The effects of forest disturbance on dissolved organic carbon in the Algoma region, central Ontario

A Thesis Submitted to the Committee on Graduate Studies in Partial Fulfillment of the Requirements for the Degree of Master of Science in the Faculty of Arts and Science

TRENT UNIVERSITY

Peterborough, Ontario, Canada

Environmental and Life Sciences M.Sc. Graduate Program

May 2024

ABSTRACT

The effects of forest disturbance on dissolved organic carbon in the Algoma region, central Ontario

Matthew G. Watkins

ABSTRACT

Many communities in Canada rely on water sourced from boreal forest headwaters for their drinking water. The Boreal Shield Ecozone is highly susceptible to climate change which threatens to exacerbate the effects of natural and human-driven disturbances such as wildfire, insect infestation and harvesting on water quality. Therefore, examining source water quality in headwater catchments within the Boreal Shield Ecozone is crucial to elucidating the potential implications of these disturbances to water treatment processes in the context of a changing climate. A synoptic water sampling investigation was conducted to evaluate how dissolved organic carbon (DOC) quantity and quality and disinfection by-product formation-potential (DBP-FP) quantity varied across space and time in the Algoma region of central Ontario. Over a five-month timeframe (June 2021 - October 2021), 168 streamflow estimates and 176 water samples were collected across 30 catchments (catchment areas from 0.2 - 106.8 km^2) which varied in their forest disturbance histories.

DOC concentration ([DOC]) ranged from 2.4 - 38.2 mg L^{-1} and tended to be higher in harvest-dominated sites, while no discernible differences in SUVA$_{254}$ were observed between catchment types. DOC export estimates ranged from 1.0 - 63.2 g C m^{-2} over a 141-day period (June 5th - Oct. 23nd, 2021). Fluorescence indices for quantifying

DOC composition suggested that all catchments were dominated by humified and terrestrially sourced carbon. DBP-FP values were positively correlated to UV-254 (r = 0.76 - 0.78) and [DOC] (r = 0.85 - 0.88), such that DBP-FP spatiotemporal patterns were strongly coupled to DOC dynamics.

Multiple linear regression analysis identified that open water was negatively related to [DOC] and $SUVA_{254}$ and explained the most variability in their spatiotemporal patterns. In addition, catchment area, which was negatively related to [DOC] and $SUVA_{254}$, and legacy insect infestation and harvesting disturbance helped improve model explanatory power. Other predictor variables, such as slope, wetland cover, coniferous forest cover and recent forest disturbance (i.e., 5-year harvesting and 5-year insect infestation), showed relatively poor explanatory power. Variability in DOC export estimates may be explained by harvesting disturbance (adjusted r^2 = 0.68 - 0.82). The results of this study emphasise that complex processes across the terrestrial-aquatic continuum, which are influenced by several factors, such as runoff, forest disturbance and landscape heterogeneity, govern the spatiotemporal patterns in water quality across boreal headwaters within the Algoma region.

Keywords: dissolved organic carbon, drinking water supply, forest disturbance, specific ultraviolet absorbance, water quality, disinfection by-products, Boreal Shield Ecozone

ACKNOWLEDGEMENTS

I would like to thank both of my supervisors, Jim Buttle and Jason Leach, for their engaging discussion, constructive criticism, guidance, and immense patience. I always wanted to be on the forefront of geoscience in some capacity and, more importantly, learn how to conduct science well, so thank you both for giving me that opportunity; it has been an amazing experience and I've grown immeasurably in numerous areas. I want to extend thanks to Erik Emilson, my supervisory committee member, for his support, suggestions, feedback and overseeing my data in the Aquatic Ecology lab at the Great Lakes Forestry Centre. In addition, this project would not have been possible without the help of many other great people at the Great Lakes Forestry Centre; namely, Laura Howden, Kara Webster, Kristi Broad, Linda Vogel and Derek Chartrand. Thank you for everything! The field component was daunting and made significantly easier by the likes of Cory, Shelby, and Danielle; I am indebted to each one of you for your hard work, support, and discussion on those long trips out on the frontier. Tom and Mark, I appreciate you guys taking the time to organise and accommodate us during the fall. Thank you to the entire forWater network for the discussion, logistical solutions, meetings, and training; the nationwide, multidisciplinary approach is unique, and I am grateful for being a small part of it. Moreover, the thoroughness and scope of this project stands on the shoulders of the network. Many thanks to Will Fines, Annie Gray, Monica Emelko, Mike Stone, Fariba Amiri, Steven Ngo, Chris Williams and Erin Cherlet. Thank you to everyone at the MNRF for helping me acquire and understand the Ontario forest harvesting dataset. Additionally, thanks to Erika Freeman for parsing out the specific land cover percentages within my catchments, and Cassidy Cameron for initially locating most of the catchments used in this study.

The vast external support network I am lucky to have has been immensely influential during this time. My family, friends, and people I have met along the way have made this journey a rewarding and successful one. Finally, many late nights working on this project (or physical restoration) were accompanied by a plethora of content (e.g., Hardcore History; Dr DisRespect, and SmashWerx) on the second monitor. Thanks for helping me find the strength to maintain and reach the top of the mountain; however, I'm literally only halfway up.

This research was funded by the Canadian Forest Service's Sustainable Forest Management program and the forWater NSERC Network for Forested Drinking Water Source Protection Technologies (NETGP-494312-16), a pan-Canadian interdisciplinary strategic network. Funding that supported this work was also provided by NSERC Discovery Grants to J. Buttle and J. Leach.

- MGW

TABLE OF CONTENTS

ABSTRACT ii
ACKNOWLEDGEMENTS iv
TABLE OF CONTENTS vi
LIST OF FIGURES viii
LIST OF TABLES xii
Chapter 1: Introduction 1
1.1 Drinking water in Canada 1
1.2 Stream DOC response after catchment disturbance in northern forested regions 8
1.3 Research objectives 14
Chapter 2: Study area and methods 16
2.1 Study area 16
2.2 Catchment selection 17
2.3 Field observations 24
2.4 Analysis 32
Chapter 3: Results 41
3.1 Regional temperature and precipitation 41
3.2 Water level and streamflow 43
3.3 Concentration - discharge relationships 45
3.4 [DOC] spatiotemporal variability 47
3.5 Instantaneous DOC flux 56
3.6 DOC export estimates 60
3.7 DOC quality 63
3.8 DBP-FP spatiotemporal variability 68
3.9 Statistical analyses 77
Chapter 4: Discussion 84
4.1 Water level and streamflow 84
4.2 DOC quantity and quality variability 88
4.3 DBP-FP 97
4.4 Uncertainty and errors 98
Chapter 5: Conclusion 104
5.1 Key findings 104
5.2 Implications for clean drinking water 105
5.3 Future work 107
REFERENCES 109

APPENDICES 123

Appendix A – Streamflow and rating curves 123
Appendix B – Statistical analysis 126
Appendix C – DOC quality, DBP-FP and fluorescence indices 130
Appendix D – Technology and instrument usage 134
Appendix E – Ancillary climate data 135

LIST OF FIGURES

Figure 2.1 Study catchments selected for synoptic water sampling and manual discharge estimation in the Algoma region of central Ontario, Canada. Water samples and discharge estimates were taken at catchment outlets near highway crossings (indicated by red circles on inset maps). Note: the clustering of the insect infestation and control catchments.

Figure 2.2 Mean daily discharge recorded at the 'Goulais River near Searchmont' monitoring site (02BF002) operated by the Water Survey of Canada for the 2021 calendar year. The blue-coloured line segment on the hydrograph and the grey rectangle indicates the timeframe (June 5th - Oct. 23rd, 2021) used to estimate DOC export in this study.

Figure 2.3 Environment and Climate Change Canada - Meteorological Service of Canada (ECCC-MSC) climate stations used to collect daily precipitation and temperature data across the Algoma region, central Ontario, Canada.

Figure 2.4 Adapted Hobo U20L logger design from Fogg et al. (2020) installed at H1.

Figure 2.5 Flowchart depicting the analysis pathway taken in this study.

Figure 2.6 Template plot depicting how the various components of the coefficient estimate plot are displayed to provide clarity and aid in interpretation of results. Note that the legend position on the arranged plot (Section 3.9.3) has been moved to the top.

Figure 3.1 Site information and mean temperature and total precipitation from ECCC-MSC climate stations across central Ontario.

Figure 3.2 Daily precipitation at ECCC-MSC climate stations across the Algoma region, central Ontario, Canada.

Figure 3.3 Adjusted water level from four sites (**A**: M2, increase; **B**: C2, decrease; **C**: H2, flashy response; and **D**: C1, flashy response) showing the three distinct streamflow patterns observed in the region. Two examples of flashy response are shown to highlight site to site differences. A discharge estimate was not taken at M2 during late October; therefore, the November date stamp is not shown.

Figure 3.4 Rating curves highlighting the range (good to poor; top left to bottom right) in stage-discharge relationship quality for six sites (M3; H2; M6; C2; M1; and M2). Regression method is indicated by colour: red = non-linear least squares regression; blue = loess fit; black = segmented regression.

Figure 3.5 C - Q relationships in log-log space for 15 sites with high quality discharge estimates across the Algoma region, central Ontario. Regression line is indicated in black.

Figure 3.6 Synoptic sampling results for [DOC] taken from June 2021 - October 2021 over six individual 'sample campaigns' at 30 sites. Boxplot summary here and throughout: the median (middle horizontal line), first and third quartiles (lower and upper hinges), 1.5 times the interquartile range (lower and upper whiskers) and outliers beyond the end of the whiskers (points) are represented with a *.

Figure 3.7 Mean **[**DOC] versus various landscape predictor variables. Catchment area is log km^2.

Figure 3.8 Mean **[**DOC] versus forest disturbance predictor variables.

Figure 3.9 Temporal variability in [DOC] for all 30 sites from June 2021 - Oct. 2021. Missing samples are a result of streams drying up.

Figure 3.10 Temporal variability in [DOC] showing individual boxplots for separate sample campaigns. Outliers are represented with a *.

Figure 3.11 Temporal variability in instantaneous DOC flux for all 30 sites from June 2021 - Oct. 2021. Missing data are a result of streams drying up, negative discharge estimates that were omitted, or discharge measurements not taken on the final sample run due to poor stage-discharge relationships established over the five previous site visits.

Figure 3.12 Temporal variability in instantaneous DOC flux showing individual boxplots for separate sample campaigns for separate sample campaigns. Outliers are represented with a *.

Figure 3.13 Mean instantaneous DOC fluxes versus various landscape predictor variables. Catchment area is log km^2.

Figure 3.14 Mean instantaneous DOC flux versus forest disturbance predictor variables.

Figure 3.15 DOC export estimates for 15 sites between June 6^{th} - Oct. 23^{rd}, 2021.

Figure 3.16 DOC export versus various landscape predictor variables. Catchment area is log km^2.

Figure 3.17 DOC export versus individual forest disturbance predictor variables.

Figure 3.18 $SUVA_{254}$ results from June 2021 - October 2021 over six individual sample campaigns at 30 sites. Outliers are represented with a *.

Figure 3.19 Temporal variability in $SUVA_{254}$ for all 30 sites from June 2021 - Oct. 2021. Missing samples are a result of streams drying up.

Figure 3.20 Temporal variability in $SUVA_{254}$ showing individual boxplots for separate sample campaigns. Outliers are represented with a *.

Figure 3.21 Mean $SUVA_{254}$ versus various landscape predictor variables. Catchment area is log km^2.

Figure 3.22 Mean $SUVA_{254}$ versus forest disturbance predictor variables.

Figure 3.23 [THM-FP] (**A**) and [HAA-FP] (**B**) results from June 2021 - October 2021 over six sample campaigns at eight sites. Outliers are represented with a *. Some [HAA-FP] samples could not be calculated due to low chlorine levels and are, therefore, missing.

Figure 3.24 Temporal variability in [THM-FP] for eight sites from June 2021 - Oct. 2021.

Figure 3.25 Temporal variability in [HAA-FP] for eight sites from June 2021 - Oct. 2021. Some September [HAA-FP] samples (n = 3) could not be calculated due to low chlorine levels and are missing.

Figure 3.26 [THM-FP] (**A**) and [HAA-FP] (**B**) versus DOC concentration at eight sites across the Algoma region.

Figure 3.27 Mean [THM-FP] versus various landscape predictor variables. Catchment area is log km^2.

Figure 3.28 Mean [THM-FP] versus forest disturbance predictor variables.

Figure 3.29 Mean [HAA-FP] versus various landscape predictor variables. Catchment area is log km^2.

Figure 3.30 Mean [HAA-FP] versus forest disturbance predictor variables.

Figure 3.31 Spearman's correlation analysis plot for physical and land cover catchment characteristics.

Figure 3.32 Principal component analysis plot results for the 19 landscape and forest disturbance predictor variables.

Figure 3.33 Coefficient results for [DOC], $SUVA_{254}$, and instantaneous DOC flux. Lines represent 95% confidence intervals.

Figure 3.34 A gap flow dam, as defined by Woo and Waddington (1990), at C11. A lodge can also be seen further up the stream, through the tree line, on the right-hand side.

Figure 3.35 Harvest residue left behind after clearcutting operations near the stream channel at H3.

Figure A1 Stage and corresponding water samples for C1 through H2. Abrupt ends in water level (at C11 and C13) are due to streams drying up and unrecoverable data.

Figure A2 Stage and corresponding water samples for H3 through M6.

Figure A3 Stage and corresponding water samples for sites with high quality stage-discharge relationships (C2 through M6).

Figure A4 Rating curves for C1 through H1.

Figure A5 Rating curves for H3 through M5.

Figure C1 [THM-FP] (**A**) and [HAA-FP] (**B**) versus $SUVA_{254}$ at eight sites across the Algoma region.

Figure C2 $SUVA_{254}$ versus [DOC] for 30 sites across the Algoma region.

Figure C3 Variability in fluorescence index (FI) across each individual study catchment within the Algoma region, central Ontario.

Figure C4 Variability in modified HIX, as per Ohno et al. (2002), across each individual study catchment within the Algoma region, central Ontario.

Figure E1 Boxplots of monthly (May to October) mean air temperature and monthly precipitation recorded at 'Sudbury A' climate station from 1990 to 2013 (monthly data was only available up to 2013). Red circles represent conditions during the 2021 late spring to fall period when the data in this investigation was collected.

Figure E2 Extraction of installed streamflow equipment at I6 on the final fall sample run which occurred from October 23rd - 26th, 2021. Photo taken by Danielle Hudson.

LIST OF TABLES

Table 1.1 Relationship between $SUVA_{254}$ and potential TOC removal (from Table 6, Health Canada, 2019).

Table 1.2 Literature summary of streamflow [DOC] response to forest disturbance in northern forested landscapes. Background colour indicates study type (blue = harvesting; red = wildfire; green = insect infestation). Percent values under "Treatment" column refer to proportion of catchment or basal area affected by a given treatment.

Table 2.1 Summary of physical and land cover catchment characteristics for all 30 sampling sites within the Algoma region.

Table 2.2 Summary of forest disturbance impact (% of catchment area) within each catchment in the Algoma region. Disturbance is broken down by type into 5-year blocks with cumulative percentage of catchment area affected calculated in the 10-, 15-, and 20-year columns. No catchment experienced a wildfire event between 2014 and 2019 so 5-year wildfire is not included.

Table 2.3 Type and quality of data collection for each study catchment.

Table 3.1 Site information and mean temperature and total precipitation from ECCC-MSC climate stations across central Ontario.

Table 3.2 C - Q relationship classification with corresponding *b* and CV_C / CV_Q values for 15 study sites.

Table 3.3 Summary of DOC quantity metrics across all 30 sampling sites in the Algoma region.

Table 3.4 AICc weights and adjusted r^2 values for models fit to mean [DOC] that included various harvest and insect infestation disturbance timeframes.

Table 3.5 AICc weights and adjusted r^2 values for models fit to mean $SUVA_{254}$ that included various harvest and insect infestation disturbance timeframes.

Table 3.6 AICc weights and adjusted r^2 values for models fit to DOC export that included various harvest and insect infestation disturbance timeframes.

Table B1 Spearman's correlation analysis values between catchment characteristic variables and water quality response variables. P-value reported in parentheses.

Table B2 Spearman's correlation analysis values between forest disturbance variables and water quality response variables in disturbed catchments. P-value reported in parentheses.

Table B3 Multiple linear regression models and their corresponding codes.

Table D1 Digital and physical technology used to complete this thesis project.

Chapter 1: Introduction

1.1 Drinking water in Canada

Provision of clean drinking water is a major public health concern in Canada. As such, provincial and territorial governments work with Health Canada to establish basic parameters for every jurisdiction to follow which ensures the safest water supply possible (Health Canada, 2020). Source water in Canada is typically of high quality; however, spatiotemporal variability in water composition often necessitates water treatment (Health Canada, 2020). Conventional methods, such as coagulation, flocculation, sedimentation, and filtration, are commonly used to treat surface water and there are guidelines in place for microbiological, radiological and chemical, and physical constituents (Health Canada, 2020; Crittenden et al., 2012). Numerous factors may influence treatment selection, design, and operation including budget, population, operator skill, finished water quality, and source water quality (Crittenden et al., 2012; Emelko et al., 2011). Consistency in source water quality is particularly important as thresholds exist for key water quality metrics such as turbidity, colour and natural organic matter (NOM; with the dissolved fraction often referred to as dissolved organic matter (DOM)). Exceedance of water quality thresholds predictably leads to greater treatment challenges, such as design and infrastructure modification, which can increase costs (Table 1.1; Crittenden et al., 2012; Emelko et al., 2011). Stable and effective water treatment operations are essential since approximately 66% of Canadians rely on surface water bodies such as lakes and reservoirs for their drinking water supply (Natural Resources Canada, 2023). Moreover, most of this surface water supply originates in forested headwater regions which are the integral providers of source water for human consumption (Natural Resources Canada, 2023).

1.1.1 The Boreal Shield Ecozone: source water and susceptibility to anthropogenic climate forcing and forest management

With over 800,000 km^2 of surface freshwater (Natural Resources Canada, 2019), the Boreal Shield Ecozone is a crucial forested source water region in Canada. Many communities, including numerous First Nations, rely on the Boreal Shield Ecozone for their water supply (Moola and Roth, 2019; Smith, 2015). Much of the headwaters within the Ontario portion of the Great Lakes Basin, which supplies approximately 80% of the province's clean drinking water, drain boreal forest landscapes (Government of Ontario, 2016). The source water provided by the forested headwaters of the Boreal Shield Ecozone is particularly susceptible to future climatic changes and resource demand which threaten to increase land disturbance, affect ecological stability, and impact water quality (Boulanger and Puigdevall, 2021; Price et al., 2013; Emelko et al., 2011; Dale et al., 2001).

Since 1948, annual average temperature has risen by 1.9 °C in Canada, which is nearly twice the global average (Natural Resource Canada, 2023). In addition, mean annual temperatures in the Boreal Shield Ecozone could significantly increase in the future which will likely affect all aspects of ecosystem function (Boulanger et al., 2023; Price et al., 2013). This is particularly concerning as these forests are expected to be less resilient to climatic shifts than other northern forests (Boulanger and Puigdevall, 2021). Large-scale natural disturbances such as wildfire, which are primarily responsible for driving canopy succession in the Boreal Shield Ecozone (Price and Apps, 1995), are already increasing in frequency and severity due to changing climate (Robinne et al., 2020; Coogan et al., 2019; Price et al., 2013). Wildfires are also expected to burn to deeper soil horizon depths which will make fire suppression efforts more challenging (Brandt et al., 2013). Shifts in insect infestation disturbance dynamics are also of concern since they are known to account for a substantial amount of wood volume loss in Canadian forests, with insect infestations affecting approximately 17.8 million ha of forested landscapes in 2020 (Natural Resources Canada, 2022; Volney and Fleming, 2000). Further, increases in regional temperature could see (a) populations of boreal forest insects rise; and (b) changes to insect behavioural dynamics, which could impact the nature of forests and tree mortality (Price et al., 2013). Thus, continuing climate perturbations threaten to exacerbate the effects of forest disturbance in the Boreal Shield Ecozone which poses a major risk to water supply and quality (Robinne et al., 2020; Emelko et al., 2011). In conjunction with industrial harvesting and its associated management activities, which have taken place in the Boreal Shield Ecozone since the early 20th century (Brandt et al., 2013), these forest disturbances have notable effects on the landscape which can significantly affect surface water dynamics. These effects include:

- increased erosion which can lead to higher total suspended solids and turbidity (Emmerton et al., 2015; Emelko et al., 2011; Tremblay et al., 2009).
- changes in fundamental hydrological processes (e.g., interception, transpiration, groundwater fluxes) leading to increased soil moisture and runoff, which, in turn,

can impact streamflow regimes (Bladon et al., 2014; Buttle, 2011; Pike et al., 2010).

- elevated stream nutrient and trace metal concentrations (Webster et al., 2022; Emmerton et al., 2015; Palviainen et al., 2015; de Wit et al., 2014; Tremblay et al., 2009).
- changes to surface vegetation and soil composition which may alter the spatiotemporal dynamics of NOM quantity and quality (Freeman et al., 2023; Kreutzweiser et al., 2008).
- stream temperature changes, particularly in small streams, which may affect aquatic species and riparian microclimate (Moore et al., 2005).
- changes to nutrient cycling processes (e.g., rates of microbial decomposition, mineralisation), which can lead to the release of substantial amounts of NOM into terrestrial and aquatic environments (Kreutzweiser et al., 2008).

Most of these effects have some level of impact on the amount and nature of NOM moving through terrestrial and aquatic systems within the Boreal Shield Ecozone. As such, shifts in NOM concentration and quality threaten to increase the number of operational challenges faced by water managers and put more strain on our water supply (Emelko et al., 2011).

1.1.2 Natural organic matter and its effect on drinking water quality

NOM primarily originates from the degradation of plants in the terrestrial and aquatic environment, and from algae and aquatic microbial exudates (Amon, 2002; Aiken and Cotsaris, 1995; Thurman, 1985). The composition and character of NOM can vary widely as it is continuously altered and transformed by a multitude of environmental processes including exposure to ultraviolet light (i.e., photodegradation), microbial decomposition and chemical fixation (United States Geological Survey, 2023; Vidon et al., 2014; Aiken and Cotsaris, 1995). For example, NOM with a relatively short residence time (e.g., transported from shallow soil layers during stormflow runoff through enriched 'export control points') will have a distinctly different composition than NOM that undergoes sorption and periods of fractionation as it percolates through multiple soil horizons (Figure 1.1; Leonard et al., 2022; Yang et al., 2015; Croué and Leenheer, 2003; McClain et al., 2003; Amon, 2002; Aiken and Cotsaris, 1995). These travel paths generate heterogeneous distributions of NOM within the environment that vary in their hydrologic connectivity to the aquatic environment which leads to fluctuating amounts in stream water (Lintern et al., 2018; Croué and Leenheer, 2003; Aiken and Cotsaris, 1995; Thurman, 1985). Ultimately, NOM is a complex, heterogenous mixture of hydrophobic and hydrophilic particulate, colloidal and dissolved compounds that primarily results from the hydrological pathway taken through the landscape (Amon, 2002; Aiken and Cotsaris, 1995).

Despite its complex nature, NOM is predominantly made up of carbon and efforts have been made to quantify various fractions such as total organic carbon (TOC), dissolved organic carbon (DOC) and particulate organic carbon (POC) (Health Canada, 2019; Croué and Leenheer, 2003; Thurman, 1985). Such measurements of organic carbon are more common than of NOM or DOM because organic matter contains other elements (e.g., oxygen and hydrogen), which complicates quantification (Thurman, 1985). Moreover, quantifying DOC is especially important as it: (1) makes up the predominant fraction of TOC in most source water (Wetzel, 2001), making it a good proxy for NOM; and (2) is the component of NOM that is chemically reactive, thereby causing significant problems for water treatment (Health Canada, 2019; Thurman, 1985).

Operationally, DOC is the fraction of organic carbon in NOM that can pass through a filter of a predefined size (e.g., 0.2 µm, 0.45 µm, or 0.7 µm (Denis et al., 2017)) and is considered a "master water quality variable" that drives aquatic ecosystem function (e.g., protecting biota through UV attenuation and complexing trace metals) (United States Geological Survey, 2023; Zarnetske et al., 2019; Oni et al., 2013; Boggs et al., 1985). DOC can also affect drinking water treatment by creating aesthetic, operational, and indirect health effect issues (Health Canada, 2019; Roulet and Moore, 2006; Edzwald, 1993; Reckhow et al., 1990; Rook, 1976). The humic substance fraction of DOC can alter water colour, while more volatile compounds (i.e., algal metabolites, which number over 200) can deteriorate water taste and produce odour (Health Canada, 2019; Watson 2003). Furthermore, DOC reacts with and consumes chemical additives (i.e., coagulant) during the coagulation process; therefore, waters rich in DOC require elevated coagulant dosages (Table 1.1; Crittenden et al., 2012; Edzwald, 1993). This coagulant amount is also not static since certain components of DOC, such as fulvic acids, require higher dosages of coagulant than others (e.g., humic acids) (Edzwald, 1993). DOC compounds also act as a source of energy for aquatic bacteria which can lead to increases in biofilm production and affect the biological nature of drinking water throughout treatment (Health Canada, 2019). Additional negative impacts occur during the disinfection stage, where DOC reacts with chemical disinfectants, such as chlorine or bromide, to form undesirable disinfection by-products (DBPs) (Reckhow et al., 1990;

Rook, 1976). Therefore, a primary goal of water managers is to control NOM (i.e., reducing NOM concentrations to a low as possible), in order to maximise water treatment effectiveness (Health Canada, 2019).

Recently, DBPs have become a topic of interest due to their proposed mutagenic, carcinogenic and genotoxic characteristics, which have negative implications for human health (Cortés, 2018; Ates et al., 2007; Richardson et al., 2007; McDonald and Komulainen, 2005; World Health Organization, 2004). Numerous DBPs are known to exist (Richardson et al., 2007; World Health Organization, 2004) with trihalomethanes (THMs) and haloacetic acids (HAAs) being the most abundant groups, and much work has been done to elucidate their relationship to the character of NOM in source water since their discovery in the 1970s (Bond et al., 2012; Nokes et al., 1999; Reckhow, Singer and Malcolm, 1990, Rook, 1976). Accordingly, methods evaluating the chemical nature of organic matter, such as ultraviolet absorbance at 254 nm (also called SAC_{254}) and specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), a surrogate measure for the DOC fraction, have become important indicators for aromaticity (i.e., aquatic humic substances), which is strongly linked to DBP formation in a given source water (Bond et al., 2012; Weishaar et al., 2003; Reckhow et al., 1990). Efforts have also been made to shift to alternative water treatment chemicals to inhibit carbonaceous DBPs from forming; however, these alternative chemicals create nitrogenous DBPs, which have been shown to pose even greater health risks (Selbes et al., 2017; Gan et al., 2013). These health risks have led to the regulation of seven DBPs in Canadian drinking water and similar regulation by the World Health Organization and the United States Environmental Protection Agency (Health Canada, 2020; United States Environmental Protection

Agency, 2006; World Health Organization, 2004). Therefore, it is important to better understand the variability in (a) the quantity and quality of DOC; and (b) the conditions (e.g., rainfall, forest disturbance) that lead to changes in the nature and reactivity of DOC since it directly contributes to disinfection byproduct synthesis (Health Canada, 2019; Reckhow et al., 1990).

Table 1.1 Relationship between $SUVA_{254}$ and potential TOC removal (from Table 6, Health Canada, 2019).

