharge-dependent and increases during storm events, and most water treatment problems occur during storms (Erlandsson et al., 2008; Hinton et al., 1997; Raymond and Saiers, 2010). Future climate scenarios indicate more intense and frequent rainfall for much of North America (Ragno et al., 2018), which underscores the importance of understanding not only how changes in forest cover affect DOC, but also how areas that have undergone land use change respond to storm events. The interaction between forest harvest and storm response has not received much attention in the literature, particularly not with high frequency measurements. In this study we monitored DOC at sub-hour intervals allowing for a more detailed description of storm response in two catchments of contrasting forest harvest history. In addition, we carried out synoptic sampling at additional forested and recently clear cut catchments to assess local variation and analyze DOC quality as well as quantity.

1.2 Research objectives

The overall objective of this thesis is to enhance understanding of the relationship between forested land use change, storm flow, and DOC. The study was carried out in the UBC Malcolm Knapp Research Forest (MKRF) near Maple Ridge, BC, which serves as an illustrative case study for small streams in the Pacific Maritime ecozone. Generally, DOC concentrations in this region are relatively low compared with other parts of North America (Mulholland and Watts, 1982). DOC concentrations are known to increase markedly during storms, and storm events are often the greatest cause for concern for drinking water treatment plants (K. Tully and A. de Boer, personal communication, May 23, 2019). Therefore, this study focuses not only on the differences between streams located in clear-cuts vs. located in relatively intact forest, but also on the response of those streams to paired storm events.

Objective 1: Compare storm responses between two streams of contrasting forest harvest history. Recent advances in instrumentation have allowed for highly temporally resolved studies of DOC (Koenig et al., 2017; Vaughan et al., 2017). In this study, we were able to capture 30-minute data over a continuous fall to spring period concurrently for two small streams of differing forest cover located only a few kilometers apart.

Objective 2: Sample from a broader range of clear-cut and forested sites to account for variation in covariate factors (e.g. drainage area size, dominant tree type, etc). One of the challenges in resolving the mechanisms of changes to DOC is the multitude of potentially significant covariates. This present study uses a two-pronged approach that investigates two sites with detailed time resolution, then also a wider array of 24 sites accounting for covariant site parameters in order to demonstrate local variation and elucidate the potential covariate effects.

Objective 3: Compare DOC character at sites of contrasting forest harvest history in base flow and storm flow. In addition to the concentration, DOC characteristics (i.e. quality) are important in drinking water and ecological contexts. Exact characterization of DOC is technically challenging, but rapidly evolving spectroscopic techniques allow for easier DOC characterization across greater numbers of samples. In this study we characterized 141 samples (approximately 6 samples for each of 24 sites) using absorbance and fluorescence spectral indices and parallel factor analysis (PARAFAC). It is not yet practical to obtain detailed characterization at 30 minute intervals, so the DOC characterization is presented for only the broad sampling portion of this thesis.

Objective 4: Discuss implications for local water treatment utilities. As the initial impetus for studying the relationship between DOC and forest harvest was the drinking water treatment context, I use the final chapter to discuss the potential implications of findings to drinking water treatment processes. Expert interviews of water treatment engineers at Metro Vancouver were conducted to use the Metro Vancouver drinking water supply as a relevant case study. We addressed the details of DOC treatment processes, how storm events and seasonality affect DOC, and what would happen if DOC changed drastically in the coming decades.

Objective 1 is addressed by analyzing temporally resolved DOC concentration data for storm responses of two headwater streams to 22 storm events (Chapter 2). Next, Objectives 2 and 3 are addressed through grab sampling analysis of DOC concentration and character at 24 sites (Chapter 3). Finally, Objective 4 is addressed through discussion of expert interviews (Chapter 4). Chapters 2 and 3 have their own introductions, which provide further background and review of relevant literature.

Chapter 2: Temporal analysis of DOC at two contrasting sites

2.1 Introduction

Dissolved organic carbon (DOC) concentration in streams is critically important for aquatic ecosystems and human water use, and is affected by changes in land use and climate. Ecologically, DOC is a food source at the base of aquatic food webs underpinning ecosystem productivity (Meyer et al., 1988; Wilcox et al., 2005). For human systems, DOC in source water is an important factor in drinking water treatment. While DOC is beneficial to ecosystems and is usually not harmful to human health, it makes drinking water treatment more challenging as it reacts with disinfectants to produce harmful byproducts (Matilainen et al., 2010; Sharp et al., 2006). Over the past few decades, several long-term studies have reported an apparent trend of increasing DOC concentrations in inland surface waters over large areas of the Northern Hemisphere (Bragée et al., 2015; Evans et al., 2005; Monteith et al., 2007).

Much of the world's drinking water supply comes from forested watersheds. Forested watersheds account for 75% of the world's accessible freshwater (Shvidenko et al., 2005), and over a third of world cities rely on them (Dudley and Stolton, 2013). Surface water provided by forested areas is naturally high quality, but forested watersheds face changes due to pressures from the forestry industry and climate change. Increased risk of wildfires, which have hugely negative impacts for water quality, has prompted more drinking watershed managers to consider active forest management for risk mitigation (Denver Water, 2018; Rio Grande Water Fund, 2014). Facing this, in recent years, there has been increasing interest in the effects of forest cover change on water quality, particularly for drinking water treatment including managing DOC levels (Emelko et al., 2011). Hydrological flow paths, such as flow across the landscape and through soils, drive DOC delivery (e.g. transport from terrestrial to aquatic ecosystems) in many headwater streams (Boyer et al., 1997; Hornberger et al., 1994) and generally DOC concentrations are highest during storm events (Raymond and Saiers, 2010; Vidon et al., 2008). Water treatment plants must plan for peak concentrations and worst-case scenarios, like high intensity storms and mass wasting events. Water supplies are subject to boil-water advisories when the water cannot be treated or cannot be treated quickly enough to keep up with demand during extreme events, which risks people's access to safe drinking water (Galway, 2016). Future climate scenarios suggest increased storm intensities (Ragno et al., 2018); thus, it is important to not only understand the effects of forest cover change but also how those changes will respond to storm events.

Mechanisms of DOC delivery to streams and the effects of disturbance at the catchment scale are not fully understood (Lambert et al., 2014; Laudon et al., 2011). Typically, in headwater streams DOC is terrestrially derived and mobilized to streams via flow paths through the soil. Vegetation, soil, and hydrologic flow paths can be altered by changes to land use or climate with implications for DOC concentration. Urbanization and agricultural land use are known to increase DOC concentrations (Manninen et al., 2018; Parr et al., 2015; Shang et al., 2018; Sickman et al., 2007; Westerhoff and Anning, 2000). Forestry operations may increase or decrease DOC concentrations as harvest operations can result in mobilization of DOC derived from slash and detrital material (Schelker et al., 2012), but in the long run may also reduce vegetative carbon inputs and speed up decomposition to decrease DOC compared to pre-treatment levels, as organic litter inputs decrease after harvesting (Kiffney and Richardson, 2010).

The complexity of DOC sources and driving mechanisms in the context of local vegetation, geology, and climate has prevented the development of generalizable DOC prediction models. Observational case studies remain an important way to assess DOC in various contexts to work toward a unified conceptualization. Past studies have found mixed results on the relationship between forestry activity and DOC concentrations, suggesting that the relationships may vary regionally. Many studies have found DOC to increase (Bertolo and Magnan, 2007; Holopainen and Huttunen, 1998; Laudon et al., 2009;

O'Driscoll et al., 2006; Pinel-Alloul et al., 2002; Schelker et al., 2012). Others have found DOC to decrease (Meyer and Tate, 1983), increase and then decrease (Plamondon et al., 1982; Startsev et al., 1998), or have no significant response (Knoepp and Clinton, 2009; Lepistö et al., 2014). Particularly for local applications, local studies of DOC dynamics are necessary.

It is understood that DOC generally increases at higher discharge (i.e. during storm events), but response of DOC concentration to storm events can be complex and vary seasonally (Knoepp and Clinton, 2009; Lepistö et al., 2014). Many past studies have looked at the effects of rain events on DOC, but DOC changes happen rapidly and may not be captured unless measurements are sub-daily (Ruhala and Zarnetske, 2017). Understanding storm responses requires high frequency recordings of DOC, but until recently this was logistically very difficult; samples were collected either by hand or with auto sampling devices (e.g. Buffam et al., 2001; Evans et al., 1999; Hinton et al., 1997; Hood et al., 2006; Raymond and Saiers, 2010; Vidon et al., 2008). In recent years, in-stream DOC measurements have allowed for a large jump in our ability to resolve DOC dynamics over time. Studies have demonstrated the usefulness of in-situ DOC-proxy sensors in single streams (Fovet et al., 2018; Jeong et al., 2012; Pellerin et al., 2012), and comparative studies are beginning to unravel differences in DOC storm responses between catchments with differing characteristics (Koenig et al., 2017; Vaughan et al., 2019; Vaughan et al., 2017).

Comparing the relationship between discharge and DOC concentration during storms, a cyclical relationship known as hysteresis often occurs, in which the relationship between variables depends on the history of inputs (i.e. the relationship between discharge and DOC concentration is different on the rising limb vs. falling limb of the storm hydrograph). The relationship between discharge and concentration is different on the rising limb versus on the falling limb of the hydrograph, creating a loop when concentration and discharge are plotted against each other. Hysteresis loops can be measured as either clockwise (concentration is higher on the rising limb) or counterclockwise (concentration is higher on the falling limb) with as few as 5 points per storm (Evans et al., 1999). Headwater streams usually exhibit clockwise hysteresis, suggesting that the DOC pool is source-limited and near-stream, but there can be significant variation between storms (Andrea et al., 2006). In this study, we describe hysteresis and flushing with normalized indices that allow for more detailed comparison between storms as well as clockwise vs. counter clockwise categorization (as in Vaughan et al., 2019). In addition to hysteresis indices, we looked at DOC response parameters like percent concentration change and rate of change, which are important to drinking water treatment processes (Sharp et al., 2006; Worrall and, 2009).

In this study, we used *in situ* submersible spectrophotometers to measure DOC by spectral proxy every 30 minutes. Highly resolved DOC time series measurements allowed us to investigate responses to storm events and compare the response at two nearby catchments of differing land use history. Our objective was to investigate the combined effects of forest cover change and storm events by comparing the storm response of two nearby headwater streams of contrasting forest harvest treatment. There are two alternative hypotheses for the base flow DOC concentration and for DOC storm response at these two sites: the clear-cut stream may be higher in DOC and/or respond more strongly to storms due to soil carbon destabilization, and the clear-cut stream may be lower in DOC and/or show a muted storm response due to reduced carbon inputs from leaf litter and root exudation.

2.2 Methods

2.2.1 Study sites

This study was conducted in Malcolm Knapp Research Forest (MKRF) located approximately 50 km east of Vancouver, BC (49°17'N, 122°36'W) in the foothills of the southern end of the Coast Mountain range (Figure 2.1). Temperatures are mild with a monthly mean temperature of 18° C in August and 3° C in December. Precipitation is predominantly rain with only very occasional snowfall at elevations below 300 m. Mean annual precipitation is about 2200 mm, 70% of which occurs from November to April (Government of Canada, 2019).

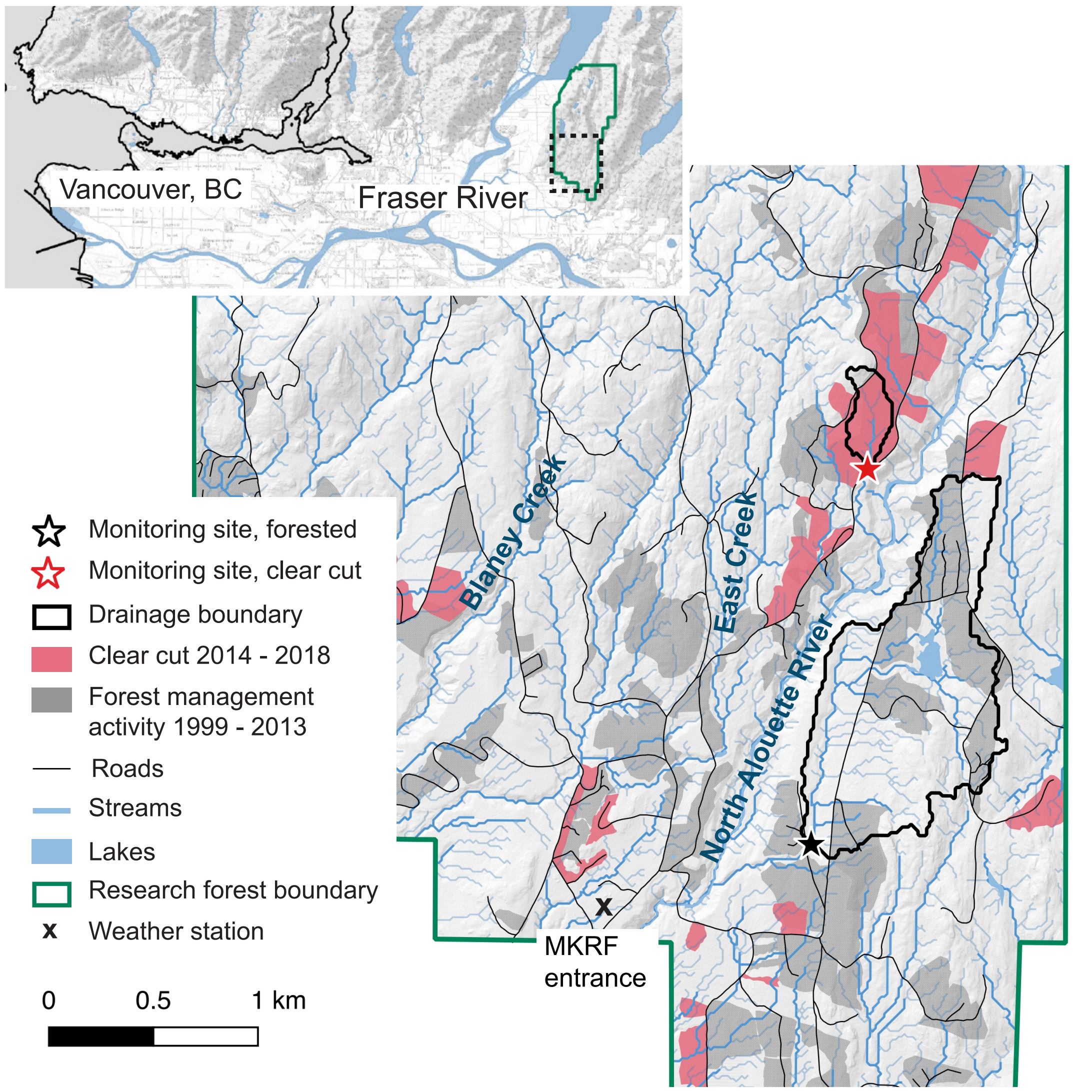

Figure 2.1. Map showing in-stream monitoring station locations within Malcolm Knapp Research Forest and clear cut history from the past 5 years (red) and from 5 to 20 years ago (grey). The research forest is located east of Vancouver, BC and drains into the Fraser River.

MKRF is situated in the Coastal Western Hemlock dry maritime (CWHdm) biogeoclimatic zone (Meidinger and Pojar, 1991). The vegetation is dominated by large conifers: western hemlock, western red cedar, and Douglas-fir. Soils are of glacial origin and generally shallow and coarse textured with acidic igneous bedrock below (Feller and Kimmins, 1979). The area of the research forest used in this study consists of 88 year old stands following large-scale fires in 1931 and successions of secondary growth following regular clear cutting since then.

Two headwater streams were selected for continuous monitoring of discharge and DOC, one in a clear cut and one in relatively mature forest. The clear-cut site was harvested in 2016 with no riparian buffer. A few meters on either side of the stream was designated as a machine free zone; no machine tracks crossed the stream, but all trees were removed leaving only some understory plants. Nearly all of the drainage area for this monitoring site was clear cut (Figure 2.1). The forested site was located in a second-growth forest last harvested in 1998 with a 10 m riparian buffer of intact forest that was not harvested. This 10 m riparian reserve was shown to contribute similar amounts of organic inputs as fully forested controls over a ten-year period (Kiffney and Richardson, 2010). Additional forest management activity including clear cutting and thinning occurred in other parts of the drainage area of the site between 2004 and 2013, but not between 2014 and 2018, shown in Figure 2.1.

Both streams have a pool-riffle morphology with cobbled stream bed, as classified following Montgomery and Buffington (1997). Elevation, slope, and drainage area were calculated using a 1 m digital elevation model provided by MKRF. The stream outlet to the clear-cut catchment is located at 283 m elevation and has an average slope of 16 degrees over a 10 m radius from the monitoring station. The stream outlet to the forested catchment is located at 193 m elevation with an average slope of 8 degrees. The forested site drains 97 ha, and the clear-cut site drains 6 ha. To account for disparity in drainage area, discharge and carbon yields are presented and discussed in absolute terms as well as in area-normalized values.

2.2.2 In-stream monitoring

Both study streams are intermittent, experiencing periods with no detectable surface flow in the summer months; thus, this study focused on the fall to spring period. At each site, a monitoring station was set up to record discharge and DOC values every 30 minutes from November 2018 to May 2019.

Discharge values were obtained using 30-minute depth measurements and rating curves. Depth was measured with CTD sensors (METER Group Inc., Pullman, USA) running on a CR1000 data logger (Campbell Scientific, Edmonton, Canada). DOC concentration was obtained using *in situ* submersible spectrophotometers (Spectrolyzer, s::can, Vienna, Austria). We developed rating curves at each site from November 2018 to February 2019 using the salt slug injection method (R. D. Moore, 2005) and a calibration constant of 0.486 mg NaCl•mg•cm/µS/L (M. Richardson, Sentlinger, Moore, and Zimmermann, 2017) following methods used by McDowell and Johnson (2018). We then fit power curves to the relationship between discharge and depth, which were used to convert depth to discharge for the entire study period. The CTD sensor calibration was verified in a lab setting prior to deployment.

We used a global calibration provided by the spectrometer manufacturer (s::can) to calculate DOC values from raw spectral fingerprints. These values were tested streamside by analyzing fresh KHP standards using the spectrometers. An adjusted three-point calibration was developed to correct the small difference observed between the global calibration values and our measurements of KHP standards. We validated this calibration by comparing in-stream readings to grab samples taken by an ISCO autosampler ($n = 24$) that were analyzed using a Shimadzu TOC analyzer within two days of collection. The TOC analyzer was calibrated using a five-point calibration with KHP standards. We found a mean standard error of 0.4 ± 0.2

mg/L for the in-stream sensor at the forested site (n = 20) and a mean standard error of 0.3 ± 0.1 mg/L at the clear-cut site (n = 24). We used the calibrated spectrolyzer measurements without further adjustment. Both monitoring stations were visited every two weeks to maintain power supplies and to clean the spectrometer sensor windows. Car batteries powered both stations; at the forested site, a hydrogen fuel cell was used to maintain battery power, and at the clear-cut site a solar panel was used. During winter months, the solar panel was able to maintain the battery power for only about two weeks, requiring exchanges with charged batteries.

We recorded 30-minute discharge and DOC from November 2018 to May 2019. There were no gaps in discharge recordings at the forested site and minimal gaps at the clear-cut site during periods of very low flow. For DOC, the dataset was cleaned to exclude data for which obstructions covered the sensor window or the sensor was measuring on air instead of water due to extremely low-flow conditions. The spectrometer software recognizes the characteristic patterns of these errors and flags them for removal. In addition, the DOC time series were checked visually and any remaining points that were 0 or highly erratic were removed as these indicated sensor fouling or measurements on air (s::can, 2011).

2.2.3 Weather data

Hourly precipitation data was obtained from the weather station located at the entrance to MKRF (Figure 2.1, 2.5 km from the clear cut and 1.0 km from the forested catchments). To delineate storms, we used the USGS Rainmaker R package (Corsi and Carvin, 2019). We used the default minimum precipitation threshold of 5 mm and a minimum event separation of 12 hours. This storm delineation was used to compare simultaneous storm responses at the two study streams. Precipitation amounts were assumed to be similar at both sites, as they are both within 5 km of the weather station and situated in similar topography.

For each storm period, 24 hours was added to the end of the Rainmaker result in order to allow enough time for discharge and DOC to return to pre-storm levels. This falling limb adjustment only affects the carbon yield and hysteresis index calculations. Because the correction was applied to both sites, the results remain comparable between sites.

2.2.4 Parameters calculated

Several storm response parameters were calculated from the in-stream DOC and discharge data. Pre-storm DOC was measured as the DOC value at the onset of the storm period. Peak DOC refers to the maximum value achieved during the storm period. Absolute difference and percent difference DOC refer to the difference from pre-storm to peak concentration. Time to reach peak DOC was the time from onset of the storm to the time when DOC concentration was at a maximum. Rate to reach peak was the absolute difference in DOC divided by the time to reach the peak. Carbon yield refers to the mass of carbon that passed downstream during the storm period, and specific C yield refers to the mass of carbon per hectare. Analysis was conducted in R version 3.5.2 (R Core Team, 2018).

Normalized indices were calculated as in Vaughan et al. (2019) [1]. Flushing index (FLI) describes the relative amount that DOC increases from the start of the storm to peak discharge and is calculated as follows:

$$DOC_{norm} = \frac{DOC_i - DOC_{\min}}{DOC_{\max} - DOC_{\min}} \tag{1}$$

[1] The acronym has been changed from FI in Vaughan et al. 2019 to FLI here to prevent confusion with fluorescence index (FI) that is commonly used in DOC literature and pre-dates Vaughan's framework.

$$FLI = DOC_{Q\max,norm} - DOC_{initial,norm} \tag{2}$$

where DOC_{norm} is the normalized parameter value ranging from 0 to 1, DOC_{max} and DOC_{min} are the maximum and minimum values reached during the particular storm, DOC_i is the concentration value at time step *i*, and $DOC_{Qmax,norm}$ is normalized concentration when discharge (Q) was at its maximum value.

Hysteresis index (HI) describes whether DOC concentration peaks before or after discharge peaks. This corresponds to the direction of hysteresis loops seen when plotting discharge versus concentration, as in Figures 2.3 and 2.4. HI values range from -1 to 1 with negative values corresponding to counterclockwise hysteresis (discharge peak occurs before concentration peak) and positive values corresponding to clockwise hysteresis. HI is also calculated as in Vaughan et al. (2017) as follows:

$$HI = mean(DOC_{j,rising} - DOC_{j,falling}) \tag{3}$$

where *j* is incremental level of specific discharge (Q) rounded to increments of 0.1 m^3/ha. Each discharge level has two corresponding DOC concentrations, one during the rising limb and one during the falling limb of the discharge time series. $DOC_{j,rising}$ refers to the normalized concentration on the rising limb, and $DOC_{j,falling}$ refers to the normalized concentration on the falling limb. HI in this study refers to the mean HI value for each storm.

To test differences in storm response parameters between the two sites, we used paired statistical tests. For normally distributed variables, we used a paired t-test. For variables that were not normally distributed, we used a Wilcoxon signed rank test with a continuity correction if the distribution was binomial. In addition, we normalized all of the variables and performed paired t-tests on all of them (paired by storm). The results were the same in both the parametric and non-parametric methods. As both methods gave the same results, the non-parametric tests are shown here, in order to discuss the unadjusted parameter values.

To investigate the effects of storm characteristics that could account for a portion of the storm response, we ran models that included antecedent discharge, storm intensity, and date of each storm. Antecedent discharge was calculated as the discharge at the onset of the storm, and storm intensity was calculated as mm rain per day. We ran an analysis of covariance (ANCOVA) including stream, storm intensity, antecedent discharge, and time for six of the storm response parameters: hysteresis index, flushing index, peak DOC, percent change in DOC from pre-storm to max concentration, rate of change in DOC, and specific carbon yield.

2.3 Results

2.3.1 Time series data

From the hourly precipitation data, 22 storm periods were identified for analysis from rain events from November 15, 2018 to April 22, 2019. Total event size ranged from 5.8 to 88.4 mm (mean = 33.5, SD = 22.9 mm) over durations of 26 to 130 hours (mean = 64 hours, SD = 26 hours). Storm intensity ranged from 0.24 to 2.56 mm/h (mean = 0.96, SD = 0.63 mm/h). Discharge averaged 0.69 ± 0.67 m^3/ha for the forested stream and 0.73 ± 0.82 m^3/ha for the clear-cut stream. DOC concentration averaged 4.27 ± 0.95 mg/L in the forested stream and 2.47 ± 0.94 for the clear-cut stream (Figure 2.2). The relationship between DOC concentration and discharge for the entire study period is shown in Figure 2.3. One representative storm is shown in Figure 2.4.

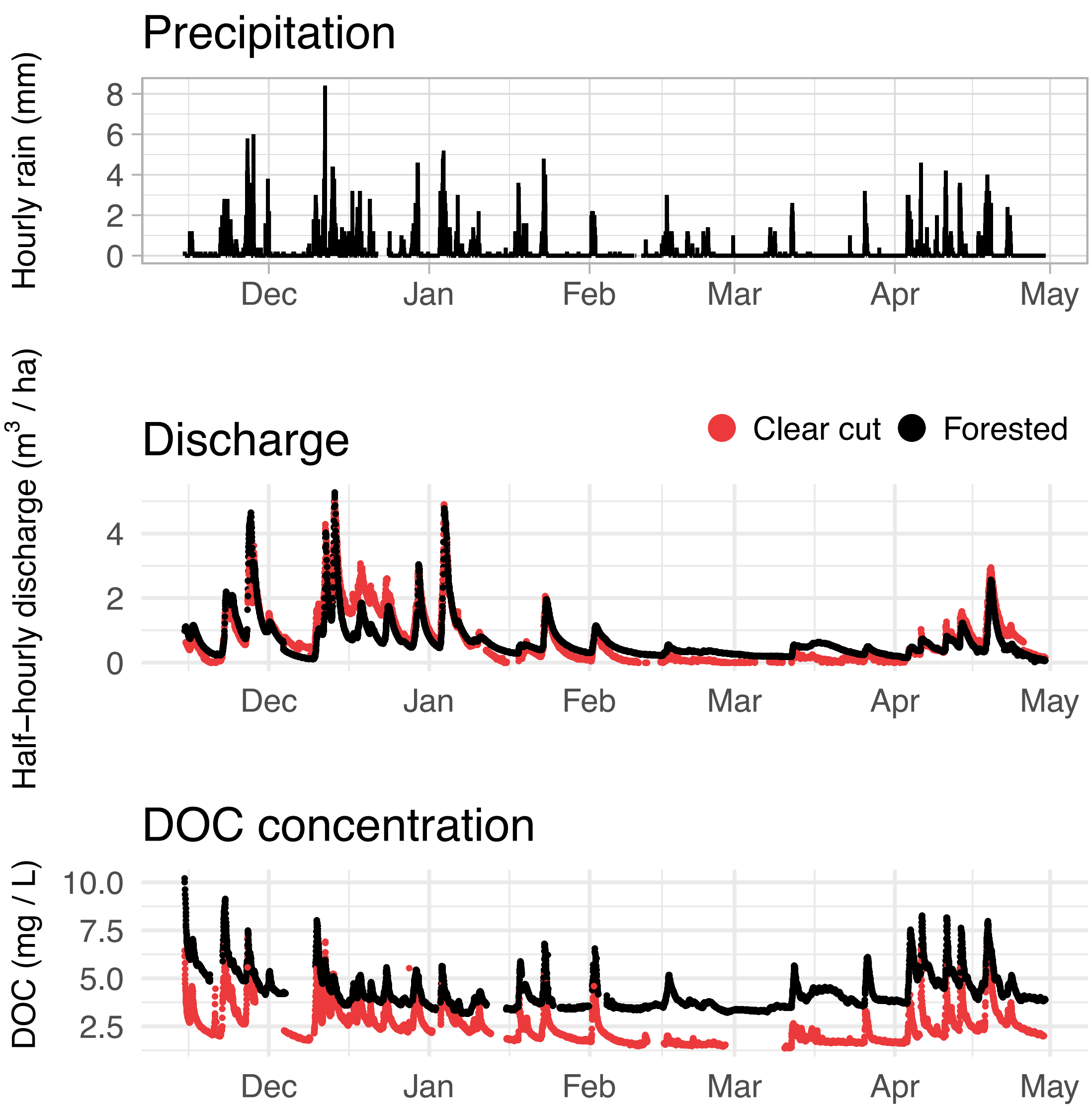

Figure 2.2. Precipitation, discharge, and DOC concentration at both MKRF stream sites over the study period. Precipitation was measured at a weather station near the entrance to the research forest (see Figure 2.1), and discharge and DOC concentration were measured every 30 minutes using in-stream sensors.

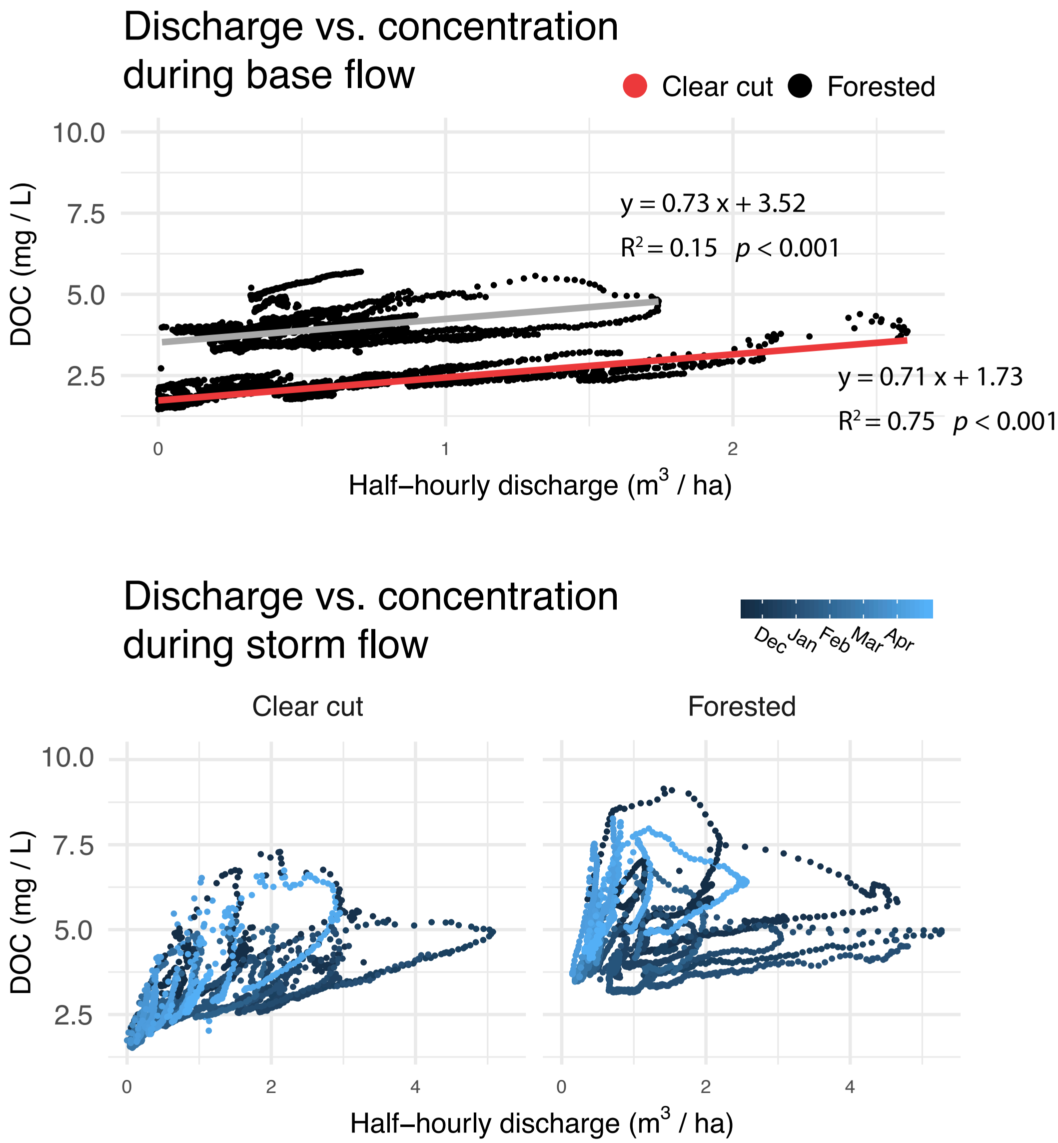

Figure 2.3. Relationship between discharge and DOC concentration during baseflow and during storm periods for both MKRF stream sites.

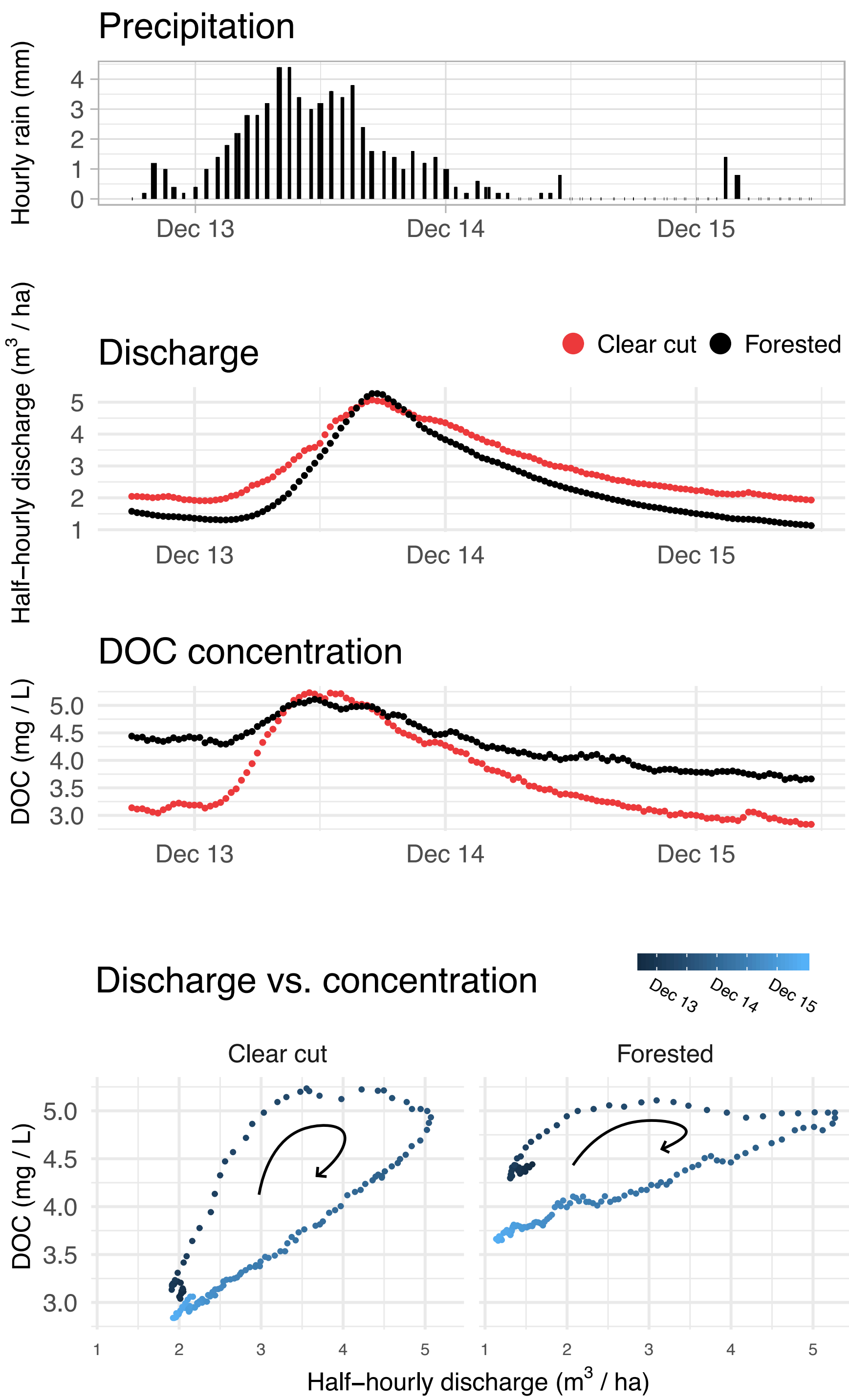

Figure 2.4. Precipitation, discharge, and DOC concentration at both monitoring sites during one representative storm event for both MKRF stream sites.

2.3.2 Paired storm responses

For each storm (n = 22), a suite of parameters was calculated for discharge and DOC response at each of the two sites. In terms of DOC concentration response parameters, we found significant differences in pre-storm DOC, peak DOC, difference and percent difference DOC, and rate to reach peak DOC (Figure 2.5, Table 2.1). Pre-storm (base flow) DOC concentration was significantly lower at the clear-cut site (2.26 ± 0.43 mg/L) than at the forested site (4.30 ± 0.83 mg/L, $p < 0.001$). Peak DOC concentration was significantly lower at the clear-cut site (4.69 ± 1.42 mg/L) than at the forested site (6.29 ± 1.45 mg/L, $p < 0.001$). Absolute difference in DOC concentration was significantly greater at the clear-cut site (2.42 ± 1.40 mg/L) than at the forested site (1.99 ± 1.16 mg/L, $p = 0.04$). Percent difference in DOC concentration was significantly greater at the clear-cut site (111 ± 69%) than at the forested site (48 ± 27%, $p < 0.001$). Time to reach peak DOC was not significantly different between the two sites. Rate to reach peak DOC concentration was significantly higher at the clear-cut site (0.16 ± 0.11 mg/L/h) than at the forested site (0.11 ± 0.09 mg/L/h, $p < 0.001$).

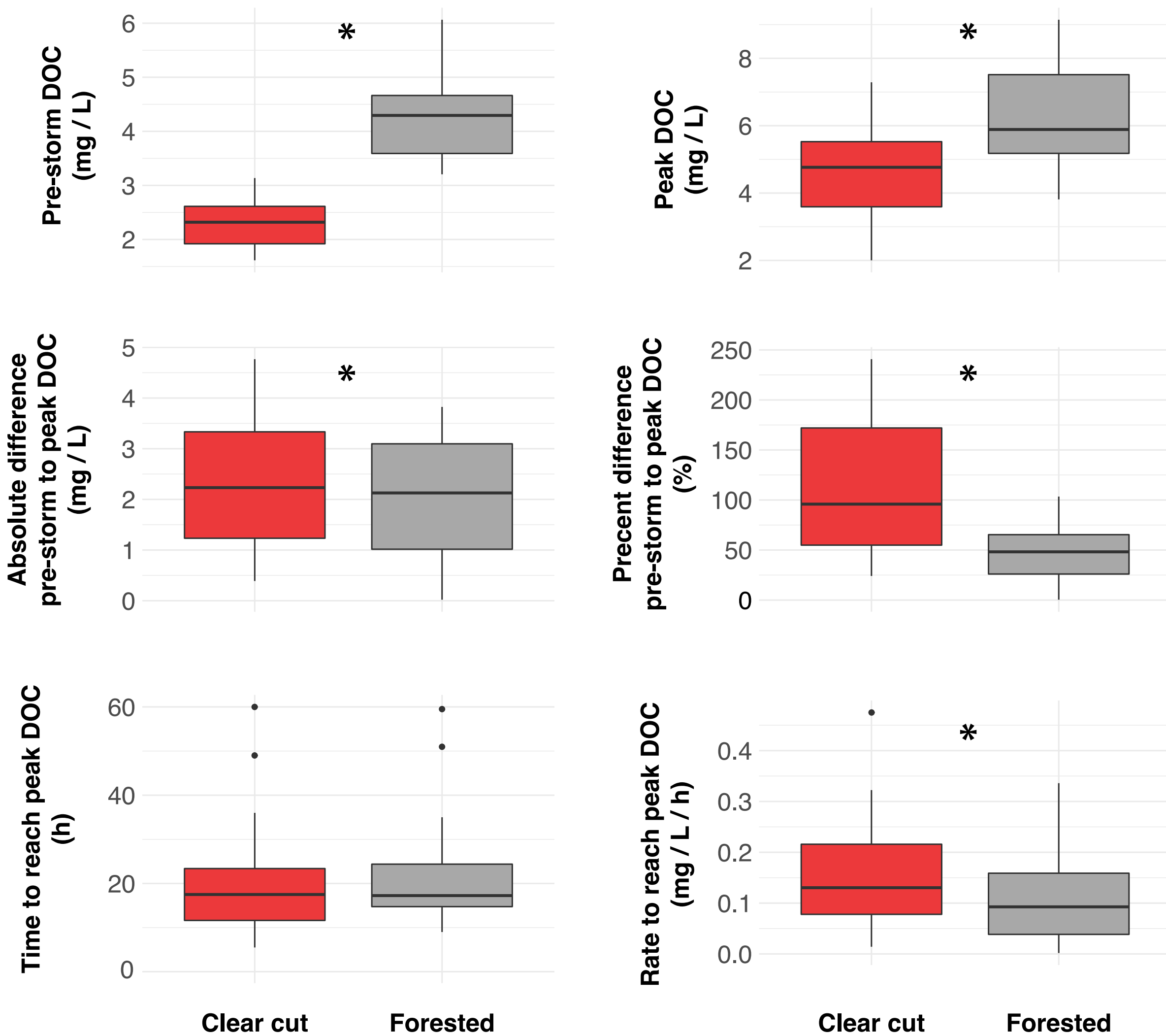

Figure 2.5. DOC concentration parameters in response to paired storms (n = 22). Asterisks indicate significant differences between responses to paired storms. Box and whisker plots show the median, quartiles, and range of data; points that exceed 1.5 times the interquartile range are shown as outliers. Statistical test results are reported in Table 2.1. Box and whisker plots show the median, quartiles, and range of data; points that exceed 1.5 times the interquartile range are shown as outliers.

Table 2.1 Statistical tests of differences between parameters for paired storms at each of the two study sites. Bold indicates *p* < 0.05. Boxplots are shown in Figures 2.4 and 2.5.

Storm response parameter	*p* value	Method
Pre-storm DOC	***	Wilcoxon signed rank test
Peak DOC	***	Paired t-test
Absolute difference DOC	*	Paired t-test
Percent difference DOC	***	Wilcoxon signed rank test
Time to reach peak DOC	0.09	Wilcoxon signed rank test with continuity correction
Rate to reach peak DOC	**	Wilcoxon signed rank test
Hysteresis index	0.20	Wilcoxon signed rank test
Flushing index	***	Wilcoxon signed rank test
Carbon yield per storm	***	Wilcoxon signed rank test
Specific carbon yield per storm	**	Wilcoxon signed rank test

*** $p < 0.001$ ** $p < 0.01$ * $p < 0.05$

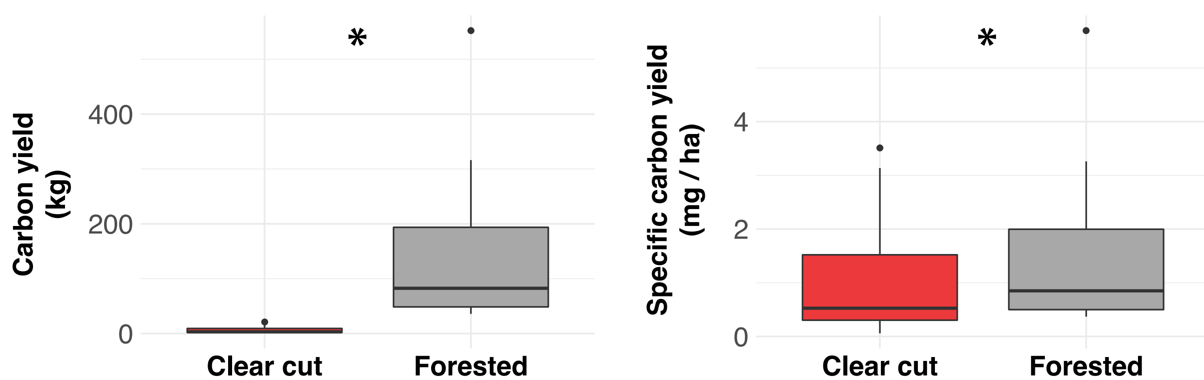

Figure 2.6. Area-normalized carbon yield was higher at the forested site for paired storms (n = 22). Box and whisker plots show median, quartiles, and range of data; points exceeding 1.5 times interquartile range are shown as outliers. Box and whisker plots show the median, quartiles, and range of data; points that exceed 1.5 times the interquartile range are shown as outliers.

Accounting for the difference in drainage area, specific carbon yield per storm was also significantly higher at the forested site (1.39 ± 1.33 kg/ha) than at the clear-cut site (1.00 ± 1.03 kg/ha, $p < 0.001$). Total carbon yield per storm was significantly higher for the forested site (134.5 ± 128.8 kg) than at the clear-cut site (6.06 ± 6.24 kg, $p < 0.001$; Table 2.1, Figure 2.6).

Flushing index (FLI), which indicates the amount by which DOC increases from storm onset to peak discharge normalized by DOC range for each storm, was significantly different between the two sites. FLI was higher at the clear-cut site (0.77 ± 0.21) than at the forested site (0.59 ± 0.29, $p < 0.001$, Table 2.1, Figure 2.7). This is consistent with the result for percent change in DOC, which measures the change in DOC from storm onset to peak DOC. Normalized index parameters are shown in Table 2.1 and Figure 2.7. Hysteresis index (HI) for each storm was not significantly different between the two sites (Table 2.1, Figure 2.7). At both sites, HI was greater than zero for all storms except for a handful of outliers (Clear cut: 0.26 ± 0.19, Forested: 0.30 ± 0.28, Figure 2.7), indicating generally clockwise hysteresis, meaning that DOC concentration peaked before discharge and the DOC source was near-stream.