SUVA	NOM composition	UV absorbance	Coagulation	Potential TOC removal
<2	Mostly hydrophilic and low molecular weight compounds	Low	NOM has little influence on coagulant dose (i.e., mainly non-coagulable NOM)	0 - 40%; higher end for waters with high TOC
2 - 4	Mixture of hydrophilic and hydrophobic compounds; mixture of molecular weights	Medium	NOM influences coagulant dose	40 - 60%; higher end for waters with high TOC
>4	Mostly hydrophobic and high molecular weight compounds	High	NOM controls coagulant dose	60–80%; higher end for waters with high TOC

1.2 Stream DOC response after catchment disturbance in northern forested regions

Disturbance regimes exert a strong control on water quality in northern forested regions (Carignan and Steedman, 2000). Accordingly, much investigation has been done on the response of stream [DOC] and DOC export after the occurrence of harvesting (usually by clearcut), wildfire and insect infestation (Table 1.2). Studies examining the relationship between forest harvesting and stream [DOC] response have shown mixed results (Freeman et al., 2023; Table 1.2). Numerous studies have found that [DOC] and DOC flux increase significantly shortly after harvest (Aaltonen et al., 2021; Schelker et al., 2012; Laudon et al., 2009; Nieminen, 2004). Conversely, several studies have reported [DOC] decreasing after recent harvest, specifically during baseflow (Mistick and Johnson, 2020), in areas of lower hydrologic connectivity (Erdozain et al., 2020) and in an outflow ditch (Palviainen et al., 2023). Furthermore, others have found increases in [DOC] in harvested areas followed by a decrease (Kreutzweiser et al., 2004), a decrease after harvesting followed by an increase (Webster et al., 2022), or no discernible difference (de Wit et al., 2014).

The response of stream [DOC] in watersheds that have been affected by wildfire is also highly variable (Robinne et al., 2020). Robinne et al. (2020) suggest that the lack of more generalised stream chemistry patterns post-wildfire is, in part, due to differences in the intensity and extent of the wildfire, reporting results, and study site characteristics. Several studies in Alberta, Canada have reported that [DOC] markedly increased in burned and salvaged-logged, and burned catchments post wildfire (Mertens et al., 2019; Emelko et al., 2011), while more subtle increases in [DOC] after recent wildfire activity have been observed in the northern United States (Mast and Clow, 2003; Minshall et al., 2001). Conversely, other investigations have noted post-fire declines in [DOC] (Rodríguez-Cardona et al., 2020; Betts and Jones, 2009). Interestingly, a review of wildfire effects on water quality in forested catchments by Smith et al. (2011) argued that although influxes of carbon into streams within wildfire-affected areas might negatively affect water treatment, [DOC] responses (in the streams and lake studies that were reviewed) were relatively minimal.

Effects of insect infestation on stream [DOC] have received little attention within northern watersheds as, to my knowledge, there is only one documented study in the Boreal Shield Ecozone, which found that spruce budworm defoliation had no effect on

[DOC] but increased aromaticity ($SUVA_{254}$) was observed in boreal and hemiboreal streams (McCaig et al., manuscript in review). Limited research in other regions have reported mixed results. While several studies have reported significant increases in [TOC] and DBP precursors in western catchments affected by mountain pine beetle (Bouillard et al., 2016; Mikkelson et al., 2013), other insect infestation work from the United States has observed stream [DOC] to increase then decrease rather quickly (Lewis and Likens, 2007) or show no significant changes (Clow et al., 2011). Additionally, a study from the Boreal Shield Ecozone that focused on lakes rather than streams found that [DOC] was significantly reduced (-27% on average) in boreal lake waters after their respective watersheds experienced insect defoliator events over a 32-year period (Woodman et al., 2021). It is unclear if this same response to insect infestation occurs in stream [DOC] within this region.

The emergence of climate change and resource-associated development has put increased stress on our forested source water regions (Webster et al., 2015). While this has sparked much investigation into the effects of forest disturbance on water quality, it is evident that more work is required to elucidate and generalise the patterns of stream [DOC] response in harvesting-, wildfire- and insect infestation-affected catchments. For instance, little work has been done investigating how these types of disturbances may affect water quality within the Boreal Shield Ecozone at the landscape scale. Moreover, many boreal catchments experience several types of disturbance of varying extent and timing or repeat disturbance events. A shortcoming of many studies is that they only look at the isolated effects of one disturbance type (Table 1.1) or a single wildfire event (Robinne et al., 2020). In a changing climate where large-scale controls on regional stream [DOC] patterns, such as mean annual temperature (Laudon et al., 2004), disturbance regime (Carignan and Steedman, 2000), and precipitation and subsequent runoff and streamflow (Raymond et al., 2016; Musolff et al., 2015; Tank et al., 2012), are becoming more unpredictable, investigating catchments that have undergone multiple types of disturbance may provide valuable insights into surface water chemistry response (Robinne et al., 2020). Furthermore, most investigations lack DBP-FP sampling which provides insight into the quantity of DBPs that may be formed in treatment facilities from a given source water (Rajamohan et al., 2012). Therefore, further clarification of the terrestrial and aquatic processes that control stream DOC quantity and quality and DBP-FP quantity within disturbed catchments across the boreal landscape is crucial to understand the implications to water supply and quality in a sensitive source water region.

Table 1.2 Literature summary of streamflow [DOC] response to forest disturbance in northern forested landscapes. Background colour indicates study type (blue = harvesting; red = wildfire; green = insect infestation). Percent values under "Treatment" column refer to proportion of catchment or basal area affected by a given treatment.

Location	Forest Type	Treatment	Catchments	Pre-treatment period	Post-treatment period	Sample frequency	Treatment effect	References
Northern Sweden	• Norway spruce • Scots pine • Birch	Clearcut	4 (11 and 320 ha)	2 years	1 year	Every 8 hrs for a total of 21 samples per week	• Increased stream water [DOC]s of up to 50% during early summer • 70% increase in DOC export	Laudon et al., 2009
Northern Sweden	• Norway spruce • Scots pine • Birch	Clearcut (63.7% with no buffer and 88.2% with a discontinuous ~10m buffer)	4 (15.6 - 156.2 ha)	2 years	4 years (2 years post-harvest and 2 years post-site preparation)	2004 - 2006: biweekly (early spring - late fall); monthly (winter)	• Median [DOC] increased by 4.5 mg L^{-1} (after clearcut) and 11.7 mg L^{-1} (after clearcut and site preparation) • Riverine C fluxes increased by 92% (after clearcut) and 195% (after clearcut and site preparation)	Schelker et al., 2012
Southern Norway	Pine- and spruce-dominated	Harvest (cut to length method; 30%)	2 (24 and 83 ha)	7 months	• 11 months (1st period) • 1-3 years (2nd period)	Biweekly / Monthly	No significant treatment effects were observed for TOC concentrations in either post-harvest period	de Wit et al., 2014
Southern Finland	Spruce-dominated	• Clearcut • CCF (continuous cover forest management)	1 (0.04 km^2)	NA	2 years	Not specified	[DOC] was lowest in clearcut and there was no difference in [DOC] between CCF and uncut catchment	Palviainen et al., 2023
Southern Finland	Norway spruce	Clearcut (40%, 40% and 72%)	5 (3.7 - 7.8 ha)	2 years	3 - 4 years	Weekly / Biweekly	• Mean [DOC] increased by 8.4 mg L^{-1}, 9.0 mg L^{-1}, and 22.8 mg L^{-1} during the first four years • Total DOC export increased by 80 kg ha^{-1} and 184 kg ha^{-1} over the first three years at two sites	Nieminen, 2004
Central Scotland	Coniferous	• Forest felling • Forest clearance and construction	2 (1.8 and 3.9 km^2)	Not specified	1 - 2 years	Monthly	Mean [DOC] was greater in the felled catchment than the catchment with wind farm construction	Zheng et al., 2018
Finland	• Norway spruce • Scots pine • Birch	Forest management (supplementary information not available)	30 (7 - 12,150 ha)	Not specified	Not specified	Weekly (spring runoff); biweekly (autumn); monthly (rest of year)	Mean annual TOC concentration and export were significantly higher in managed catchments	Aaltonen et al., 2021
Central Ontario, Canada	• Sugar maple (90%) • Yellow birch (9%) • Various conifers (1%)	• Clearcut (100%) • Selection cut (100%) • Shelterwood (70%)	7 (4.5 - 68.9 ha)	15 years	21 years	Daily during snowmelt and biweekly during the rest of the year	• Stream DOC was below pre-harvest conditions for the first few years post-harvest • Sustained elevated concentrations between four- and nine-years post-harvest	Webster et al., 2022
Central Ontario, Canada	• Sugar maple • Yellow birch	• Diameter limit harvest (89% basal area) • Selection harvest (29% basal area) • Shelterwood (42% basal area)	8 (4.6 - 130 ha)	2 years	3 years	Daily (spring runoff) and weekly or biweekly during the rest of the year	[DOC] increased slightly one year after harvest and declined by two years post-harvest	Kreutzweiser et al., 2004
British Columbia, Canada	Conifer-dominated	Clearcut	2 (6 - 97 ha)	NA	Not specified	High (in-situ measurements every 30 minutes)	Lower [DOC] in the clearcut catchment during baseflow; larger and faster [DOC] response to storms in the clearcut catchment	Mistick and Johnson, 2020
New Brunswick, Canada	• Softwoods (42%) • Softwood-cedar (15%) • Mixedwoods (18%) • Hardwood (25%)	Harvest (clearcut and partial; 18.8% - 49.9%)	14 (50.9 - 176.7 ha)	NA	0 - 5 years	Not specified	[DOC] concentrations were significantly lower at sites with higher hydrological connectivity	Erdozain et al., 2020
Central Siberia	Larch	Wildfire	17 (3.7 - 254.3 km^2)	NA	3 - >100 years	Not specified	Post-fire decline in stream water [DOC] (approximately 50-year recovery time)	Rodríguez-Cardona et al., 2020
Montana, United States	Conifer-dominated	Wildfire (0.4% - 73%)	5	NA	0 - 4 years	Variable (twice weekly - monthly)	Mean DOC slightly higher in burned catchment (1.1 mg L^{-1} to 0.7 mg L^{-1}). Low [DOC]s in general	Mast and Clow, 2003
Idaho, United States	Fir-, and pine-dominated	Wildfire (trace - 91%)	11	NA	0 - 1 year	Single grabs with periods of multiple samples taken within 20-72 hour timeframes	[DOC] higher in burned catchments. Low [DOC] concentrations in general	Minshall et al., 2001
Southern Alberta, Canada	Not specified	• Wildfire (21,000 ha) • Salvage-logging	7 (3.59 - 13.15 km^2)	NA	1 - 4 years	Dataset 1: Variable Dataset 2: High	• Increased median [DOC]s in burned and salvage-logged catchments in the first two years and remained elevated in the third- and fourth-years post-wildfire • 95th percentile [DOC]s were elevated	Emelko et al., 2011

Table 1.2 Continued.

Location	Forest Type	Treatment	Catchments	Pre-treatment period	Post-treatment period	Sample frequency	Treatment effect	References
Southern Alberta, Canada	Not specified	• Wildfire (21,000 ha) • Salvage-logging	7 (3.59 - 13.15 km2)	NA	8 years	Two weeks	[DOC]s were highest in burned and salvage-logged catchments and next highest in burned catchments eight years post-wildfire	Mertens et al., 2019
Alaska, United States	Hardwood-dominated	Wildfire (65%)	4 (5.2 - 10.0 km^2)	2 - 3 years	3 years	Daily	[DOC] declined from 5.7 mg L^{-1} to 5.1 mg L^{-1}	Betts and Jones, 2009
Pennsylvania, United States	Eastern hemlock- and American beech-dominated	Insect defoliation	2 (299 and 450 ha)	~ 1 year	0 - 4 years	Variable	[DOC] concentrations were highest just weeks after defoliation (44-69% and 100-163% greater than pre-treatment concentrations). DOC concentrations were similar to pre-defoliation levels two-three months after defoliation had occurred.	Lewis and Likens, 2007
Colorado, United States	Pine forest	Insect infestation	9	NA	0 - 7 years	Quarterly intervals	Significantly higher TOC and DBP concentrations at facilities using source water from mountain pine beetle affected areas	Mikkelson et al., 2013
Colorado, United States	Pine forest	Insect infestation	14	NA	NA	2 - 6 samples per site across one snowmelt period	No significant changes in streamwater [DOC]	Clow et al., 2011

1.3 Research objectives

The main research objectives for this study were to: (1) examine the spatial and temporal dynamics of DOC quantity and quality and DBP-FP quantity in catchments with complex disturbance histories (i.e., predominantly intermixed harvesting and insect infestation events that varied in extent and timing); and (2) determine which physical, land cover and disturbance characteristics help explain observed patterns of DOC quantity and quality. Multiple working hypotheses (Chamberlin, 1890) were considered for each research objective. For objective 1, expected outcomes were:

- large variability in [DOC] and DOC export across space due to landscape heterogeneity (Health Canada, 2019; Jantze et al., 2015; Oni et al., 2013; Lyon et al., 2012; Dawson et al., 2011; Buffam et al., 2008; Creed et al., 2008, Temnerud and Bishop, 2005; Moore, 2003; Thurman, 1985).
- elevated [DOC] and $SUVA_{254}$ during high flow periods as, typically, more labile DOC tends to be flushed during stormflow (Raymond et al., 2016; Hinton et al., 1997) due to an increase in the water table, which shifts the main flow path from groundwater to more surficial pathways that mobilise different organic matter source pools (Mistick and Johnson, 2020; Creed et al., 2015; Yang et al., 2015).
- elevated [DOC] and DOC export in catchments that have experienced recent (1 - 3 years) harvest events (Table 1.1) due to: (1) soil disturbance; (2) elevated water tables that lead to the saturation of organic rich surficial soil layers coupled with lower evapotranspiration and increased runoff; and (3) increased decomposition and leaching (e.g., harvest residues) associated with increases in forest floor

moisture and temperature (Shah et al., 2022; Schelker et al., 2013; Schelker et al., 2012; Buttle, 2011; Laudon et al., 2009; Kreutzweiser et al., 2008).

- a strong positive correlation between [DOC] and [THM-FP] and [HAA-FP] due to: (1) organic matter in source water being the primary precursor to disinfection by-product formation (Health Canada; Rook, 1974); and (2) strong correlations being observed in numerous studies (Yang et al. 2015; Rajamohan et al., 2012; Engelage et al., 2009; Chow et al., 2007) and forWater network datasets (Monica Emelko, pers. communication).

For objective 2, expected outcomes were:

- lower [DOC] and $SUVA_{254}$ in catchments with upstream lake presence as carbon quality may change through lake passage and significant amounts of organic carbon have been reported to be lost within boreal lakes (i.e., mineralised or outgassed); thereby decreasing [DOC] downstream (Vidon et al., 2014; Larson et al., 2007; Algesten et al., 2004; Molot and Dillon, 1996).
- elevated [DOC] and DOC export in catchments with greater wetland percentage as wetland percentage is perhaps the most important predictor of DOC export up to the regional scale; strong associations between [DOC], DOC export and wetland percentage have been well-documented in several boreal studies (Casson et al., 2019; Creed et al., 2008; Laudon, Köhler, and Buffam, 2004; Dillon and Molot, 1997).

Chapter 2: Study area and methods

2.1 Study area

The study was conducted in the Algoma region of Ontario, Canada which is located within the south-central portion of the Boreal Shield Ecozone. This area marks the transitional boundary between predominantly mixed-forest (Great Lakes - St. Lawrence) to the south and conifer-dominated forest (Boreal) to the north (Rowe, 1972). White and black spruce (*Picea glauca*, *Picea mariana*), jack pine (*Pinus banksiana*) and balsam fir (*Abies balsamea*) are characteristic tree species of the boreal landscape, while eastern hemlock (*Tsuga canadensis*), yellow birch (*Betula alleghaniensis*), sugar maple (*Acer saccharum*), and eastern white and red pines (*Pinus strobus*, *Pinus resinosa*) – along with several other broadleaved and boreal species – characterise the Great Lakes - St. Lawrence forest (Rowe, 1972). Critical drivers of ecosystem dynamics within these forests are disturbances such as insect infestation, disease, wildfire and commercial harvesting (e.g., shelterwood, clear-cut) which often vary in extent, intensity and length (Brandt et al., 2013; Oliver and Larson 1996; Price and Apps 1995).

The region is underlain by an assemblage of Precambrian rocks; primarily east-west striking metasedimentary belts intermixed with gneisses and metavolcanics (Geological Survey of Canada, 1989). Thin tills (usually <4m), of two origins, metavolcanic and Paleozoic carbonate, generally overlie much of the bedrock (Geological Survey of Canada, 1989). Soil parent material is relatively young due to the recent influence of the Laurentide ice sheet during the Pleistocene and much of the Quaternary deposition within the region is glaciofluvial in origin (Geological Survey of Canada, 1989). As such, eskers and moraines are common landforms (Geological Survey of Canada, 1989). Although variations in the intensity of podsolisation are seen across the landscape (Thiffault, 2019), humo-ferric podzols are common under dense canopies while organic-rich soils tend to dominate wetlands (DeAngelis, 2008).

The climate is strongly continental, characterised by a short growing season, cold winters (-20 °C or lower), and warm summers (20 °C or higher) which tend to have higher amounts of rainfall than other seasons (Environment Canada, 2023; Thiffault, 2019; Brandt et al., 2013; DeAngelis, 2008). Climate normals between 1981 and 2010 at multiple Environment Canada meteorological stations (e.g., Wawa, Timmins) suggest a relatively strong west to east precipitation gradient (i.e., ~950 mm near Lake Superior declining to ~800 mm inland) across the region (Environment Canada, 2023). Snowfall accounts for approximately 35% of the annual precipitation in the region (Environment Canada, 2023).

2.2 Catchment selection

Catchments in this study were selected to cover a range of forest disturbance that varied in type, extent, and timing across the Boreal Shield Ecozone. Initially, all streams that crossed under each major highway – Highways 556, 129 and 101 – were located on ArcGIS Pro (version 2.7). Catchments were then delineated using the stream crossing as the outlet and characterised based on terrain properties (e.g., mean elevation) from these locations using the Ontario Flow Assessment Tool. Land cover data (e.g., tree species) were extracted from the Ontario GeoHub (Forest Resources Packaged Products – Version 2) and converted into percentage coverage within each catchment using Python (Erika Freeman, pers. communication; Table 2.1). To capture large heterogeneity in forest disturbance across the region, data dating back to 2000 (i.e., <20 years) were assessed. In addition, this threshold allowed the removal of legacy disturbances (i.e., >20 years), which was not a focus of this study. Harvesting data up to 2019 were obtained through the Ontario's Ministry of Natural Resources and Forestry repository. The 2019/2020 fiscal year of harvesting data was currently undergoing review and was not available during the time of data acquisition (Larry Watkins, pers. communication). Therefore, some of the study catchments may have undergone more recent harvesting events which could not be captured by this investigation. Insect infestation, abiotic (e.g., ice storms, wind damage) and wildfire data were collected from Natural Resources Canada and Ontario GeoHub repositories, respectively (Government of Ontario, 2020; Natural Resources Canada, 2020). The effects of drought, which was another disturbance type included in the abiotic dataset, on streamflow and stream chemistry were not considered as drought impact is estimated to be regional; thus, every study catchment was assumed to experience similar effects (Dale et al., 2001). A forest disease dataset (of predominantly brown spot needle blight of pine and septoria leaf spot and canker) was also examined; however, no events occurred in any of the study catchments over this timeframe. These data were then dissolved and subsequently intersected with catchment boundaries to establish percent area cover of each disturbance type. Individual disturbance events had a corresponding year of occurrence which enabled the creation of unique disturbance histories for each catchment (Table 2.2).

Table 2.1 Summary of physical and land cover catchment characteristics for all 30 sampling sites within the Algoma region.

Catchment ID	Group	Latitude	Longitude	Drainage Area (km²)	Elevation (m a.s.l.)	Slope (°)	Wetland Cover (%)	Open Water (%)	Total Productive Forest (%)	Deciduous Forest (%)	Coniferous Forest (%)
C12	Control	47.9442	-84.3909	106.8	440.3	13.3	3.1	6.1	93.9	56.5	38.1
C6	Control	47.8628	-83.9045	69.3	459.5	4.5	5.9	4.3	89.7	22.3	41.7
C14	Control	47.9912	-84.7646	44.1	339.3	12.2	0.8	17.8	69.4	41.6	56.1
C11	Control	47.9587	-84.3672	39.3	394.9	12.2	4.0	2.9	95.3	55.7	39.8
C5	Control	47.8651	-83.8316	20.5	454.7	3.7	6.9	29.5	61.1	23.7	53.4
C8	Control	47.8958	-84.0497	15.6	465.9	7.8	6.7	3.0	88.2	37.6	39.0
C4	Control	47.8506	-83.7701	13.1	464.8	5.5	3.9	17.3	76.3	41.0	57.1
C13	Control	48.0317	-84.6484	12.8	365.4	8.6	3.7	8.4	86.1	42.6	57.0
C9	Control	47.926	-84.1079	4.6	454.1	7.2	10.1	0.0	88.0	35.1	64.6
C1	Control	47.7486	-83.3875	3.5	455.5	3.3	6.9	9.6	74.9	38.5	14.9
C10	Control	47.9653	-84.3485	1.8	385.3	6.2	3.0	2.4	92.2	57.2	27.7
C2	Control	47.7697	-83.4481	1.5	457.6	4.9	10.3	6.1	82.5	43.8	39.5
C7	Control	47.8627	-83.9047	1.2	449.3	4.5	11.3	5.5	82.6	9.7	30.8
C3	Control	47.7727	-83.4525	0.2	454.8	3.8	0	0	99.4	34.4	42.3
H3	Harvest	47.8059	-83.6341	5.2	473.2	4.6	7.5	0.6	88.2	27.4	72.6
H2	Harvest	47.8084	-83.6291	1.8	483.2	7.2	6.9	0.4	91.9	53.1	46.2
H1	Harvest	46.8176	-83.3279	1.7	455.2	13.1	2.9	1.1	94.0	76.5	19.8
H4	Harvest	47.9423	-84.1805	0.5	427.5	6.3	13.8	0	85.6	39.0	58.4
I6	Infestation	47.4367	-83.2054	65.3	464.9	4.1	3.7	9.5	85.5	49.2	29.8
I2	Infestation	47.127	-83.1423	46.0	477.5	12.1	2.5	7.3	87.4	59.1	10.3
I5	Infestation	47.3853	-83.2007	36.0	482.3	6.0	4.9	3.8	89.7	48.9	40.4
I1	Infestation	46.7571	-83.8506	11.6	393.5	14.3	1.6	3.0	94.9	46.9	28.9
I4	Infestation	47.3524	-83.2099	2.7	459.5	3.6	14.2	4.4	79.9	48.4	31.3
I3	Infestation	47.1577	-83.1542	1.2	469.7	13.1	5.4	0.5	93.6	51.6	13.0
M5	Mixed	47.6937	-83.3088	25.5	461.4	2.0	2.4	1.8	91.2	25.7	53.9
M3	Mixed	47.2757	-83.2036	19.6	514.1	9.9	3.6	1.9	93.2	57.0	10.6
M2	Mixed	46.7965	-83.322	16.0	434.3	14.2	4.2	1.4	92.9	36.3	32.4
M1	Mixed	46.746	-84.1009	14.2	422.6	10.7	4.3	2.1	93.0	52.9	28.4
M4	Mixed	47.5089	-83.2127	9.1	471.2	3.3	2.4	0.7	94.1	45.8	32.7
M6	Mixed	47.9431	-84.1747	2.1	431.0	7.5	0.1	0.8	100.0	36.7	56.6

Selection of treatment catchments was based on several criteria: catchment size, type and extent of disturbance, timing of disturbance, and accessibility. All harvesting was conducted using clearcutting while insect infestations were predominantly Large Aspen Tortrix, Birch Skeletonizer, Bruce Spanworm, Forest Tent Caterpillar and Aspen Twoleaf Tier. Spruce Budworm and Jack Pine Budworm infestations were also present, albeit less frequent in this region. Abiotic events consisted of ice storms and blowdown. To prioritise the effects of recent disturbance on water quality within the region, treatment sites affected by recent (i.e., <5 years) disturbance events were to only be selected; however, this proved limiting and events that occurred within the last 10 years were considered to include more sites of all treatment types. In one case, disturbance within the last 13 years was considered in order to include a mixed-disturbance site affected by wildfire since wildfire occurrence after the year 2000 was rare in the study region. Catchments experiencing greater than 20% disturbance to their catchment area during this time were selected since the hydrochemical effects of forest disturbances are typically assumed to be undetected below this threshold (Wei et al., 2021; Bosch and Hewlett, 1982). Sites were subdivided into harvest-dominated, insect-dominated (herein referred to as insect infestation) and mixed-disturbance groups; two candidate wildfire-dominated sites were removed after field reconnaissance confirmed their inaccessibility. Forest disturbance was broken down into three timeframes: (1) disturbance occurring within the last 5 - 7 years, (2) disturbance occurring between 8 and 10 years ago; and (3) 10 or more years since disturbance. Harvest-dominated classifications were assigned to sites that had experienced harvesting events that exceeded 20% catchment coverage in the 5 - 7 year or the 8 - 10 year timeframe. Insect-infestation classifications were assigned to sites that had experienced insect infestations that exceeded 20% catchment coverage in the 5 - 7 year or the 8 - 10 year timeframe. Mixed-disturbance classification was assigned to sites that had experienced: (1) two different disturbance types that both exceeded 20% catchment coverage in the same timeframe or in different timeframes; or (2) one disturbance type that exceeded 20% catchment coverage and a different disturbance type that exceeded 10% catchment coverage in the same timeframe. Control catchments were those that experienced no more than 5% cumulative disturbance. The only exception to this threshold was C7, which experienced a harvest event in 2002 that affected 9% of its catchment area. This 5% threshold was selected for two reasons: (1) completely undisturbed catchments were rare given the extensive disturbance across the region during this timeframe; and (2) catchments at or below this threshold were assumed to behave like undisturbed catchments (Bosch and Hewlett, 1982). These control catchments were also assumed to be fully recovered from a 2002 Spruce Budworm infestation that had covered the entire study region. Overall, this synoptic approach covered a large geographical extent and captured a variety of disturbance conditions across a wide range of catchment size (0.2 - 106.8 km^2).

Table 2.2 Summary of forest disturbance impact (% of catchment area) within each catchment in the Algoma region. Disturbance is broken down by type into 5-year blocks with cumulative percentage of catchment area affected calculated in the 10-, 15-, and 20-year columns. No catchment experienced a wildfire event between 2014 and 2019 so 5-year wildfire is not included.

Catchment ID	Group	5-year Harvest	5-year Infestation	5-year Abiotic	10-year Wildfire	10-year Harvest	10-year Infestation	10-year Abiotic	15-year Wildfire	15-year Harvest	15-year Infestation	15-year Abiotic	20-year Wildfire	20-year Harvest	20-year Infestation	20-year Abiotic
C9	Control	0	0	0	0	1.2	0	0	0	1.2	0	0	0	1.2	100	0
C4	Control	0.1	0	0	0	0.1	0.5	0	0	0.1	0.5	0	0	1.5	100	0
C14	Control	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0
C13	Control	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0
C10	Control	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0
C11	Control	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0
C12	Control	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0
C7	Control	0	0	0	0	0	0	0	0	0	0	0	0	9.0	100	0
C5	Control	0	0	0	0	0	0	0	0	0	0	0	0	1.3	100	0
C3	Control	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0
C1	Control	0	2.0	0	0	0	2.0	0	0	0	2.0	0	0	0	100	0
C2	Control	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0
C6	Control	0	0	0	0	0	0	0	0	0.4	0	0	0	1.9	100	0
C8	Control	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0
H4	Harvest	52.5	0	0	0	52.5	0	0	0	52.5	0	0	0	52.5	0	0
H3	Harvest	38.3	1.2	0	0	38.3	94.3	0	0	38.3	94.3	0	0	38.3	98.5	0
H1	Harvest	0	0	0	0	23.9	0	0	0	23.9	0	0	0	23.9	0	0
H2	Harvest	21.4	0	0	0	21.4	95.3	0	0	21.4	95.3	0	0	21.4	98.3	0
I5	Infestation	4.4	9.8	1.1	0	7.3	91.9	1.1	0	10.9	91.9	1.1	0	20.2	91.9	1.1
I6	Infestation	3.7	2.5	0.8	0	5.0	57.1	0.8	0	7.3	57.8	0.8	0	14.9	57.8	0.8
I1	Infestation	0	46.3	0	0	1.3	46.3	0	0	15.6	46.3	0	0	24.2	46.3	0
I4	Infestation	0	18.0	0	0	0	100	0	0	0	100	0	0	24.4	100	0
I3	Infestation	0	0	0	0	0	38.6	0	0	0	38.6	0	0	0	38.6	0
I2	Infestation	0	2.7	0	0	0	30.8	0	0	0	30.8	0	0	0	30.8	0
M6	Mixed	32.3	0	0	25.3	32.3	0	0	25.3	32.3	0	0	25.3	32.3	100	0
M1	Mixed	6.1	44.5	0	0	25.1	44.5	0	0	25.1	46.0	0	0	35.9	46.0	0
M3	Mixed	16.1	7.8	4.3	0	16.1	98.5	4.3	0	16.1	98.5	4.3	0	16.1	98.5	4.3
M5	Mixed	1.5	13.8	0.8	0	11.8	32.4	0.8	0	18.5	32.4	0.8	0	20.2	100	0.8
M2	Mixed	0	0	0	0	3.0	2.8	0	23.0	7.9	2.8	0	23.0	21.1	2.8	0
M4	Mixed	0	16.7	23.0	0	0	16.7	23.0	0	10.2	16.7	23.0	0	10.2	16.7	23.0

Sampling sites (n = 30) were primarily located at stream crossings along Highways 556, 129 and 101 between the cities of Sault Ste. Marie, Chapleau, and Wawa (Figure 2.1). Two sites were located 2 km west of Highway 101 on a forest service road. The sites sampled an area of approximately 14,200 km^2 and spanned three Ministry of Northern Development, Mines, Natural Resources and Forestry (NDMNRF) Forest Management Units: Algoma Forest, Northshore Forest and Martel Forest.