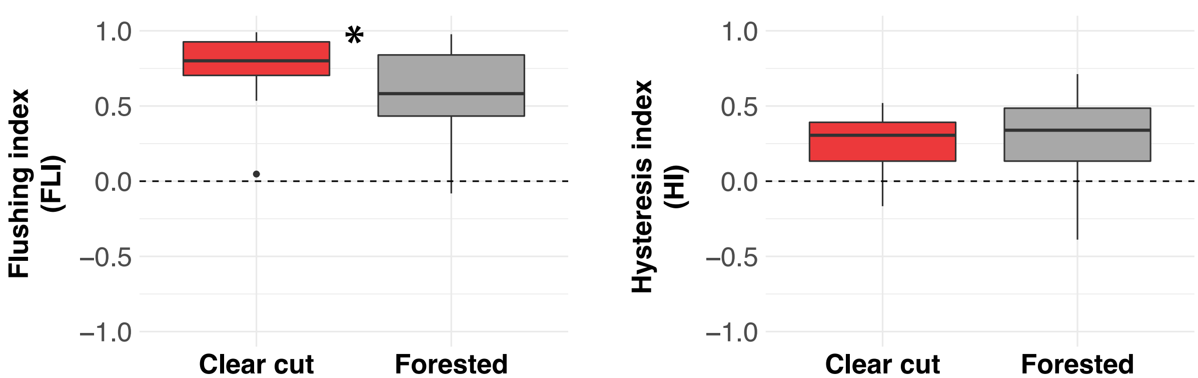

Figure 2.7. Normalized indices in response to paired storms (n = 22). Hysteresis index > 0 indicates clockwise hysteresis. Box and whisker plots show the median, quartiles, and range of data; points that exceed 1.5 times the interquartile range are shown as outliers. Statistical test results are reported in Table 2.1. Box and whisker plots show the median, quartiles, and range of data; points that exceed 1.5 times the interquartile range are shown as outliers.

2.3.3 Discharge dynamics and carbon yield

For the total study period duration, the clear-cut stream produced very similar total discharge per hectare as compared with the forested stream (Table 2.2). A greater proportion of discharge occurred during storms in the clear-cut site. For the clear cut, 75% of discharge occurred during storm periods, whereas for the forested site 71% of total discharge occurred during storms. The forested site produced higher carbon yield per hectare: 20 kg/ha produced by the forested stream and 15 kg/ha produced by the clear-cut stream (Table 2.2). As with discharge, a greater proportion of the carbon yield occurred during storms at the clear cut (82%) than at the forested site (75%). For both sites, carbon yield responded more strongly to storms than discharge did.

Table 2.2. Summary of total discharge and carbon yield during the study period. Total precipitation during the study period was 1,207 mm.

Parameter	Clear-cut site	Forested site
Total discharge (m^3/ha)	4,498	4,363
Discharge during storms (%)	75.4	70.5
Total specific carbon yield (kg/ha)	15.01	20.49
Specific carbon yield during storms (%)	81.5	74.8
Runoff ratio	0.37	0.36

2.3.4 ANCOVA analysis

Of ten ANCOVAs of storm response parameters with site as well as antecedent discharge, storm intensity, and date as predictors, five showed site as a significant variable (Table 2.3). Peak DOC, carbon yield, and flushing index were explained by site alone, without any significance to the covariate factors. Percent change in DOC was related to both site and antecedent discharge. Hysteresis index was predicted only by date. Rate of change in DOC was predicted by storm intensity and antecedent discharge. Specific carbon yield was predicted by antecedent discharge and date (Table 2.3).

Percent change in DOC concentration and rate to reach peak DOC concentration decreased with antecedent discharge, while specific carbon yield increased significantly with antecedent discharge (Figure 2.8). Rate to reach peak DOC increased with storm intensity. Hysteresis index and specific carbon yield decreased over the course of the study period (Figure 2.8).

Table 2.3. ANCOVA analysis for storm response parameters with site, storm intensity, and antecedent discharge (discharge at storm onset) as predictors. Parameters with at least one significant model are shown in Figure 2.7.

	***P* values for model predictors**			
Storm response parameter	**Site**	**Storm intensity**	**Antecedent discharge**	**Date**
Pre-storm DOC	***	0.93	*	0.57
Peak DOC	***	0.08	0.52	0.56
Absolute difference DOC	0.24	*	0.05	0.70
Percent difference DOC	***	0.14	*	0.74
Time to reach peak DOC	0.72	0.33	0.09	*
Rate to reach peak DOC	0.09	**	*	0.06
Hysteresis index	0.54	0.28	0.43	*
Flushing index	*	0.19	0.12	0.11
Carbon yield per storm	***	0.87	0.06	*
Specific carbon yield per storm	0.15	0.81	***	**

*** $p < 0.001$ ** $p < 0.01$ * $p < 0.05$

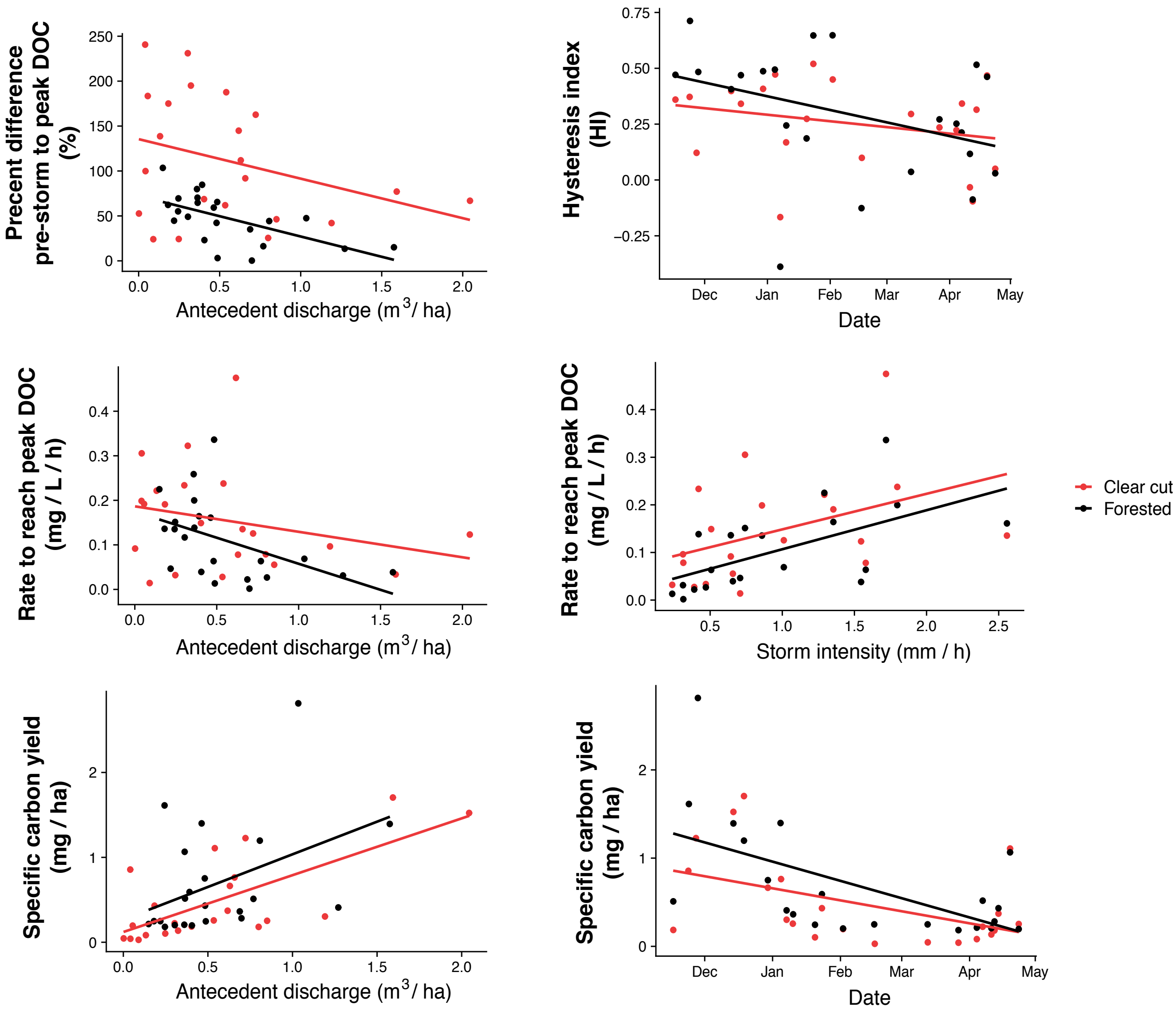

Figure 2.8. Linear trends for significant predictors of storm response parameters from ANCOVA analysis using storm intensity, antecedent discharge, and date as predictors. *P* values from ANCOVA analysis are shown in Table 2.3.

2.4 Discussion

2.4.1 Overall discharge and carbon yield

In this study, we observed significantly different DOC storm responses at two nearby headwater streams of contrasting forest harvest history. Overall, we observed slightly higher discharge per unit drainage area at the clear cut but substantially more discharge as storm flow. This is consistent with other studies, which have found post-harvest hydrology to exhibit increased discharge due to reduced interception and uptake by the vegetation (Carr and Loague, 2012; Mohr et al., 2013). Though, this is not always the case as condensation of fog on dense tree stands can contribute to discharge in the Pacific Northwest (R Dan Moore and Wondzell, 2005). For both sites, the majority of discharge occurred during storms. Discharge during storms was 7% higher at the clear-cut site (75.4%) than at the forested site (70.5%), indicating that the system was more responsive to rain events, as would be expected post-harvest. Clear cutting generally reduces soil infiltration and increases the speed of flow paths to the stream, further contributing to a ‘flashier' storm response (Birkinshaw et al., 2011; Jones and Grant, 1996).

Throughout the season in baseflow conditions, DOC concentration was lower at the clear-cut site than at the harvested site, supporting the hypothesis that baseflow DOC decreases after clear cutting treatment due to the reduction of organic inputs from leaf litter, increased discharge, or both. This was a relatively surprising result given that many other studies have found DOC to increase after forest harvest (Laudon et al., 2009; O’Driscoll, et al., 2006; Schelker et al., 2012), though some have found DOC to decrease (Judy L. Meyer and Tate, 1983b). Our clear-cut site was harvested 2 years prior to this study, and it is possible the effect of harvest differed immediately following harvest compared to our study period.

We observed lower overall specific carbon export from the clear-cut site. This is consistent with another paired watershed study conducted two years after clear cutting that found DOC concentration and flux to be lower at the clear-cut site (Meyer and Tate, 1983). We observed specific discharge to be higher at the clear-cut site, thus DOC concentration may have been lowered in part by dilution. However, because the overall specific carbon export was lower, we know dilution alone was not responsible for the lower DOC concentration. Other studies which have found increased DOC concentration in the first few years after clear-cut harvesting also found increased DOC flux (Laudon et al., 2009; Schelker et al., 2012). However, in other cases DOC concentration has been found to increase while export remained constant (Piirainen et al., 2002). In our case, DOC concentration and flux were found to both be lower, supporting the hypothesis that reduced carbon inputs may be an important mechanism by which clear cutting affects DOC for production forests in this region.

2.4.2 Storm response dynamics

Storm responses were significantly different between the two sites, consistent with other studies that have shown significant differences in storm responses for streams of varying land use (Koenig et al., 2017; Vaughan et al., 2017). In our study, although baseflow DOC was lower at the clear-cut site, the response to storms was larger. In the clear-cut site, we found larger changes in DOC concentration and higher rates of concentration change, which could be due to increased number and speed of flow paths after clear cutting. Just as the hydrology was flashier in the clear cut than the forested site, the DOC concentration response was also flashier with larger and faster changes at the clear-cut site. This is in contrast with a previous study from a boreal forest site where higher DOC and smaller changes in DOC during storms were measured in the first season after clear cutting (Laudon et al., 2009), underscoring the potential importance of regional differences of DOC responses to forest management. The magnitude of changes in DOC during storms is important in the context of water treatment, because inputs for chemically-assisted DOC filtration need to be constantly adjusted based on concentration, and rapid changes can be more difficult to manage because the effectiveness of the particular chemical inputs needs to be monitored and can be difficult to predict if the quality of DOC is also changing (Matilainen et al., 2010).

The hysteresis index (HI), the degree to which DOC concentration differs on the rising limb compared with the same level of flow on the falling limb, was not significantly different between the two sites. The DOC sources are similarly supply-limited and near-stream. Positive HI indicated proximal, quickly mobilized sources at both sites. Studies of HI comparing watersheds of varying land use type have also found no difference in mean HI between sites (Vaughan et al., 2019; Vaughan et al., 2017). In describing the discharge-concentration plot of a storm event (as in Figures 2.3 and 2.4), HI captures the directionality and width of the hysteresis loop, while flushing index (FLI) describes the slope of the rising limb portion. FLI was positive for both of our sites, and significantly greater at the clear-cut site. Significantly more positive FLI at the clear-cut site indicated a greater change in DOC during the rising limb of the hydrograph. Other studies using this definition of flushing index have also found predominantly positive values for forested catchments (Butturini et al., 2008; Vaughan et al., 2019).

Higher antecedent discharge dampened the effects of storms on DOC concentration. The change in DOC happened more slowly and resulted in a smaller percent change when discharge was high prior to storms. Alternatively, low antecedent discharge and re-wetting of relatively dry soil resulted in more DOC being mobilized more quickly. Some studies have found antecedent discharge to improve models explaining peak DOC during storm events (Gellis, 2013), while others have found discharge level to be insignificant (Wymore et al., 2019). We found peak DOC to be predicted by site only, but we found significance of antecedent discharge for other storm response parameters: percent difference DOC concentration, rate to reach peak concentration, and specific carbon yield. Interestingly, antecedent discharge was not significantly related to HI as was found by Vaughan et al. (2019). The significance of storm response parameters other than peak DOC underscores the importance of examining response parameters in addition to peak concentration, especially parameters such as rate of change and carbon yield, which are of interest to management of drinking water treatment processes.

Higher storm intensities resulted in larger changes in DOC from pre-storm to peak concentration. Other studies have found peak DOC to be significantly correlated with storm intensity (Dawson et al., 2008; Dhillon and Inamdar, 2014; Jung et al., 2012). We found peak DOC to be significantly predicted only by stream site, but change in DOC and rate of change in DOC were significantly predicted by storm intensity. More intense storms create faster flows that have more capacity to mobilize DOC into the stream and resulted in larger changes and faster rates of change.

2.4.3 Potential site covariates

While the streams in this observational study are relatively similar in their location, geology, climate, vegetative species, and stream morphology, they are different in ways that could affect some of our observations. The clear-cut site was slightly higher (283 m vs. 193 m), steeper (16 degrees vs. 8 degrees), and drains a smaller area (6 ha vs. 97 ha). There is a small bog lake within the catchment area of the forested site, which likely contributes to elevated DOC. Differences in area were accounted for by normalizing discharge and carbon yields by unit area. However, we did not make adjustments for the difference in elevation and slope. Smaller, steeper catchments generally have faster flow paths to the stream which is related to increased storm response (Hewlett and Hibbert, 1967). Rainfall typically increases with elevation (Osborn, 1984). An elevation difference of 90 m likely does not make a substantial difference, but it is possible.

2.4.4 Conclusions and future directions

Future climate predictions point toward higher storm intensities around the world (Bengtsson et al., 2009; Prein et al., 2017). It is important to understand not only impacts now, but also how these impacts may change in the near future. In the Pacific Maritime region, models predict drier summers and increased storm intensity with a shift to a more rain-dominated hydrology (Salathé et al., 2014; Trenberth, 1999).

These changes are likely to increase DOC concentrations. Percent change in DOC and rate of change significantly were predicted by antecedent discharge and storm intensity in our study. We saw larger and faster changes in DOC when pre-storm flow was lower and when storm intensity was higher. Higher DOC concentrations are costly for water treatment processes because more chemical inputs are required. High rates of change can be a challenge, because the amounts and ratios of treatment chemicals need to be constantly adjusted and can be hard to predict if the type of DOC is also changing over time.

Under predictions for higher storm intensity, flux totals are likely to increase as well. We found that nearly 10% more overall carbon flux occurred during storms at the clear-cut site than at the forested site. Increased carbon yield would have substantial consequences for ecosystems and for human uses. For water treatment, the total volume of organic carbon that is filtered out of source water needs to be transported off site, which can require expensive infrastructure upgrades. On the other hand, elevated soil temperatures could increase microbial processing of DOC reducing carbon flux to streams. Overall, future climate predictions are likely to bring changes to DOC in forested, headwater streams. It is crucial to understand the impacts of both land use change and storm response on DOC concentration and consider the implications for human and ecological systems.

Chapter 3: DOC concentration and characterization for synoptic sampling in base flow and storm flow for catchments differing in forest management history

3.1 Introduction

Dissolved organic carbon (DOC) plays a key role in aquatic ecosystem functioning as well as in human infrastructure. Ecologically, DOC provides a food source for microorganisms. In the human context, DOC is often a crux of drinking water treatment as it is costly and difficult to remove. While it is not inherently harmful, DOC is removed because it interacts with disinfectants to produce a diversity of disinfection byproducts (DBPs). There are regulatory limits for many DBPs, some of which are known carcinogens (Villanueva et al., 2004; Li and Mitch, 2018; Philip C. Singer, 1994). Additionally, DOC is detrimental as it encourages growth of microbes in drinking water distribution systems, which can create health risks as well as colour and taste issues (Smith et al., 2002). DOC concentration is often monitored in water treatment plants, but characterization of the type of DOC present in water is more difficult to measure and is less frequently considered. DOC composition is important because different functional types of DOC can have different implications for ecosystems and water treatment.

DOC is comprised of potentially thousands of different, often complex, molecules, making it difficult to directly measure molecular composition. In general, DOC in stream water is comprised mainly of two broad types of components. The first is DOC derived from terrestrial soils. This allochthonous DOC varies in humification, generally becoming more humic and recalcitrant with time (Ohno 2002). Allochthonous DOC is relatively high molecular weight, hydrophobic, and humic-like (Croué, 2004). The other predominant type of DOC is freshly produced in-stream by microbial organisms or root exudation (Zsolnay et al., 1999). Autochthonous DOC tends to be more biologically available (labile), lower molecular weight, and hydrophilic.

Because these two categories of DOC (humic-like and microbial-like) have different chemical structures, they play different roles in the ecosystem and in drinking water treatment. More labile, "fresh" DOC is most beneficial as an ecosystem energy source (Hessen et al., 2004), but it carries a higher risk of enabling microbial growth in pipes (Frias et al., 2001). Humic DOC is resistant to microbial degradation and typically has a longer residence time in rivers than more bioavailable forms of DOC (Hansell, 2013). Though humic DOC generally accounts for the majority of DOC in rivers, it is less bioavailable than microbially produced DOC (Andersson et al., 2013; Søndergaard and Middelboe, 1995). For DBP formation, more humic DOC generally poses more of a problem than fresh or algal DOC (Singer, 1999). For example, humic-like DOC can lead to increased trihalomethanes (THMs) following disinfection compared with fresh DOC, which produces nitrogen-containing DBPs that are not yet regulated but may also be carcinogenic (Li and Mitch, 2018). If DOC composition is shifting over time with changing climactic or land use variables, drinking water utilities will need to plan for potential implications for the safety of their water supply.

Exact characterization of DOC molecular structures is technically challenging (Kirilenko and Sedjo, 2007). Alternatively, bulk analysis of spectral properties of DOC can be used to estimate DOC character (Coble, 1996) and techniques are rapidly evolving (Fellman et al., 2010; Hansen et al., 2016). Optical indices and parallel factor analysis (PARAFAC) are two common ways to assess DOC character based on spectral properties. This study combines both methods and integrates their results to give a comprehensive view of DOC character.

DOC composition has been shown to vary spatiotemporally and respond to anthropogenic and climate drivers in some, but not all cases (Filella and Rodríguez-Murillo, 2014; Parr et al., 2019; Stanley et al., 2012). DOC concentration and composition are determined by many overlapping factors that can be difficult to unravel. Some studies have found higher DOC in summer and lower in winter, with differences attributed to warmer summer temperatures causing faster decomposition and microbial activity (Dawson et al., 2008). Others have found no seasonality (van den Berg et al., 2012). The mechanisms for these trends depend on ecological, biogeochemical, and hydrological factors that can be difficult to control for and vary across regions, necessitating additional case studies.

In this study, we looked at the variation of DOC concentration and characterization as it relates to contrasting forest management history (streams in clear cuts vs. forested streams) as well as climactic, topographical, and vegetative covariates. We hypothesized that DOC concentration would be higher in recently clear-cut catchments than in forested catchments, higher during stormflow than during baseflow, and higher during the first fall rains at the start of our study period than later in winter or spring. We included as many sampling sites as possible with a range of landscape covariates in order to determine whether the differences between clear-cut and forested sites were significant in the context of local variation. We expected forest harvest to increase protein-like DOC derived from microbial processes by increasing surface temperatures and light levels, which encourages microbial activity. We expected DOC in harvested catchments to be characterized by humic-like components, coming from terrestrial DOC and litter leachate, to either increase due to soil erosion or decrease due to the reduction in litter inputs and root exudation.

Our first objective was to determine whether there were differences in DOC among streams for three main categorical variables covering land use (clear-cut vs. forested areas), flow conditions (stormflow vs. baseflow), or seasonality (month). The second objective was to investigate other landscape covariates like topography, hydrology, and vegetation type to determine what role they may play in mechanisms of DOC origin and fate.

3.2 Method

3.2.1 Study sites

This study was conducted in Malcolm Knapp Research Forest (MKRF), located approximately 50 km east of Vancouver, British Columbia, Canada (49°17'N, 122°36'W) in the southern Coast Mountain range (Figure 3.1). The hydrology of the area is rain dominated with an average precipitation of 2200 mm per year, 70% of which occurs from November to April (Government of Canada, 2019). Temperatures are mild with a monthly mean temperature of 18° C in August and 3° C in December. The soil is of glacial origin, generally shallow, and overlays igneous bedrock (Feller and Kimmins, 1979). MKRF is situated in Coastal Western Hemlock dry maritime (CWHdm) biogeoclimatic zone (Meidinger and Pojar, 1991). The vegetation consists of predominantly large conifers including western hemlock, western red cedar, and Douglas-fir. Site photos are provided in Appendix A.