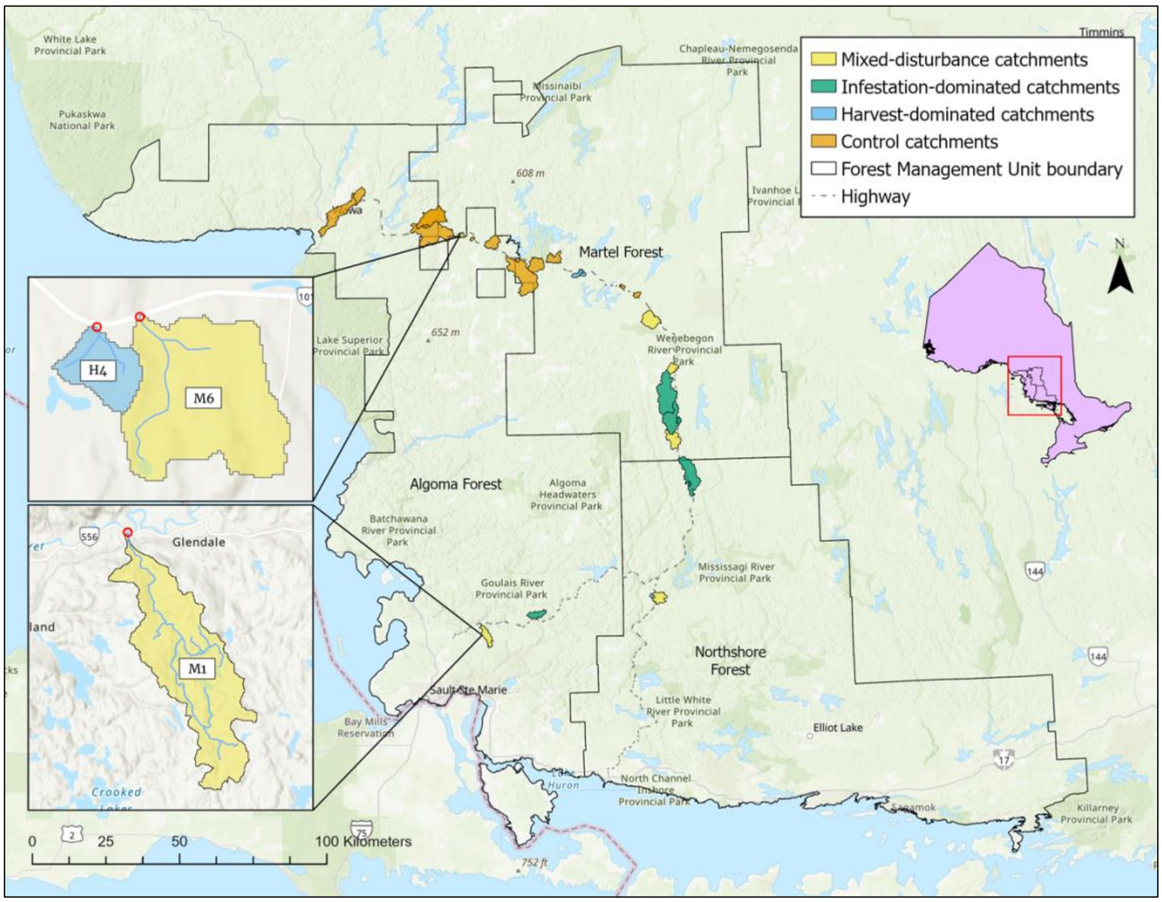

Figure 2.1 Study catchments selected for synoptic water sampling and manual discharge estimation in the Algoma region of central Ontario, Canada. Water samples and discharge estimates were taken at catchment outlets near highway crossings (indicated by red circles on inset maps). Note: the clustering of the insect infestation and control catchments.

2.3 Field observations

Data collection occurred from late May 2021 to late October 2021 (herein referred to as the study period) to capture a range of flow conditions. Suitable areas for manual streamflow measurements and locations for hydrometric instrument installation were identified during site reconnaissance prior to data collection.

2.3.1 Hydrological and meteorological overview

Annual mean discharge data was obtained from the 'Goulais River near Searchmont' monitoring station (02BF002) operated by the Water Survey of Canada for the 2021 calendar year. This station was selected to gain an understanding of hydrological regime within the region and to estimate what percentage of the annual runoff occurred during the study period, which was calculated to be 30% (Figure 2.2). Due to the lack of currently active climate stations within the study region, five nearby stations (Massey, Pukaskwa (AUT), Sault Ste. Marie Airport, Sudbury Climate, and Timmins Climate) were used to characterise air temperature and precipitation conditions during the study period (Figure 2.3).

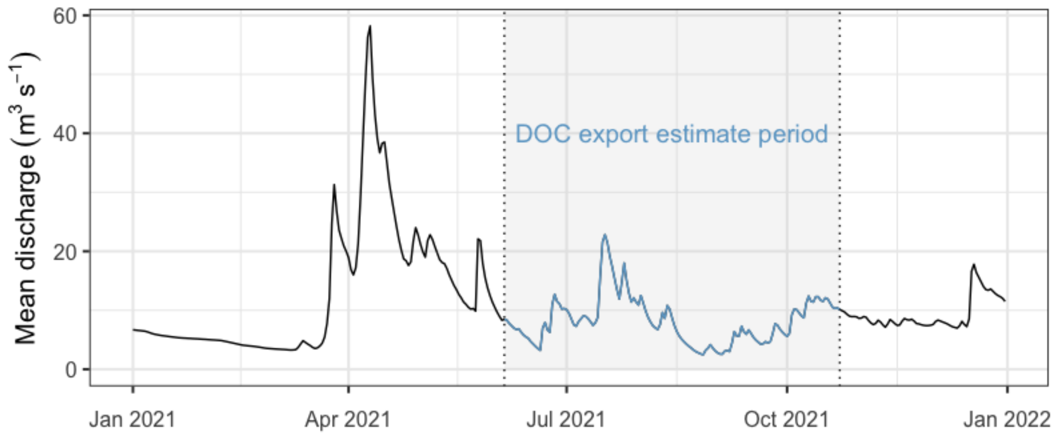

Figure 2.2 Mean daily discharge recorded at the 'Goulais River near Searchmont' monitoring site (02BF002) operated by the Water Survey of Canada for the 2021 calendar year. The blue-coloured line segment on the hydrograph and the grey rectangle indicates the timeframe (June 5th - Oct. 23rd, 2021) used to estimate DOC export in this study.

Figure 2.3 Environment and Climate Change Canada - Meteorological Service of Canada (ECCC-MSC) climate stations used to collect daily precipitation and temperature data across the Algoma region, central Ontario, Canada.

2.3.2 Water level and streamflow

Rebar stakes (1.8 m length) were installed into the streambed at all sites for stage measurements. The height from the top of the rebar to both the bed of the channel and the stream surface was measured at each site using a measuring tape. These measurements were taken concurrently with spot measurements of stream discharge. Unvented Hobo U20L loggers – housed in 20 cm sections of PVC pipe (3.2 cm diameter) and fastened with eye bolts – were secured to each stake with hose clamps and measured water level at 10-minute intervals (Figure 2.4). This adapted design was chosen due to its long-term reliability and low impact on the aquatic ecosystem (Fogg et al., 2020).

Figure 2.4 Adapted Hobo U20L logger design from Fogg et al. (2020) installed at H1.

At nine sites, a second Hobo U20L was secured to the base of a tree near the stream to record barometric pressure in order to correct the unvented stream stage measurements. Unfortunately, there were not enough U20Ls to record barometric pressure at each of the remaining 21 study sites. Therefore, one U20L was installed at a marked, forested location along the highway between two or sometimes three sites within 5 km of each other. In all instances, near-ground, shady locations were selected to minimise sunlight exposure to the sensor; in cases where the overhead canopy was thin, brush and bark were used to shade the logger.

Manual measurements of stream discharge were made 168 times across 26 sites throughout the study period. An average of six measurements were taken at each site, with a maximum of seven and a minimum of two at one site. Measurements could not be made at four sites as stream depth was too deep to gauge safely. Measurements were made on a bi-weekly basis from May to early July and shifted to tri-weekly and monthly measurements from late July to late October. Measurement locations were selected along channel reaches that were: (1) relatively straight and unobstructed; and (2) had high potential for sustained streamflow throughout the field season (Turnipseed and Sauer, 2010). Cross-sectional area of each stream was calculated and mean flow velocity was measured using a SonTek FlowTracker2 or an Ott MF Pro following the area-velocity method (B.C. Ministry of Environment and Climate Change Strategy, 2018; Sanders, 1998). Panel discharge estimates were computed by the equal-area method and summed to obtain total streamflow for each site (Sanders, 1998).

Water pressure was calculated by subtracting barometric pressure from the total pressure measured by in-stream loggers. Subsequently, mean hourly values of water pressure (kPa) were computed by averaging each 10-minute measurement and converted to water depth in metres. Corresponding manual rebar measurements were matched to each site's hourly water depth record by date and time. Since loggers were removed twice for data collection, offsets were made to correct the stage time series. At sites where the rebar was physically moved due to low flows or stream drying, two separate adjusted water levels records were generated.

Stage-discharge relationships were derived from measured streamflow and corresponding hourly mean water depth. Depending on the stage-discharge relationship, loess, non-linear least-squares, or segmented regression models were fit for each site to generate hourly discharge records. Stage data of "high" quality were given to sites that exhibited uninterrupted water levels for the entire study period (Table 2.3). Sites that had missing data (either from low flows or stream drying) were deemed of "partial" quality, and "low" stage quality was assigned to sites where excessive noise was observed in the data rendering it unusable. Continuous discharge estimates from reliable stage-discharge relationships were deemed high quality. Partial discharge quality was assigned to sites that had shown reliable stage-discharge relationships for the period prior to physical relocation of the logger, and low discharge quality was assigned to sites that had hourly estimates generated from poorly developed rating curves.

2.3.3 Water quality

Water samples were manually collected at all 30 sites (concurrent with spot discharge measurements) in triple-rinsed 1 L high-density polyethylene wide mouth bottles. To minimise road influence on water quality, samples were collected at least 25 m upstream of road crossings (United States Geological Survey, 2006). At sites where wading was deemed safe, an effort was made to sample as close to the center of the stream as possible in areas that had well-mixed flow (United States Geological Survey, 2006). Where stream depth and pervasive wetlands prevented wading, samples were taken while positioned at the top of the culvert on the upstream side of the road.

Eight of the sampling sites were selected for additional DBP-FP sampling (Table 2.3). Six disturbed sites (two of each catchment treatment type) were chosen primarily based on differences in forest disturbance extent and timing whereas two control sites were selected based on differences in catchment size and landscape characteristics (e.g., forest type, slope). Since only a limited number of sites could be sampled due to lab analysis costs, an attempt was made for these sites to be distributed throughout the study region and represent a range of conditions (forest disturbance and hydrological) seen across the ecozone.

A portion (20 mL) of each DOC sample was filtered within 48 hours of sampling through 0.7 µm glass fibre filters into scintillation vials and sealed for DOC quality analysis. All samples were transported in coolers with multiple ice packs and subsequently refrigerated overnight. DOC samples were delivered to the Great Lakes Forestry Centre in Sault Ste. Marie and refrigerated until analysis. UV absorbance at 254 nm (m^{-1}) was measured on a Cary 60 UV-Vis spectrophotometer and used to calculate $SUVA_{254}$ by dividing by DOC in mg L^{-1}. Three-dimensional fluorescence scans were run on an Agilent Cary Eclipse at 5 nm excitation steps from 220 to 450 nm, and emissions were read at 2 nm steps from 300 to 600 nm. Spectral corrections and calculation of indices was conducted with the 'staRdom' R package. Two fluorescence indices were calculated: the humification index (HIX; Ohno, 2002) and the fluorescence index (FI; McKnight et al., 2001). DBP-FP samples were sent on ice to the Department of Civil and Environmental Engineering at the University of Waterloo in sealed coolers for subsequent analysis (i.e., [THM-FP] and [HAA-FP] measurements were conducted on a HP 6890 Series Gas Chromotagraph and a TELEDYNE Tekmar Atomx 15-000-1000 following the P&T/GC/MS and LLE/GC/MS methods adapted from US EPA 501.1 and 552.3, respectively).

Table 2.3 Type and quality of data collection for each study catchment.

Catchment ID	Group	Stage Quality	Discharge Quality	DBP-FP Sampling
C14	Control	High	High	No
C12	Control	High	High	Yes
C9	Control	High	High	No
C2	Control	High	High	Yes
C4	Control	High	High	No
C8	Control	High	High	No
C7	Control	Low	Not taken	No
C5	Control	High	Not taken	No
C6	Control	Low	Not taken	No
C11	Control	Partial	Partial	No
C13	Control	Partial	Low	No
C10	Control	High	Low	Yes
C3	Control	High	Low	No
C1	Control	High	Low	No
H3	Harvest	High	Low	No
H2	Harvest	High	Low	No
H4	Harvest	High	Not taken	No
H1	Harvest	High	Low	Yes
I4	Infestation	High	High	No
I3	Infestation	High	High	Yes
I2	Infestation	High	High	No
I1	Infestation	High	Low	Yes
I6	Infestation	High	Low	No
I5	Infestation	High	Low	No
M6	Mixed	High	High	Yes
M5	Mixed	High	High	No
M4	Mixed	High	High	No
M3	Mixed	High	High	No
M1	Mixed	High	Low	Yes
M2	Mixed	High	Low	No

2.4 Analysis

2.4.1 Instantaneous DOC flux and DOC export

For days with manual discharge estimates, instantaneous DOC flux was computed by multiplying the manual discharge estimate and [DOC] from the spot water sample. In addition to the instantaneous flux estimates, a subset of 15 sites had high quality discharge records (Table 2.3) and a minimum of five [DOC] samples, which were used to estimate DOC flux for the period of June 5th to October 23rd, 2021 (i.e., 141 days) which corresponded to the dates with the most overlapping data across the sites. Over this timeframe, DOC export was computed using daily [DOC] estimated by: (1) linear interpolation between sample points; (2) assuming all days had equal concentrations to the maximum [DOC] measured at the site; and (3) assuming all days had concentrations equal to the minimum [DOC] measured at the site. Methods (2) and (3) were used to capture uncertainty in the export estimate. A fourth method, linear regression between discharge and [DOC], was also used; however, poor relationships between daily discharge and [DOC] made flux estimates inaccurate; therefore, this method was excluded. DOC export was standardised by catchment area.

Volume-weighted [DOC]s were compared to unweighted [DOC]s which resulted in a strong correlation ($r = 0.95$); therefore, the main findings from this study should not differ regardless of which method is employed.

2.4.2 Concentration - discharge relationships

Relationships between solute concentration and stream discharge (herein referred to as C - Q) are often used to provide insights into how catchments hydrochemically respond to changes in runoff (McPhail et al., 2023; Godsey et al., 2009). Therefore, preliminary C - Q relationships were determined for 15 sites with high quality discharge estimates to quantify basic response patterns and help elucidate solute transport and delivery mechanisms in previously ungauged catchments across the Boreal Shield Ecozone. [DOC] and instantaneous discharge were log transformed to derive power law relationships which enabled C - Q behaviour to be categorised primarily based on the exponent *b* (McPhail et al., 2023; Bieroza et al., 2018; Creed et al., 2015; Godsey et al., 2009). In addition, the coefficient of variation was calculated for [DOC] (CV_C), and instantaneous discharge (CV_Q) such that the ratio (CV_C/CV_Q) could be utilised as an additional categorisation threshold (McPhail et al., 2023). Accordingly, following Beiroza et al.'s (2018) chemostatic behaviour threshold of $|b| <0.1$ and McPhail et al.'s (2023) additional CV_C/CV_Q ratio stipulations, C - Q relationships were defined as:

1. Chemostatic behaviour when $|b| <0.1$ and $CV_C/CV_Q <0.5$
2. Transport-limited (i.e., flushing) behaviour when $b > 0.1$
3. Source-limited (i.e., dilution) behaviour when $b < -0.1$
4. Chemostochastic behaviour when $|b| <0.1$ and $CV_C/CV_Q >0.5$

2.4.3 Correlation analysis

Exploratory scatterplots were produced to examine relationships between: (1) water quality response variables (mean [DOC], mean instantaneous DOC flux, DOC export, mean $SUVA_{254}$, mean [THM-FP], and mean [HAA-FP]) and predictor variables (physical and land cover catchment characteristics, and forest disturbance timeframes); and (2) mean discharge, CV_C, and CV_C/ CV_Q and catchment area (Figure 2.5). Spearman's correlation analysis was then conducted to determine the direction, strength, and significance of these relationships. Spearman's correlation analysis was selected because: (1) some data violated the assumption of normality; (2) the sample size was small; and (3) it is more robust to outliers than Pearson's correlation coefficient test. The significance threshold used in this analysis was set at $p = 0.05$.

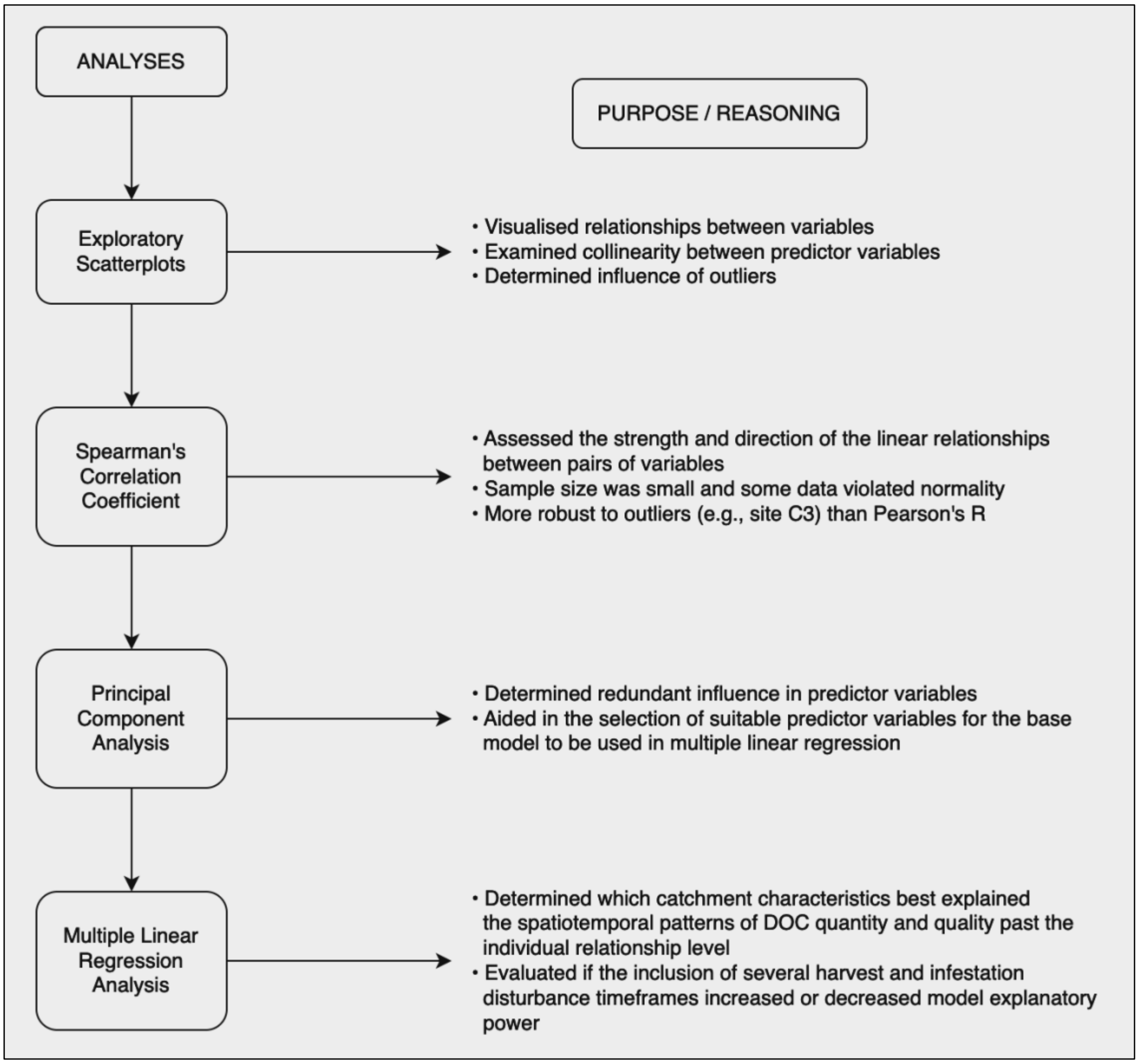

Figure 2.5 Flowchart depicting the analysis pathway taken in this study.

2.4.4 Multiple linear regression analysis

A principal component analysis (PCA) was used (from the 'stats' R package) to assess predictor variable redundancy and helped determine which suite of variables was to be retained in the multiple linear regression analysis (MLRA). Prior to conducting the PCA, several variables were excluded for the following reasons:

- 5-year wildfire disturbance (which had a value of zero for every study catchment).

- 20-year wildfire disturbance (values were identical to 15-year wildfire disturbance).
- Total productive forest % (this variable contained considerable uncertainty and is defined as: "area that has the potential for tree growth which may or may not have timber currently growing as it is dependent on the development stage" (Ministry of Natural Resources, 2009)). As such, it was assumed that coniferous forest % and deciduous forest % were more accurate representations of current forest cover in the region.
- 10-, 15-, and 20-year abiotic disturbance (values were identical to 5-year abiotic disturbance).

MLRA was used to further elucidate if certain landscape characteristics or forest disturbance (either categorical or a specific type and timeframe) had a strong positive or negative relationship with DOC quantity and quality in this study. The goal was to create a 'base model' of predictor variables that: (1) contained several land cover characteristics that were assumed to influence DOC quantity and quality in northern headwaters; (2) minimised multicollinearity; and (3) to a reasonable degree, followed the other statistical assumptions of multiple regression such as normally distributed data, linearity, and no outliers (Uyanuk and Güler, 2013; Tabachrick and Fidell, 1996). Ultimately, five predictor variables were retained for the MLRA. Predictor variables were standardised using the *z-score* function (from the 'mosaic' R package) for efficient plotting and comparison.

Stream networks within boreal forest landscapes tend to have elevated [DOC] and DOC export in catchments with a significant percentage of wetlands; therefore, the sum of open and treed wetlands was retained as **wetland cover (%)** (Creed et al., 2003; Laudon et al., 2003; Dillon and Molot, 1997). Previous work has also shown that forest coverage (and even specific forest types (Freeman et al., 2023)) can influence DOC quality (Piirso et al., 2012). Moreover, dense coniferous coverage can result in acidic, organic-rich soils (Buffam et al., 2008). Therefore, **coniferous forest cover (%)**, which showed stronger simple linear relationships to mean [DOC] and DOC export than deciduous forest cover, was retained. **Slope (°)** was retained as it exerts an important influence on particulate and dissolved solute mobilisation and delivery into stream networks (Lintern et al., 2018). In addition, topographic characteristics such as slope tend to be particularly important influences on stream water solute concentrations during dry periods, which was a focus in this study (Lintern et al., 2018). **Catchment area (km^2)** was included as heterogeneity in hydrology across space can significantly influence solute delivery (Lintern et al., 2018). **Open water (%)** was retained due to its strong influence on DOC quantity and quality, which was addressed in Section 1.3. Open water includes lakes, ponds, reservoirs and wide rivers (Ministry of Natural Resources, 2009). Rivers > 10 m in width are defined as wide rivers and mapped as polygons, whereas rivers < 10 m in width are mapped as linear features (Ministry of Natural Resources, 2009). Accordingly, only certain channel sections of C12 would be considered a wide river. Therefore, nearly the entire percentage of open water calculated in this study is in the form of lakes.

Excluded predictor variables included **deciduous forest %** as it showed weaker relationships with mean [DOC] and DOC export than coniferous forest %, while also being collinear with slope and negatively related to coniferous forest %; **latitude (DD)** due to collinearity with coniferous forest % and, to a lesser degree, collinearity with elevation; **longitude (DD)** since collinearity was observed with elevation and, to a lesser degree, coniferous forest %; **elevation (m a.s.l.)** as the catchments had a small range (~150 m) in relief which was assumed to not significantly influence hydrological processes; and many **forest disturbance timeframes**, such as 5-year wildfire and 20-year infestation, due to: (1) the strong influence of single events; (2) zero catchment coverage at many sites for these timeframes; or (3) negligible differences in disturbance percentage with other timeframes.

The base model was run on each individual sampling campaign (SC) for [DOC], $SUVA_{254}$, and instantaneous DOC flux. In addition, the base model was also run on mean [DOC], mean $SUVA_{254}$ and DOC export computed for the full study period. Due to low sample numbers, there was not enough statistical power to run the base model on either [THM-FP] or [HAA-FP]. C3 was removed from the MLRA as it contained many anomalous (i.e., high) [DOC] values, which had a strong influence on the modelling results.

Numerous model variations (i.e., the base model with various forest disturbance timeframes) were also fit to mean [DOC], mean $SUVA_{254}$ and DOC export to determine if recent and legacy insect infestation and harvest disturbance increased explanatory power. A full list of models (including the base model, their variables and corresponding codes) is included in Table B3 (Appendix B). Akaike's information criterion (AIC) was used to determine if any of the model variations better explained the variability in the spatiotemporal patterns of mean [DOC], mean $SUVA_{254}$, and DOC export relative to the base model (Burnham and Anderson, 2004). Models were ranked by AICc, a second-order bias correction that is a refinement of AIC for small sample data, and weights of the model variations were compared to the weight of the base model to determine if improvements, no changes or worsening in explanatory power occurred (Burnham and Anderson, 2004; Section 3.9.3.2).

2.4.4.1 Coefficient estimate plot overview

MLRA results were displayed in a multiple plot format that indicated each response variable on the top of their respective plot, each predictor variable individually listed on the y-axis, and the coefficient estimate (spanning a numerical range) on the x-axis. Each SC (i.e., 1 through 6), as well as the mean across all SCs, was represented by an individual dot and line combination which corresponded to a unique colour indicated on the legend at the top of each arranged plot. An example plot (Figure 2.6), shown at the bottom of this section, was created for clarity purposes. It is important to understand that:

1. A point to the right of zero (on the x-axis) indicates a **positive** relationship and a point to the left of zero indicates a **negative** relationship.
2. The further a point is away from zero in either direction, the **stronger** the relationship is.
3. When the solid line attached to each SC's coefficient estimate **does not cross zero,** the estimate is significantly different from 0 at $p = 0.05$. Conversely, when the solid line attached to each SC's coefficient estimate **does cross zero**, the estimate is not significantly different from 0.