We selected 24 sites for sampling that represent a range of headwater streams in close proximity to one another with all study sites situated within a 5 km radius. There has been active forest harvest activity in MKRF before it became a research forest in 1949 and continually since, resulting in mixed age classes ranging from 140-year-old stands to recent clear cuts. For this study, we selected 6 streams in 2-3 year old clear cuts within an elevation limit of 350 m, as higher areas risk access issues due to snow; sites used in this study ranged from 49 to 348 m elevation. In addition to the clear cut sites, we selected 18 streams in relatively mature forest, defined as reaches that had not been touched by forest management in at least 20 years. The forested sites represent a range of stream sizes at a range of slopes and elevations, with various stream morphology and vegetation. Distributions of site descriptors are shown in Figure 1. The range of sites chosen allowed us to run multivariate models and assess the effects of covariates as well as forest management history.

For each site, six covariate parameters were calculated: slope, elevation, drainage area, specific discharge, stream morphology, and vegetation (Appendix B.1). Slope, elevation, and drainage area were calculated based on a 1 m digital elevation model provided by MKRF. Slope and elevation were calculated R (R Core Team, 2018). Sampling sites had an average elevation of 198 ± 85 m and average slope of 15.7 ± 6.3 degrees. Drainage area contributing to the sampling sites was calculated in QGIS (QGIS Development Team, 2016) using the GRASS package (GRASS Development Team, 2016) and averaged 163 ± 387 ha. Stream morphology was classified according to Montgomery and Buffington (1997). All streams in this study were categorized as step pool, pool riffle, plane bed, or cascade (Appendix B.1).

We conducted discharge measurements during baseflow, defined as discharge sustained between rain events with at least 3 days having passed since the last event, (n = 22; collected February 4-5, 2019) for the purpose of catchment characterization. Depending on which were appropriate, we used at least one of three methods: volumetric analysis method, velocity-area method, and salt injections. For very small streams that had a culvert going under the road (n = 9), we were able to calculate discharge by volumetric analysis as the time required to fill a 5 L bucket. For streams that were turbulent and well-mixed (n = 12) we used the salt slug injection method (Moore, 2005) and a calibration constant of 0.486 mg NaCl mg•cm/µS/L (Richardson et al., 2017) following methods used by McDowell and Johnson (2018). For streams that were deep enough to accommodate a velocity probe and wide enough for at least five cross sectional measurements (n = 5), we computed discharge using the velocity-area method and a velocity meter (Gore and Banning, 2017). For streams where multiple methods were used (n = 4), the average value was used; the difference between multiple measurements was 20 ± 9%. Two of the 24 sites were too deep to measure using our methods. Average discharge was 22.0 ± 37.8 L/s. Based on the one-time discharge measurements, we calculated specific discharge as discharge per unit drainage area. Average specific discharge for the sites was 0.34 ± 0.18 L/s/ha.

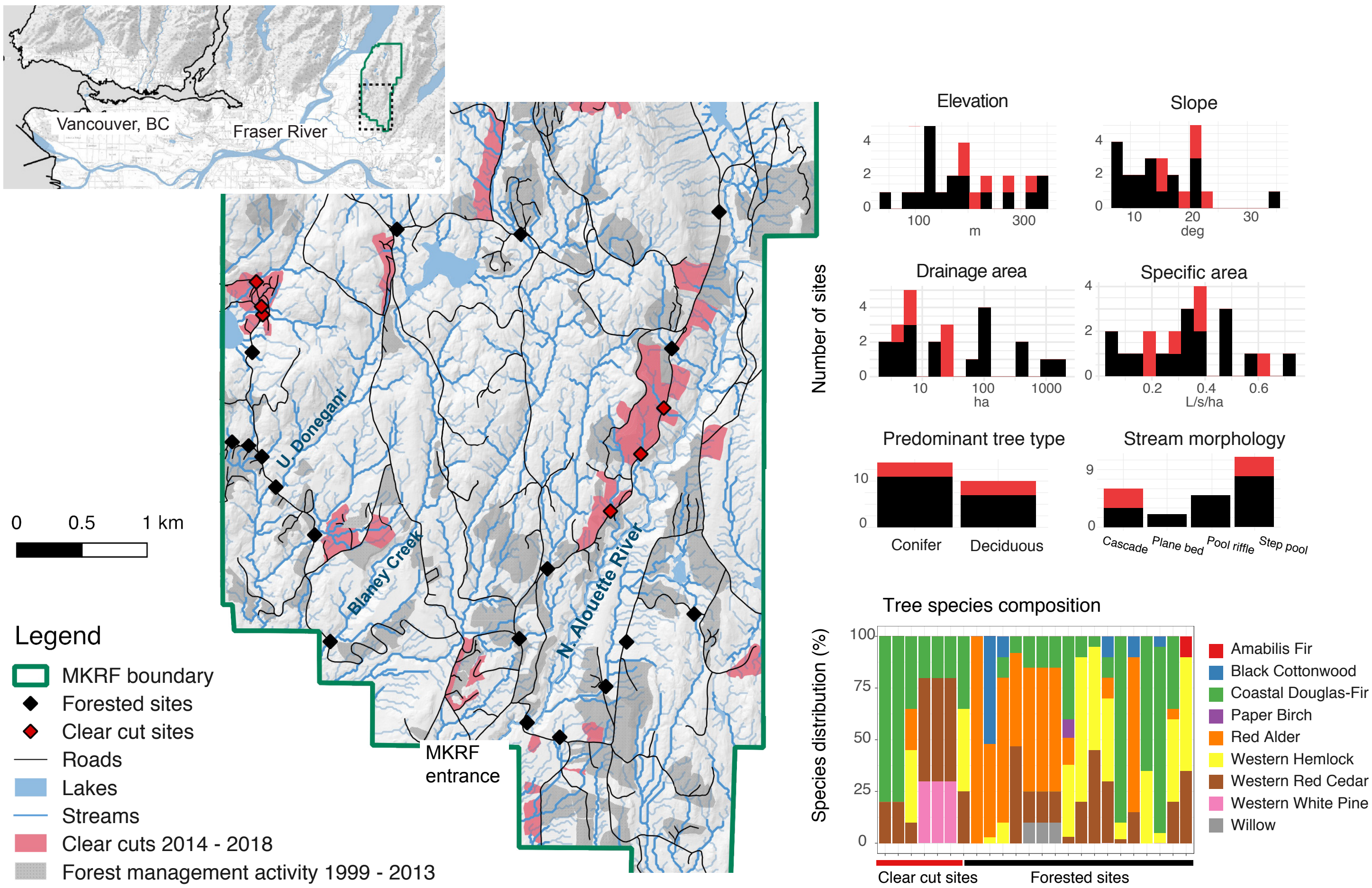

Figure 3.1 Map showing sites where grab samples were taken from headwater streams in Malcolm Knapp Research Forest (MKRF) located approximately 50 km east of Vancouver, British Columbia, Canada. Study sites were located in recent clear cuts (n = 6) and relatively mature forest (n = 18). Sites were located within a 5 km radius and represent a range of clear-cut and forested headwater streams. Distributions of covariates are shown on the right with clear-cut sites represented in red and forested sites in black.

We extracted tree species composition data from the MKRF GIS database (MKRF database, 2019), and reduced this information to predominant tree type: conifer or deciduous, based on which tree type accounted for more than 50% of the vegetative cover at the site (Figure 3.1). Five coniferous species were present: Amabilis Fir, Coastal Douglas-Fir, Western Hemlock, Western Red Cedar, and Western White Pine and four deciduous species: Black Cottonwood, Paper Birch, Red Alder, and Willow.

3.2.2 Stream sampling

Grab samples of water were collected at baseflow and stormflow conditions during three distinct hydrological periods (early wet season, mid-wet season, late wet season), resulting in six collections for each of the 24 sites. Specifically, sampling campaigns were planned based on projected storm events with samples collected first at baseflow and then again within 1 week during stormflow conditions. First, baseflow condition samples were taken on a day when there had been little to no rain for the previous 3 days, then stormflow samples were taken from the same sites (n = 24) during a storm that was forecast to have at least 20 mm of rain in 24 hours. Samples were collected during the rainy season from November 2018 to March 2019. All 24 sites were sampled in one day within approximately 5 hours. Samples were stored in 250 mL opaque containers on ice until they were returned to a refrigerator within a few hours of completing the round of sample collection.

3.2.3 Sample analysis

All chemical analyses were performed within three days of sample collection. First, samples were filtered with 0.7 μm glass fiber filters and separated into two vials. One vial was used for DOC concentration measurements with a TOC-VCSN total organic carbon analyzer (Shimadzu Inc., Kyoto, Japan). The other was used for absorbance and fluorescence characterization analysis using an AquaLog fluorometer (HORIBA, Kyoto, Japan). The remaining sample (~100 mL) was analyzed using a scanning spectrophotometer (Spectrolyzer, s::can, Vienna, Austria) and related software to derive DOC concentrations analogous to those determined using the TOC analyzer.

Samples run in the TOC analyzer were acidified with 1000 µL of 2 M HCl to lower pH below 2 prior to analysis. Samples were placed in an autosampler from which the machine drew sample and sparged it to remove dissolved inorganic carbon, leaving only non-purgeable organic carbon (NPOC), referred to hereafter as DOC. Sparged samples were then combusted and the resulting CO_2 was measured to calculate the concentration of DOC present. The Shimadzu instrument was calibrated using a five-point calibration with potassium hydrogen phthalate (KHP) standards.

For fluorescence measurements, samples were not acidified and were brought up to room temperature before analysis. Measurements were taken for excitation and emission wavelengths from 240 to 600 nm with a 3.3 nm increment and 2.0 s integration time, using a 10 mm quartz cuvette. Excitation-emission matrices (EEMs) and absorbance spectra were recorded for each sample, which were used to calculate indices and components related to DOC functional characteristics.

The Spectrolyzer instrument was used for redundancy with the Shimadzu TOC analyzer. The TOC analyzer is more accurate but more prone to mechanical maintenance needs. We established a linear empirical relationship ($R^2 = 0.82$) between the Spectrolyzer and Shimadzu instruments. Samples from one campaign set were analyzed only using the Spectrolyzer as the Shimadzu was undergoing maintenance.

3.2.4 DOC characterization by optical properties

3.2.4.1 Pre-processing

Prior to calculating indices and performing PARAFAC analysis, we prepared and corrected the EEMs in R statistical software (R Core Team, 2018) using the eemR package (Massicotte, 2017). We corrected for inner-filter effects, performed blank subtraction, removed negative fluorescence intensities, removed scattering, and normalized to Raman units (Murphy et al., 2013; Stedmon and Bro, 2008).

3.2.4.2 Optical indices

Optical indices have been established in the literature as useful proxies to describe the functional composition of DOC (Hansen et al., 2016), and they can be used as a standardized metric that is comparable across studies. We calculated three fluorescence indices: humification index (HIX), biological index (BIX), and fluorescence index (FI), on corrected EEMs using the eemR package (Massicotte, 2017). As shown in Table 3.1, HIX is defined as emission intensity from 435 to 480 nm divided by emission intensity from 300 to 345 nm, and signifies the degree of humification of the DOC pool. Higher HIX values represent more humification (Ohno, 2002). BIX is defined as the ratio of emission at 380 nm and 430 nm at a fixed excitation of 310 nm. BIX characterizes biological production of DOC and increases with more fresh-like DOC (Huguet et al., 2009). FI is defined as the ratio of emission at 450 nm and 500 nm at a fixed excitation of 370 nm. FI is indicative of the source of DOM. Higher values represent more microbial DOC and lower values represent more terrestrial DOC (McKnight et al., 2001).

Table 3.1. Definition of optical indices used in this study.

DOC character index	Reference	Definition	Purpose
Humification index (HIX)	Ohno (2002)	Emission intensity 435-480 divided by emission intensity 300-345	Used to characterize the degree of humification of DOM. Ranges from 0 to 1 increasing with higher humic content
Biological index (BIX)	Huguet et al. (2009)	Ratio of emission at 380 nm and 430 nm at fixed excitation 310 nm	Used to characterize biological production of DOM. Increases with greater autotrophically produced DOM
Fluorescence index (FI)	McKnight et al. (2001)	Ratio of emission at 450 nm and 500 nm at fixed excitation 370 nm	Indicates source and aromaticity of DOM. Higher values indicate more microbial and lower values more terrestrial. Values < 1.4 are generally terrestrial.
Slope ratio (SR)	Helms et al. (2008)	Ratio between absorbance slopes from 275-295 nm and 350-400 nm	Proxy for molecular weight. Higher values indicate lower molecular weight compounds.

One absorbance index, slope ratio (SR), was computed from absorbance spectra determined on the Aqualog (R Core Team, 2018). SR is defined as the ratio between absorbance from 275-295 nm where lower molecular weight DOC absorbs, and absorbance from 350-400 nm where higher molecular weight DOC absorbs. SR is thus used as a proxy for molecular weight, where higher SR values signify lower molecular weight DOC composition (Helms et al., 2008).

3.2.4.3 Parallel factor analysis

To extract chemical components from EEM data, we used a parallel factor analysis (PARAFAC) in MATLAB (MathWorks Inc., 2016) using tools in the N-way and drEEM toolboxes as in Murphy et al. (2013). PARAFAC is a multi-way method to extract components from a dataset. Here, we used three-way analysis of EEM arrays to decompose samples into chemical components. For each sample, scores were assigned that represent the relative abundance of each modeled component in that sample.

In addition to the EEM pre-processing done in R, we smoothed the dataset and removed outliers using built in functions of the drEEM toolbox following Murphy et al. Appendix A (2013). We then ran split-half PARAFAC models with varying numbers of components until we found the largest number of components that could be validated.

PARAFAC components are directly attributable to chemical signatures. Spectral loadings of resulting components can be compared to components reported in published literature, so the character of particular components can be inferred from their similarity to other described datasets. We used the OpenFluor database (Murphy et al., 2014) to facilitate matches to the literature and compare our components to those with the closest similarity.

3.2.4.4 Principal component analysis

To describe how the parameters in our suite of characterization metrics (optical indices and PARAFAC components) are related to one another, we used a principal components analysis (PCA) using the stats package in R (R Core Team, 2018). PCA uses linear correlation coefficients to reduce the correlated variables to a set of principal components. The number of significant principal components was determined with a Kaiser-Guttman rule (Kaiser, 1960).

3.2.5 Statistical methods

3.2.5.1 Inferential statistics

To test whether the distributions of water quality parameter measurements were significantly different for categorical groupings, non-parametric inferential tests were used. For variables with one degree of freedom (land use status and streamflow status as baseflow or storm flow), we used Wilcoxon rank sum tests. For variables with more than one degree of freedom (seasonality) we used Kruskal-Wallis rank sum tests.

3.2.5.2 Generalized linear mixed models

To determine significant predictors of DOC concentration and character, we ran generalized linear mixed models (GLMM) using the lme4 package (Bates et al., 2014). For DOC concentration and each DOC characterization output parameter, we considered three fixed effects: land use status, flow condition, and seasonality, and six random effects: slope, elevation, drainage area, specific discharge, vegetation type, and stream morphology were included in the GLMM. T-tests using Satterthwaites's method were used to determine significance of the fixed effects (Kuznetsova et al., 2017). To assess the significance of including random effects in the models, likelihood ratio tests (LRT) were used to compare GLMM models with GLM models that included fixed effects only. Single term deletion LRTs were used to assess significance of specific random effects in the models (Scheipl et al. 2008). Slightly larger than usual *p* values may be considered significant for single term deletion models, as LRT is known to give conservative results with empirical *p* values about twice as large as for simulated data (Pinheiro and Bates, 2000).

3.2.5.3 Categorization and regression trees

Regression tree models provide a powerful and flexible approach to multivariate analysis. Categorization and regression trees (CART), which can include categorical and continuous variables as in this study, are optimized decision trees built by recursively partitioning a dataset. CART is advantageous because unlike traditional methods it inherently accounts for interactions and is non-parametric. CART can handle any number of non-normal and skewed variables without any transformation or further categorization, and accounts for all interactions between all variables (Breiman, 1984). Comparisons between multiple regressions and CART have shown CART to perform better than multiple regressions for small, noisy datasets and when categorical variables are present (Razi and Athappilly, 2005).

Due to high variance in regression tree algorithms, ensemble methods are often used where many trees are essentially averaged into one larger model. We used bootstrap aggregation (i.e., "bagging") to combine the predictions of many models that were all trained on a random 50% subset of the data. Our bagged model contained an ensemble of 500 unpruned (i.e. all predictors included) regression trees. We computed the bagged CART model using Breiman's random forest algorithm (Breiman, 2001) using the randomForest package in R (Liaw and Wiener, 2002).

To assess the relative importance of various predictors in the model, we calculated variable importance as a percent contribution to sum of squared errors (SSE). This is done by algorithms in the randomForest package by removing the predictors one at a time and measuring the increase in prediction error (Breiman, 2001).

3.3 Results

3.3.1 Sampling conditions

Base flow samples were collected on November 20, January 15, and March 10. Storm flow samples were collected November 27, January 18 and March 12. Samples were taken on all six occasions for 22 of 24 sites. One site was inaccessible in March due to a road closure, and one site was not sampled in November base flow. This resulted in a total of 141 samples used in this study. Storm intensity through the study period and on sampling days is shown in Figure 3.2. In our statistical models, flow condition is a binary variable indicated as either base flow or storm flow. Air temperature through the study period is also shown in Figure 3.2.

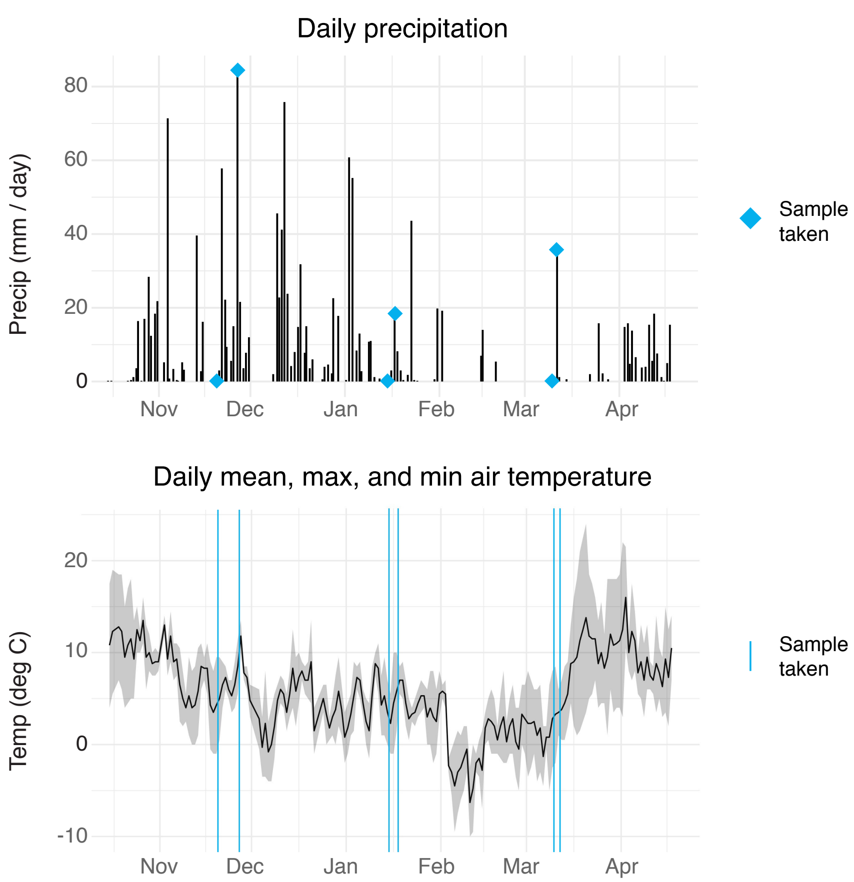

Figure 3.2 Precipitation and air temperature throughout the study period

3.3.2 DOC concentration

DOC concentration overall was relatively low for these streams ranging from 1.3 to 5.7 mg/L with a mean of 2.6 mg/L and standard deviation of 0.8 m/L. Mean DOC concentration was not significantly different between clear-cut and forested sites (Clear cut: 2.7 ± 0.9 mg/L, Forested: 2.4 ± 0.7 mg/L; p = 0.17; Figure 3.3; Table 3.2). During baseflow, mean DOC concentration was 2.4 ± 0.6 mg/L and during stormflow it was significantly higher at 2.9 ± 0.9 mg/L (p < 0.001; Figure 3.3; Table 3.2). Average DOC in November was 3.0 ± 0.8 mg/L, in February was 2.7 ± 0.9 mg/L, and in March was 2.2 ± 0.6 mg/L. DOC concentration declined significantly by month (p < 0.001; Figure 3.3; Table 3.2). All sampling results are reported in Appendix B.2.

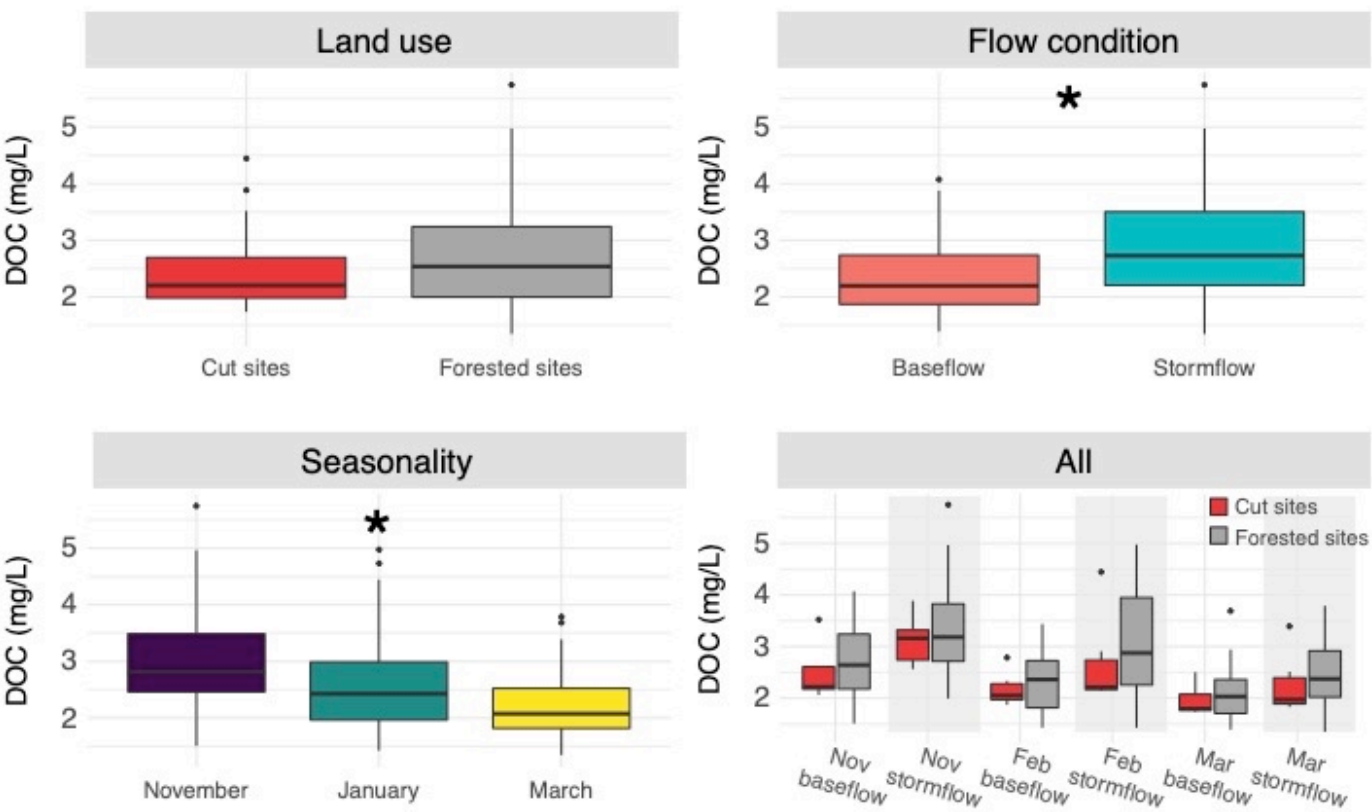

Figure 3.3 DOC concentration for all samples (n = 141). Asterisks in the top and left panels indicate significant difference between groups. See Table 3 for statistical test results. Box and whisker plots show the median, quartiles, and range of data; points that exceed 1.5 times the interquartile range are shown as outliers.