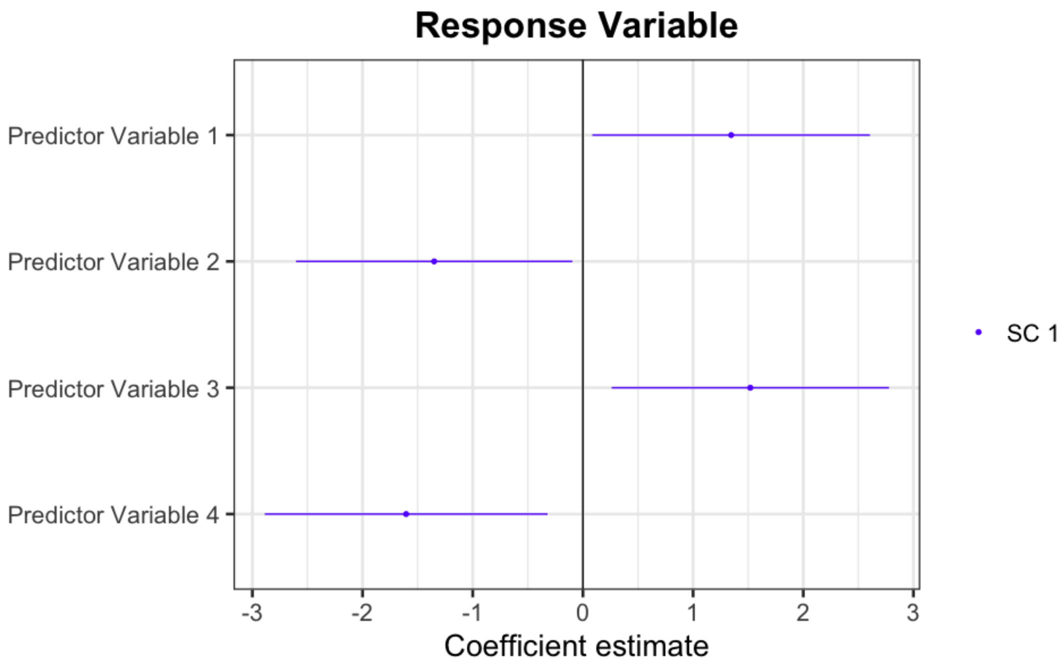

Figure 2.6 Template plot depicting how the various components of the coefficient estimate plot are displayed to provide clarity and aid in interpretation of results. Note that the legend position on the arranged plot (Section 3.9.3) has been moved to the top.

Chapter 3: Results

3.1 Regional temperature and precipitation

Mean air temperature ranged from 12.7 - 15.7 °C and total precipitation ranged from 393.3 - 568.4 mm over the duration of the study period (Table 3.1). Temperatures generally peaked in June (apart from Sault Ste. Marie Airport, where temperatures peaked in August) and were lowest in late October (Figure 3.1). Temperatures in October were anomalously high relative to historical averages (Appendix E). Daily precipitation ranged from 0 - 55.4 mm (Massey) and the highest daily precipitation amounts were generally seen from June - August (Figure 3.2). Breaks in the mean daily air temperature graph indicate days with missing data. Historical climate data (i.e., average monthly air temperature and precipitation) is documented in Appendix E.

Table 3.1 Site information and mean temperature and total precipitation from ECCC-MSC climate stations across central Ontario.

Station name	Elevation (m asl)	Latitude (DD)	Longitude (DD)	Mean air temperature (°C)	Total precipitation (mm)
Pukaskwa (AUT)	191.5	48.61	-86.29	12.7	393.3
Sault Ste. Marie Airport	187	46.48	-84.52	14.9	506.9
Massey	200	46.19	-82.02	15.7	568.4
Timmins Climate	294.4	48.56	-81.39	13.6	442.9
Sudbury Climate	348	46.63	-80.79	15.0	546.4

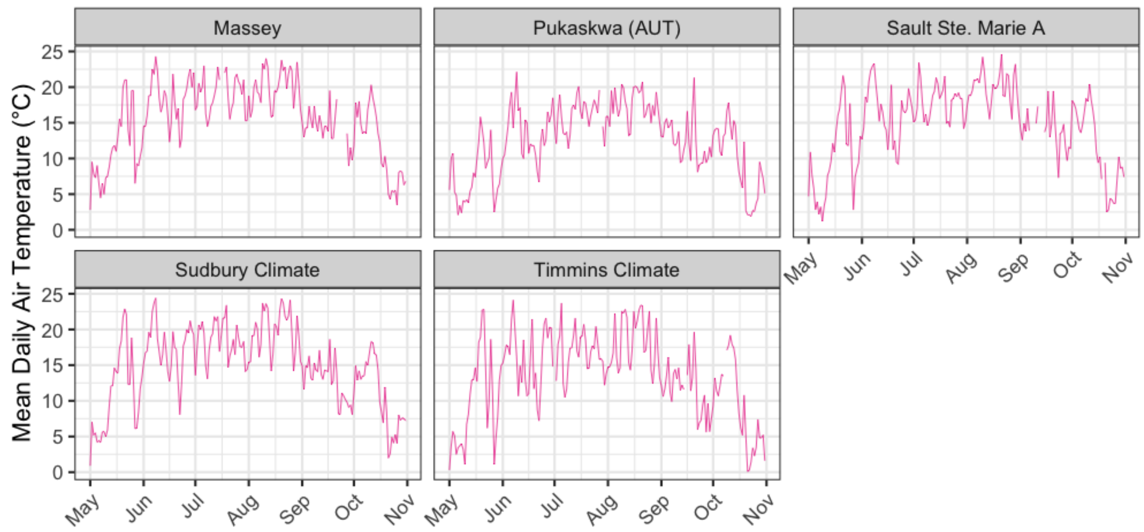

Figure 3.1 Mean daily temperature at ECCC-MSC climate stations across the Algoma region, central Ontario, Canada.

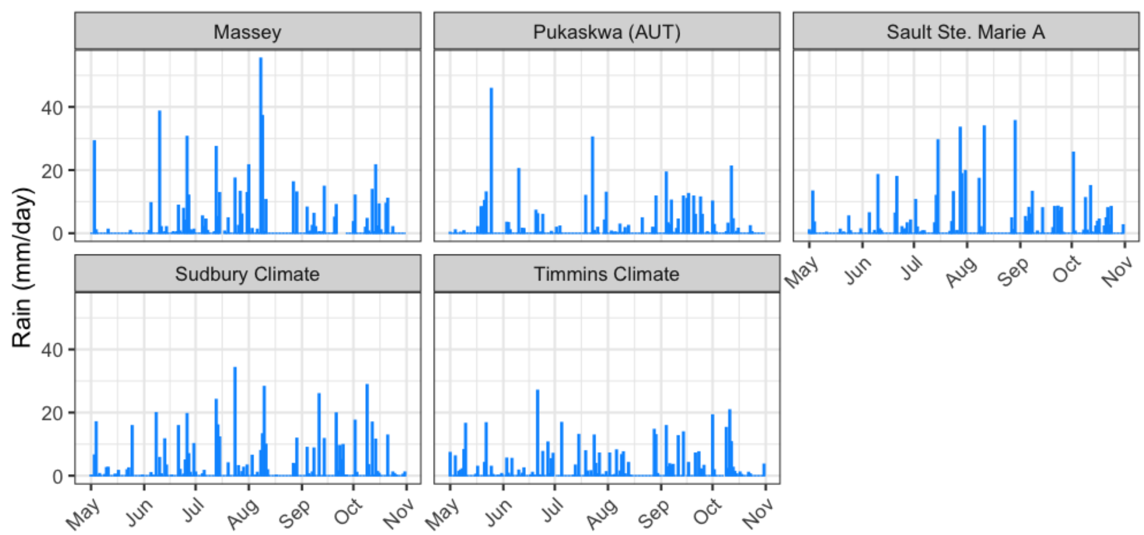

Figure 3.2 Daily precipitation at ECCC-MSC climate stations across the Algoma region, Ontario, Canada.

3.2 Water level and streamflow

Study catchments exhibited one of three general streamflow regimes: (1) overall increases in water level likely associated with increases in discharge (Q) during the study period; (2) overall decreases in water level likely associated with decreases in Q during the study period; and (3) flashy regimes associated with precipitation events (Figure 3.4; Appendix A). Four streams displayed increases in water level over time, while four other streams showed general decreases in water level over that same period. Most catchments that were monitored in the study behaved in a relatively flashy nature. Unfortunately, streamflow regimes could not be determined at C6 and C7, due to a lake effect caused by a partially intact beaver dam, and C13 as it dried up in mid-July.

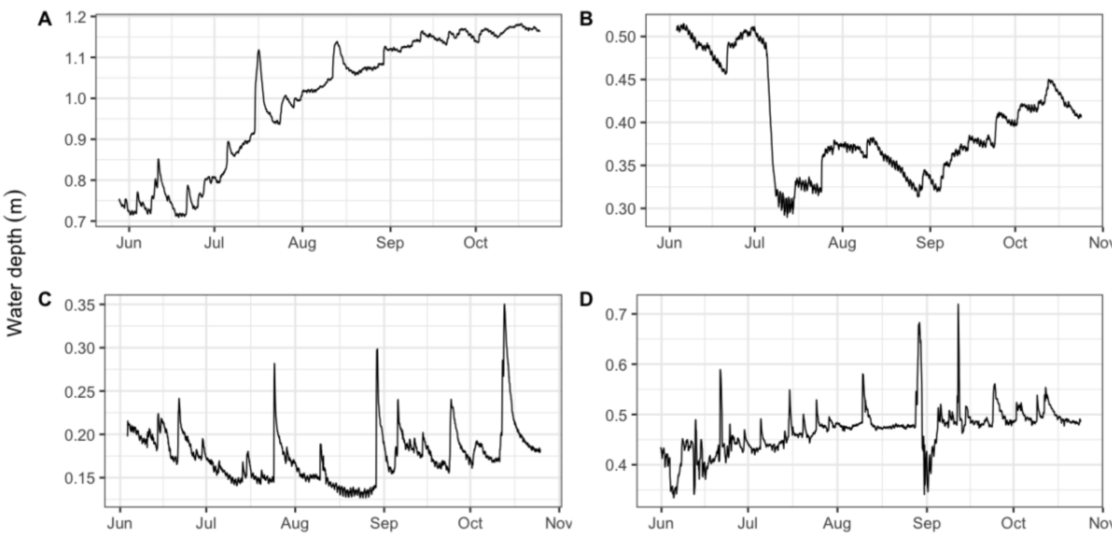

Figure 3.3 Adjusted water level from four sites (**A**: M2, increase; **B**: C2, decrease; **C**: H2, flashy response; and **D**: C1, flashy response) showing the three distinct streamflow patterns observed in the region. Two examples of flashy response are shown to highlight site to site differences. A discharge estimate was not taken at M2 during late October; therefore, the November date stamp is not shown.

For the 26 catchments where streamflow was measured, the lowest and highest streamflow estimates were 0.1 and 1511 L s^{-1} at C8 and C13, respectively. Four negative measurements were observed, likely due to mud and vegetation interfering with the instrument sensor, and were omitted. Fifteen sites were deemed to have high quality discharge estimates (i.e., a well-defined rating curve relationship), 10 sites were deemed to have low quality discharge estimates (i.e., unreliable rating curves) and one site had partial high quality discharge estimates as the logger location was changed (due to low flows) resulting in some unrecoverable data.

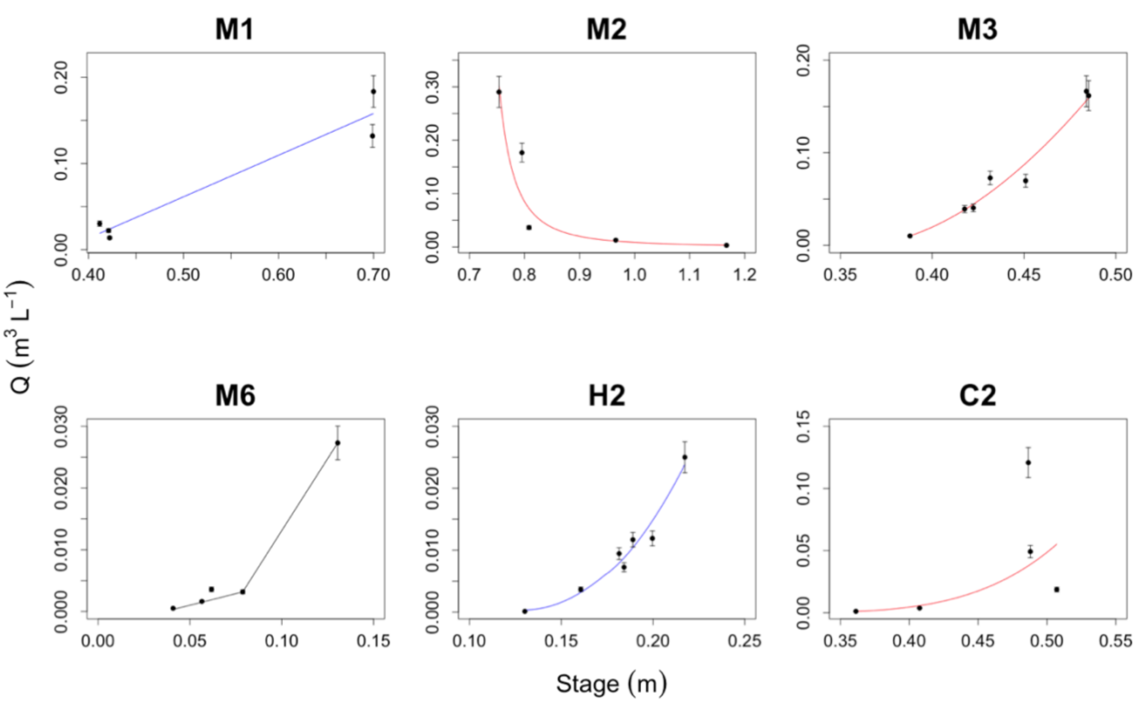

Figure 3.4 Rating curves highlighting the range in stage-discharge relationship quality across six sites. Regression method is indicated by colour: red = non-linear least squares regression; blue = loess fit; black = segmented regression.

3.3 Concentration - discharge relationships

Across the study region, chemostatic, transport-limited, and chemostochastic C - Q behaviour was observed coupled with relatively wide ranges in values for *b* and CV_C / CV_Q ratios, respectively (Table 3.2; Figure 3.5). Chemostatic (47% of sites) and transport-limited (40% of sites) were the most common patterns of solute behaviour, whereas chemostochastic behaviour was restricted to one site, M6. No sites displayed source-limited behaviour. Disturbed sites showed the greatest proportion of chemostatic behaviour, while control sites favoured transport-limited behaviour. Transport-limited sites tended to have greater variability in C relative to Q, whereas lower variability in C relative to Q was seen at chemostatic sites.

Table 3.2 C - Q relationship classification with corresponding *b* and CV_C / CV_Q values for 15 study sites.

Catchment ID	*b*	CV_C / CV_Q	C - Q Behaviour
C2	-0.001	0.026	Chemostatic
C4	-0.027	0.065	Chemostatic
H3	0.08	0.16	Chemostatic
I3	0.061	0.21	Chemostatic
I4	0.078	0.28	Chemostatic
M3	0.056	0.22	Chemostatic
M5	0.047	0.15	Chemostatic
M4	0.007	0.69	Chemostochastic
I2	Could not determine	0.22	N/A
C8	0.33	0.71	Transport-limited
C9	0.35	0.46	Transport-limited
C12	0.3	0.53	Transport-limited
C14	0.2	0.47	Transport-limited
H2	0.25	0.37	Transport-limited
M6	0.27	0.34	Transport-limited

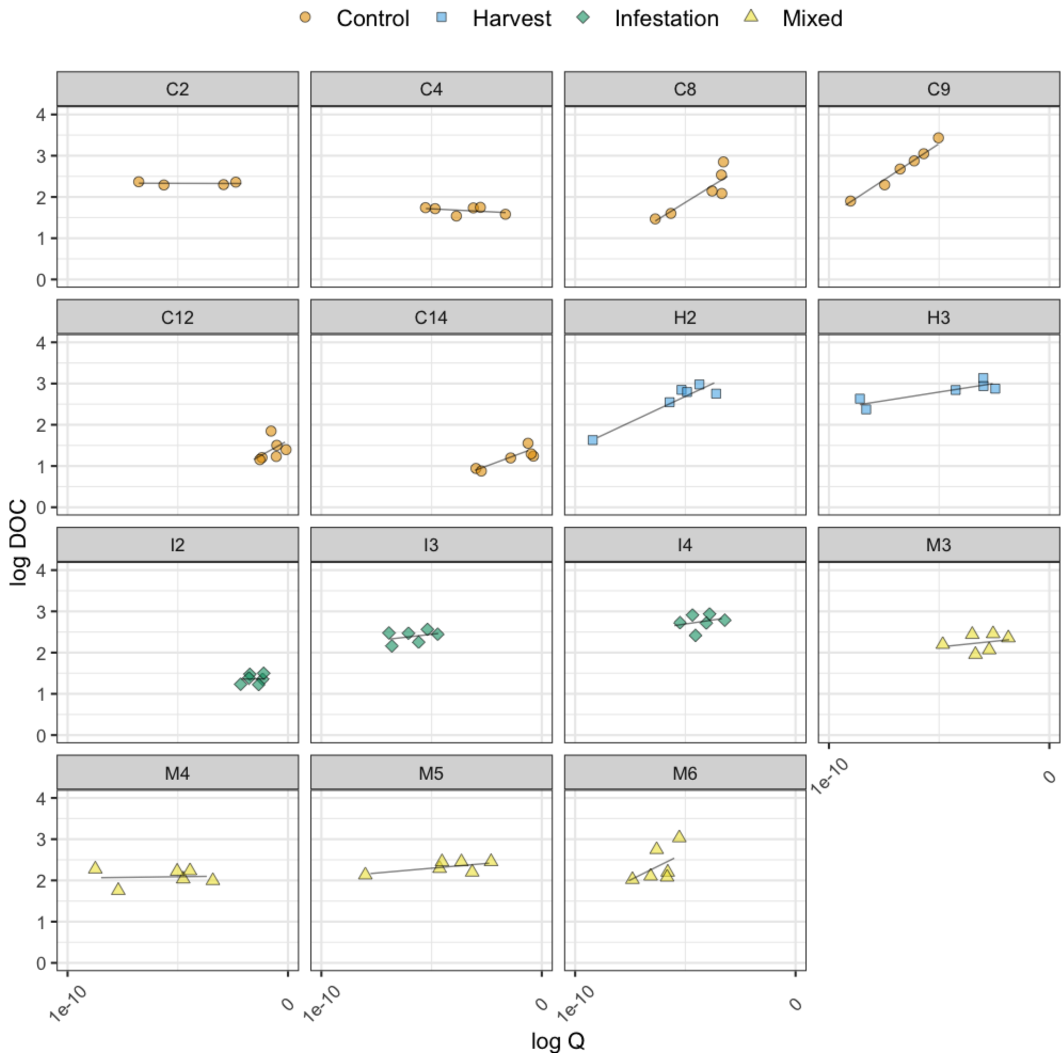

Figure 3.5 C - Q relationships in log-log space for 15 sites with high quality discharge estimates across the Algoma region, central Ontario. Regression line is indicated in black.

3.4 [DOC] spatiotemporal variability

DOC concentration measured across all sites during the five-month study period ranged between 2.4 and 38.2 mg L^{-1} (Figure 3.6). The highest [DOC]s were observed at the smallest (0.2 km^2) catchment, (C3; n = 6, mean = 27.7 mg L^{-1}) while the lowest [DOC]s were recorded at C14 (n = 6, mean = 3.4 mg L^{-1}). The greatest range in [DOC] was observed at C9 (n = 6, sd = 8.7 mg L^{-1}), and the lowest range in [DOC] was observed at C2 (n = 6, sd = 0.4 mg L^{-1}) (Table 3.3).

Table 3.3 Summary of DOC quantity metrics across all 30 sampling sites in the Algoma region.

Catchment ID	Group	*n*	Mean DOC (mg L^{-1})	Standard Deviation (mg L^{-1})	Coefficient of Variation
C3	Control	6	27.7	7.4	0.3
C9	Control	6	16.8	8.7	0.5
C10	Control	5	14.3	2.0	0.1
C2	Control	6	10.3	0.4	0
C8	Control	6	9.3	4.9	0.5
C7	Control	6	7.4	3.1	0.4
C6	Control	6	7.4	3.4	0.5
C5	Control	5	6.8	3.7	0.5
C4	Control	6	5.4	0.5	0.1
C13	Control	3	5.1	1.0	0.2
C11	Control	6	5.1	1.0	0.2
C12	Control	6	4.1	1.2	0.3
C1	Control	6	3.6	1.2	0.3
C14	Control	6	3.4	0.8	0.2
H3	Harvest	6	18.1	3.3	0.2
H2	Harvest	6	14.5	5.1	0.4
H1	Harvest	6	13.7	1.5	0.1
H4	Harvest	6	6.1	1.1	0.2
I4	Infestation	6	15.8	2.8	0.2
I5	Infestation	6	14.6	2.0	0.1
I3	Infestation	6	11.1	1.6	0.1
I6	Infestation	6	6.6	0.5	0.1
I1	Infestation	6	5.1	2.1	0.4
I2	Infestation	6	3.9	0.5	0.1
M6	Mixed	6	11.5	5.4	0.5
M5	Mixed	6	10.4	1.4	0.2
M3	Mixed	6	9.6	1.9	0.2
M4	Mixed	6	8.2	1.5	0.2
M2	Mixed	6	8.2	1.3	0.2
M1	Mixed	6	7.5	1.5	0.2

[DOC] in control catchments ranged from 2.4 to 38.2 mg L^{-1} (n = 80, mean = 9.1 mg L^{-1}); 5.1 to 22.9 mg L^{-1} (n = 24, mean = 12.8 mg L^{-1}) in harvest-dominated catchments; 2.9 to 18.8 mg L^{-1} (n = 36, mean = 9.5 mg L^{-1}) in insect infestation-dominated catchments; and 5.8 to 20.7 mg L^{-1} in mixed-disturbance catchments (n = 36, mean = 9.2 mg L^{-1}). Mean and median [DOC] were higher in harvest-dominated catchments relative to the other three catchment types, whose mean and median [DOC] values were relatively similar.

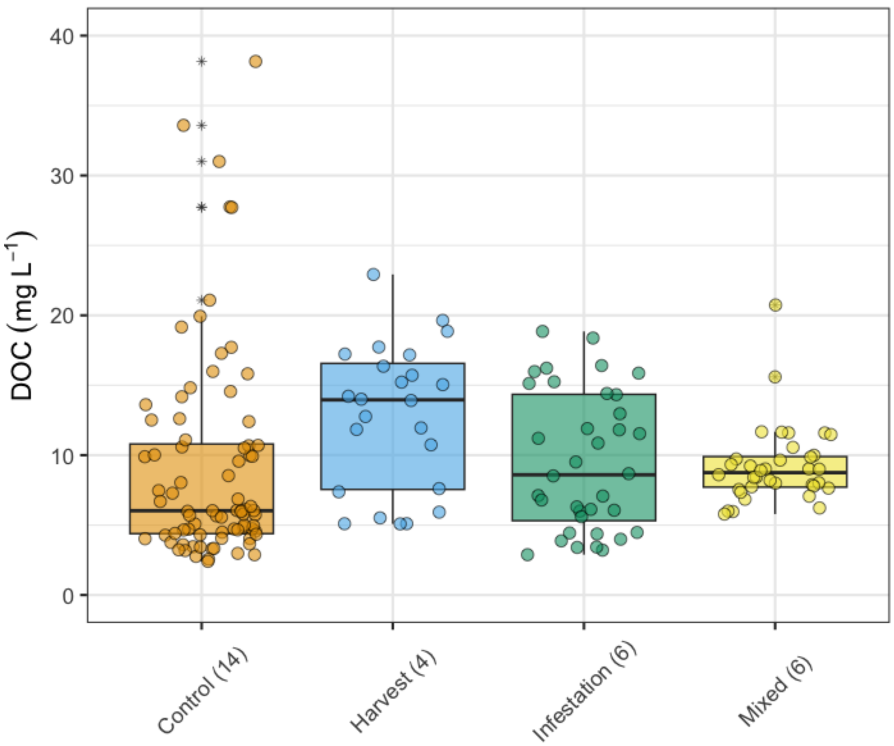

Figure 3.6 Synoptic sampling results for [DOC] taken from June 2021 - October 2021 over six individual 'sample campaigns' at 30 sites. Boxplot summary here and throughout: the median (middle horizontal line), first and third quartiles (lower and upper hinges), 1.5 times the interquartile range (lower and upper whiskers) and outliers beyond the end of the whiskers (points) are represented with a *.

Mean [DOC] had significant positive correlations with elevation ($r = 0.35$; $p < 0.001$), and longitude ($r = 0.31$; $p < 0.001$). Conversely, mean [DOC] had significant negative correlations with catchment area ($r = -0.47$; $p < 0.001$), open water % ($r = -0.45$; $p < 0.001$) and slope ($r = -0.28$; $p < 0.001$).

In disturbed catchments, mean [DOC] had a significant positive correlation ($r = 0.51$, $p = 0.05$) with 20-year insect infestation % (Figure 3.8). All other correlations between mean [DOC] and forest disturbance predictor variables were not significant (Appendix B).

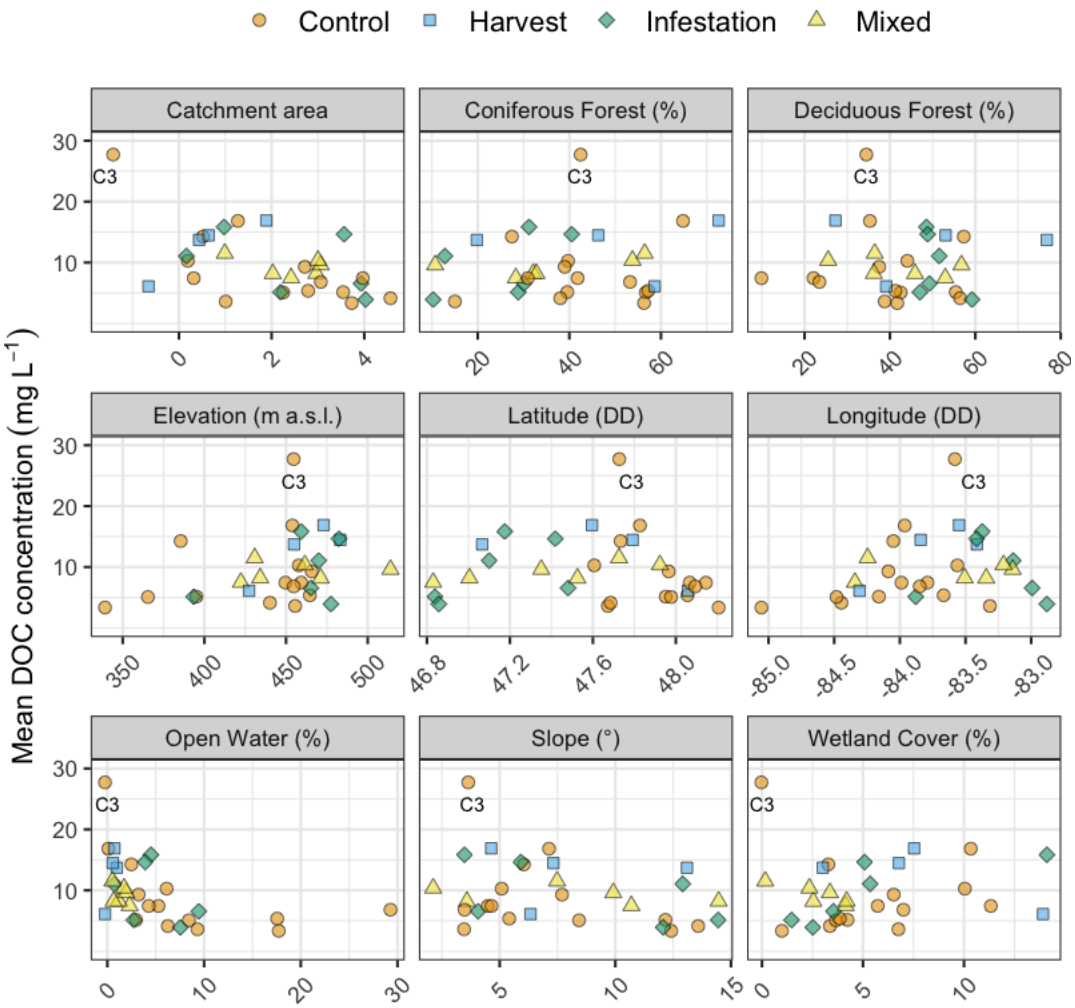

Figure 3.7 Mean [DOC] versus various landscape predictor variables. Catchment area is log km^2.