Table 3.2. Results of statistical tests comparing samples by land use, flow condition, and seasonality. DOC parameters include concentration, spectral indices (HIX, BIX, SR, FI), and PARAFAC components (C1-C4). Tests of land use and flow condition were carried out with Wilcoxon rank sum tests, and tests of seasonality were carried out using Kruskal-Wallis rank sum tests.

DOC parameter	Land use	Flow condition	Seasonality
	p value	*p* value	*p* value
DOC (mg/L)	0.17	***	***
HIX	0.87	***	***
BIX	*	**	*
SR	0.46	0.30	*
FI	*	**	0.08
C1	0.77	**	***
C2	0.44	***	***
C3	0.67	0.54	***
C4	0.50	**	***

*** $p < 0.001$ ** $p < 0.01$ * $p < 0.05$

From the GLMM model, we found that flow condition and seasonality were statistically significant predictors of DOC concentration, but land use status was not (Table 3.3). DOC increased with stormflow and decreased over the course of the study period. The GLMM model, which included random effects, was significantly higher quality than a model of DOC concentration including the fixed effects only (Fixed effects only: AIC = 30, BIC = 48; GLMM: AIC = -123, BIC = -89; $p < 0.001$; Table 3.4). However, while the random effects were significant in aggregate, none were significant alone based on single term deletion LRT (Appendix C). Drainage area returned a *p*-value of 0.19, and was the only term to give a *p*-value less than 1.

In a split-half bagged CART model, we found drainage area to have the highest contribution for the model, contributing to 34% of SSE (Figure 3.4). The next most important predictors of DOC concentration were season (20%), flow condition (13%), and slope (12%). The remaining predictors each accounted for less than 10% of model SSE.

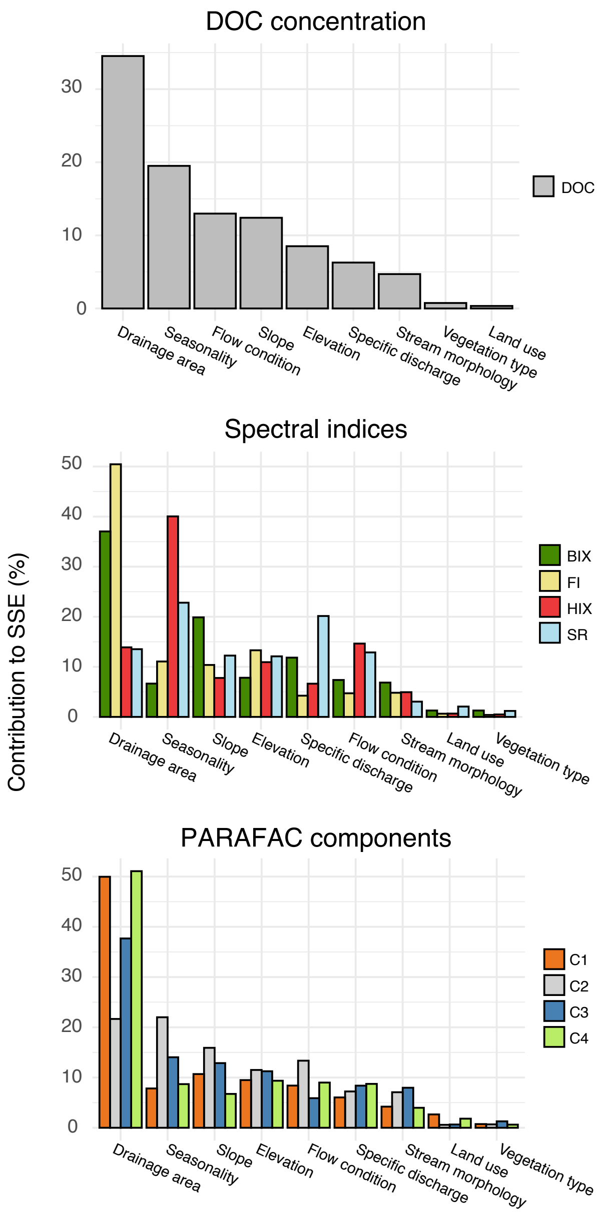

Figure 3.4 Relative contribution of predictors to sum of squared errors (SSE) in bootstrap aggregated split-half CART models of DOC concentration and each characterization parameter for 141 samples taken from streams in Malcolm Knapp Research Forest.

3.3.3 DOC characterization

3.3.3.1 Optical indices

BIX and FI were slightly but significantly higher for samples taken from streams in clear cuts than from forested streams, indicating DOC characterized by more fresh, autotrophically produced, and microbially derived DOC in cut vs. forested areas. BIX was 0.59 ± 0.04 for streams in clear cuts and 0.57 ± 0.05 for forested streams ($p = 0.049$; Figure 3.5; Table 3.2). FI was 1.18 ± 0.05 for streams in clear cuts and 1.16 ± 0.06 for forested streams ($p = 0.028$; Figure 3.5; Table 3.2). These are the only two parameters in this study that showed significant differences based on forest management history. HIX and SR were not significantly different between clear-cut and forested streams.

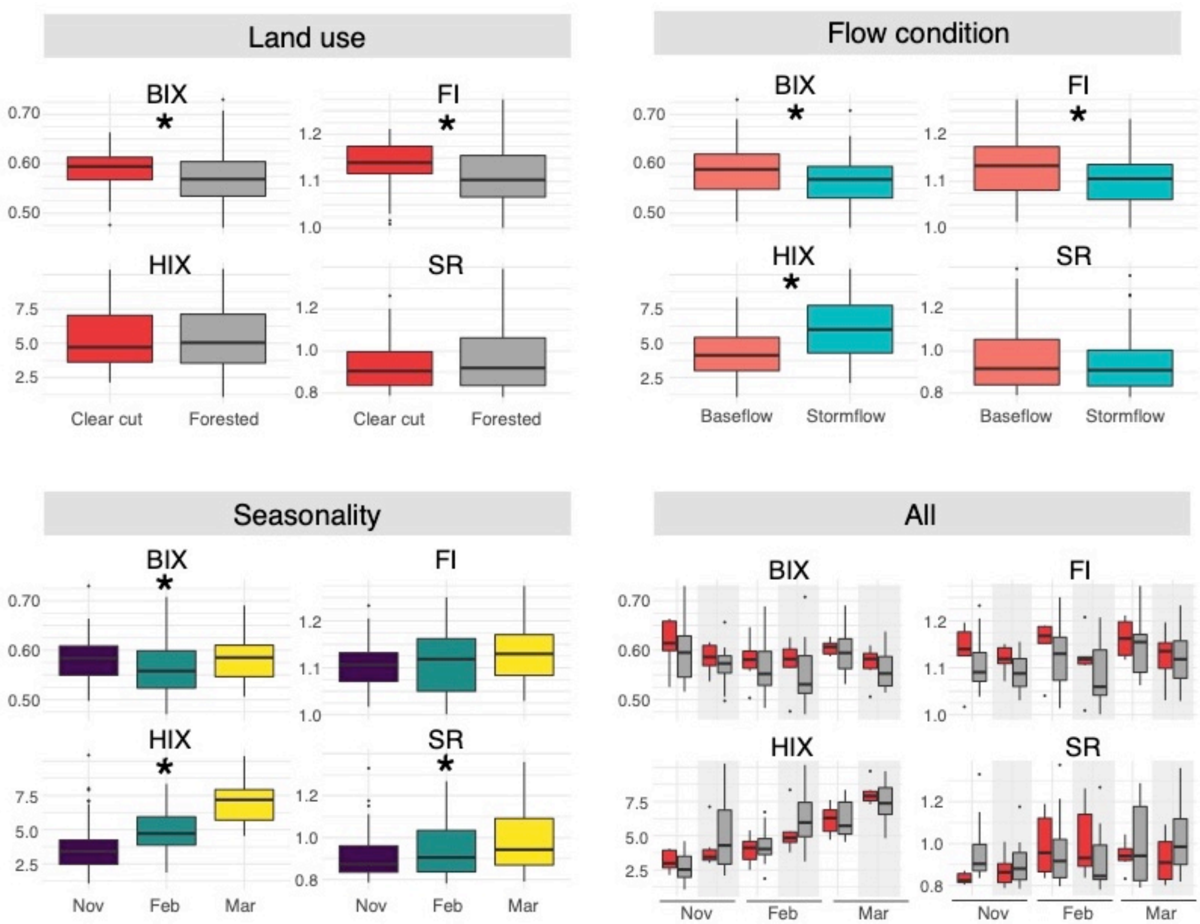

Figure 3.5. Optical indices for all samples (n = 141). Box and whisker plots show median, quartiles, and range of data; points exceeding 1.5 times interquartile range are shown as outliers.

HIX was significantly higher during stormflow than during baseflow (Figure 3.5; Table 3.2), indicating more humic DOC during storms. BIX and FI were significantly lower during storms, indicating less fresh autochthonous DOC during storms (Figure 3.5; Table 3.2).

BIX, HIX, and SR were significantly different by month (Figure 3.5; Table 3.2). BIX first decreased then increased, meaning autochthonous DOC first decreased as the winter season progressed then increased, possibly as temperature began to increase (See temperature in Figure 3.2). HIX and SR increased over time, meaning the proportion of humic content and low molecular weight compounds both increased.

For GLMM models of optical indices, we found that flow condition and seasonality were significant predictors for HIX, BIX, and FI; seasonality, but not flow condition, was significant for SR (Table 3.3). The GLMM was a better fit than fixed effects alone for HIX, BIX, and FI, but was not significantly better for SR (HIX: <0.05, BIX: <0.001, FI: <0.001, SR: 0.16; Likelihood ratio tests; Table 3.4). Of the random effects, we found none to be statistically significant based on single deletion LRT (Appendix C). Drainage area showed some reduction in model error for BIX, FI, and SR but the difference was not significant. As we saw for DOC concentration, the magnitude of standard deviation for drainage area was close to the coefficients for the fixed effects, indicating this could be a driving factor, but we do not have enough evidence to conclude significance of this factor in the GLMM.

In CART models of optical indices (Figure 3.4), drainage area was most important for BIX (37% of model SSE) and FI (50%) whereas season was most important for HIX (40%) and SR (23%). Slope, elevation, specific discharge, and flow condition were generally next most important. Specific discharge was more important for SR than the other indices. Flow condition was more important for HIX and SR than the other indices. Surprisingly, vegetation type and land use were the least important variables across all optical indices (Figure 3.4).

Table 3.3 GLMM results for fixed effects of DOC concentration and characterization parameters.

Fixed effects	Estimate	*SE*	*t*	*p*
DOC concentration				
Land use	0.08	0.12	0.65	0.52
Flow condition	0.20	0.02	10.90	***
Seasonality	-0.19	0.02	-11.77	***
HIX				
Land use	0.02	0.10	0.16	0.88
Flow condition	0.38	0.05	7.76	***
Seasonality	0.55	0.04	12.90	***
BIX				
Land use	-0.02	0.02	-0.80	0.44
Flow condition	-0.03	<0.01	-5.96	***
Seasonality	0.02	<0.01	4.32	***
FI				
Land use	-0.02	0.02	-0.94	0.36
Flow condition	-0.03	0.01	-5.80	***
Seasonality	0.02	0.01	3.98	***
SR				
Land use	0.06	0.04	1.52	0.15
Flow condition	-0.03	0.02	-1.25	0.21
Seasonality	0.05	0.02	2.42	*
C1				
Land use	-0.05	1.26	-0.04	0.97
Flow condition	2.95	0.56	5.27	***
Seasonality	6.30	0.49	12.87	***
C2				
Land use	0.70	1.39	0.50	0.62
Flow condition	3.26	0.36	8.96	***
Seasonality	1.83	0.32	5.74	***
C3				
Land use	-0.43	0.85	-0.51	0.62
Flow condition	-0.35	0.34	-1.02	0.31
Seasonality	3.80	0.30	12.71	***
C4				
Land use	-0.07	0.13	-0.56	0.58
Flow condition	-0.46	0.07	-6.59	***
Seasonality	-0.75	0.06	-12.27	***

*** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$

Table 3.4 Fit indices of GLMM models and GLM models including only fixed effects (land use, flow condition, and seasonality). Likelihood ratio tests compare the goodness of fit of the GLMM versus fixed effect only models. Significant *p* values indicate the GLMM was significantly higher quality than fixed effects alone.

DOC parameters	GLMM		Fixed effects only		Likelihood ratio test
	AIC	BIC	AIC	BIC	*P* value
DOC (mg/L)	-123	-89	30	48	***
HIX	83	117	87	105	*
BIX	-515	-481	-420	-403	***
FI	-458	-423	-371	-354	***
SR	-117	-83	-120	-103	0.16
C1	718	752	718	735	0.06
C2	630	665	697	715	***
C3	594	628	610	627	***
C4	172	206	170	187	0.10

3.3.3.2 PARAFAC model

We validated four components in our PARAFAC analysis representing the most common classes of molecular structures found in the fluorescent DOC. Using the OpenFluor database (Murphy et al., 2014), we matched our components to those in other published PARAFAC analyses. The components listed in Table 3.4 share excitation and emission loading curves that match our components with at least 97% similarity. Based on these matches, we drew conclusions about the likely molecular makeup of these components (Table 3.5). Components 1-3 were humic-like and terrestrially derived (Figure 3.6). Component 1 was high molecular weight, component 3 was low molecular weight, and component 2 was fulvic-acid-like. Component 4 was protein-like and tyrosine-like (Figure 3.6). Component similarities to traditional Coble peaks are also reported in Table 3.5.

Table 3.5. Comparison of PARAFAC components with previously identified sources.

Component	EEM peak location (Ex_{max} / Em_{max})	Traditional peak (Coble, 1996)	Comparable components from other studies	Description
C1	335 / 443	Peak C	C1: Stedmon et al., 2007 C1: Gueguen et al., 2014	High molecular weight, humic-like, terrestrially derived
C2	383 / 508	Near peak C	C2: Stedmon et al., 2007 C2: Wunsch et al., 2018	Humic-like, high molecular weight, aromatic, fulvic-acid like, terrestrially derived
C3	308 / 397	Peak M	C2: Shutova et al., 2014 C2: Goncalves-Araujo et al., 2016	Humic-like, low molecular weight, terrestrially derived
C4	272 / 303	Peak B	C3: Chen et al., 2017 C1: Wheeler et al., 2017	Protein-like, tyrosine-like, authochthonous, microbially derived

3.3.3.3 PARAFAC components

None of the PARAFAC components showed significant difference between clear-cut and forested sites (Figure 3.7, Table 3.2). Two of the humic-like components, C1 and C2 were higher during stormflow and the protein-like component, C4, was lower during stormflow (Figure 3.7, Table 3.2). All components were significantly different by month with the humic-like components generally increasing and protein-like components decreasing (Figure 3.7, Table 3.2).

Results of GLMM for PARAFAC components showed similar results to the optical indices in that season was significant for all components, and flow condition was significant for C1, C2, and C4 (Table 3.3). The GLMM was higher quality than fixed effects alone for C2 and C3, but was not significantly better for C1 or C4 (C1: 0.06, C2: <0.001, C3: <0.001, C4: 0.10; Likelihood ratio tests; Table 3.4). Of the random effects, again none were significant according to single deletion LRT (Appendix C). Drainage area contributed to reduction in model error in C4, but not a significant amount.

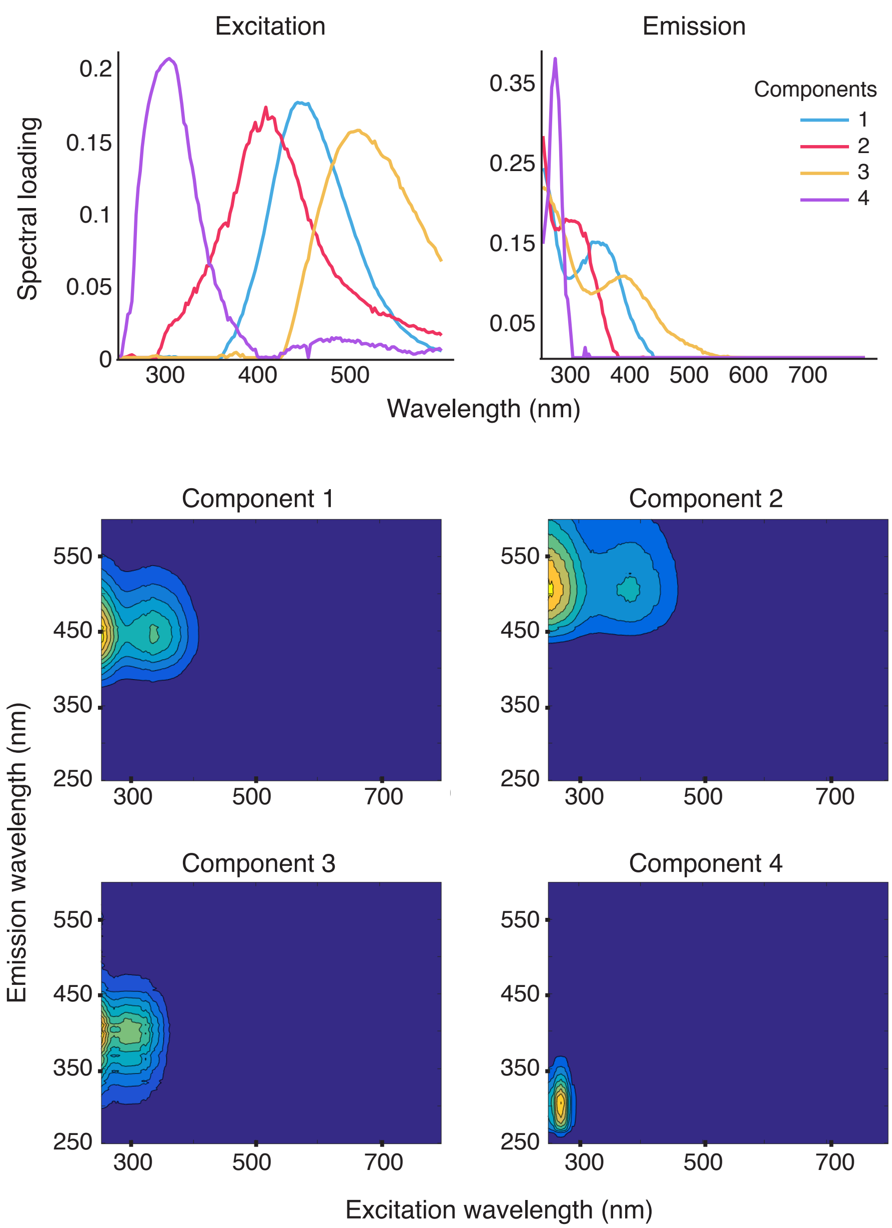

Figure 3.6. Spectral loadings and fingerprints of four components identified by PARAFAC analysis for samples taken in Malcolm Knapp Research Forest (n = 141).

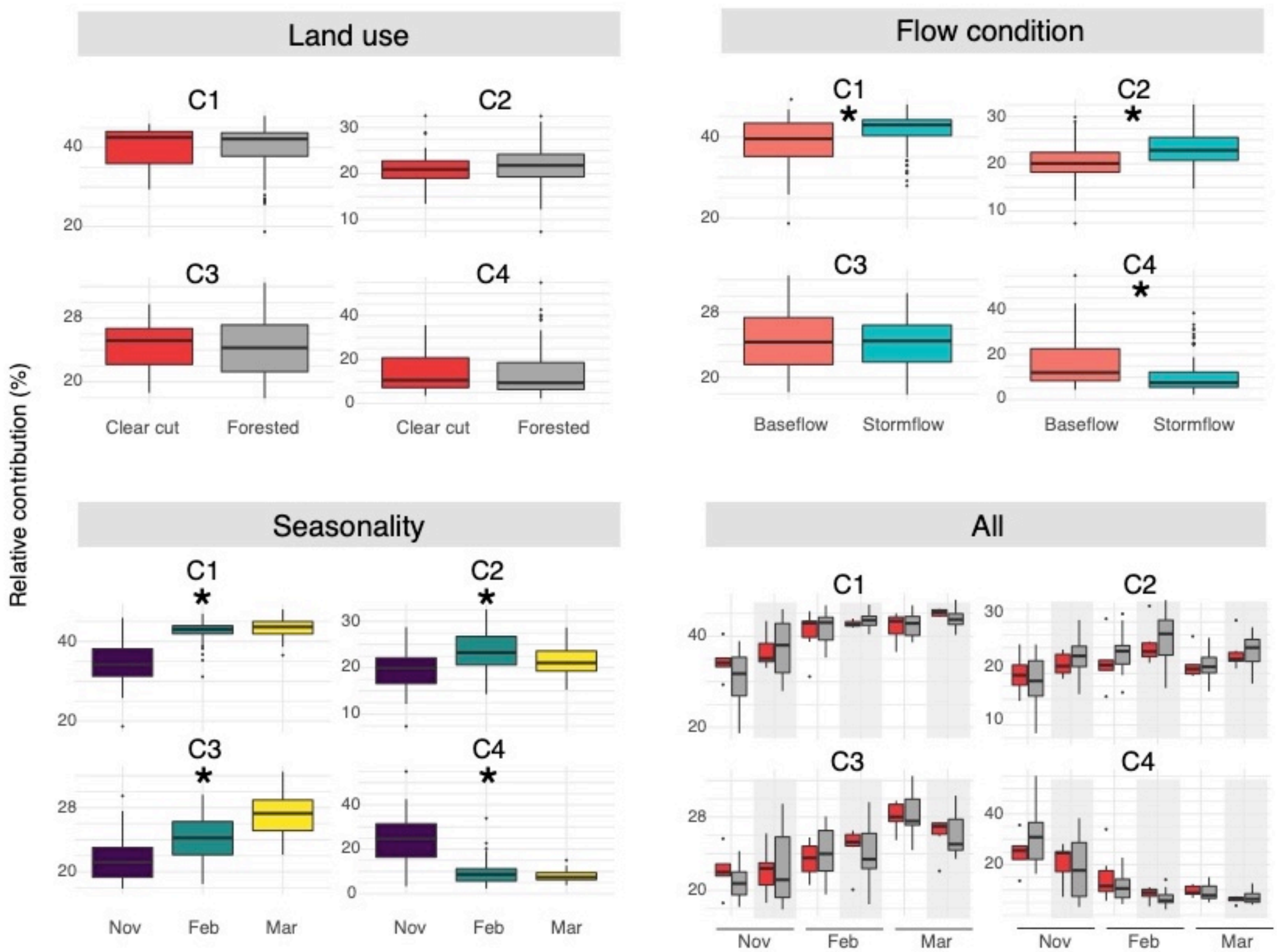

Figure 3.7. Relative contribution of PARAFAC components C1-C4 (n = 141 samples). Asterisks in the top and left panels indicate significant difference between groups.

In CART models, the pattern of significance is broadly similar to the optical indices in that month and drainage area are the most important variables. Season was more important for the humic-like components, C1, C2, C3, than for the protein-like component, C4. Drainage was more important for the protein-like component than for the other three. Again, we found land use to be the least important variable (Figure 3.4).

3.3.3.4 Correlation analysis

As we have combined an optical index analysis with PARAFAC modeling, it is likely that some of our parameters are describing the same attributes of the DOC pool, rather than independent measures. We found two significant factors from a Kaiser-Guttman test of a PCA analysis (Figure 3.8A). Factor 1 accounted for 49.8% of variance, and factor 2 accounted for 30.3% of variance. Factor loadings indicate whether the parameters (i.e. HIX, BIX, etc.) are positively or negatively correlated with one another in relation to that factor (Figure 3.8B). Factor 1 appeared to differentiate between humic and fresh-like components. HIX, C1, C2, C3, and SR have positive factor 1 loadings while BIX, FI, and C4 have negative factor 1 loadings. SR would have been predicted to group with BIX and FI, but it is the close to zero indicating relatively weak correlation. For factor 2, we saw that C2 and C4 are negatively correlated with the remainder of the parameters. The mechanism for this is not immediately clear. However, the humification process may explain the strong negative correlation between C2 and C4. As tyrosine-like compounds undergo humification they become more fulvic-acid-like (Dong et al., 2017). C4 has been shown to indicate tyrosine-like material and C2 has been shown to indicate fulvic-acid-like material (Table 3.5).

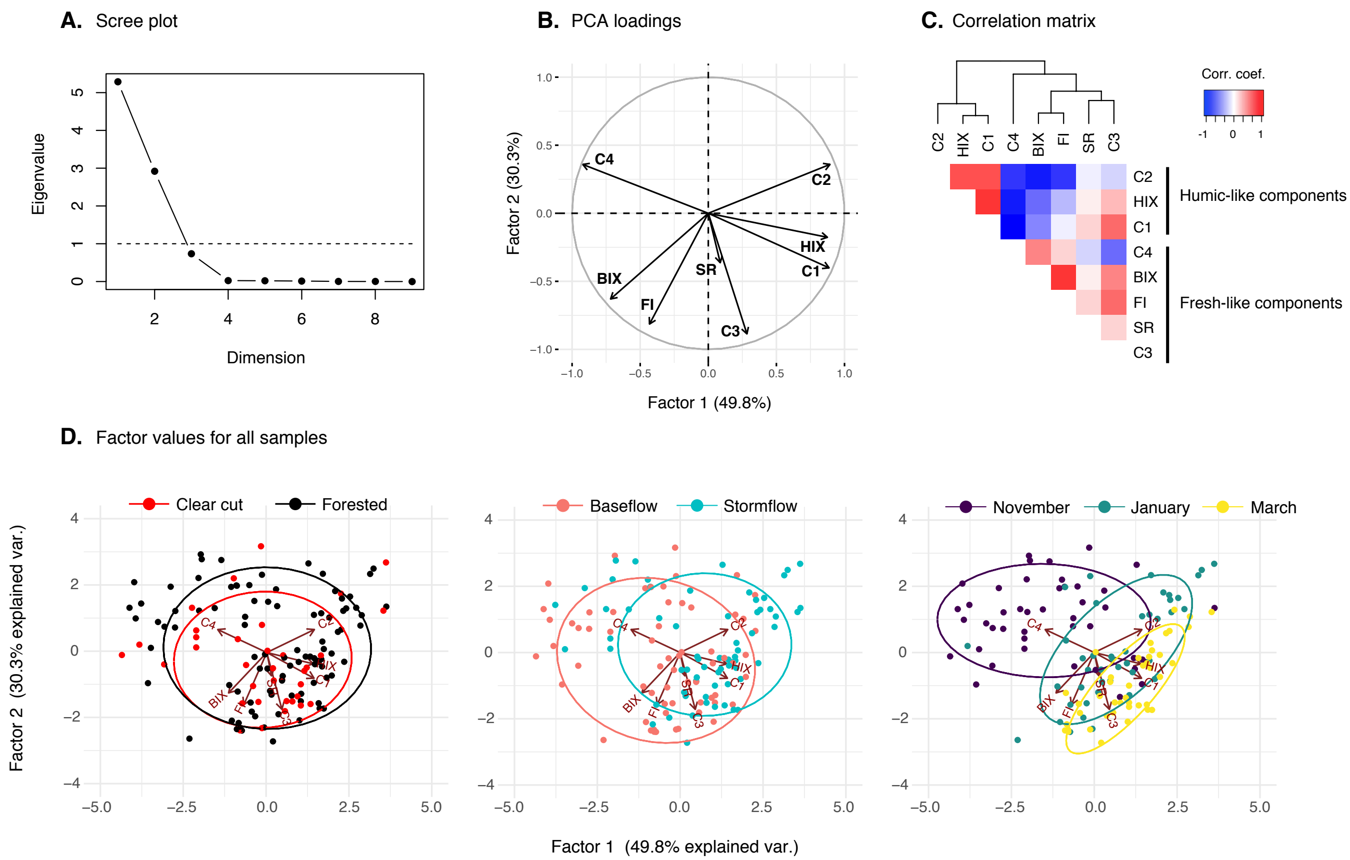

Figure 3.8. Correlation analysis for DOC characterization parameters. A.) Eigenvalues for principle component analysis (PCA) reveal two significant groupings according to a Kaiser-Guttman test. B.) Factor loadings for all DOC characterization parameters. Arrow length indicates relative contribution to component. C.) Correlation matrix for all parameters showing grouping trees that indicate parameters most highly correlated with one another. D.) All samples plotted according to their factor 1 and factor 2 values and grouped by categorical variables: land use, flow condition, and seasonality. Ellipses represent normal probability ellipsoids of the groups. Note that the PCA loadings in all panels are the same.

A correlation matrix between the variables shows two primary groupings that also align generally with the humic vs. protein-like dichotomy (Figure 3.8C). One group includes HIX, C1, and C2 and the other includes BIX, FI, SR, C3, and C4. These groups are almost completely consistent with our expectations for where the parameters fall within the two broad types of DOC contents. Group 1 includes the humic-like components. This group is humic-like, terrestrially-derived, larger molecular weight, allochthonous DOC. Group 2 includes protein-like components. The compounds in this portion of the DOC pool are labile, autotrophically-derived, autochthonous DOC. The only parameter that did not fall out as expected was C3. We had expected C3 to group with the humic components rather than with the fresh components, because other studies have described similar PARAFAC components as humic-like (Table 3.4). However, this component is also described as low molecular weight, which may be related to it correlating more closely with low-molecular weight fresh compounds.

Plotting the sample results in the factor 1 and 2 space of the PCA (Figure 3.8D), we can look at whether our samples cluster in certain regions of the plot based on other grouping variables. We do not see substantial grouping based on land use. We see some trend toward the humic-like variables during stormflow (Figure 3.8D), and toward higher factor 2 values, indicating that values of C2 were higher during stormflow than values of C3. C3 are lower molecular weight compounds that may group more closely with fresh material, so this result is consistent with expectations. Looking at the samples by collection month, we see the groups move along the axis from C4 toward C1. Earlier in the winter season protein-like components are more substantial. As the winter season progresses the low-molecular weight compounds (C4) are no longer produced as biological activity slows, leaving the high molecular weight, terrestrially derived compounds (C1).

3.4 Discussion

3.4.1 DOC concentration

The values we found for DOC concentration are in line with other measurements for small, forested watersheds in baseflow conditions (Bernal et al., 2002). Although some studies have found DOC concentration to increase after forest harvest activity (Bertolo and Magnan, 2007; Laudon et al., 2009; Schelker et al., 2012), we did not find a significant difference in DOC concentration at baseflow between land use types, even after accounting for covariates in multivariate models. This is consistent with other studies that have found no significant effect of harvesting in paired catchments (Knoepp and Clinton, 2009; Lepistö et al., 2014). It is possible that some impact occurred subsequent to harvest, but without lasting effect. Each of the clear-cut sites used in this study were cut 2 to 3 years prior to sampling, which could be enough time to attenuate the effects of soil disruption and other harvest-related factors that can increase DOC. Some studies have shown recovery to pre-harvest sedimentation levels in as little as 2.5 years (Nitschke, 2005), though other have measured significant differences in DOC over longer time scales (Schelker et al., 2014). On the other hand, DOC has also been shown to decrease after cutting, for example in old growth vs. plantation sites in small watersheds where removing older vegetation reduces carbon inputs from woody debris, leaf litter, and root excretion (Lajtha and Jones, 2018). Thus, the impacts of forest harvest on DOC concentration are potentially confounded between opposing mechanisms that (1) increase DOC via soil disruption, increased temperature, and increased light levels, or (2) decrease DOC by removing carbon inputs from older vegetation.

Flow condition is commonly a driver of DOC concentration in small catchments, with DOC increasing as flow levels rise in response to precipitation inputs or snowmelt (Raymond and Saiers, 2010). The particularities of the relationship between discharge (Q) and concentration (C) have been long studied (Hinton et al., 1997; Vaughan et al., 2019), as the Q-C relationship can give information about DOC source. Our findings confirmed our expectation that DOC would increase with stormflow as higher discharge mobilized DOC likely sourced from woody detritus and shallow soil layers. DOC mobilization during storms is relatively high in the Pacific Northwest in part due to very high levels of C storage in vegetation and soil (Smithwick et al., 2002). Our stormflow samples were taken during the first 24 hours of a storm event, indicating that the lag time for DOC response is relatively short and DOC sources are thus likely near-stream. In larger rivers, lag times may be up to a few days following discharge events, but rapid response is common in smaller watersheds (Shultz et al., 2018).

Seasonality of DOC concentration appears to vary in response to changing hydrological conditions. We found DOC to decrease from early to late wet season, which has been previously described for rain-dominated landscapes (Lajtha and Jones, 2018), though there can be variation (Dawson et al., 2008). DOC concentrations peak with a first flush at the onset of the early-wet season, then DOC levels taper off as material is flushed by consistent winter rain. At the end of the wet season, DOC reaches a minimum due to source limitations, a condition which is maintained through the summer low flows. In the summer, source material like leaf litter, woody debris, and soil matter accumulate, but discharge is lower and transport capacity is reduced. This contrasts snowmelt-dominated systems, where DOC is lowest in the winter and peaks in the spring once snowmelt increases discharge levels, frozen soils become mobile, and microbial activity increases (Shultz et al., 2018; Köhler et al., 2008).

3.4.2 Humic-like and protein-like DOC

Forest harvest has variable impacts on DOC concentration, and likewise may vary in its impact on DOC composition in relation to the DOC source and the degree of degradation it has undergone. Our expectation was that protein-like DOC would be higher in harvested catchments due to higher microbial activity enabled by higher surface temperatures and light levels, however during the winter there is less light which could explain the lack of differences observed. Humic components could have increased or decreased after clear cutting depending on whether soil erosion or reduction in litter inputs were the dominant mechanism. Other recent studies have found higher protein-like fluorescent DOC in harvested catchments and higher humic-like components even several decades after harvesting (Lee and Lajtha, 2016). In our sites, we found significantly higher BIX and FI, which indicates more protein-like DOC associated with microbial activity. We did not find any significant difference in humic-like components. Opposing mechanisms of soil erosion and source depletion may be counteracting each other, and improvements to forestry practice may play a role. Increases in humic-like DOC found by Lee and Lajtha (2016) were attributed to decomposing woody debris in the harvested landscape. However, that study was conducted on 50-year-old clear cuts, and best management practices for forestry operations have evolved markedly since, with a prominent focus on reducing soil erosion (Cristan et al., 2016).

Other studies have noted that climatic variables can be more influential on DOC than land-use change (Lepistö et al., 2014). Flow condition, the only climactic variable in our analysis, was a significant predictor of DOC concentration and character. DOC mobilized during high flow can make up the majority of annual DOC export for small catchments (Raymond and Saiers, 2010). Assuming flow paths and hydrologic source areas change during storm events, the character of event DOC changes as well, generally shifting to more terrestrial humic-like signatures as sub-surface flow through riparian soil increases. This would cause higher portions of humic-like DOC in storm water, as has been measured for other small, forested watersheds (Toosi et al., 2014; Wilson et al., 2016).

Consistent with previous studies, we found humic-like components to increase during event flow. HIX, C1, and C2 were all significantly higher during storms than in baseflow. Humic-like DOC has been seen to increase during storms uniformly across different land use types (Vidon et al., 2008). We did not observe a significant difference in HIX response between sites of contrasting land use type in this study. Also, per expectation, we found an inverse relationship between microbial-like and humic-like DOC. Humic components increased during storms, while microbial components decreased. During baseflow, longer residence times likely allowed for DOC to be processed by microbes, leading to microbial-like signatures in DOC content. Conversely, increased contact time with surficial soils during stormflow likely increased humic-like DOC content.

Studies have demonstrated that event water may transport DOC that is more bioavailable (Buffam et al., 2001), but correlations between fluorescence characterization and bioavailability are increasingly questioned in part due to variability in microbial assemblages. In streams dominated by humic-like DOC, like small forested headwater streams, microbial communities may be adapted to utilizing humic-like DOC (Wilson et al., 2016). Our finding that microbial-like DOC decreased during storms does not necessarily equate to reductions in bioavailability, and further study is warranted. Whether event water is more or less bioavailable could have major impacts for downstream ecosystems and drinking water systems.

Downstream impacts of DOC in small, forested watersheds on water supplies and ecosystems are substantial, thus our finding of increased humic-like DOC and decreased protein-like DOC during storms has important implications. As much as 85% of annual DOC flux is mobilized during storm events (Raymond and Saiers, 2010). This rapid export has been described as a "pulse-shunt" transport mechanism (Raymond et al., 2016). Large pulses of event water DOC move rapidly down the river network unchanged by biodegradation, uptake, or other in-stream processing, arriving downstream in a much more unchanged form than they would have under baseflow conditions. According to the river continuum concept, downstream ecosystems are adapted to use upstream byproducts and inefficiencies (Vannote et al. 1980). As storm events have the potential to shift water quality profiles downstream, changes to storm strength or frequency (especially under future climate scenarios) risk destabilizing these ecosystem processes. DOC character during storm events represents the majority of DOC that is exported to larger rivers and reservoirs that are used for drinking water supplies.

3.4.3 Covariate site characteristics

In GLMM models, we demonstrated that including site characteristics other than land use, flow condition, and season as random effects significantly improved models of DOC concentration and some aspects of DOC character. While no single factor was found to be statistically significant, the total model was significantly better than the model with fixed effects alone. Standard deviations of drainage area in the model were the largest of the random effects, indicating drainage area may play the largest role of those factors. We found drainage area to be an important predictor of DOC in CART models, as concentration increased with drainage area. Previous studies have found DOC concentration to increase downstream (i.e. with larger drainage area) for first order streams (Billett et al, 2006). At larger stream network scale, DOC concentrations decrease once larger rivers are reached, mainly due to biological uptake and photodegradation taking place as residence time of DOC increases (Raymond et al., 2016). Typically DOC is less labile downstream due to rapid uptake by bacteria, especially during warmer months as metabolisms are faster and there is more photodegradation of the DOC (Tiwari et al., 2014). In the present study, we found that for CART models of DOC character, drainage area was more important for BIX and FI (indicators of microbial-like DOC) than for other optical indices.

Although not significant in our models, we observed some slight trends in the relationships between DOC and covariates that could be investigated in further studies. DOC decreased slightly for reaches with greater slope, consistent with Connolly et al. (2018), and decreased slightly with higher elevation, consistent with Larouche et al. (2015). DOC also decreased with specific discharge (i.e. discharge normalized for area). Catchments with high specific discharge have relatively high discharge for their size, likely imparting a dilution effect on DOC concentration. In this study, vegetation type and stream morphology did not predict DOC concentration or character.

3.4.4 Source water protection implications

Removal of DOC from source water is often a high-cost step in water treatment processes (Li and Mitch, 2018). Though not toxic on its own, organic matter can contribute to taste, colour, and odour issues, encourage microbial growth in pipes, and react with disinfectants to produce harmful disinfection byproducts (DBPs). DBPs have been shown to have a strong correlation with bladder cancer, low birth weight, and miscarriages (Villanueva et al., 2004). Just as there is a large diversity of DOC composition, there is a large diversity of subsequent DBPs, 11 of which are government-regulated (as of Li and Mitch 2018), primarily trihalomethanes (THM) and haloacetic acids (HAA). The primary precursors of DBPs in organic matter are humic substances (Singer, 1999), particularly humic-like compounds (Parr et al., 2019).

Lower humic-like DOC generally reduces THMs, but other protein-like DOC can cause algal blooms and nitrogen based DBPs (N-DBPs) which are not yet regulated, but are increasingly studied and found to be harmful even at small concentrations (Li and Mitch, 2018; Shah and Mitch, 2012; U.S. Environmental Protection Agency, accessed August 2019). As more DBPs are found to have harmful effects on human health, regulations could continue to become more stringent and drinking water utilities may pay closer attention to the composition of DOC in raw water. Land management implications, as considered in this study, are an important management strategy for optimizing protection of drinking source water supplies (Emelko et al., 2011).

Our observation of elevated DOC concentration and humic-content during storms underscores the importance of analysis of future climate scenarios and risks of change to storm patterns in order to manage drinking water security. Impacts of land use, as observed in this study, may be relatively less harmful to drinking water processes, though further study of the ecological impacts of changes to DOC is needed. Forest harvest can be detrimental to biodiversity and ecosystem services (Chaudhary et al., 2016;

Pohjanmies et al., 2017; Williams et al., 2016), so an abundance of caution is necessary in its application as a source water protection tool. We found no significant difference in DOC concentration for harvested sites, and the only significant difference in characterization we found was elevated microbial-like DOC. This type of DOC may be less harmful for drinking water processes, but could increase autotrophic activity in fluvial ecosystems.

Chapter 4: Water treatment discussion

4.1 Overview

In this thesis, I have considered the effects of landscape change, storm events, seasonality, and other factors on DOC for forested headwater streams (Chapters 1-2). There is an important link to human systems in the management of stream DOC, as DOC must be removed from drinking water supplies through processes that are complex and expensive. This is a common management concern, as over a third of world cities rely on forested watersheds drinking water supplies, and all natural waters contain DOC (Dudley and Stolton, 2013). Access to safe water for drinking has been one of the greatest achievements in the history of public health, and will always be a critical resource for communities. Treatment facilities are costly, so decisions must be made to optimize costs while maintaining high quality standards. In this chapter, I use the Metro Vancouver drinking water supply system as a case study to explain how DOC is removed from source water and how changes to DOC affect those processes.

4.2 Typical drinking water treatment processes

The primary goal of treating water is to kill pathogens (i.e. disinfection) and to remove heavy metals and other toxins. Secondarily, treatment aims to improve taste, colour, and odour, to meet the consumer's desire for not only clean but also clear and appealing water. There are three main methods for water disinfection: chlorination, ozonation, and UV irradiation, each of which deactivates most harmful bacteria, protozoa, and viruses. There are pros and cons to each disinfection method, but chlorine is the least expensive and remains the most widely used in North America (EPA, 2013; Health Canada, 2009). The downside of chlorine is that its use typically results in harmful residuals called disinfection byproducts (DBPs) that must be minimized. Ozone is a more effective disinfectant than chlorine, but it requires higher capital and operational costs, and does not persist in the distribution system so a small amount of chlorine must be added regardless. Residual disinfectant is almost always added to guard against microbial growth from leaks in the distribution system (Clark, 2019). Ozonation systems have been built with the intention of reducing DBPs, but are still less common than chlorination (Langlais et al., 2019). UV treatment similarly does not produce harmful byproducts, but often requires additional chlorine to mitigate microbial and biofilm growth in the distribution system (Pūle, 2016). An additional disadvantage of UV treatment is that is requires very low turbidity to be effective, necessitating higher quality filtration before disinfection (Pūle, 2016).

Steps leading up to disinfection, collectively known as the treatment process train, are carried out to remove materials from the source water in order to minimize byproducts and maximize disinfection efficacy (Gerba, 2009). The bulk of solutes in natural waters are natural organic material (NOM), which includes DOC and larger particulate organic matter. In a conventional water treatment process, the treatment train consists of coagulation, flocculation, sedimentation, and filtration before disinfection. Coagulation is the addition of chemicals like aluminum and iron salts to raw water in order to neutralize the charge of raw water solutes, allowing them to collide and aggregate (Matilainen et al., 2010). The majority of NOM is negatively charged. Coagulants have high positive charge and thus adsorb onto and neutralize negatively charged material. Flocculation is the process of vigorous mixing to encourage the coagulated material to collide and form larger particles called flocs (Gregory and O'Melia, 1989). After mixing, the flocs are removed by sedimentation and/or filtration. Sedimentation is done in large holding tanks where the flocs settle out by gravity over time and the clear water is piped out from above the sediment. Filtration forces water through a small pore material such as sand or membranes (Gerba, 2009). After filtration, one or more disinfection methods are used. When the finished water leaves the plant, it enters the distribution system where there is risk for contamination through leaks. A substantial portion of waterborne disease outbreaks in the last decades have been attributed to contamination in the distribution system (Blackburn et al., 2004; Clark, 2019). To minimize that risk, chemical disinfectant that will persist for a longer period of time, usually chlorine, is added to the water as a final step in the treatment process.