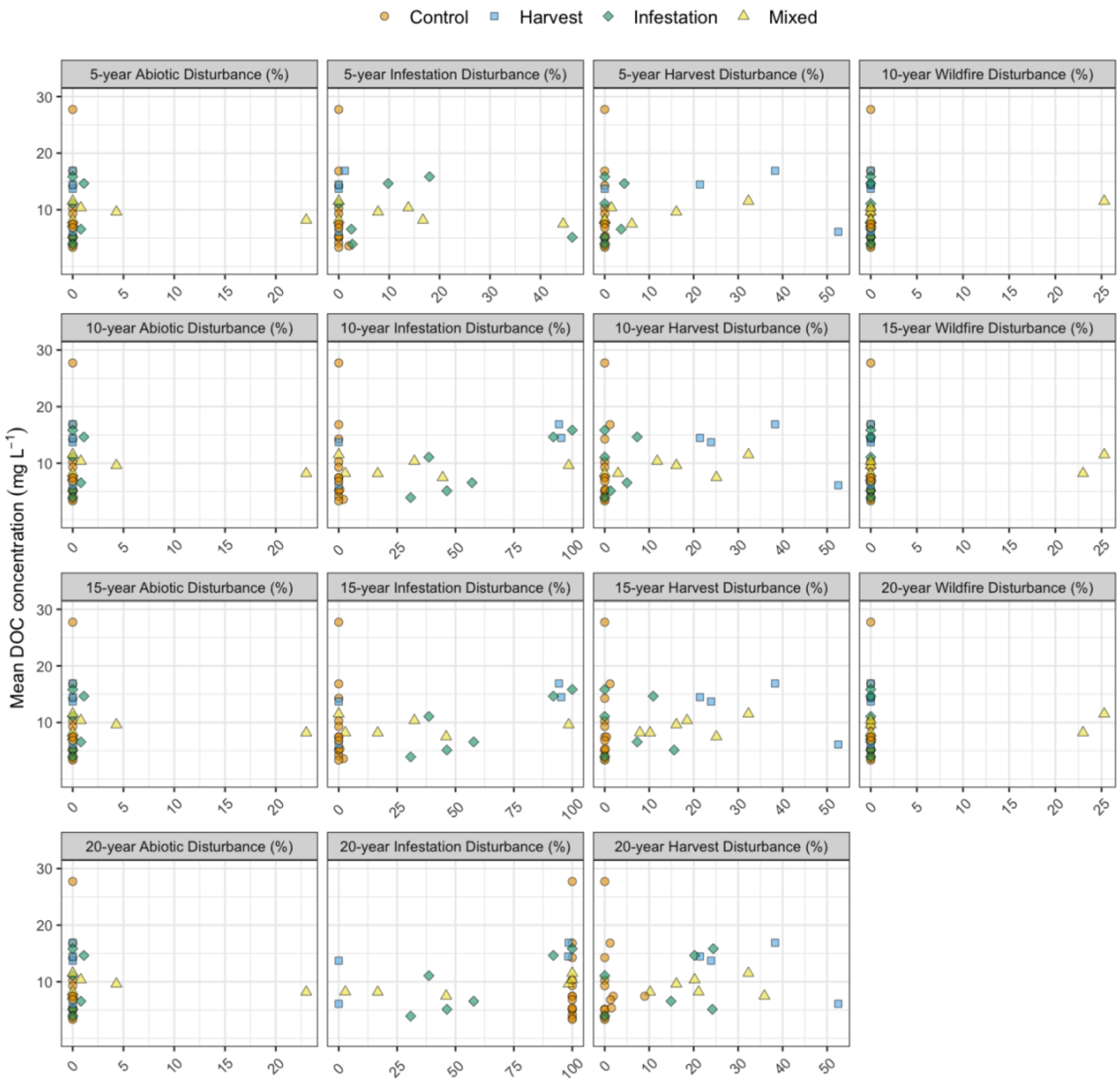

Figure 3.8 Mean **[**DOC] versus forest disturbance predictor variables.

Individual site analysis (Figure 3.9) indicated that control catchments exhibited the most variation in [DOC] over time. [DOC] at some sites (e.g., C6 through C9, H3, and M6) tended to decrease from May to August and significantly increase in September and October. High within-group consistency was observed for mixed-disturbance catchments; however, a linear increase was observed at M1. In addition, [DOC] remained relatively stable at M2, I6 and C1 (Appendix A). In other cases, several sites, such as I2, I6, C2, and C4, exhibited little fluctuation in [DOC] over time. More mixed patterns were observed at sites where water level tended to increase and restabilise over the course of the study period (Appendix A).

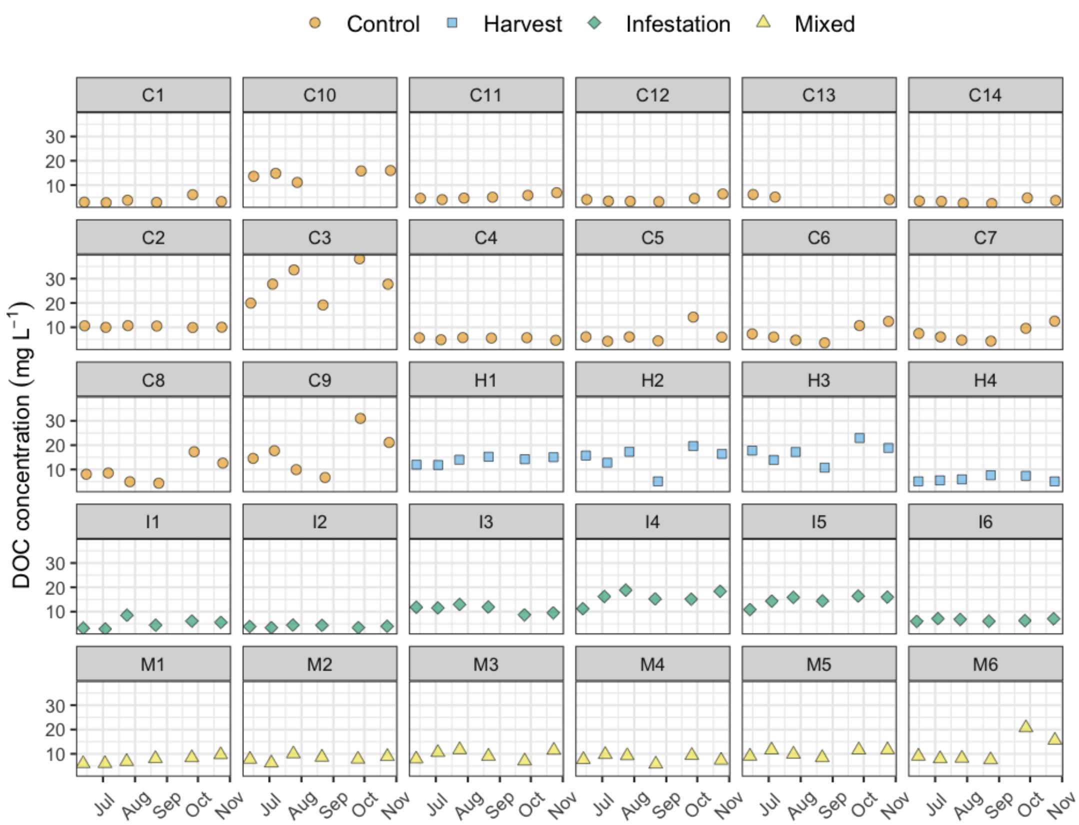

Figure 3.9 Temporal variability in [DOC] for all 30 sites from June 2021 - Oct. 2021. Missing samples are a result of streams drying up.

Overall, median [DOC] tended to decrease in control catchments from June - August and markedly increase in September and October (Figure 3.10). Variability in control catchment [DOC] was also notably lower in late August relative to the rest of the study period. Harvest-dominated catchments experienced relatively stable [DOC], except for SC 4 (late August), when it declined. Additionally, in five out of six SCs, H4 had a markedly lower [DOC] than the other three harvest catchments. Insect infestation-dominated catchments exhibited no consistent changes in [DOC] over time; however, some slight fluctuations in [DOC] variability were observed between successive sample campaigns. Mixed-disturbance sites displayed much lower variability in [DOC] relative to the other catchment types. The lowest [DOC]s were observed at the peak of the dry season (July and August) during the lowest baseflow observed in this study (Appendix A). [DOC] slightly increased into the fall and peaked in late September (end of the water year), when baseflow is typically at its lowest (United States Geological Survey, 2023). Mean [DOC] was highest in SC 5 (12.4 mg L^{-1}) in late September, followed by SC 6 (10.9 mg L^{-1}) in late October, and was lowest in SC 4 (7.7 mg L^{-1}) in late August. Little variation in mean [DOC] was seen across the first three SCs (8.6 - 9.8 mg L^{-1}) in June and July, respectively. Overall, mean [DOC] was lower in the late spring and summer period (8.8 mg L^{-1}) compared to the fall (11.6 mg L^{-1}); however, nearly twice as many samples were collected during the late spring and summer (n = 117) than in the fall (n = 59).

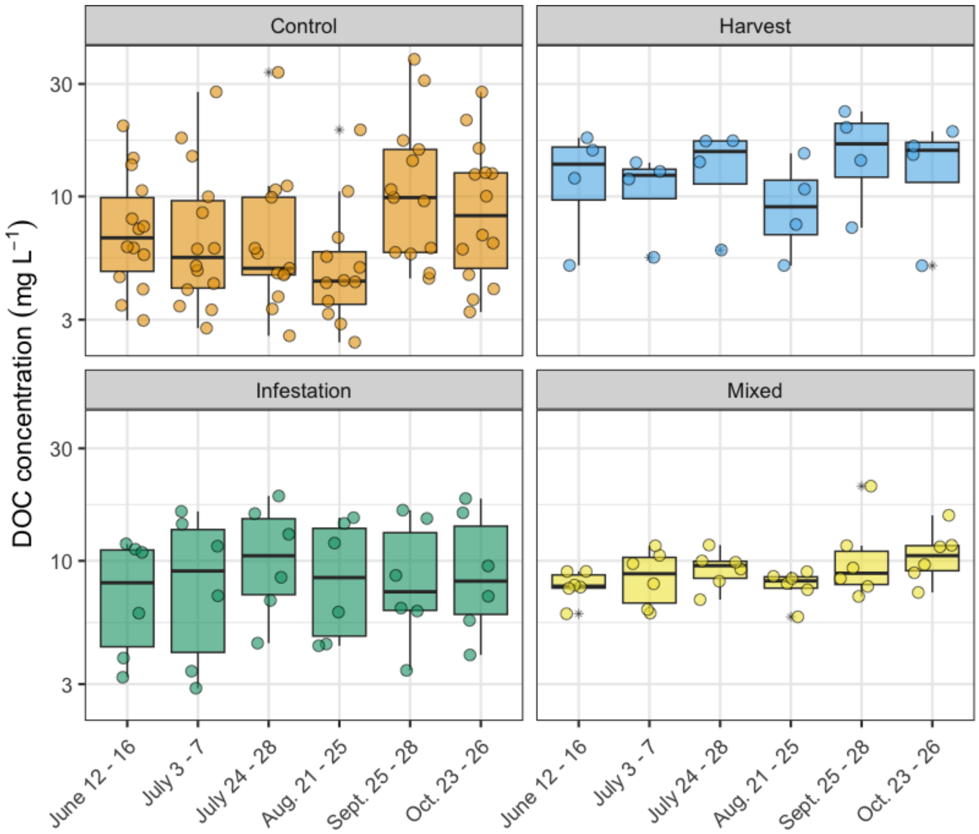

Figure 3.10 Temporal variability in [DOC] showing individual boxplots for separate sample campaigns. Outliers are represented with a *.

3.5 Instantaneous DOC flux

Instantaneous DOC flux ranged from 0.1 mg s^{-1} km^{-2} to 3877 mg s^{-1} km^{-2}. The highest flux was observed at C3, and the lowest flux was observed at M5 (Figure 3.11). For many sites, flux decreased from June to August and increased in September and October. Cyclical behaviour (e.g., I3, C4 and I6) was also observed, while fluxes at other sites, such as H1 and C1, remained relatively stable over time. H2, H3, and to a lesser degree, M4, experienced significant reductions in flux during July and August.

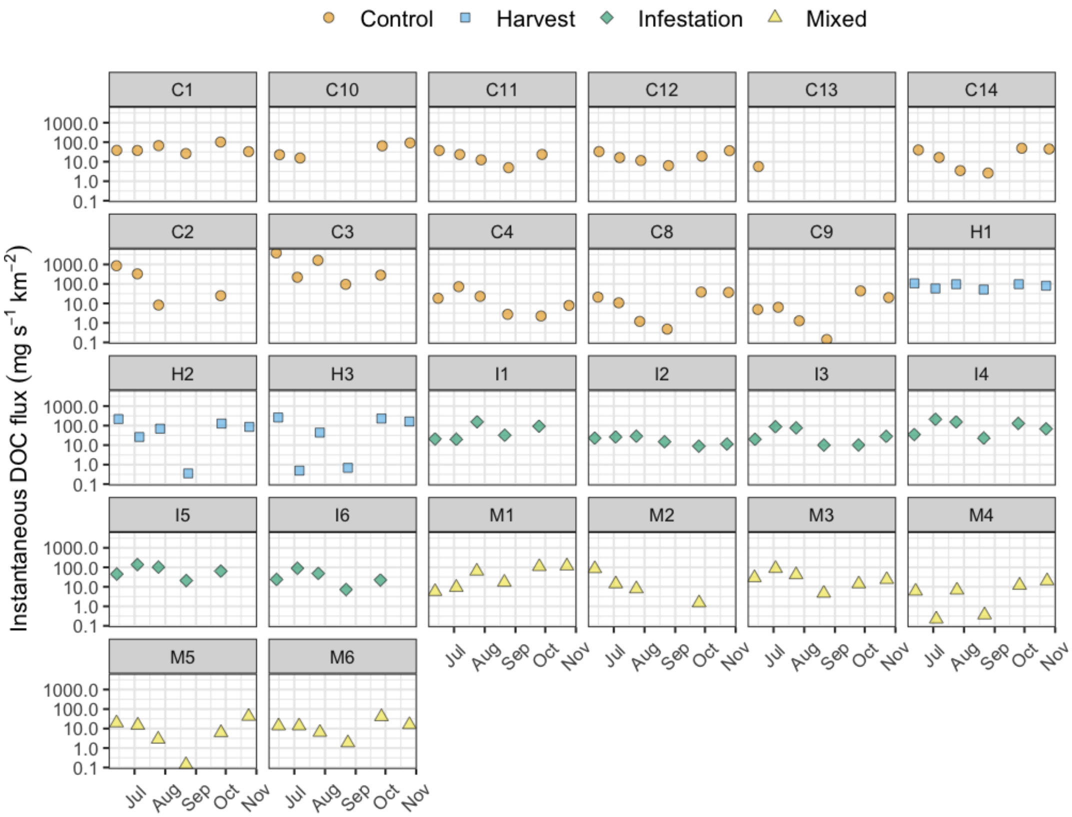

Figure 3.11 Temporal variability in instantaneous DOC flux for all 30 sites from June 2021 - Oct. 2021. Missing data are a result of streams drying up, negative discharge estimates that were omitted, or discharge measurements not taken on the final sample run due to poor stage-discharge relationships established over the five previous site visits.

Instantaneous flux tended to decrease from June to August and increase in September and October in control, harvest-dominated and mixed-disturbance catchments (Figure 3.12). Conversely, fluxes from insect infestation-dominated catchments tended to increase from June to late July, which was followed by slightly lower fluxes seen in August through October. The highest inter-site variability in flux was observed in harvest-dominated catchments, which had notable increases in early July and late August relative to other SCs. Mixed-disturbance catchments also saw larger variability in August, relative to early July and October in particular. Control and insect infestation-dominated catchment flux variability did fluctuate as well, but to a lesser degree.

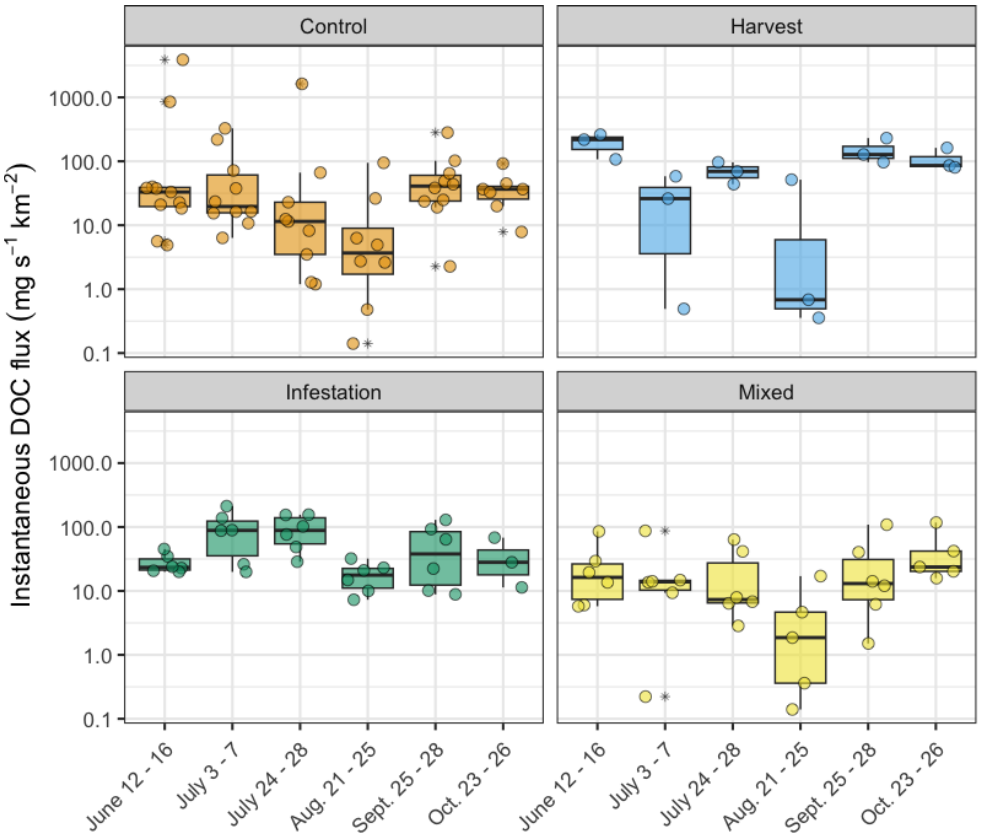

Figure 3.12 Temporal variability in instantaneous DOC flux showing individual boxplots for separate sample campaigns. Outliers are represented with a *.

Instantaneous DOC flux tended to have relatively weak correlations with most landscape predictor variables (r = -0.36 - 0.29) (Figure 3.13; Appendix B); however, it did have a significant negative correlation with catchment area (r = -0.46; p = 0.02). Additionally, flux variability tended to increase with increasing latitude, longitude, and wetland cover and tended to decrease with increasing open water %. C3, due to its small catchment size and elevated [DOC], was influential in determining the strength of these relationships.

In disturbed catchments, mean instantaneous DOC flux was significantly positively correlated with 10- and 15-year insect infestation % (r = 0.59) and 20-year harvest % (r = 0.53) (Figure 3.14). All other correlations between mean instantaneous DOC flux and forest disturbance predictor variables were not significant (Appendix B).

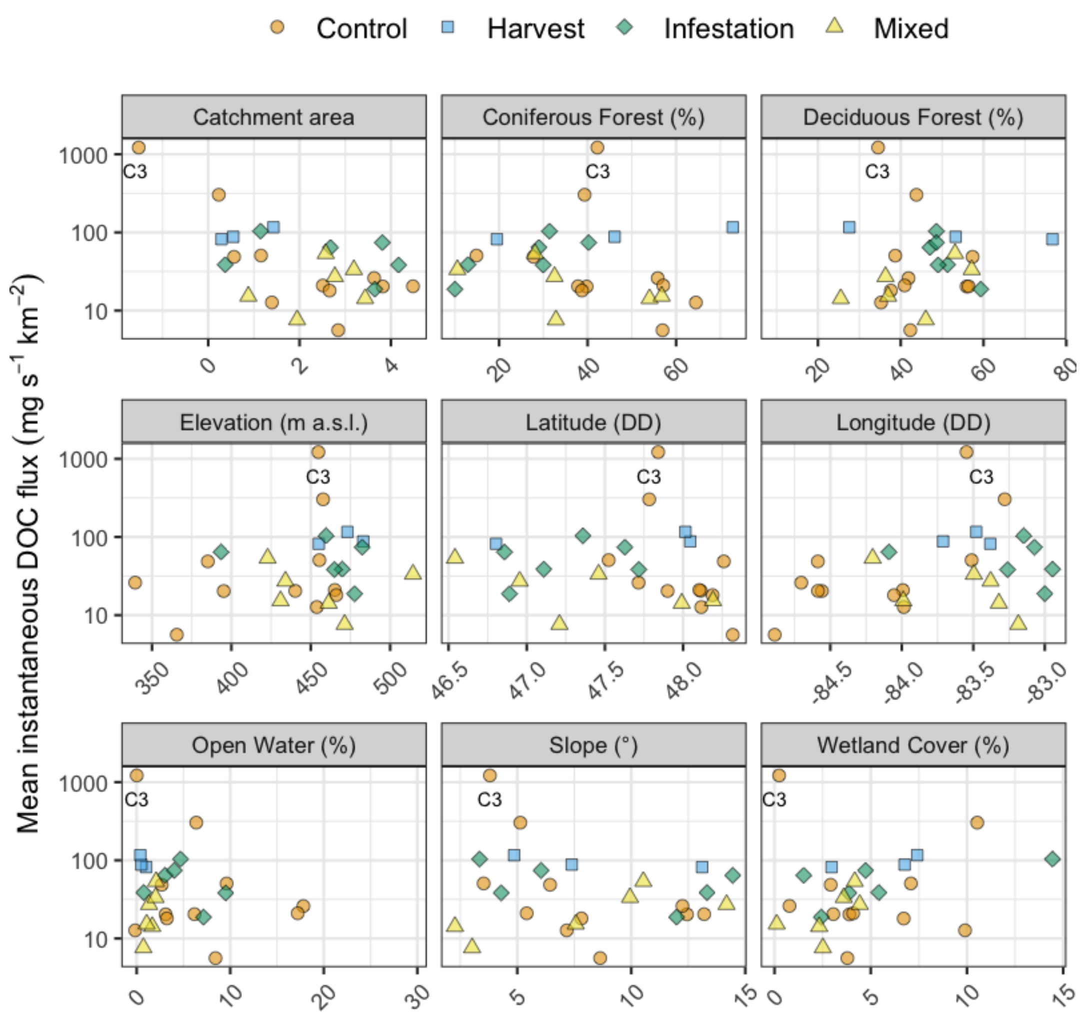

Figure 3.13 Mean instantaneous DOC flux versus various landscape predictor variables. Catchment area is log km^2.

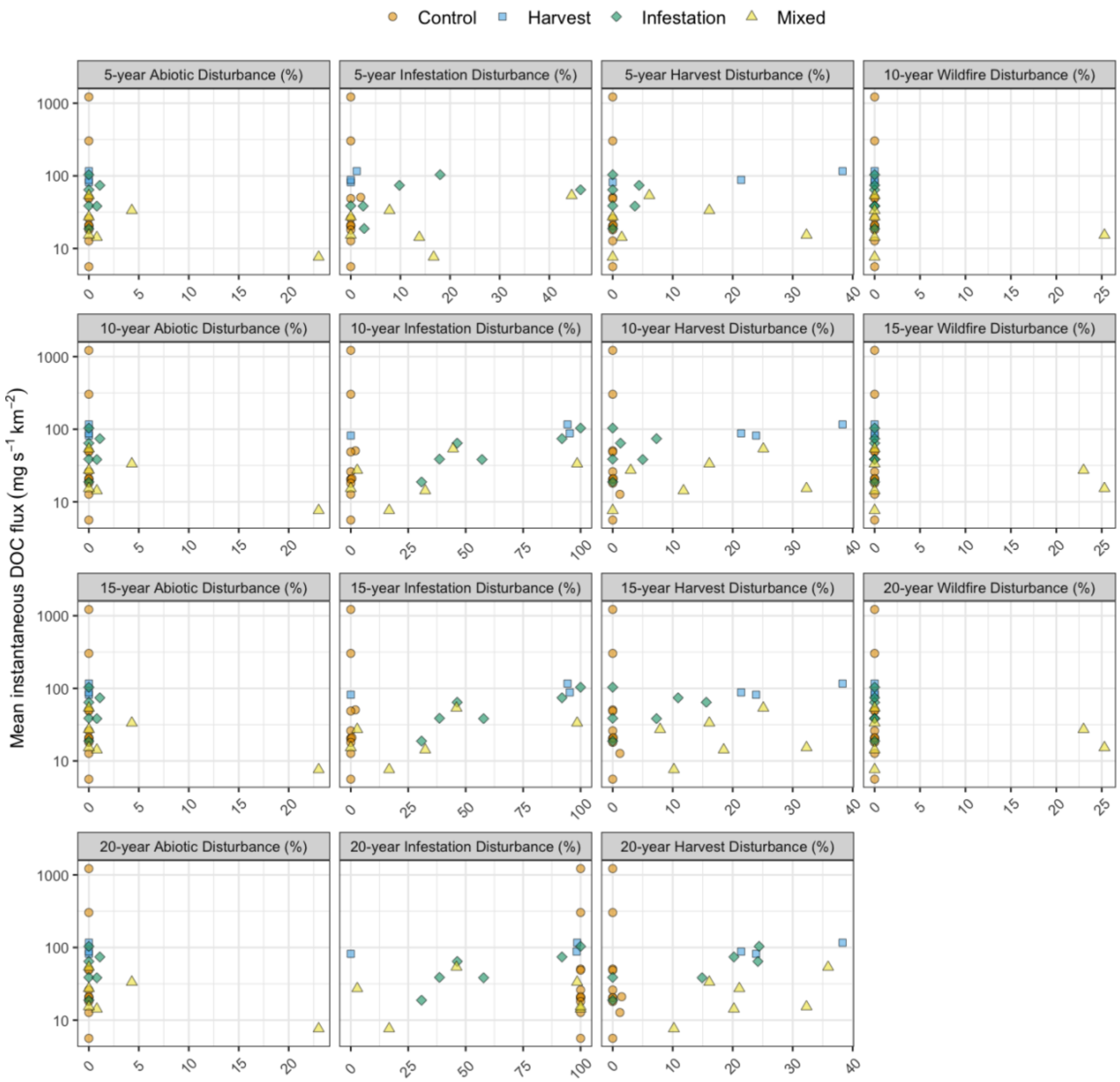

Figure 3.14 Mean instantaneous DOC flux versus forest disturbance predictor variables.

3.6 DOC export estimates

The maximum and minimum estimated DOC export was 63.2 g C m^{-2} and 1.0 g C m^{-2} over a period of 141 days (Section 2.4.1) at H3 and C9, respectively (Figure 3.15). Interpolated DOC export estimates ranged from 3.0 - 51.7 g C m^{-2} over the same timeframe; control catchments ranged from 3.0 - 23.3 g C m^{-2}, while harvest-dominated catchments ranged from 24.5 - 51.7 g C m^{-2}, insect infestation-dominated catchments ranged from 5.4 - 36.6 g C m^{-2}, and mixed-disturbance catchments ranged from 5.6 - 44.9 g C m^{-2}. H3, M6, H2 and I4 had the most variability in DOC export estimates while C2, C4, I2 and M5 had highly consistent export estimates for all methods used. Corresponding hydrographs and DOC samples are included in Appendix A.

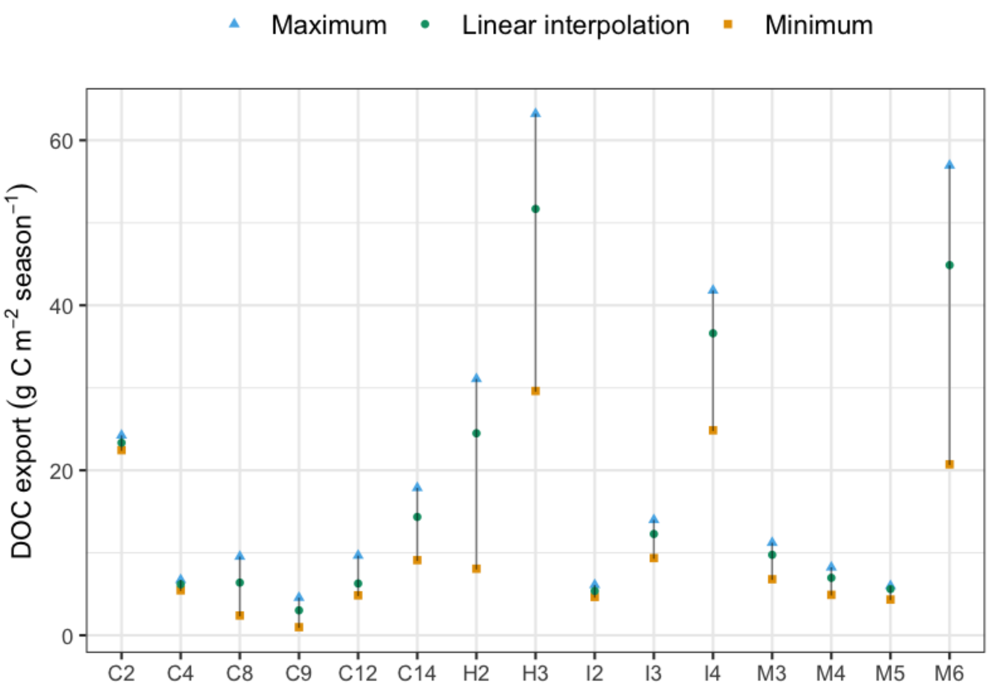

Figure 3.15 DOC export estimates for 15 sites between June 6th - Oct. 23rd, 2021.

3.6.1 DOC export spatial variability

There were no statistically significant relationships between any landscape variables and DOC export (Figure 3.16; Appendix B). DOC export tended to increase and be highly variable in small catchments (~ <5km^2). In larger catchments, DOC export showed no discernible correlation, but tended to become smaller and less variable. Increased variability in DOC export was seen in catchments with little (<5%) to no open water % while export estimates tended to decrease with increasing open water %.

DOC export in disturbed catchments was positively correlated with 20-year harvest % ($r = 0.82$; $p = 0.007$) (Figure 3.17; Appendix B). All other correlations between DOC export and forest disturbance predictor variables were not significant (Appendix B).

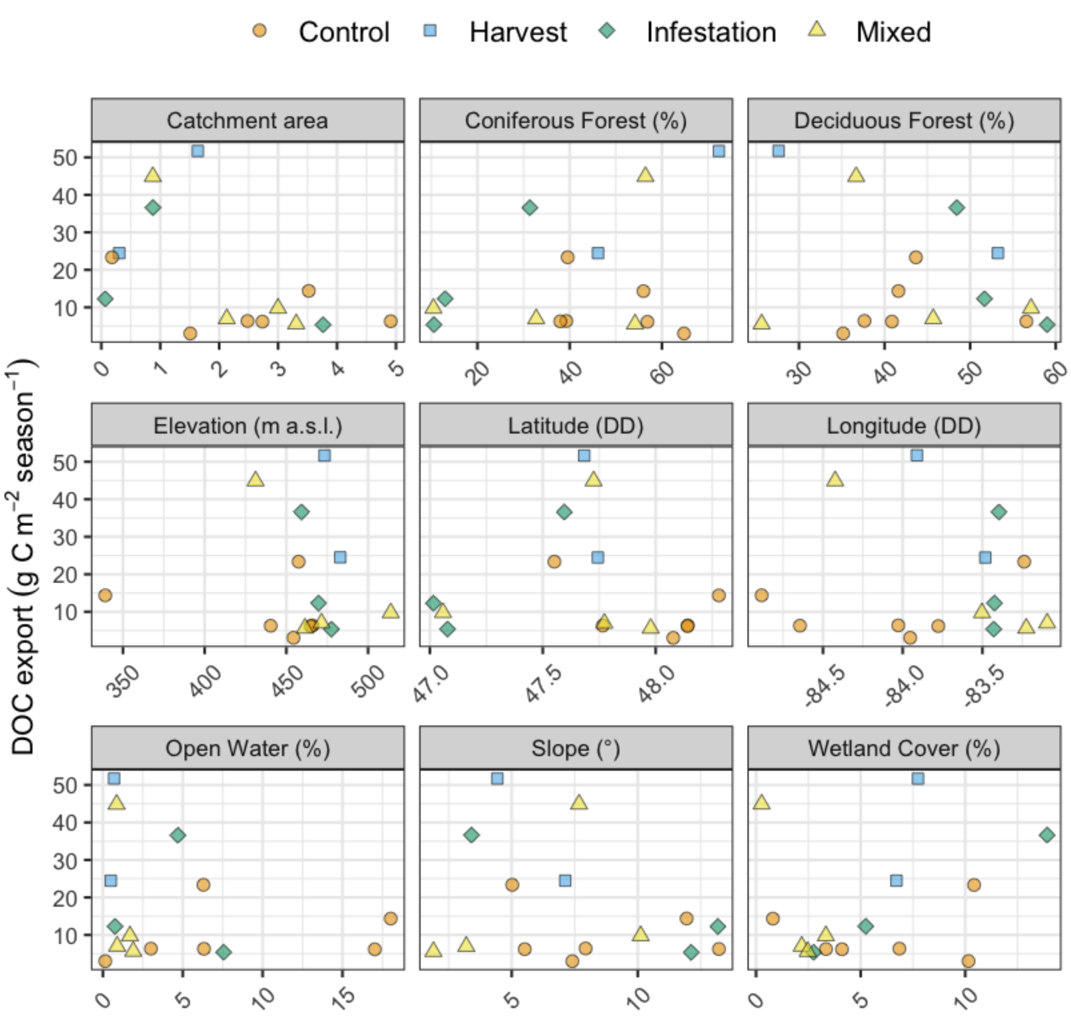

Figure 3.16 DOC export versus various landscape predictor variables. Catchment area is log km^2.

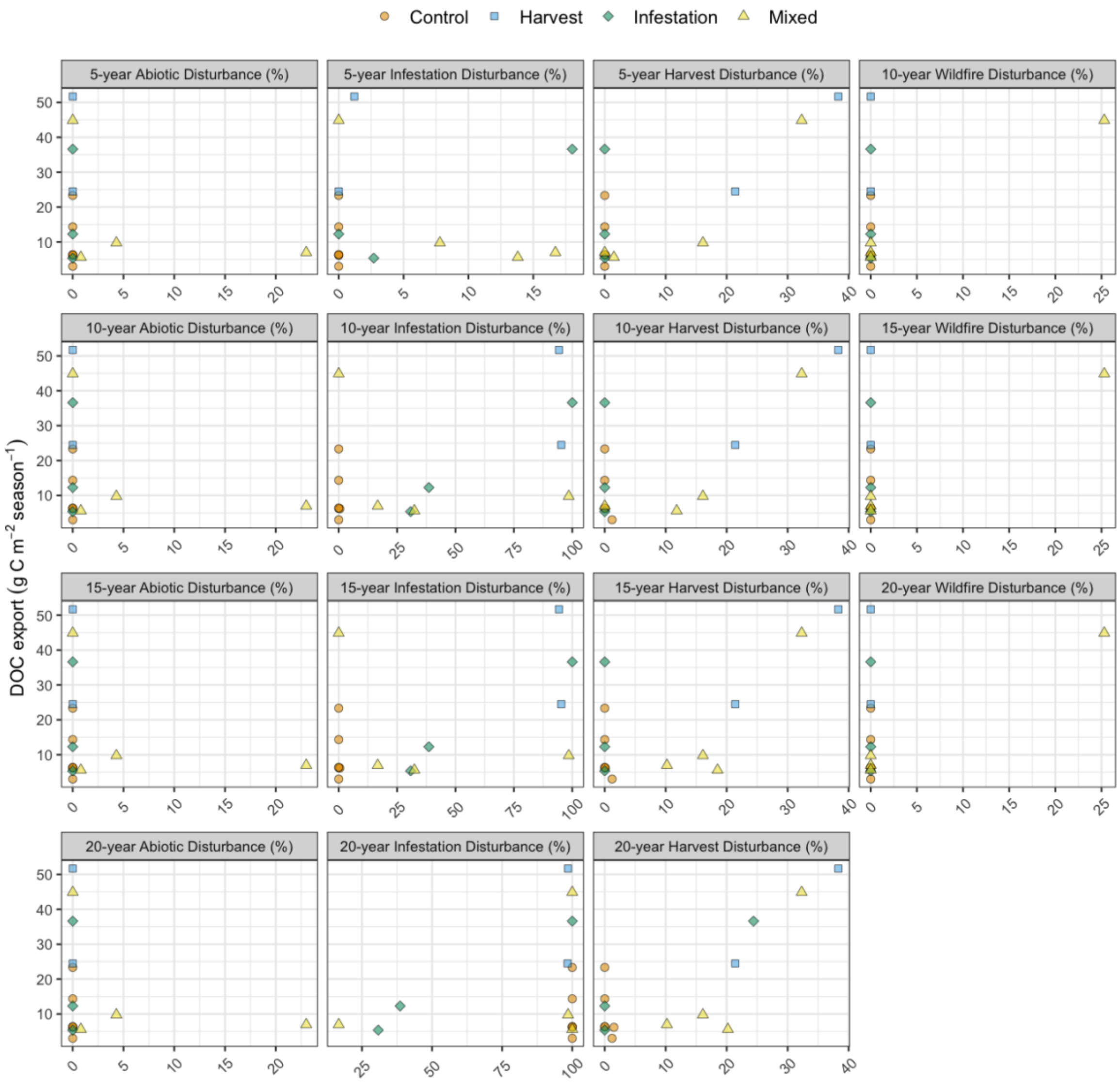

Figure 3.17 DOC export versus forest disturbance predictor variables.

3.7 DOC quality

SUVA254 ranged from 1.6 to 10.1 L mg^{-1} m^{-1} across the study region. Values ranged from 1.6 to 10.1 L mg^{-1} m^{-1} in the control catchments; from 1.8 to 5.6 L mg^{-1} m^{-1} in harvest-dominated catchments; from 2.9 to 5.1 L mg^{-1} m^{-1} in insect infestation-dominated catchments; and from 3.8 to 8.9 L mg^{-1} m^{-1} in mixed-disturbance catchments. SUVA254 was slightly higher in harvest-dominated and mixed-disturbance catchments relative to control and insect infestation-dominated catchments; however, these differences were not significant. The majority (59%) of $SUVA_{254}$ calculations exceeded a value of 4 L mg^{-1} m^{-1}, 40.9% fell between the values of 2 and 4 L mg^{-1} m^{-1}, and two values were below 2 L mg^{-1} m^{-1}. Additional DOC quality results (i.e., fluorescence indices) are presented in Appendix C.

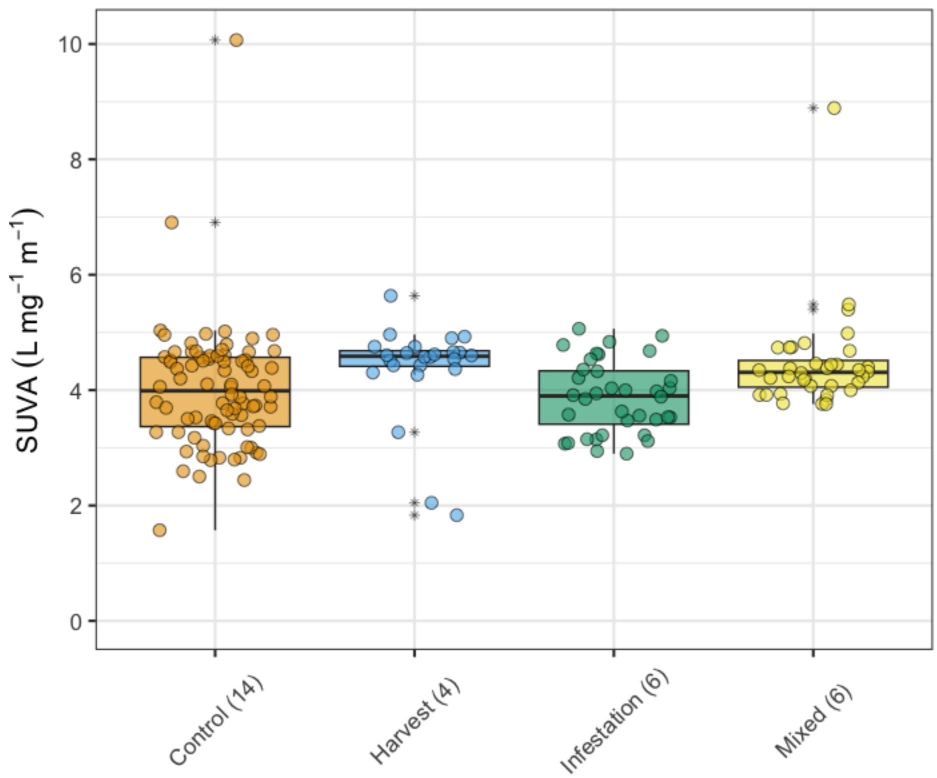

Figure 3.18 $SUVA_{254}$ results from June 2021 - October 2021 over six individual sample campaigns at 30 sites. Outliers are represented with a *.

Many sites experienced little fluctuation in $SUVA_{254}$ variability overall (Figure 3.19); however, slight decreasing trends were observed for I3, I6 and C2, while other sites, such as C1 and C5, experienced more cyclical behaviour. Notably, C11 experienced a large spike in $SUVA_{254}$ in late July and other anomalous increases and decreases in

$SUVA_{254}$ were seen in late August for M6, C8, H3 and H4. Later samples in sites that experienced an anomalous spike or reduction in $SUVA_{254}$ value returned to the range of previously calculated values observed earlier in the study period.

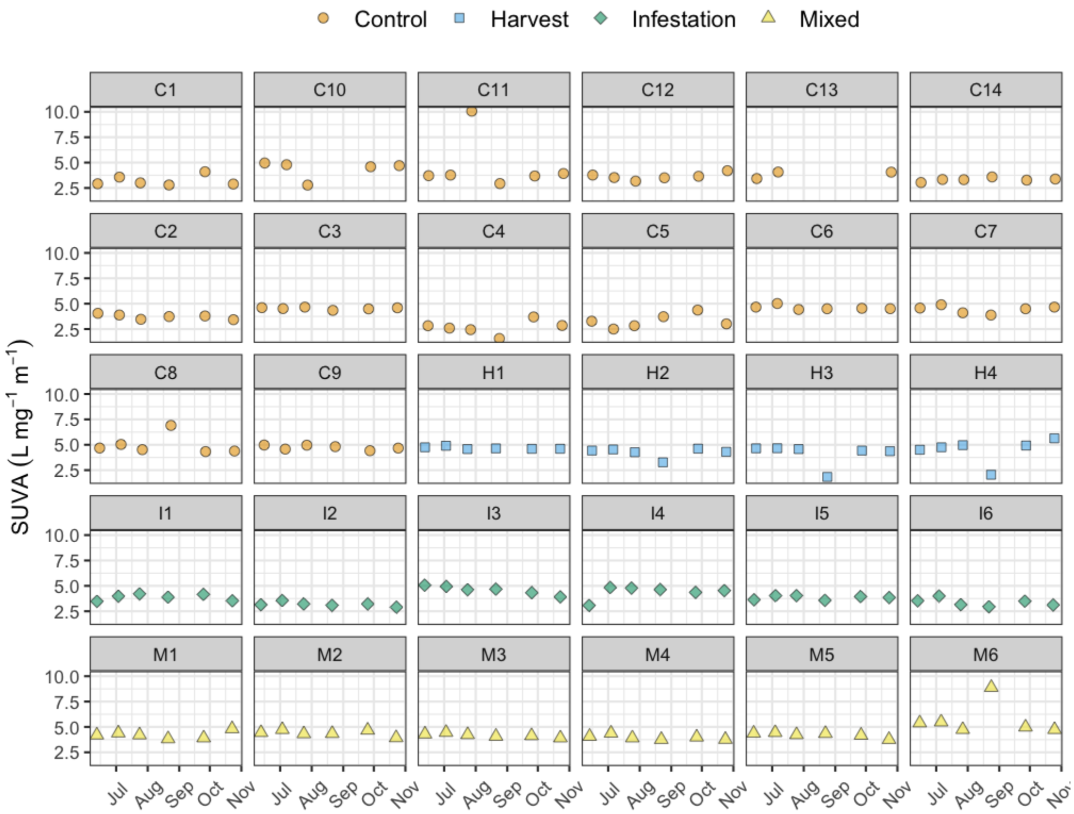

Figure 3.19 Temporal variability in $SUVA_{254}$ for all 30 sites from June 2021 - Oct. 2021. Missing data are a result of streams drying up.

Harvest-dominated sites experienced a decrease in $SUVA_{254}$ in late August, which was accompanied by an increase in variation (Figure 3.20). Additionally, a slight increase in variability during October was observed in the harvest-dominated sites. $SUVA_{254}$ values for mixed-disturbance catchments slightly increased in variability from June to October but were otherwise relatively stable. In insect infestation-dominated catchments, $SUVA_{254}$ variability tended to increase during July and August. Conversely, control catchments experienced lower $SUVA_{254}$ variability during September. Across all sites, the largest and smallest $SUVA_{254}$ values were observed in July and August.

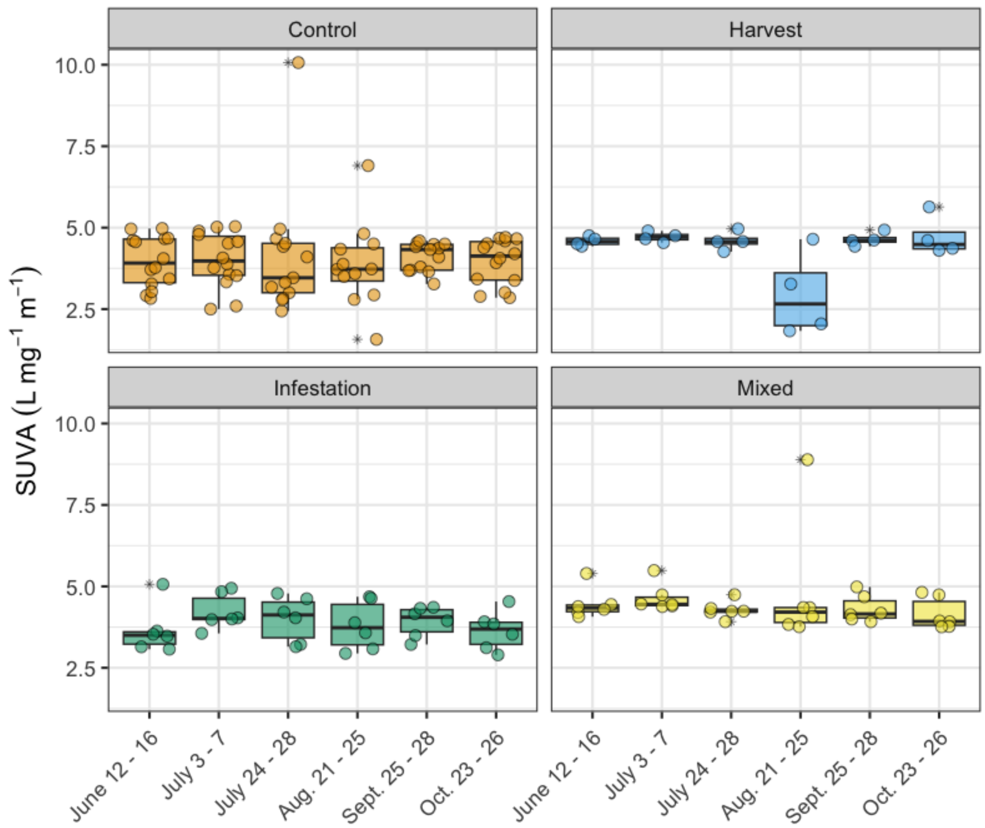

Figure 3.20 Temporal variability in $SUVA_{254}$ showing individual boxplots for separate sample campaigns. Outliers are represented with a *.

Mean $SUVA_{254}$ had significant negative correlations with open water % ($r = -0.69$; $p < 0.001$) and catchment area ($r = -0.39$; $p = 0.03$) (Figure 3.21). Non-significant correlations were seen between mean $SUVA_{254}$ and all other catchment characteristic variables (Appendix B).

Mean $SUVA_{254}$ in disturbed catchments had significant negative correlations with 5-year insect infestation ($r = -0.58$, $p = 0.02$) and all abiotic disturbance timeframes ($r = -0.49$, $p = 0.05$) (Figure 3.22). Non-significant relationships were observed between $SUVA_{254}$ and all other forest disturbance predictor variables (Appendix B).

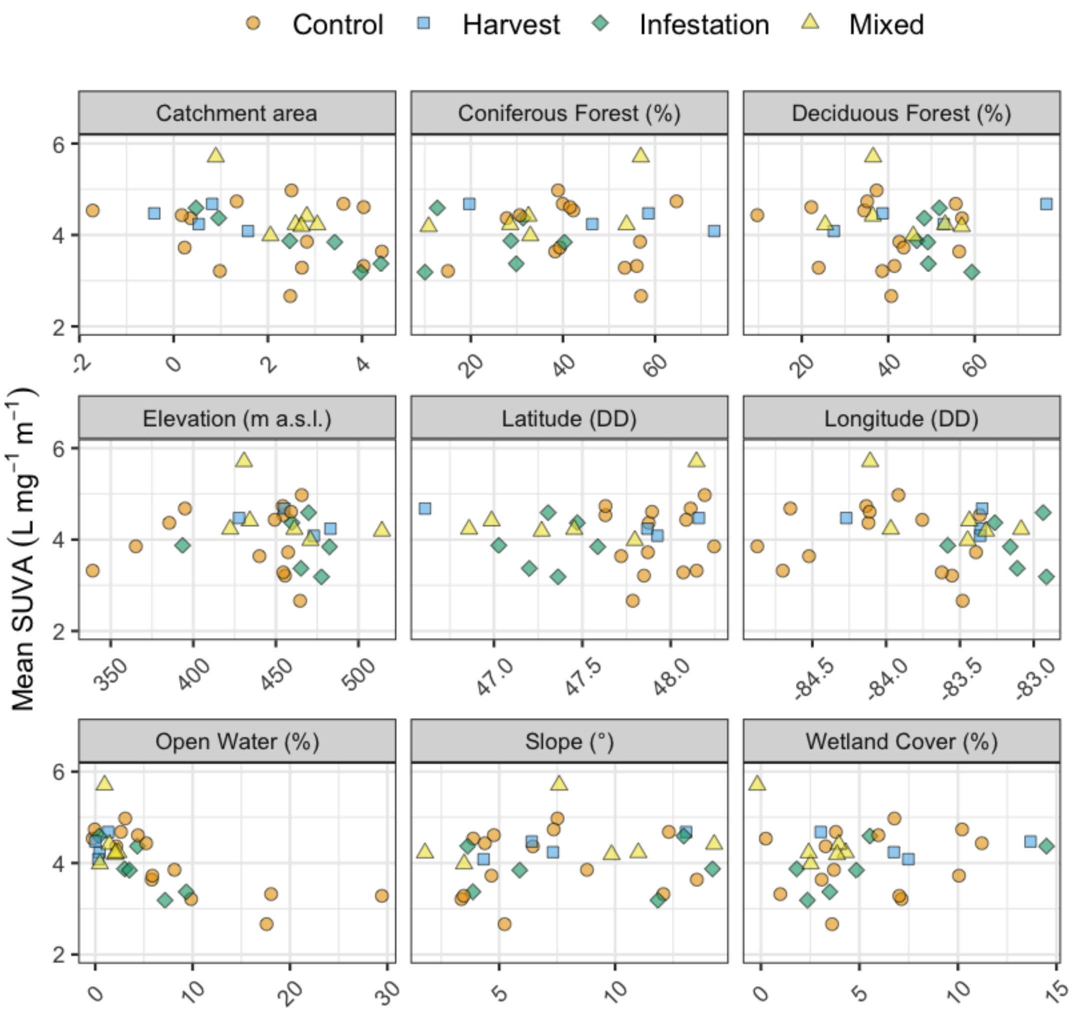

Figure 3.21 Mean $SUVA_{254}$ versus various landscape predictor variables. Catchment area is log km^2.

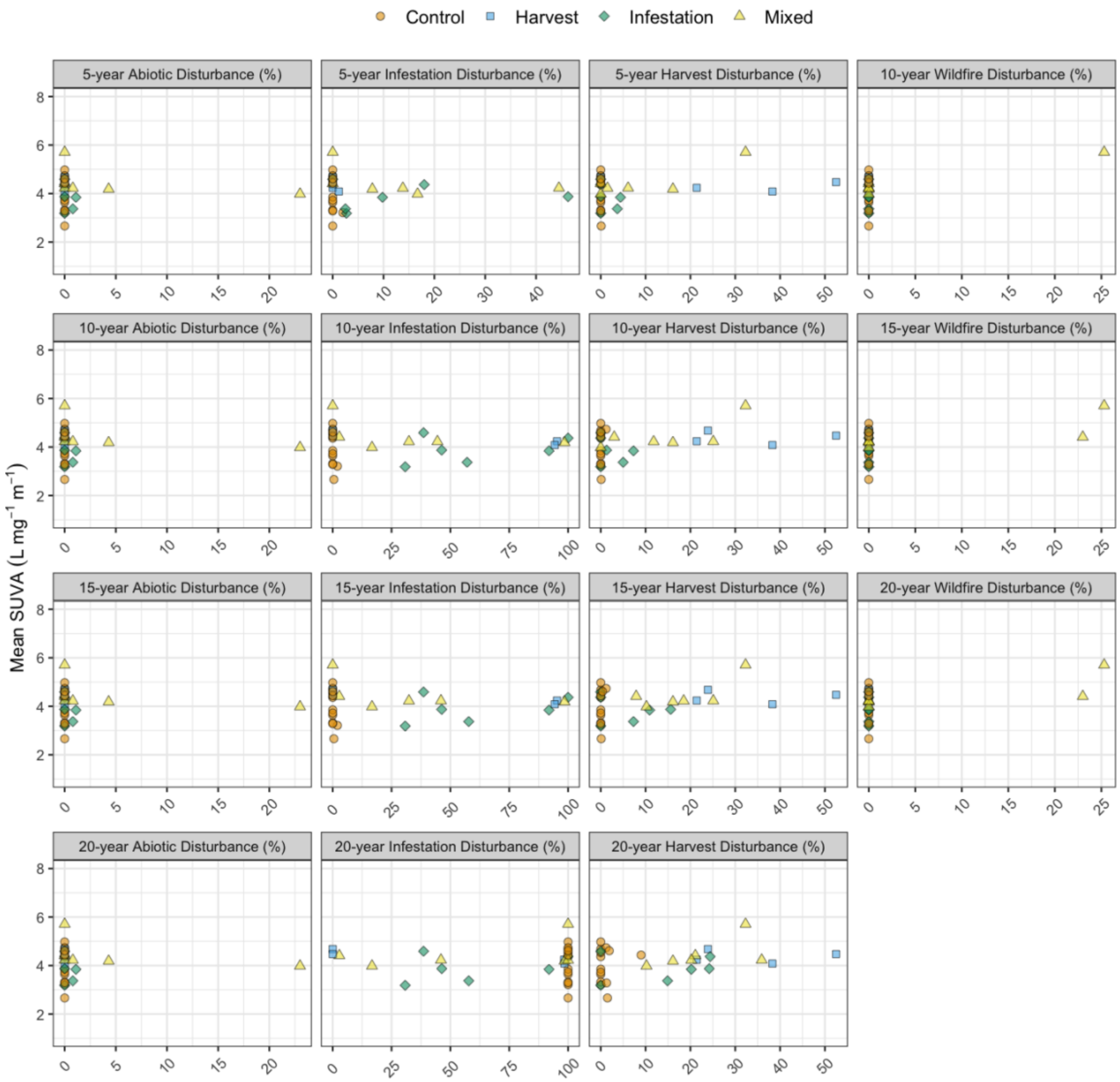

Figure 3.22 Mean $SUVA_{254}$ versus forest disturbance predictor variables.