The chemical quality of the raw water, including NOM concentration and character, determines the appropriate type and dosage of chemicals used for coagulation. NOM enters the water from organics in the soil (humic-like, allotchonous DOC) and from biological processes in streams (protein-like, autochthonous DOC). Protein-like DOC is more hydrophilic, and humic-like DOC, which usually accounts for more than half of the DOC present, is more hydrophobic (Matilainen et al., 2010b). Hydrophobic portions of DOC carry high negative surface charge, thus the positively charged coagulants are effective in neutralizing them. Low molecular weight, non-humic components of DOC are not as amenable to coagulation, thus a large percentage of this type of DOC (low molecular weight, hydrophilic, and likely protein-like) is not removed during treatment (Liu et al., 2010; Zhao et al., 2009). Removal rates can be improved through pH adjustments (Volk, 2000). There are alternative treatment methods that remove more of this portion of DOC, namely magnetic ion exchange, activated carbon, and membrane filtration, but even they do not remove all DOC, and they are significantly more expensive. Most plants use coagulation only, rather than these more advanced methods (Matilainen et al., 2011). In order to remove as much DOC as possible, coagulant doses are increased with increasing DOC concentration, and increased even more with higher hydrophilic content, but always with the goal of using only just as much coagulant as necessary. Overall, drinking water treatment plants must balance optimization for maximum NOM removal, minimal residual coagulant, minimal sludge production (material that is removed in filtration), and minimal operating cost (Edzwald, 1993).

4.3 Metro Vancouver case study

For the case of Metro Vancouver in particular, water treatment processes are a bit different from conventional water treatment, because the source water is cleaner and more protected than average. UV and ozone are used as primary disinfectants, with some chlorine added secondarily for the distribution system. Because the source water is generally very clean and low in NOM, filtration was not used at all until 2009 and is now used for only one of two treatment plants. Metro Vancouver supplies safe drinking water to over 2.5 million people from three protected sources: the Seymour, Capilano, and Coquitlam watersheds (Metro Vancouver, 2011). These watersheds are located north of the Region of Vancouver and have been protected since the early 20th century with a complete ban on forest harvest since 1999 (Greater Vancouver Water District, Water Committee, 1999). Water from Seymour and Capilano reservoirs provides about 70% of water in the system. These sources are combined at the Seymour Capilano Water Filtration Plant. In the plant, first an aluminum-based coagulant (poly aluminum chloride) and a coagulant aid polymer are added. Next, the water undergoes flocculation to increase the particle size of material in the water. Next a filter aid polymer is added, and the water is filtered through a medium of anthracite and sand (Metro Vancouver, 2018a). The resulting filtered water is then disinfected with UV irradiation. As there is coagulation/flocculation but no sedimentation step in the treatment train, this is a chemically assisted direct filtration process. When commissioned, it was the largest direct filtration plant in Canada and the largest UV system in the world (Stantec, 2010). After UV treatment, sodium hypochlorite (as chlorine), CO_2, and lime are added for microbe and corrosion control in the distribution system (Metro Vancouver, 2016).

In the Coquitlam watershed, which provides roughly 30% of the region's water, coagulation and flocculation are not used. Water from the Coquitlam reservoir is routed to the Coquitlam UV Disinfection Facility, where ozone is used as the primary disinfectant (Metro Vancouver, 2019). Ozone can only be used without filtration when NOM levels are very low. Average DOC values for all three reservoirs are similar (2018 averages: Coquitlam 1.6 mg/L, Seymour 1.7 mg/L, Capilano 1.6 mg/L), but Coquitlam is less prone to spikes during storm events (Metro Vancouver, 2018). In the Coquitlam plant, after ozonation the water is also disinfected with a UV system, and sodium hypochlorite (chlorine) is added for distribution. Though the Coquitlam watershed has a lower propensity for landslides and sedimentation, there is always some risk. Vancouver is fortunate to have multiple supply areas, so if there were a concern in the Coquitlam watershed, the Seymour and Capilano sources are available as a backup supply. The microclimates of Coquitlam and the other two source areas are generally different enough that the risk of all three supplies becoming problematic is low, and the Seymour Capilano Filtration plant can handle relatively high levels of DOC if needed.

In a personal interview with senior staff at Metro Vancouver, I was able to gain insight into how DOC affects drinking water treatment for Metro Vancouver. The objective of the interview was to ascertain **(1) how DOC is measured and how necessary adjustments are made, (2) how storm events and seasonality affect DOC and treatment processes, and (3) what would happen if DOC increased or changed substantially in the coming decades.**

Proxies for DOC are measured continuously and changes to coagulant dosing are computer-automated. At the Seymour Capilano Filtration plant, DOC is monitored by UV transmittance at 254 nm (UVT). UVT is a proxy for DOC concentration that is calibrated on a site-by-site basis measured as the percent UV light at 254 nm that passes through a sample. This is similar to SUVA254 (absorbance of UV light at 543 nm normalized by DOC concentration), but does not require a concentration measurement. In addition to the UVT proxy, direct measurements of DOC are done weekly at the Seymour Capilano Filtration plant. Though UVT is monitored, it is not used for control. The chemical dosing is fully automated at the plant based on measurements by streaming current detector (SCD) (K. Tully and A. de Boer, personal communication, May 23, 2019). SCDs measure net surface charge, thereby informing how much coagulant should be added to the raw water (Jiang, 2015). An SCD measuring the finished water is set to keep the chemical dose within 5-10% of target levels, and operators intervene if measurements go out of that range (K. Tully and A. de Boer, personal communication, May 23, 2019). With this system, the Seymour Capilano Filtration Plant is able to remove greater than 50% of organics, and this percent removal is consistent so that DOC residual concentration varies; residual concentration is higher when

DOC in the raw water was higher. Therefore disinfection byproduct concentrations rise during storms as well. There are regulations limiting haloacetic acids (HAAs), which are the most common DBP produced in the Seymour Capilano plant. Currently HAA levels are measured quarterly as required by regulations (K. Tully and A. de Boer, personal communication, May 23, 2019).

For the Metro Vancouver watersheds, DOC increases markedly during storms. Typically, DOC changes at most about 1 mg/L in 24 hours (0.04 mg/L/hr) (K. Tully and A. de Boer, personal communication, May 23, 2019). From the sites with in-stream sensors described in Chapter 2 of this thesis, the rate of change in DOC during storms was 0.16 mg/L/hr for the stream located in a clear cut and 0.11 mg/L/hr for the forested stream. These streams changed faster than what is generally seen for the Metro Vancouver reservoirs, likely because they are orders of magnitude smaller and they are streams rather than reservoirs. Usually the yearly maximum DOC concentration in the Seymour and Capilano reservoirs is around 3.5 mg/L, and the highest recorded in recent decades was 11 mg/L during a landslide in 2017. When DOC increases, dosing of both the coagulant and coagulant aid polymer increase, and filter aid polymer level is left constant. Turbidity is removed from water in the same way as DOC, and it is often decoupled from the DOC storm response. Metro Vancouver often observes DOC concentration peaking before turbidity. The effects of rainstorms typically last up to a week before returning to baseline level. When the reservoir level prior to the storm is low, the DOC response is generally greater, as there is less stored water present to dilute the new DOC coming in (K. Tully and A. de Boer, personal communication, May 23, 2019). This is in agreement with what is generally understood about the effects of antecedent flow on DOC, and what I measured in Chapter 2. The Metro Vancouver reservoirs may be even more susceptible to heightened effects during low antecedent flow, because their banks are less stable than natural lakes and are thus more prone to erosion and bank instability when being re-wetted. The Coquitlam reservoir is largely underlain by bedrock, so its DOC levels do not respond as strongly to storms. Having multiple separate watershed sources is advantageous for Metro Vancouver. If one reservoir suffers a quality issue such as a major landslide, water from the others can be used (K. Tully and A. de Boer, personal communication, May 23, 2019).

From season to season, DOC concentration varies, but DOC character does not vary enough to impact water treatment in the Metro Vancouver system. DOC concentration is highest in the fall after the first rains, and then decreases through the rest of the year with anther smaller uptick during spring snowmelt (Metro Vancouver, 2018b). DOC character (e.g. the portion of DOC that is protein-like vs. humic-like) is not measured by Metro Vancouver (K. Tully and A. de Boer, personal communication, May 23, 2019), and is assumed to not change much over time. While I did find significant changes in DOC character in this thesis (Chapter 3), the changes may be small in the larger scheme of what matters for water treatment. I measured fluorescence index (FI) values ranging from 1.1 to 1.3. FI values around 1.4 are generally considered terrestrial and FI around 1.9 are considered microbial. I found significant differences in FI between streams with different land use status and during stormflow vs. during baseflow, but this variation was all well below the threshold for what is considered terrestrial-like along a scale of FI values. Currently, phosphorous in the Metro Vancouver watersheds is extremely low and there has never been measureable algae (K. Tully and A. de Boer, personal communication, May 23, 2019). However, there still may be potential for algal growth to increase with increasing temperatures. Finished drinking water in Vancouver contains more HAAs than THMs, the opposite of what is observed in the Canadian prairies (K. Tully and A. de Boer, personal communication, May 23, 2019). This is assumed to be due to differences in DOC character. Overall, changes in DOC character are not currently a problem for Metro Vancouver, but as water quality standards are becoming stricter with additional limits on more DBPs (Matilainen et al., 2011), DOC characterization may need to be done in the future.

If DOC concentration in the Metro Vancouver watersheds were to increase markedly, operational costs for chemical supplies and removal of waste material would increase. DOC is not predicted to increase enough in the coming decades for major changes to the plant to become necessary (K. Tully and A. de Boer, personal communication, May 23, 2019), but it is important to understand potential changes in budgeting for the plant's operation. Chemical costs alone account for about 30% of water treatment plant costs, about $800k per year in the case of Metro Vancouver. At very high DOC levels, the direct filtration system would no longer be appropriate and sedimentation tanks would be to be added, but this is unlikely to happen. The most limiting factor in the current infrastructure is the capacity to process and transport residual material left over after the treatment process (K. Tully and A. de Boer, personal communication, May 23, 2019).

DOC levels during storms are predicted to likely increase as storm intensity increases and reservoirs are kept lower with increasing demand from a growing population. Although storm events may become more expensive to treat, discrete events are easier to deal with than consistently high DOC levels. DOC concentration in the Metro Vancouver watersheds is typically highest during the first flush in the fall and the snowmelt in the spring. But, because these are not the times of highest treated water demand, even if concentrations are elevated the total residual waste produced would still likely be lower than what is produced during high summer water demand (K. Tully and A. de Boer, personal communication, May 23, 2019). Following a landslide in 2017, an additional ~$100k in chemical costs was required, a ~12% increase in the annual chemical budget from a single rain event (K. Tully and A. de Boer, personal communication, May 23, 2019). The sum of chemical costs for the Coquitlam plant is similar to the cost of coagulants in the Seymour Capilano plant per unit water produced. Ozone is only effective at low levels of DOC, so if DOC were to increase in this watershed that water could not be treated with the current plant. There is little risk for this happening and if something were to happen temporarily, water would be drawn from the other two watersheds (K. Tully and A. de Boer, personal communication, May 23, 2019).

In summary, I was able to gain insights on all three of the expert interview objectives. First regarding DOC measurement and process control, DOC concentration at the Seymour Capilano Filtration Plant is monitored continuously using net surface charge and UVT as proxies, and DOC concentration is measured directly once per week in a laboratory. Adjustments to coagulant dosing based on DOC content are done based on net surface charge measured and controlled by a streaming current detector (SCD). HAA levels are measured quarterly as is required by current regulations.

Regarding storm events and seasonality, I confirmed our expectation that storm events have a substantial effect on DOC levels for the Metro Vancouver reservoirs. The rate of change in DOC typically measured in the reservoirs is much slower than what we found in MKRF (Chapter 2). In our study streams, we measured changes in DOC concentration roughly 3x faster. For the Metro Vancouver reservoirs, the increase in DOC concentration in response to storms is typically greater when antecedent flow was low, which is consistent with what we found in MKRF. DOC concentration varies seasonally in the Metro Vancouver reservoirs. Concentration generally peaks during the first fall rains then decreases over the winter with a small uptick during spring snowmelt. This is also consistent with what we found in MKRF.

DOC character is measured only by UVT, which is an indicator of humic-like DOC content. It is not known whether DOC character in the Metro Vancouver reservoirs varies seasonally or with storm events, but it is assumed to not change much over time. In Chapter 3, I found significant differences in DOC character based on flow condition, season, and land use condition. As understanding of the health effects and precursors of DBPs improve, new regulations could require more thorough understanding of DOC character. For example, N-DBPs that are associated with protein-like DOC are not currently regulated, but may be in the future (Li and Mitch, 2018; Shah and Mitch 2012). Protein-like precursor material is not measured by UVT, and other measurement techniques may be needed to monitor DOC.

In terms of future outlook, I learned that DOC is not expected to change enough in the coming decades to require any changes to the Metro Vancouver drinking water treatment plants. The current infrastructure can support much higher DOC loads, but chemical costs would increase if DOC concentration increased substantially. Chemical costs currently account for about 30% of water treatment plant costs. The most limiting and potentially most costly effect of very high DOC would be the need for processing and transporting additional residual waste. DOC levels during storms may rise as storm intensity is predicted to increase under future climate scenarios (Bengtsson et al., 2006; Prein et al., 2017), and reservoirs may be lower with increasing demand from a growing population. These changes are unlikely to cause any need for infrastructure upgrades, but may cause water treatment to become more expensive.

Chapter 5: Conclusions

Dissolved organic carbon (DOC) is important to ecosystem productivity (Meyer et al., 1988; Wilcox et al., 2005) and drinking water treatment (Matilainen et al., 2010; Sharp et al., 2006). DOC concentration and character have been shown to depend on land use change (Laudon et al., 2009; Schelker, et al., 2012), but the mechanisms driving this relationship remain poorly understood and are complicated by regional differences and the multitude of factors effecting DOC. In this thesis, I investigated the relationship between recent clear-cutting and DOC concentration and characterization for a case study near Vancouver, British Columbia, Canada. I used a two pronged observational approach by measuring (1) highly resolved temporal data at two contrasting streams (one in a clear cut and one in relatively mature forest), and (2) less frequent low and high discharge grab samples at a 18 additional forested sites and 6 additional clear-cut sites within a 5 km radius. To discuss the results in the context of drinking water treatment systems, particularly for the local municipality, I completed expert interviews with water treatment engineers at Metro Vancouver.

From the temporal analysis using in-stream sensors at two sites, I found base flow DOC concentration and DOC response to storm events to be significantly different between the two sites. Mean base flow DOC just before storm onset was 2.26 ± 0.43 mg/L at clear-cut site, substantially lower than at the forested site, which measured 4.30 ± 0.83 mg/L. This was a surprising result considering many studies have found DOC to increase after clear cutting (Bertolo and Magnan, 2007; Pinel-Alloul, et al., 2002), though not all have found this (Meyer and Tate, 1983; Startsev et al., 1998). The grab sampling portion of this project confirmed a trend of lower DOC concentration at 6 clear-cut sites than at 18 similar forested sites, but the difference was not statistically significant. For the forested in-stream sensor site, a small bog lake upstream in the catchment may have contributed to more elevated DOC base flow concentration. The relatively low DOC concentration at the clear-cut site suggested the removal of carbon inputs like leaf litter and root exudation may have been the primary mechanism by which clear cutting affected DOC.

In terms of storm response, DOC concentration at the clear-cut site reacted more strongly than the forested site. DOC increased on average 2.42 mg/L during storms in the clear-cut site versus only 1.99 mg/L at the forested site. The time to reach peak concentration during the storm was similar at the two sites, thus the rate of change in DOC was also significantly higher at the clear-cut site. Though the base flow DOC concentration was lower, DOC concentration increased more and faster at the clear cut than in the stream located in mature forest. This could have been due to the speed and number of flow paths increasing after clear cutting. Speed and magnitude of DOC response to storms are important for managing drinking water treatment facilities, and larger faster changes can be more difficult and more expensive for utilities (Sharp et al., 2006; Worrall and Burt, 2009).

From the broad sampling analysis across 24 stream sampling sites, I found DOC concentration to depend significantly on flow condition and seasonality, but not on land use condition (i.e. clear-cut vs. forested sites). As was expected (Lajtha and Jones, 2018; Raymond and Saiers, 2010; Vaughan et al., 2018), DOC concentration increased during storms and decreased through the fall to spring study period. On average across sites, DOC was 2.4 ± 0.6 mg/L during base flow and increased to 2.9 ± 0.9 mg/L during storm flow. Average DOC decreased from 3.0 mg/L in November to 2.7 mg/L in February and 2.2 mg/L in March. We observed the same trend that DOC concentration was higher on average at the forested sites, but across 24 sites the difference was not statistically significant.

For DOC characterization of grab samples across 24 sites, I characterized DOC content using 8 parameters derived from fluorescence and absorbance measurements. The various characterization parameters can be generally grouped as either humic-like or fresh-like DOC. Parameters indicating fresh-like DOC (BIX and FI) were significantly higher for the clear-cut sites than forested sites. Increased surface temperatures and light levels after harvesting may have contributed to elevated fresh-like DOC

(Lee and Lajtha, 2016), and the difference may be even greater during summer months, though summer flows in the study streams are very low. Humic-like components (HIX, C1, C2) were higher during stormflow, likely due to changes in flow paths to mobilize more DOC from soils. When random factors were included in a GLMM, land use was no longer a significant predictor of any DOC character parameters. In comparing the relative importance of covariates using CART, we found drainage area to be the most important predictor.

In expert interviews with Metro Vancouver water treatment engineers, I learned that the utility continuously monitors a UV transmittance proxy for DOC and adjustments to treatment chemical dosing are computer-automated. Their observations of seasonal variation in DOC concentration and response to storms were broadly consistent with what was measured in our study in MKRF. Interestingly, DOC characterization is not measured at the Metro Vancouver drinking water treatment plant. The differences we found in DOC character may be too small to matter for treatment processes, or DOC character may not fluctuate as much in a large reservoir even during storm events. The treatment plant is able to accommodate changes in DOC by adjusting chemical dosing, but chemical costs are a substantial part of their budget with single mass wasting events costing upwards of $100k in chemical costs (12% of annual budget). Upgrades to the plant to accommodate higher concentrations are not predicted to be necessary in the coming decades. If base flow DOC concentrations were to increase, the greatest expense would be in the processing of residual waste produced as DOC is removed.

Overall, this thesis has made an important contribution in demonstrating that recently clear-cut sites can show similar or significantly lower DOC concentration than nearby similar forested sites, even though the opposite is more commonly reported in the literature (Bertolo and Magnan, 2007; Laudon et al., 2009; J. Schelker et al., 2012). This work is also at the forefront of highly resolved time series analysis for the relationship between DOC concentration and land use condition. Though studies have reported differences between forested, agricultural, and urban settings (Vaughan et al., 2017; Vaughan et al. 2018), this thesis is the first known synoptic sub-hour frequency study of DOC at comparable sites of contrasting forest harvest history. Our finding that protein-like DOC character was more prominent in clear-cut sites is also a key finding, and has implications for water treatment. Though the DOC pool is primarily humic-like, humic-like DOC is much easier to remove by coagulation whereas protein-like DOC is not easily removed and persists into the disinfection stage more so than humic-like constituents. Disinfection byproducts (DBPs) created by the interactions between protein-like DOC and disinfectants are relatively understudied. If these DBPs are harmful to human health, increasing protein-like DOC due to forest harvest will be of even greater interest to water treatment managers.

There are many ways this work might be expanded and built upon to improve understanding of the relationship between landscape change and water treatability. First, knowing now that net surface charge is the primary metric measured and used to control coagulant dosing for Metro Vancouver (K. Tully and A. de Boer, personal communication, May 23, 2019), it would be interesting to test how surface charge relates to DOC concentration, DOC character, and potential explanatory variables like land use, flow condition, or other site parameters. There may be opportunities to continue our relationship with Metro Vancouver and conduct research in the drinking supply watersheds in collaboration with their research questions and needs. While the Metro Vancouver watersheds are protected from land use change, it would be interesting to install submersible spectrometers and compare storm response to what we observed in MKRF (Chapter 2). However, storm response has been found to be highly variable even within sites (Butturini et al. 2008; Vaughan et al 2017), so it may be difficult to compare responses with much certainty. For this reason, it would be valuable also to repeat monitoring with the submersible spectrometers at the same MKRF sites to assess annual variability in DOC concentration and storm response.

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Appendices

Appendix A: Site photos

These photos were taken in May, 2019 after the end of the study period and after spring leaf out had begun. Vegetation obscures the stream in many photos, but they give a general idea of stream size and morphology for this study. Stream sampling sites beginning with **C** are located in recent clear cuts, and sites beginning with **F** are located in relatively intact forest.

Site C1

Site F9

Site F8

Site C2

Site C3

Site F6

Site C4

Site C5

Site C6

Site F17

Site F16

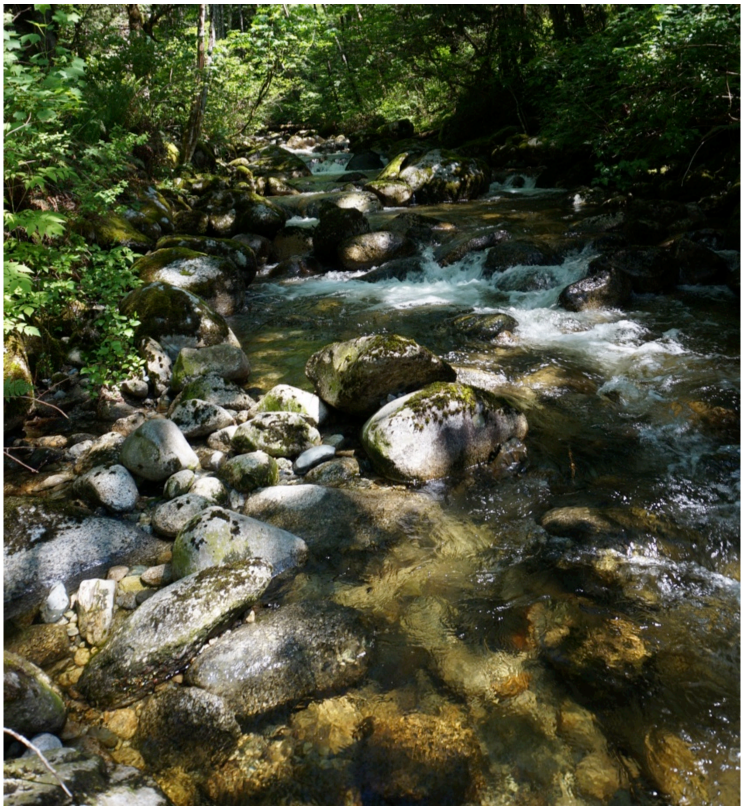
Site F15

Site F14

Site F13

Site F12

Site F11



Site F10

Site F7

Site F3

Site F1

Site F2

Site F4

Site F5

Site F18

Appendix B: Grab sampling dataset

B.1. Site description parameters

Site	Land use	Elevation (m)	Slope (deg)	Drainage area (ha)	Specific discharge (L/s/ha)	Predominant tree type	Stream morphology
C1	Clear cut	283.00	15.96	6.06	0.101	conifer	step pool
C2	Clear cut	328.21	18.35	4.24	0.045	conifer	cascade
C3	Clear cut	244.70	15.78	20.63	0.018	conifer	step pool
C4	Clear cut	219.41	23.65	24.72	0.016	deciduous	cascade
C5	Clear cut	191.47	20.28	5.98	0.046	deciduous	cascade
C6	Clear cut	191.03	20.42	20.63	0.010	deciduous	step pool
F1	Forested	192.82	7.60	97.01	0.004	conifer	pool riffle
F2	Forested	232.58	13.89	5.73	0.042	conifer	step pool
F3	Forested	279.54	7.49	6.96	0.045	conifer	step pool
F4	Forested	161.14	10.48	4.31	0.133	conifer	plane bed
F5	Forested	130.09	34.24	1708.56		deciduous	cascade
F6	Forested	202.33	9.89	82.47	0.004	conifer	step pool
F7	Forested	159.75	8.51	97.01	0.005	conifer	pool riffle
F8	Forested	347.56	13.74	16.83	0.043	conifer	pool riffle

Site	Land use	Elevation (m)	Slope (deg)	Drainage area (ha)	Specific discharge (L/s/ha)	Predominant tree type	Stream morphology
F9	Forested	329.12	20.67	2.64	0.022	conifer	cascade
F10	Forested	137.46	12.12	325.90	0.001	deciduous	pool riffle
F11	Forested	49.03	17.41	948.27	0.000	deciduous	step pool
F12	Forested	92.42	15.97	73.96	0.006	deciduous	pool riffle
F13	Forested	108.61	21.81	85.80	0.004	conifer	step pool
F14	Forested	117.91	11.18	5.51	0.021	deciduous	step pool
F15	Forested	117.77	16.36	14.94	0.022	deciduous	step pool
F16	Forested	120.04	13.32	3.62	0.137	deciduous	step pool
F17	Forested	180.29	21.41	2.92	0.019	conifer	cascade
F18	Forested	340.31	7.32	354.40		conifer	plane bed

B.2. Water quality results

Site	Land use	Flow condition	Seasonality	DOC (mg/L)	BIX	FI	HIX	SR	C1	C2	C3	C4
C1	Clear cut	Baseflow	November	2.173	0.66	1.25	2.13	0.82	29.38	13.44	21.57	35.62
C1	Clear cut	Stormflow	November	3.176	0.62	1.20	3.42	0.79	34.23	18.74	22.26	24.77
C1	Clear cut	Baseflow	January	2.002	0.65	1.23	2.50	0.85	31.13	14.31	20.58	33.98
C1	Clear cut	Stormflow	January	2.219	0.63	1.26	3.78	0.89	41.93	20.65	26.33	11.10
C1	Clear cut	Baseflow	March	1.770	0.61	1.26	5.96	0.83	43.08	18.36	29.70	8.86
C1	Clear cut	Stormflow	March	2.038	0.57	1.25	7.29	0.81	46.02	19.57	26.89	7.52
C2	Clear cut	Stormflow	November	2.604	0.57	1.17	7.11	0.88	43.37	23.17	26.22	7.25
C2	Clear cut	Baseflow	January	1.959	0.60	1.20	3.00	1.16	42.73	21.02	24.91	11.35
C2	Clear cut	Stormflow	January	2.154	0.60	1.17	4.49	1.20	42.56	23.45	25.36	8.63
C2	Clear cut	Baseflow	March	1.815	0.59	1.22	6.96	1.04	44.44	19.20	27.50	8.85
C2	Clear cut	Stormflow	March	1.883	0.61	1.21	8.33	0.94	44.24	21.50	27.45	6.80
C3	Clear cut	Baseflow	November	2.608	0.60	1.19	2.99	0.86	34.14	18.31	21.98	25.57
C3	Clear cut	Stormflow	November	3.142	0.60	1.17	3.02	0.85	33.04	18.81	20.03	28.12
C3	Clear cut	Baseflow	January	2.336	0.56	1.20	4.08	0.91	38.77	19.21	22.49	19.54
C3	Clear cut	Stormflow	January	2.907	0.56	1.17	5.32	1.26	43.40	24.69	24.73	7.17
C3	Clear cut	Baseflow	March	2.159	0.59	1.20	6.62	0.94	43.52	19.75	28.46	8.27

Site	Land use	Flow condition	Seasonality	DOC (mg/L)	BIX	FI	HIX	SR	C1	C2	C3	C4
C3	Clear cut	Stormflow	March	2.510	0.56	1.14	7.85	0.88	44.24	22.96	25.89	6.90
C4	Clear cut	Baseflow	November	2.060	0.66	1.23	2.65	0.87	33.28	16.45	22.88	27.39
C4	Clear cut	Stormflow	November	2.561	0.61	1.20	3.15	0.91	35.32	17.66	22.51	24.52
C4	Clear cut	Baseflow	January	1.867	0.58	1.24	4.16	1.19	43.06	19.43	25.77	11.74
C4	Clear cut	Stormflow	January	2.135	0.57	1.16	4.57	0.84	42.17	22.10	26.53	9.20
C4	Clear cut	Baseflow	March	1.734	0.63	1.26	5.11	0.99	39.66	18.14	29.79	12.42
C4	Clear cut	Stormflow	March	1.903	0.59	1.18	7.45	0.80	45.20	20.92	27.11	6.77
C5	Clear cut	Baseflow	November	2.217	0.61	1.18	3.94	0.81	40.50	20.25	25.64	13.62
C5	Clear cut	Stormflow	November	3.365	0.57	1.16	4.14	0.80	39.44	22.58	23.16	14.82
C5	Clear cut	Baseflow	January	2.097	0.58	1.24	4.73	0.84	45.49	21.19	24.58	8.73
C5	Clear cut	Stormflow	January	2.202	0.60	1.17	5.10	0.95	42.51	21.71	25.19	10.59
C5	Clear cut	Baseflow	March	1.763	0.61	1.17	7.61	0.91	45.05	20.48	27.58	6.89
C5	Clear cut	Stormflow	March	1.825	0.59	1.19	7.94	1.03	45.93	21.17	27.42	5.49
C6	Clear cut	Baseflow	November	3.520	0.53	1.07	4.06	0.81	35.19	24.15	18.61	22.06
C6	Clear cut	Stormflow	November	3.887	0.54	1.12	3.46	1.01	34.92	21.28	18.63	25.18
C6	Clear cut	Baseflow	January	2.781	0.50	1.09	5.39	1.01	43.40	28.94	21.90	5.76
C6	Clear cut	Stormflow	January	4.444	0.48	1.06	8.34	0.91	43.88	32.56	20.08	3.48
C6	Clear cut	Baseflow	March	2.504	0.60	1.17	4.71	0.94	36.55	25.64	25.48	12.33

Site	Land use	Flow condition	Seasonality	DOC (mg/L)	BIX	FI	HIX	SR	C1	C2	C3	C4
C6	Clear cut	Stormflow	March	3.389	0.51	1.08	10.37	1.09	45.37	28.66	22.12	3.85
F1	Forested	Baseflow	November	3.436	0.64	1.14	2.04	0.84	26.25	17.74	24.30	31.70
F1	Forested	Stormflow	November	3.714	0.55	1.12	2.80	0.84	31.21	19.92	17.91	30.96
F1	Forested	Baseflow	January	2.748	0.55	1.12	3.65	0.82	35.30	21.25	20.67	22.78
F1	Forested	Stormflow	January	3.550	0.51	1.09	5.81	0.81	43.58	27.77	22.19	6.46
F1	Forested	Baseflow	March	2.741	0.57	1.20	5.72	0.79	42.83	20.80	27.56	8.81
F1	Forested	Stormflow	March	3.350	0.51	1.08	8.93	0.97	44.94	26.37	23.69	5.01
F10	Forested	Baseflow	November	2.794	0.54	1.13	3.41	0.87	34.28	21.05	20.60	24.07
F10	Forested	Stormflow	November	4.046	0.53	1.11	4.37	0.91	38.06	24.20	21.19	16.55
F10	Forested	Baseflow	January	2.469	0.56	1.21	3.62	0.81	39.29	23.30	25.98	11.44
F10	Forested	Stormflow	January	3.820	0.52	1.09	7.45	0.78	43.50	28.42	22.92	5.16
F10	Forested	Baseflow	March	2.048	0.62	1.22	5.09	0.81	40.17	19.19	29.12	11.53
F10	Forested	Stormflow	March	2.727	0.54	1.13	6.97	0.89	43.57	23.52	25.78	7.13
F11	Forested	Baseflow	November	3.877	0.55	1.10	3.88	0.98	37.19	20.98	22.09	19.73
F11	Forested	Stormflow	November	5.747	0.50	1.09	10.43	0.99	45.95	28.74	22.03	3.28
F11	Forested	Baseflow	January	3.162	0.52	1.10	4.87	0.87	44.47	25.26	23.90	6.37
F11	Forested	Stormflow	January	3.594	0.52	1.09	7.27	0.83	45.11	26.00	23.49	5.40
F11	Forested	Baseflow	March	2.939	0.54	1.13	7.89	1.09	46.81	20.92	27.12	5.15

Site	Land use	Flow condition	Seasonality	DOC (mg/L)	BIX	FI	HIX	SR	C1	C2	C3	C4
F11	Forested	Stormflow	March	2.914	0.54	1.13	8.87	1.12	45.67	23.78	25.43	5.12
F12	Forested	Baseflow	November	2.035	0.60	1.19	1.89	0.90	27.14	13.38	19.90	39.59
F12	Forested	Stormflow	November	2.528	0.61	1.17	2.09	1.01	27.95	14.73	18.97	38.34
F12	Forested	Baseflow	January	1.773	0.64	1.18	2.93	1.02	39.10	19.88	26.56	14.46
F12	Forested	Stormflow	January	2.208	0.59	1.14	4.99	0.85	42.19	22.84	26.24	8.73
F12	Forested	Baseflow	March	1.696	0.62	1.22	5.44	0.92	38.64	19.89	29.78	11.68
F12	Forested	Stormflow	March	1.964	0.58	1.18	5.93	0.83	41.84	20.91	27.76	9.49
F13	Forested	Baseflow	November	2.132	0.61	1.14	1.88	0.87	26.46	14.68	18.57	40.30
F13	Forested	Stormflow	November	2.697	0.57	1.13	7.08	0.96	43.06	23.79	26.79	6.36
F13	Forested	Baseflow	January	1.876	0.55	1.23	3.06	0.94	43.00	20.41	23.02	13.57
F13	Forested	Stormflow	January	2.930	0.52	1.07	6.00	1.64	43.27	27.40	23.27	6.05
F13	Forested	Baseflow	March	1.702	0.59	1.18	5.12	1.55	39.41	19.19	29.96	11.44
F13	Forested	Stormflow	March	2.258	0.56	1.14	7.84	1.55	44.41	24.90	24.27	6.42
F14	Forested	Baseflow	November	1.861	0.65	1.23	1.66	1.00	25.80	12.20	19.38	42.63
F14	Forested	Stormflow	November	2.580	0.60	1.21	6.89	0.91	43.01	22.09	27.58	7.32
F14	Forested	Baseflow	January	1.693	0.63	1.28	4.06	1.00	43.45	18.97	27.36	10.21
F14	Forested	Stormflow	January	1.818	0.63	1.22	3.86	1.27	42.40	20.90	26.77	9.92
F14	Forested	Baseflow	March	1.531	0.69	1.32	5.57	1.29	42.16	18.21	32.50	7.13

Site	Land use	Flow condition	Seasonality	DOC (mg/L)	BIX	FI	HIX	SR	C1	C2	C3	C4
F14	Forested	Stormflow	March	1.635	0.64	1.26	7.13	1.09	43.95	19.76	28.26	8.03
F15	Forested	Baseflow	November	2.453	0.61	1.19	2.58	0.95	32.01	15.61	20.34	32.05
F15	Forested	Stormflow	November	3.838	0.58	1.18	3.61	0.80	36.45	19.69	19.50	24.36
F15	Forested	Baseflow	January	2.249	0.56	1.22	5.11	1.21	46.80	22.48	25.17	5.54
F15	Forested	Stormflow	January	2.670	0.57	1.19	7.38	1.00	46.95	24.61	24.93	3.52
F15	Forested	Baseflow	March	1.983	0.61	1.22	8.26	0.96	46.45	19.61	27.92	6.02
F15	Forested	Stormflow	March	2.370	0.59	1.21	9.06	1.19	45.56	23.48	26.19	4.76
F16	Forested	Baseflow	November	1.882	0.65	1.26	2.29	0.99	32.21	14.13	23.93	29.72
F16	Forested	Stormflow	November	2.766	0.58	1.18	8.01	0.83	45.15	22.15	27.18	5.52
F16	Forested	Baseflow	January	1.730	0.62	1.30	3.07	0.87	44.29	18.32	26.43	10.97
F16	Forested	Stormflow	January	1.863	0.60	1.20	4.54	0.83	44.13	20.30	27.46	8.11
F16	Forested	Baseflow	March	1.545	0.66	1.24	5.57	0.82	39.47	18.76	29.97	11.80
F16	Forested	Stormflow	March	1.645	0.59	1.25	5.94	0.90	42.89	20.47	29.15	7.50
F17	Forested	Baseflow	November	2.488	0.58	1.17	2.47	1.15	31.32	16.71	19.03	32.94
F17	Forested	Stormflow	November	2.858	0.57	1.16	7.89	0.80	43.16	23.75	25.89	7.21
F17	Forested	Baseflow	January	2.170	0.55	1.20	4.66	0.98	46.04	23.47	23.84	6.65
F17	Forested	Stormflow	January	2.395	0.55	1.17	5.92	1.10	45.39	25.22	24.35	5.04
F17	Forested	Baseflow	March	1.899	0.58	1.16	7.71	1.25	45.82	21.69	27.34	5.15

Site	Land use	Flow condition	Seasonality	DOC (mg/L)	BIX	FI	HIX	SR	C1	C2	C3	C4
F17	Forested	Stormflow	March	2.018	0.55	1.28	8.50	1.09	48.03	22.43	24.39	5.15
F18	Forested	Baseflow	November	2.816	0.59	1.16	2.47	0.87	31.54	14.30	23.88	30.27
F18	Forested	Stormflow	November	3.003	0.60	1.13	5.36	0.82	38.19	20.47	29.46	11.88
F18	Forested	Baseflow	January	2.641	0.60	1.16	3.89	0.85	41.03	20.50	27.25	11.22
F18	Forested	Stormflow	January	2.816	0.58	1.14	5.18	0.85	42.15	21.86	28.14	7.85
F18	Forested	Baseflow	March	2.527	0.63	1.21	4.97	0.92	40.22	16.01	31.50	12.27
F18	Forested	Stormflow	March	2.568	0.59	1.17	5.69	1.00	41.09	18.45	29.39	11.07
F2	Forested	Baseflow	November	1.505	0.73	1.28	1.07	0.89	18.68	7.37	18.93	55.02
F2	Forested	Stormflow	November	1.989	0.66	1.20	2.36	0.96	31.06	15.63	21.72	31.59
F2	Forested	Baseflow	January	1.425	0.69	1.21	1.86	1.35	39.14	15.08	28.07	17.71
F2	Forested	Stormflow	January	1.424	0.71	1.26	3.11	1.58	40.40	15.91	29.63	14.06
F2	Forested	Baseflow	March	1.386	0.68	1.28	4.70	1.17	41.32	15.26	32.32	11.10
F2	Forested	Stormflow	March	1.345	0.63	1.22	4.81	0.93	40.29	16.74	30.34	12.63
F3	Forested	Baseflow	November	4.072	0.53	1.12	4.60	1.07	37.75	24.13	21.76	16.36
F3	Forested	Stormflow	November	3.358	0.57	1.14	2.81	0.79	31.67	19.95	19.21	29.16
F3	Forested	Baseflow	January	3.417	0.55	1.15	4.70	0.83	38.22	24.01	21.02	16.76
F3	Forested	Stormflow	January	4.976	0.51	1.11	7.85	1.05	43.47	29.50	21.76	5.26
F3	Forested	Baseflow	March	3.685	0.53	1.13	8.35	0.82	44.44	25.39	24.39	5.79

Site	Land use	Flow condition	Seasonality	DOC (mg/L)	BIX	FI	HIX	SR	C1	C2	C3	C4
F3	Forested	Stormflow	March	3.788	0.51	1.10	7.99	0.84	43.67	26.52	23.44	6.37
F4	Forested	Baseflow	November	2.469	0.64	1.17	1.94	1.11	26.82	15.44	19.87	37.88
F4	Forested	Stormflow	November	2.912	0.58	1.14	6.81	0.95	42.19	24.22	25.65	7.94
F4	Forested	Baseflow	January	1.790	0.60	1.25	3.88	1.39	43.27	20.46	27.36	8.91
F4	Forested	Stormflow	January	1.876	0.62	1.22	3.39	2.28	41.87	20.80	26.15	11.18
F4	Forested	Baseflow	March	2.030	0.58	1.19	7.23	1.20	43.40	21.53	27.22	7.85
F4	Forested	Stormflow	March	2.372	0.55	1.18	7.37	1.12	43.93	25.06	24.60	6.41
F5	Forested	Baseflow	November	3.548	0.52	1.09	4.27	2.21	38.94	23.49	21.07	16.50
F5	Forested	Stormflow	November	4.965	0.51	1.08	5.47	0.96	40.17	26.77	18.60	14.47
F5	Forested	Baseflow	January	3.435	0.48	1.06	6.72	1.56	46.13	29.90	19.54	4.43
F5	Forested	Stormflow	January	4.732	0.47	1.05	10.18	2.51	46.73	32.48	18.48	2.31
F5	Forested	Baseflow	March	2.168	0.56	1.12	6.98	1.07	43.61	23.09	26.60	6.70
F5	Forested	Stormflow	March	2.416	0.53	1.13	6.55	1.36	42.08	24.89	24.48	8.55
F6	Forested	Baseflow	November	3.247	0.55	1.10	2.69	0.84	30.58	19.81	18.19	31.43
F6	Forested	Stormflow	November	3.785	0.56	1.09	3.27	0.86	32.92	21.59	18.22	27.27
F6	Forested	Baseflow	January	2.729	0.53	1.10	4.03	0.92	36.72	23.22	19.81	20.24
F6	Forested	Stormflow	January	4.256	0.50	1.06	7.67	0.83	43.52	31.17	21.50	3.81
F6	Forested	Baseflow	March	2.359	0.54	1.11	7.45	1.29	44.34	23.64	24.66	7.36

Site	Land use	Flow condition	Seasonality	DOC (mg/L)	BIX	FI	HIX	SR	C1	C2	C3	C4
F6	Forested	Stormflow	March	3.073	0.53	1.13	9.71	0.82	44.99	27.36	23.48	4.17
F7	Forested	Baseflow	November	3.216	0.53	1.11	3.69	0.90	35.75	21.94	20.90	21.42
F7	Forested	Stormflow	November	4.058	0.55	1.10	3.48	1.18	34.10	21.90	19.26	24.74
F7	Forested	Baseflow	January	2.713	0.52	1.15	6.34	0.80	43.75	26.51	23.46	6.28
F7	Forested	Stormflow	January	4.064	0.52	1.10	6.85	0.78	42.69	28.79	22.98	5.55
F7	Forested	Baseflow	March	2.312	0.56	1.14	7.08	0.83	43.69	22.19	26.60	7.52
F7	Forested	Stormflow	March	3.130	0.53	1.12	7.95	0.94	42.97	26.25	24.51	6.27
F8	Forested	Baseflow	November	2.306	0.61	1.13	2.67	0.84	32.61	19.08	22.48	25.83
F8	Forested	Stormflow	November	2.337	0.59	1.14	2.30	0.83	29.19	17.58	19.93	33.30
F8	Forested	Baseflow	January	1.967	0.53	1.18	4.81	1.07	43.04	23.57	24.09	9.31
F8	Forested	Stormflow	January	2.460	0.54	1.10	4.91	0.98	42.48	26.26	23.30	7.96
F8	Forested	Baseflow	March	1.824	0.60	1.22	4.54	0.89	39.28	18.27	27.36	15.08
F8	Forested	Stormflow	March	2.102	0.53	1.18	7.26	1.20	42.59	23.06	25.04	9.30
F9	Forested	Baseflow	November	2.792	0.56	1.12	3.53	1.33	36.26	21.35	21.65	20.74
F9	Forested	Stormflow	November	3.452	0.57	1.17	4.21	0.83	38.00	21.99	21.11	18.90
F9	Forested	Baseflow	January	2.545	0.51	1.07	4.02	0.84	41.61	28.67	21.82	7.89
F9	Forested	Stormflow	January	3.987	0.50	1.05	7.68	0.84	44.45	31.28	20.72	3.55

Appendix C: GLMM single term deletions for random effects

In addition to LRT comparing GLMM and GLM with fixed effects alone (Table 3.4), we conducted single term deletion tests where random effects were removed from the model one at a time. LRT was used to determine whether removal each variable had a significant effect on model quality. We found no significance for these tests.

Table C.1. Results of single term deletion LRT for random effects for DOC concentration.

Random effects	DOC concentration	
	St. dev.	*p*
Slope	0.08	1
Elevation	0.07	1
Drainage area	0.20	0.19
Specific discharge	0.05	1
Stream morphology	<0.01	1
Vegetation type	<0.01	1

Table C.2. Results of single term deletion LRT for random effects for optical indices.

Random effects	HIX		BIX		FI		SR	
	St. dev.	*p*	St. dev.	*p*	St. dev.	*p*	St. dev.	*p*
Slope	0.15	1	0.02	1	0.03	1	<0.01	1
Elevation	0.01	1	<0.01	1	0.02	1	<0.01	1
Drainage area	<0.01	1	0.03	0.45	0.03	0.50	0.05	0.35
Specific discharge	0.09	1	0.02	1	0.01	1	<0.01	1
Stream morphology	<0.01	1	<0.01	1	<0.01	1	0.05	0.56
Vegetation type	<0.01	1	<0.01	1	<0.01	1	<0.01	1

Table C.3. Standard deviation and p-values from LRT on random effects for PARAFAC components.

Random effects	C1		C2		C3		C4	
	St. dev.	*p*	St. dev.	*p*	St. dev.	*p*	St. dev.	*p*
Slope	0.35	1	1.08	1	0.94	1	0.17	1
Elevation	0.48	1	2.54	1	0.32	1	0.12	1
Drainage area	1.70	0.85	<0.01	1	1.13	0.45	<0.01	1
Specific discharge	1.17	1	0.34	1	0.01	1	0.01	1
Stream morphology	<0.01	1	<0.01	1	<0.01	1	<0.01	1
Vegetation type	<0.01	1	<0.01	1	<0.01	1	<0.01	1