3.8 DBP-FP spatiotemporal variability

Based on 48 stream samples taken from eight sites (Section 2.3.3), [THM-FP] ranged from 124.6 - 2079 mg L^{-1}, while [HAA-FP] ranged from 166.7 - 2302.7 mg L^{-1} (Figure 3.23). The highest concentrations of THM-FP and HAA-FP were observed at M6, while the lowest concentrations of THM-FP and HAA-FP were recorded at C12. Median THM-FP and HAA-FP concentrations were higher in all treatment catchment types relative to control catchments. Large differences in [HAA-FP], and to a lesser degree, [THM-FP], were observed between the harvest-dominated sites (H1 and H4), which increased overall variability within that catchment type.

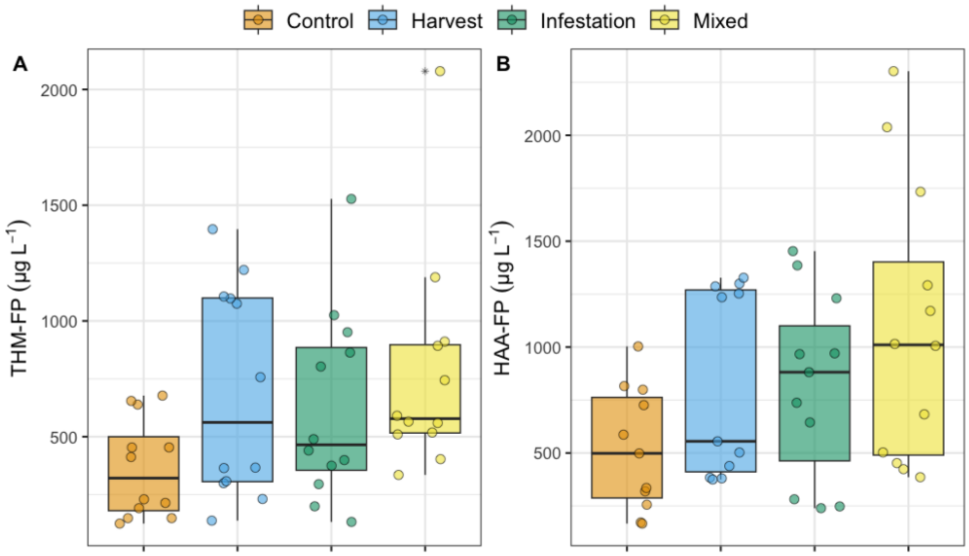

Figure 3.23 [THM-FP] (**A**) and [HAA-FP] (**B**) results from June 2021 - October 2021 over six sample campaigns at eight sites. Outliers are represented with a *. Some [HAA-FP] samples could not be calculated due to low chlorine levels and are, therefore, missing.

[THM-FP] temporal variability was relatively low for C12, H1, H4 and M1 (Figure 3.24); however, [THM-FP] in H1 tended to be consistently elevated, with a noticeable drop in concentration in late September. The largest [THM-FP] variability was observed at M6. I3 and C2 experienced decreasing trends over time and I1 had a spike in [THM-FP] during late July but otherwise concentrations were relatively low.

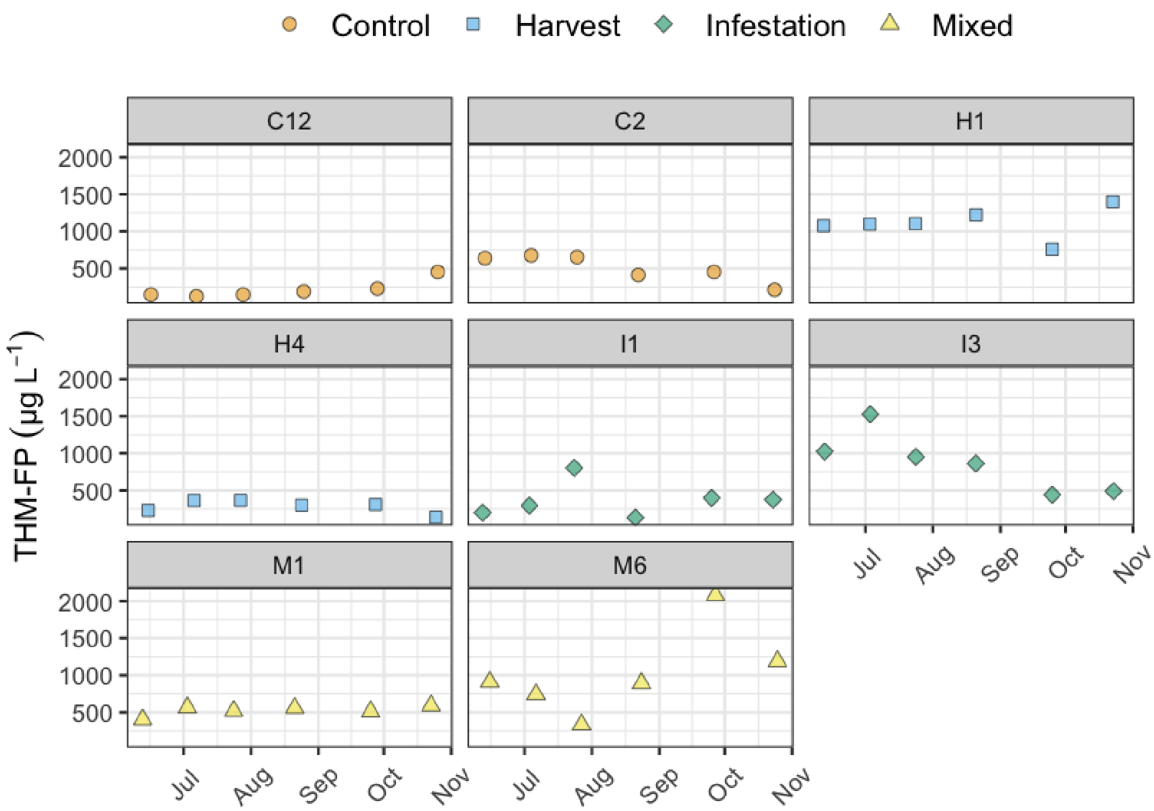

Figure 3.24 Temporal variability in [THM-FP] for eight sites from June 2021 - Oct. 2021.

[HAA-FP]s were relatively stable over time in C12, H1 and H4; however, H1 had elevated [HAA-FP] relative to C12 and H4 (Figure 3.25). The largest variability in [HAA-FP] over time was observed at M6, which also had the highest concentration (late October). Overall, increasing trends in [HAA-FP] were observed at M1 and M6 whereas decreasing trends were seen at C2 and I3; however, both C2 and I3 both experienced small increases in the October sample.

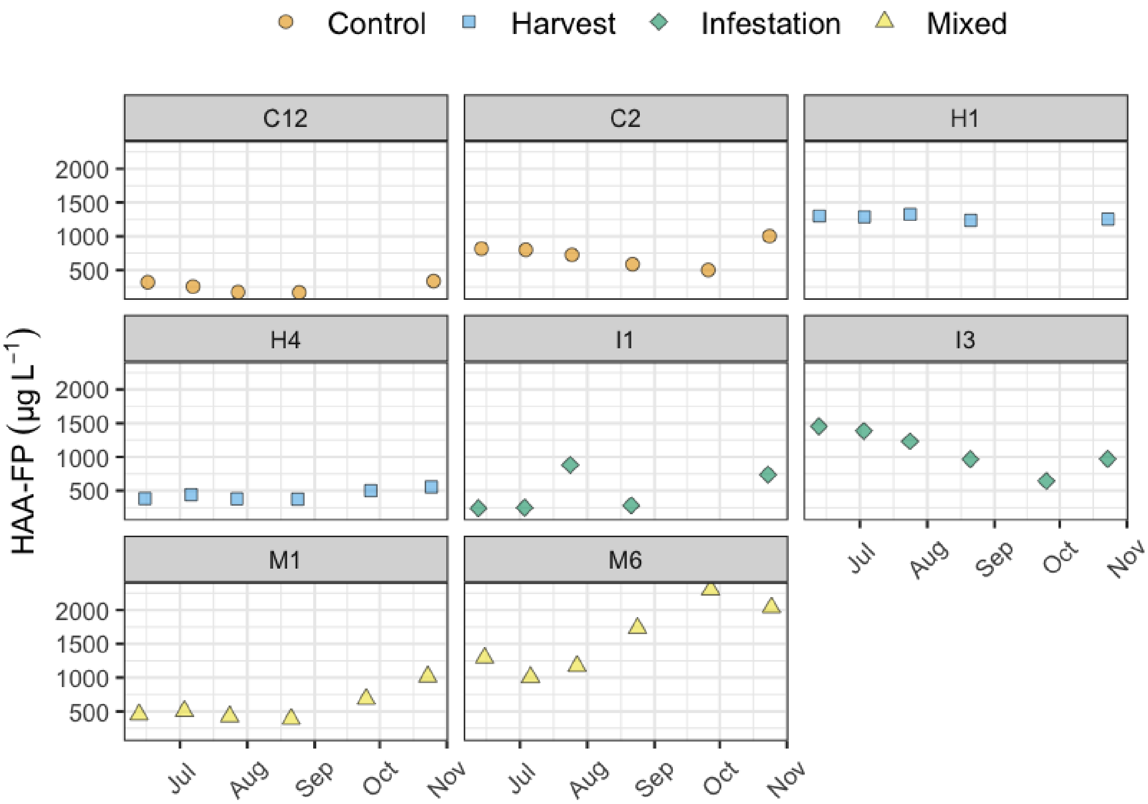

Figure 3.25 Temporal variability in [HAA-FP] for eight sites from June 2021 - Oct. 2021. Some September [HAA-FP] samples (n = 3) could not be calculated due to low chlorine levels and are missing.

3.8.1 Relationships between [DBP-FP] and [DOC], catchment characteristics, and forest disturbance

[THM-FP] (r = 0.88) and [HAA-FP] (r = 0.85) were positively correlated with [DOC]. The relationship between [DOC] and [HAA-FP] tended to be most variable in mixed-disturbance catchments. [HAA-FP] was also positively correlated with $SUVA_{254}$ (Appendix C).

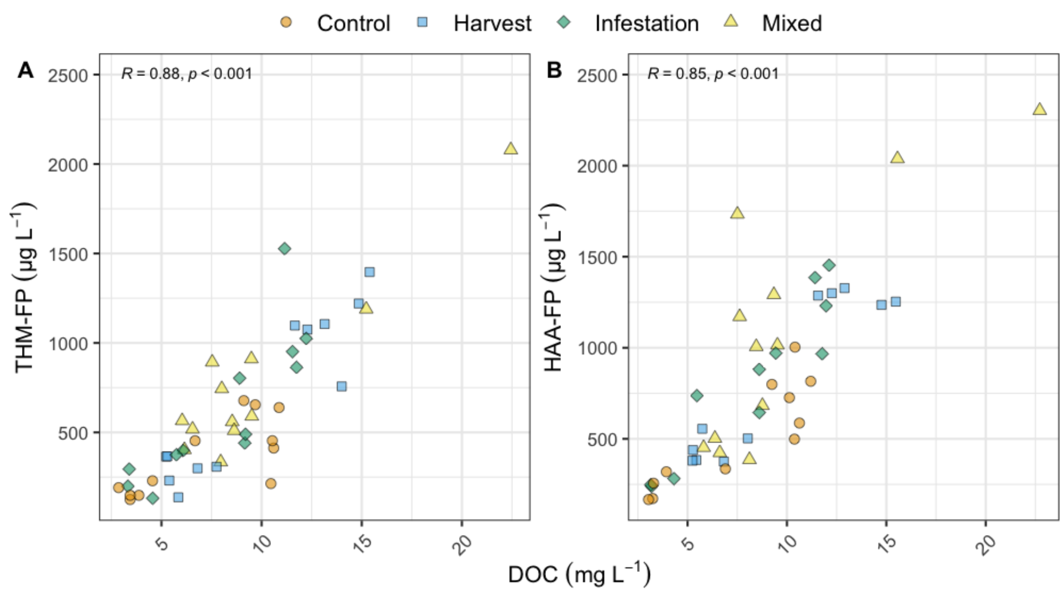

Figure 3.26 [THM-FP] (**A**) and [HAA-FP] (**B**) versus [DOC] at eight sites across the Algoma region.

Mean [THM-FP] had a significant positive correlation with longitude (r = 0.51; p < 0.001) and elevation (r = 0.38; p < 0.01) (Figure 3.27; Appendix B). Significant negative correlations occurred between mean [THM-FP] and catchment area (r = -0.52; p < 0.001), and open water % (r = -0.42; p < 0.01). Additionally, as with mean [THM-FP], mean [HAA-FP] had significant positive correlations with longitude (r = 0.48; p <0.001) and elevation (r = 0.4; p < 0.01) (Figure 3.29). Notable significant negative correlations were also observed between [HAA-FP] and catchment area ($r = -0.6$; $p < 0.001$), and open water % ($r = -0.44$; $p < 0.01$), respectively. There were no significant correlations observed between either mean [THM-FP] or mean [HAA-FP] and any of the forest disturbance predictor variables (Figure 3.28; Figure 3.30; Appendix B).

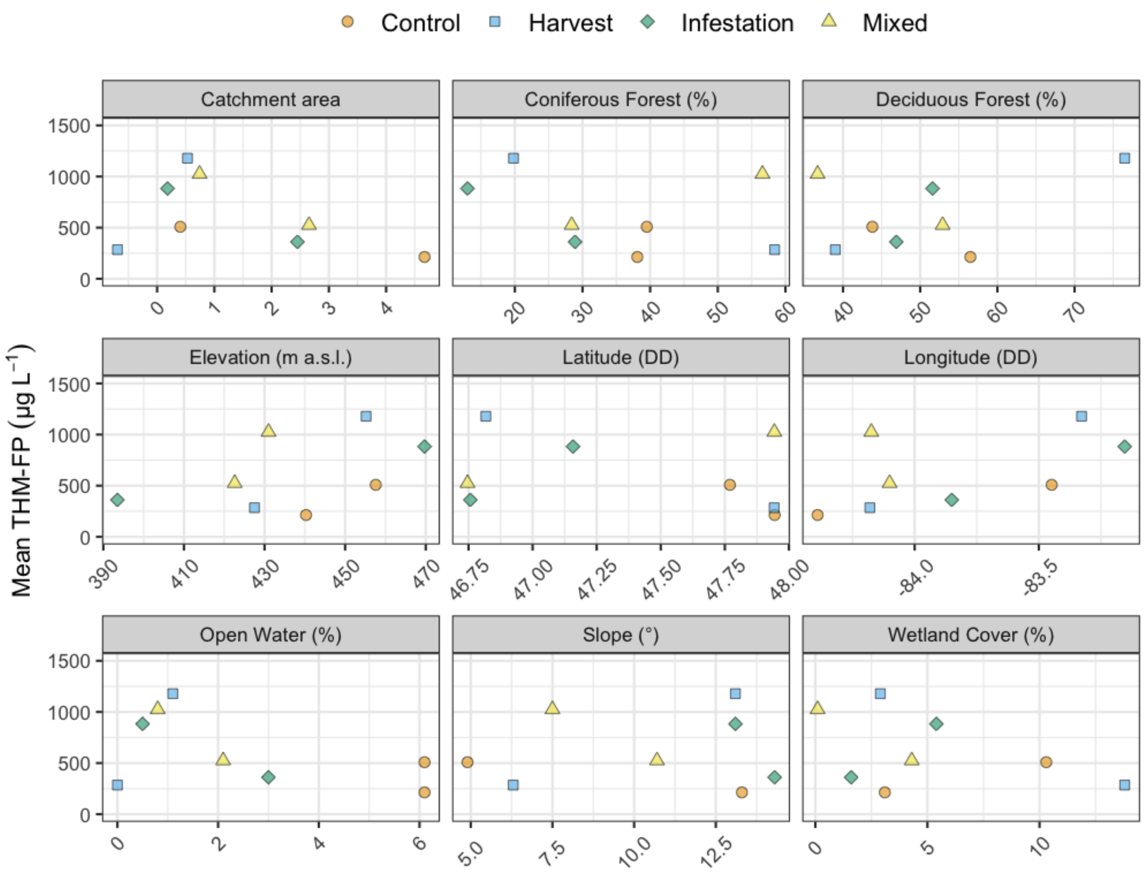

Figure 3.27 Mean [THM-FP] versus various landscape predictor variables. Catchment area is given on a logarithmic scale.

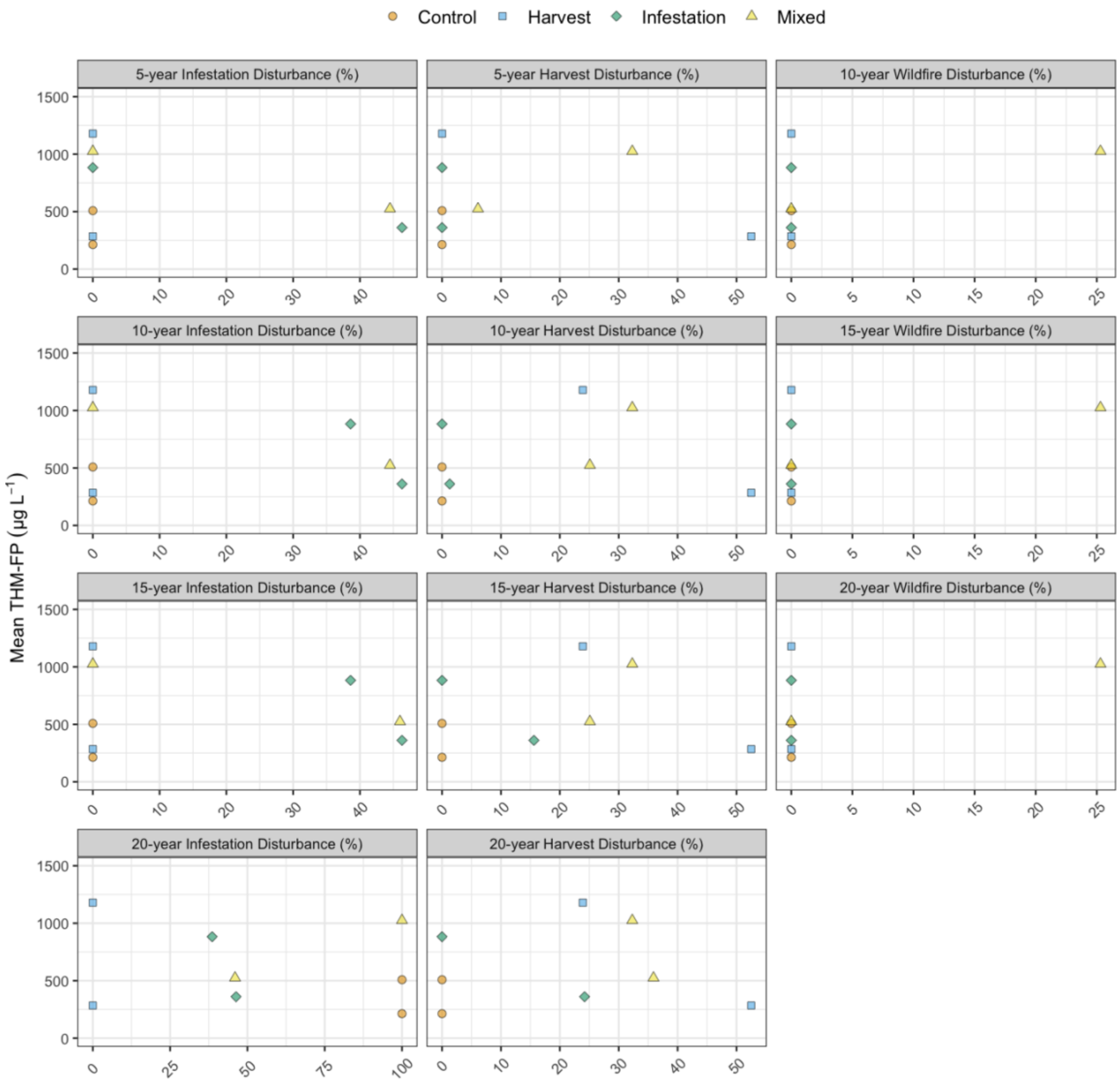

Figure 3.28 Mean [THM-FP] versus forest disturbance predictor variables.

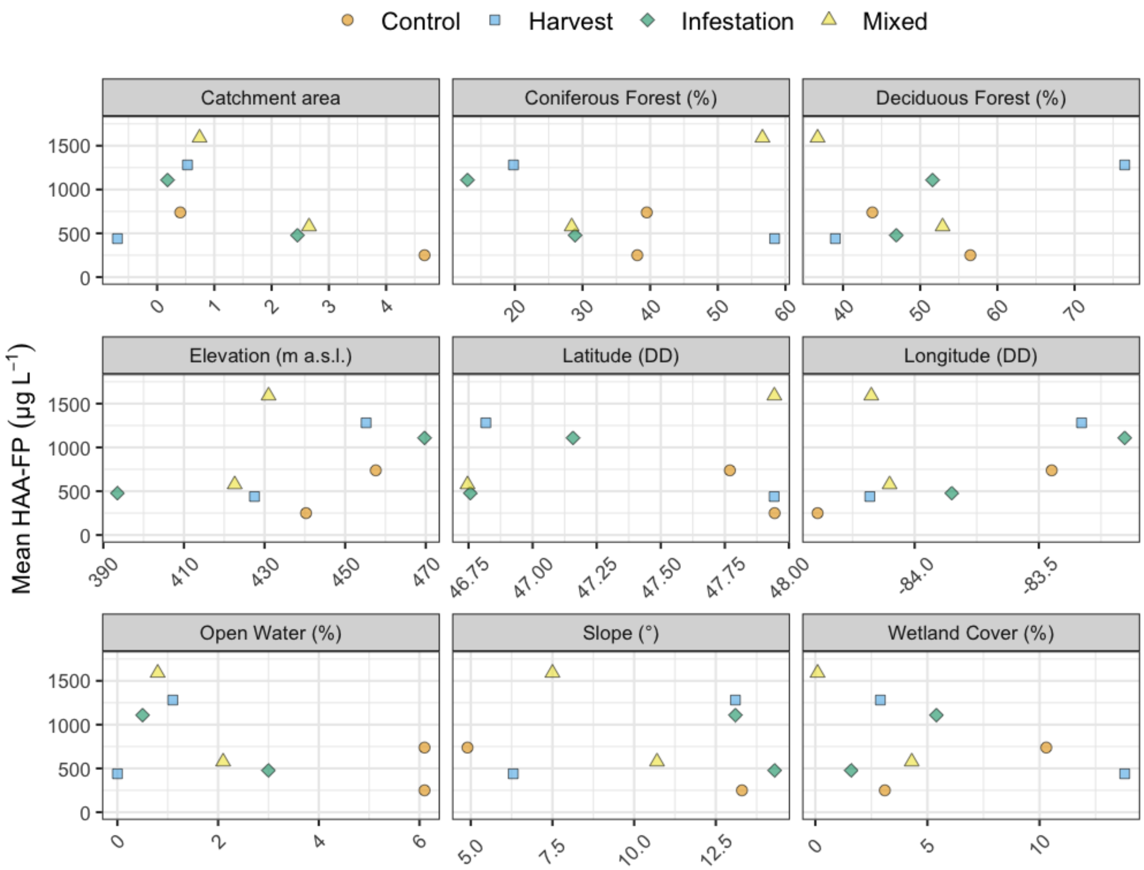

Figure 3.29 Mean [HAA-FP] versus various landscape predictor variables. Catchment area is given on a logarithmic scale.

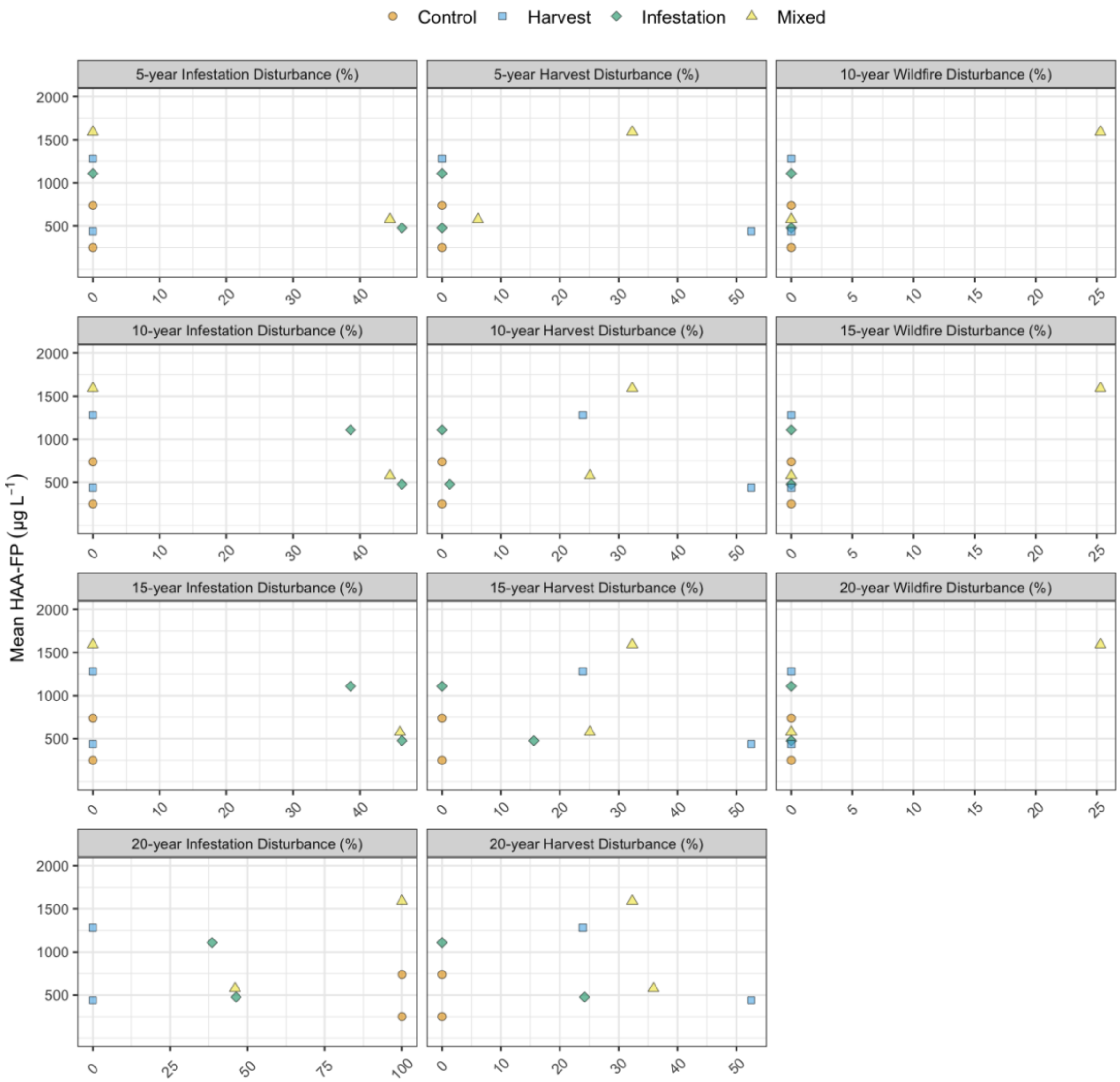

Figure 3.30 Mean [HAA-FP] versus forest disturbance predictor variables.

3.9 Statistical analyses

3.9.1 Spearman correlation analysis – catchment characteristics and multicollinearity

Spearman's correlation coefficients between catchment characteristics ranged widely (r = -0.79 - 0.78) (Figure 3.31). The strongest positive correlation was observed between longitude and elevation (r = 0.78). Lesser positive correlations were seen between latitude and coniferous forest % (r = 0.6), catchment area and open water % (r = 0.52), deciduous forest % and slope (r = 0.5), total productive forest % and slope (r = 0.41), and deciduous forest % and total productive forest % (r = 0.31). The strongest negative correlation was observed between latitude and longitude (r = -0.79). Other notable negative correlations included those between total productive forest % and open water % (r = -0.63), coniferous forest % and deciduous forest % (r = -0.58), total productive forest % and wetland cover % (r = -0.55), coniferous forest % and longitude (r = -0.48), and latitude and elevation (r = -0.43).

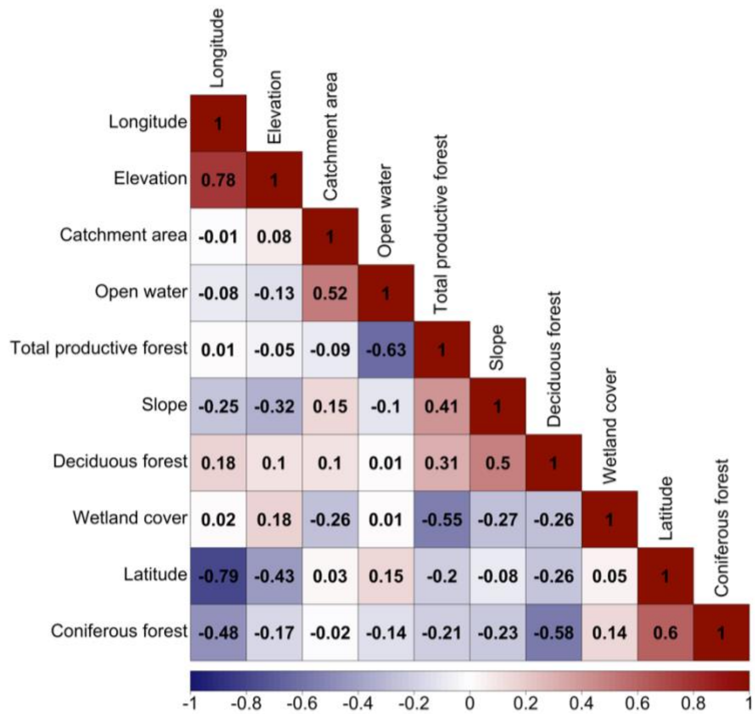

Figure 3.31 Spearman's correlation analysis plot for physical and land cover catchment characteristics.

3.9.2 Principal component analysis

Results of the PCA were used to identify redundancy in predictor variables and drove the selection of the most important variables for inclusion in the multiple regression base model (Figure 3.32). Redundant variable groups (i.e., variables that tended to cluster together) included:

- 10- and 15-year insect infestation disturbance and elevation.
- 5-, 10-, and 15-year harvest disturbance.
- Longitude and 5-year insect infestation disturbance.
- Wetland cover %, 20-year harvest disturbance, and 15-year wildfire disturbance.
- Deciduous cover % and slope.

- 5-year insect infestation disturbance and longitude.

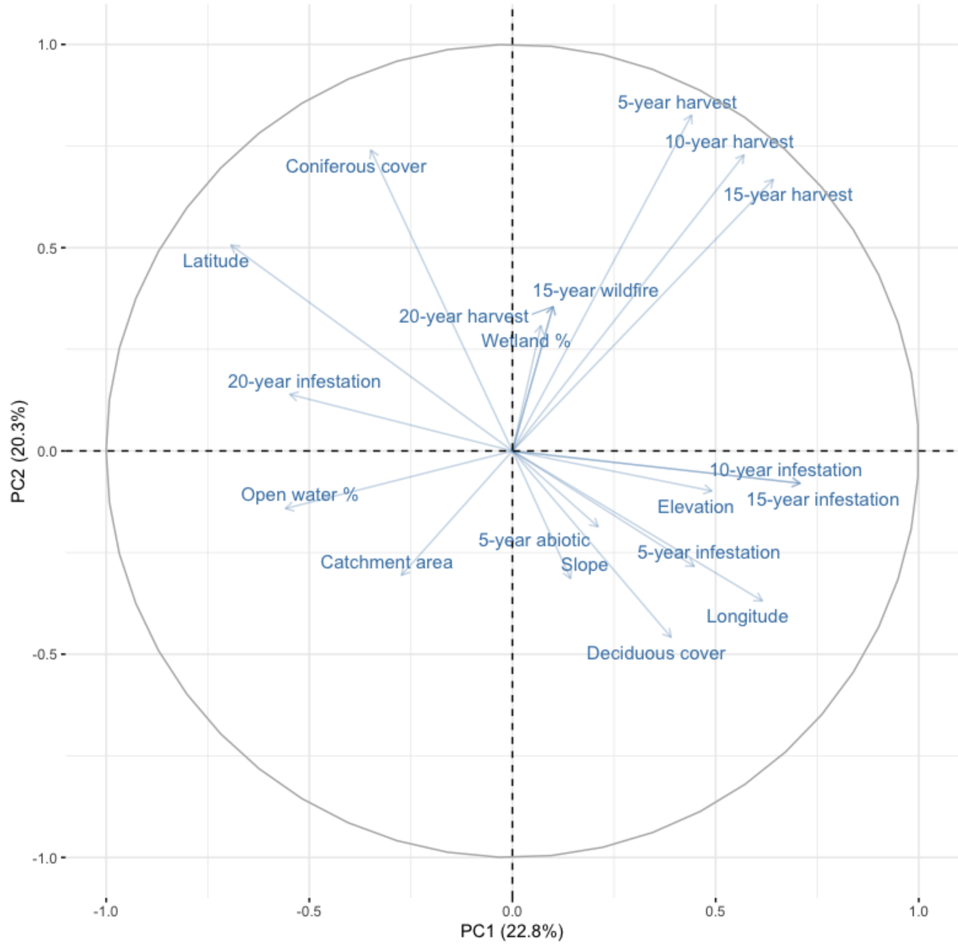

Figure 3.32 Principal component analysis plot results for the 19 landscape and forest disturbance predictor variables.

3.9.3 Multiple linear regression analysis – landscape influence on water quality

3.9.3.1 Base model

The base model, which was fit to DOC export (Section 3.9.3.2) and various sample campaigns of [DOC], $SUVA_{254}$ and instantaneous DOC flux (Figure 3.33), resulted in adjusted r^2 values ranging from -0.2 - 0.54. [DOC] had the strongest negative relationship with open water %. In addition, open water % had numerous significant negative relationships with $SUVA_{254}$ which highlighted its strong explanatory power on DOC quality. All other predictor variables had little explanatory power on DOC quality. Instantaneous DOC flux was observed to have the strongest negative relationship with catchment area and the strongest positive relationship with wetland cover %.

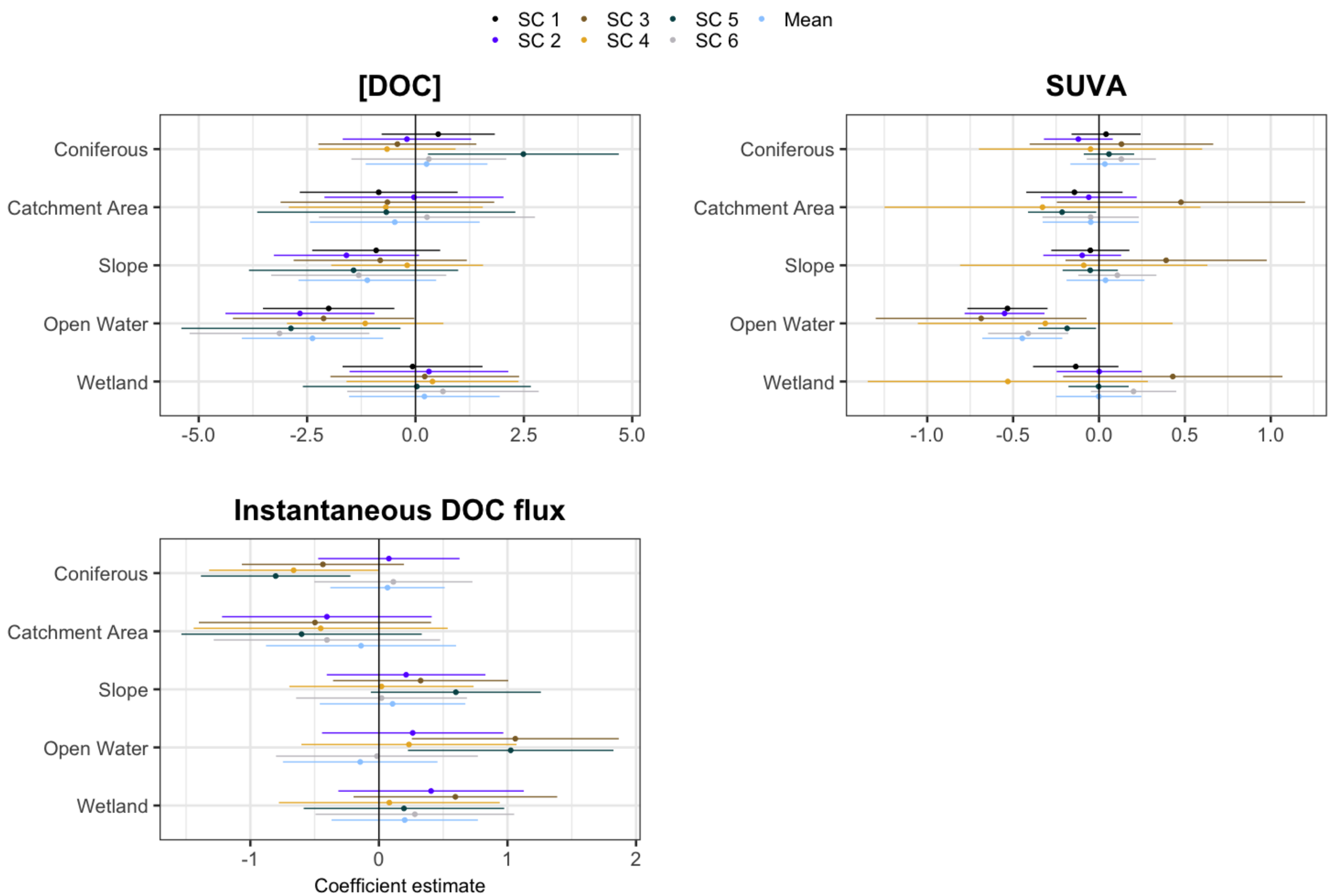

Figure 3.33 Coefficient estimates for [DOC], $SUVA_{254}$, and instantaneous DOC flux. Lines represent 95% confidence intervals.

3.9.3.2 Forest disturbance inclusion

Recent forest disturbance did not help explain much of the variability in mean [DOC]; however, the 15I and 15H legacy disturbance models improved model explanatory power for mean [DOC] the most (i.e., increasing adjusted r^2 by 0.11 - 0.23) (Table 3.4). This was primarily driven by insect infestation, but, to a lesser degree, harvesting contributed as well. In addition, the legacy harvesting model (20H) explained more variation in mean $SUVA_{254}$ than the base model; however, other disturbance and land cover predictor variables had little explanatory power (Table 3.5). DOC export was best explained by the 15H legacy harvesting model followed by the 10H, 5H, and 5H and 5I models, which were all improvements over the base model (Table 3.6). Legacy insect infestation also helped to explain some of the variability; however, to a lesser degree than harvesting. However, when compared to the more consistent results of mean [DOC] and mean $SUVA_{254}$, the small sample size (n = 15) of the DOC export dataset likely led to several statistical issues (e.g., poor model fit, high sensitivity to forest disturbance data, and inconsistencies in AICc weights).

Table 3.4 AICc weights and adjusted r^2 values for models fit to mean [DOC] that included various harvest and insect infestation disturbance timeframes.

Model	AICc	Adjusted r^2
15H + 15I	156.72	0.6
10H + 10I	160.52	0.55
10I	161.74	0.48
15I	161.79	0.48
Base model	165.97	0.37
5H	167.04	0.37
15H	167.75	0.36
10H	168.74	0.34
5I	169.72	0.31
20H	169.82	0.31
5H + 5I	171.13	0.35

Table 3.5 AICc weights and adjusted r^2 values for models fit to mean $SUVA_{254}$ that included various harvest and insect infestation disturbance timeframes.

Model	AICc	Adjusted r^2
20H	51.67	0.50
Base model	53.11	0.42
10I	54.30	0.45
15I	54.30	0.45
15H	55.59	0.42
5H	56.22	0.41
5I	56.41	0.41
10H	56.47	0.41
15H + 15I	58.09	0.43
10H + 10I	58.51	0.43
5H + 5I	59.84	0.40

Table 3.6 AICc weights and adjusted r^2 values for models fit to DOC export that included various harvest and insect infestation disturbance timeframes.

Model	AICc	Adjusted r^2
15H	135.38	0.74
5H	137.62	0.7
10H	138.66	0.68
5H + 5I	141.78	0.82
Base model	146.78	0.05
15H + 15I	148.28	0.73
10I	149.30	0.35
15I	149.30	0.35
10H + 10I	152.56	0.64
20H	153.04	0.16
5I	155.63	0

Chapter 4: Discussion

4.1 Water level and streamflow

The majority of sites in close spatial proximity exhibited hydrologic similarity (Blöschl, 2005); however, several sites, such as M2 and C4, experienced dampened peak flow responses relative to nearby sites, which was likely a function of upstream lake presence and larger catchment areas. In addition, upstream lakes tended to reduce the size of peak flows several kilometres downstream of their respective outlets, which support findings by Leach and Laudon (2019). Generally, it is accepted that peak flows can be less pronounced in catchments that have more open water coverage (Hudson et al., 2021; Leach and Laudon, 2019; FitzGibbon and Dunne, 1981). Moreover, lake storage can play a key role in reducing runoff response (FitzGibbon and Dunne, 1981).

The four sites (C2, C3, C4 and I2) that experienced streamflow decreases over time were all linked to nearby lake systems which likely exerted a strong control over their streamflow regime. Typically, lake water level fluctuates over time as a result of variability in catchment water balance (Wrzesiński and Ptak 2016; Polderman and Pryor, 2004); however, despite observing overall reductions in these catchment outflows, examining whether evapotranspiration exceeded precipitation (Figure 3.2) and groundwater inputs to lakes, which would result in lake water level drops, was outside the scope of this study. Alternatively, these streamflow reductions may have been the result of upstream beaver activity (i.e., an increase in water storage).

Streamflow increases over time were observed at three sites (I5, I6 and M2). These patterns likely resulted from beaver dam construction downstream, which is known to increase stage (Westbrook et al. 2006; Woo and Waddington, 1990). The water level rises observed at I5, I6 and M2 are similar to a hydrograph from a stream that was affected by downstream beaver dam construction in northern Ontario (Woo and Waddington, 1990). Although no dams or ponds were visible at I5, I6 or M2, evidence of beaver was observed at many other sites, such as C11 (Figure 3.34). The effect of beaver was not considered in the design of this study; however, beaver likely influence hydrologic connectivity and water storage in these boreal systems, which may in turn affect water quality (Moore 2003; Woo and Waddington, 1990; Nieman, 1982).

Figure 3.34 A gap flow dam, as defined by Woo and Waddington (1990), at C11. A lodge can also be seen further up the stream, through the tree line, on the right-hand side.

4.1.1 Concentration – discharge relationships

Chemostatic solute behaviour has been commonly observed for [DOC] in river systems (McPhail et al., 2023; Fazekas et al., 2020; Bieroza et al., 2018; Creed et al., 2015). The dominance of chemostatic behaviour seen across the boreal landscape in this study thus agrees with these previous investigations into C - Q patterns (McPhail et al., 2023; Fazekas et al., 2020; Bieroza et al., 2018; Creed et al., 2015). The relatively high prevalence (40%) of transport-limited C - Q relationships also support the notion that [DOC] may exhibit non-chemostatic behaviour as well (McPhail et al., 2023). Event-based flows typically pulse labile DOC from more surficial sources into stream networks as solute transport shifts away from subsurface pathways (Raymond et al., 2016; Yang et al., 2015). This suggests that localised DOC stores are relatively inexhaustive at some sites and discharge limits delivery to streams (Musolff et al., 2015); however, it is clear that [DOC] in certain catchments within the region is more sensitive to changes in flow path during storm events than others (Appendix A). As Lintern et al. (2018) suggest, this may be attributed to the proximity of source areas to the stream or the overall distribution of landscape features within each catchment. Although DOC may be relatively homogeneously distributed across the landscape (i.e., lack of source-limited C - Q relationships), distant source pools could decrease the likelihood of hydrological connection during water table elevation (Lintern et al., 2018), and thus reduce the tendency for [DOC] to increase with discharge.

Moatar et al. (2017) used physical catchment (e.g., catchment area) and land use characteristics in an attempt to explain variability in C - Q relationships for some French catchments. Their results showed that biological processes may influence C - Q behaviour at low flows while hydrology tends to control C - Q behaviour at high flows. McPhail et al. (2023) also attempted to explain differences in C - Q relationships by examining catchment characteristics; however, their selected physiographic indices exhibited little explanatory power. Although variability in C - Q behaviour was present in this study (Figure 3.5), catchment area had negligible correlations with CV_C and CV_C/CV_Q. These relationships remained statistically weak despite having the greater range in catchment area than that examined by McPhail et al. (2023).

C - Q relationships in this study were derived from a small sample size (Figure 3.5) and much longer-term datasets have been used in previous work (McPhail et al. 2023, Moatar et al. 2017; Creed et al. 2015). As such, more data from these streams would permit the estimation of more robust C - Q relationships.

4.2 DOC quantity and quality variability

[DOC] varied between 2.4 mg L^{-1} and 38.2 mg L^{-1} across the landscape, which was relatively unsurprising due to the general expectation of variation in [DOC] in aquatic systems (Thurman, 1985). Additionally, the observed range in [DOC] agreed with many previous water chemistry studies in northern forested environments (Lupon et al., 2023; Oni et al., 2013; Dawson et al., 2011; Laudon et al., 2011; Buffam et al., 2008; Temnerud & Bishop, 2005; Moore, 2003).

Interpolated DOC export, which ranged from 3.0 - 51.7 g C m^{-2} over the study period, agreed with the spatial variability observed in previous boreal investigations (Burd et al., 2018; Mengistu et al., 2013; Olefeldt et al., 2012; Creed et al., 2008; Laudon et al., 2003; Dillon and Molot, 1997; Clair et al., 1994); however, exports from several catchments equalled or exceeded previously reported values (Urban et al., 1989; Naiman, 1982). Unfortunately, other studies primarily report DOC export estimates in annual averages, which cannot be directly compared to the results of this investigation, which only captured a 141-day period from the late spring to fall. Smaller catchments (<5 km^2) tended to have highly variable and relatively large exports. Due to their close connection to source areas (Freeman et al. 2007), small headwater catchments act as the primary entry point to the aquatic system for terrestrial DOC, thus having a large influence on DOC export (Ågren et al., 2007).

$SUVA_{254}$ ranged from 1.6 to 10.1 L mg^{-1} m^{-1}, which was consistent with several other studies (Inamdar et al., 2007). Such heterogeneity in DOC quality tends to be driven by the spatiotemporal variability in hydrological connections to nearby terrestrial source areas in low order streams (Creed et al., 2015; Freeman et al., 2007). This may in part explain why there were no discernable differences in DOC quality between catchment types across the region.

4.2.1 DOC and catchment characteristics

Open water % had significant negative correlations with mean [DOC] and mean $SUVA_{254}$ and also explained the most variability in mean [DOC] and mean $SUVA_{254}$ in the MLRA. Several boreal studies have reported that significant amounts of terrestrial organic carbon entering aquatic ecosystems can be retained and subsequently lost (i.e., via sedimentation or CO_2 emission) in lakes (Algesten et al., 2004; Molot and Dillon 1996). Significant negative relationships between upstream lakes and stream TOC have also been reported in numerous (n = 86) catchments with low lake coverage (range = 0.5 - 26%; mean = 9%) (Mattsson et al., 2005). Longer water residence times in lakes, relative to rivers, also allows for terrestrial DOC to undergo various degrees of transformation and can significantly increase the amount of carbon lost (Algesten et al., 2004; Mash et al., 2004). In conjunction with retention and mineralisation of terrestrially derived DOC, lakes have high production rates of autochthonous DOC through algal or macrophyte activity (Creed et al., 2015; Mash et al., 2004). As such, lakes contribute large amounts of autochthonous DOC downstream, which differs in composition (e.g., less absorbance capacity, more hydrophilic) from terrestrially derived DOC (Health Canada, 2019; Martin et al., 2005; Mash et al., 2004). These processes likely explain why such strong decreases in [DOC], $SUVA_{254}$ and generally lower quantity and variability in DOC export occurred in streams sampled below lakes in this study.

The smallest catchment (C3) had the highest mean [DOC], which was significantly higher than every other study site. This supports the findings of Gough (2014) where the highest mean [DOC] was recorded at the smallest upland catchment in northern Wales. Catchment area also had significant negative correlations with mean [DOC] and mean $SUVA_{254}$ but exhibited significantly less explanatory power than open water % in the MLRA; however, results indicate no discernable difference in mean [DOC] with increasing catchment area if C3 is removed (Figure 3.7), which would support previous findings (Ågren et al., 2013; Temnerud and Bishop 2005; Mitchell and McDonald, 1995). In addition, DOC export had a weak negative relationship with catchment area which supports the negative relationships found in other studies (Ågren et al., 2007; Mattsson et al., 2005). Increased solute transport time due to longer flow paths in larger catchments likely leads to higher retention, decomposition, and mineralisation of DOC (Mattsson et al., 2005). Catchment area also tends to positively covary with lake presence, which increases DOC retention (Algesten et al. 2003; Molot and Dillon, 1996); however, the elevated exports observed in the smaller catchments are likely influenced by recent disturbance events which may explain the weak relationship seen with catchment area (Section 4.2.2).

Overall, slope and wetland cover % were relatively poor explanatory predictor variables of DOC quantity and quality across the landscape; however, a significant positive correlation was observed between mean [DOC] and slope which suggests that it may in part influence the mobilisation and delivery of solutes to the stream network within these catchments (Lintern et al., 2018). The absence of relationships between wetland coverage and DOC quantity and quality was unexpected given that increasing wetland coverage has been shown to be strongly correlated with stream [DOC] and DOC export in other northern forested region studies (Casson et al., 2019; Hanley et al., 2013; Laudon et al., 2011; Creed et al., 2008; Laudon et al., 2004; Dillon and Molot, 1997). Due to water retention and frequent anoxic conditions, most forested wetlands accumulate and store large quantities of DOC, thereby acting as principal sources of carbon to nearby streams (Casson et al., 2019; Creed et al., 2008; Creed et al., 2003; Dillon and Mollot, 1997). Periods of dryness lead to hydrologic disconnection between streams and surrounding wetlands likely leading to more proximal sources, such as surficial soil layers in the riparian zone, serving as the dominant source of DOC during these times (Lintern et al., 2018; Ledesma et al., 2015; Laudon et al., 2009).

Another important aspect of wetlands is their proximity to streams, and work by Laudon et al. (2011) called for examination into how wetland location within the catchment affects DOC dynamics. Andersson and Nyberg (2008) found no significant correlation between DOC flux and wetlands located within 50 m of the stream and statistical models that included near-stream wetland proportion were found to be poor predictors of DOC in central Ontario catchments (Casson et al., 2019). Ultimately, catchment topography may serve as a better overall predictor of DOC flux than wetland extent and their location within the catchment (Andersson and Nyberg, 2008). Perhaps a more important factor is the influence of cryptic wetlands on DOC export (Creed et al., 2003); however, accurate ground surveys would have to be conducted across this landscape to better examine the role of cryptic wetlands on DOC quantity.

4.2.2 DOC and forest cover and disturbance

Coniferous forest cover % did not have a significant relationship with DOC export in this study which disagrees with the notion that coniferous forest coverage tends to be a positive influence on DOC export (Ågren et al., 2007). Additionally, coniferous forest cover % showed little explanatory power on DOC quantity and quality within the MLRA. Nevertheless, acidic, organic-rich soils tend to develop below thick coniferous canopies and this, coupled with higher rates of terrestrial DOC production in the summer months due to increases in temperature and soil respiration, may lead to more DOC leaching from these areas relative to deciduous canopies (Buffam et al., 2008; Ågren et al., 2007). The negligible effect deciduous forest cover had on DOC export was also consistent with findings by Ågren et al. (2007) despite a greater range in catchment coverage (9.7 - 76.5%) of deciduous forest in this study.

Three of the four harvest-dominated catchments in this study, which were sampled between two and eight years after their respective clearcut events, showed elevated [DOC]s relative to control catchments and other disturbed catchments. Generally, rises in [DOC] tend to occur in the first few years after harvesting significant amounts of forested watersheds (Freeman et al., 2023; Shah et al., 2022; Nieminen et al., 2015; Palviainen et al., 2015; Schelker et al., 2012; Laudon et al., 2009; Kreutzweiser et al., 2008; Nieminen, 2004). Conversely, stream [DOC] in harvested catchments in the nearby Turkey Lakes Watershed declined for the first few years post-harvest and only rose 4 - 9 years post-disturbance (Webster et al., 2022). Shah et al. (2022) also noted that elevated [DOC]s may persist for longer than 3 - 4 years post-harvest. Elevated stream [DOC] post-harvest is generally attributed to soil disturbance and the decrease in evapotranspiration from tree loss leading to higher water tables and hydrologic connectivity (Palviainen et al., 2022; Shah et al., 2022; Laudon et al., 2009; Kreutzweiser et al., 2008). Alternatively, leaching from slash or the release of DOC from other harvest residues, such as burn piles or remaining logs, may also contribute to elevated concentrations (Laudon et al., 2009; Kreutzweiser et al., 2008). Indeed, near stream areas observed at some harvested sites in this study contained abundant source material (Figure 3.35). Increased surface temperatures in logged areas can lead to elevated decomposition rates that may release more labile DOC (Palviainen et al., 2022; Shah et al., 2022 Kreutzweiser et al., 2008); however, while soils may become enriched with carbon post-harvest, large amounts have been shown to be retained in surficial horizons (Piirainen et al., 2002).

Figure 3.35 Harvest residue left behind after clearcutting operations near the stream channel at H3.

The significant positive correlation exhibited by legacy harvesting on DOC export suggests that this form of disturbance may have explained the variability in export from several catchments, which is consistent with other investigations (Nieminen et al. 2015; Nieminen, 2004; Lundin 2000; Lundin, 1999). Annual DOC exports have been observed to increase by 8.0 - >20 g C m^{-2} in catchments several years following harvest in northern regions (Nieminen et al. 2015; Nieminen, 2004). Due to the complex response of hydrological processes to forest disturbance (Buttle, 2011), attributing such changes (i.e., increases in DOC export) to any one single metric seems unlikely; rather a combination of factors is likely responsible. Urban et al. (1989) noted that differences in water yield were the main control on large inter-catchment variation in DOC export. Indeed, the review by Buttle (2011) noted that water yield tends to increase after harvesting, with the largest increases seen in smaller catchments. As runoff is a primary control on DOC export (Meybeck, 1982), this may explain why export variability and magnitude were higher in smaller catchments that had experienced > 24% harvest in this study. Alternatively, Naiman (1982) speculated that pervasive beaver activity (Section 4.1) may have influenced high DOC export at one boreal site. Thus, although the results of this study suggest that harvesting and its associated effects on fundamental hydrological processes (Buttle, 2011) may exert the most noticeable control on DOC export, other landscape factors, such as local biological, soil, and hydrogeological conditions, may also be important influences (Davidson et al., 2019; Schiff et al., 1997).

At the group classification level, catchments that experienced a range (25% - 100%) of insect infestation intensity over the last 20 years had relatively similar DOC quantity and quality compared to that of mixed-disturbance and control catchments. Conversely, 10- and 15-year insect infestation increased model explanatory power in the MLRA, and although recent insect infestation (i.e., 5-year) did not explain much of the variability in mean [DOC] and mean $SUVA_{254}$ in the same models, it did have a significant negative correlation with mean $SUVA_{254}$. This significant negative relationship observed between 5-year insect infestation and mean $SUVA_{254}$ may be attributed to the reduction of forest canopy cover (Woodman et al., 2021). Woodman et al. (2021) noted that, during the growing season, insect infestation outbreaks tended to reduce leaf area index in 12 catchments across Ontario, Canada from 1985 to 2016. Moreover, defoliator feeding tends to peak in mid-summer, whereas leaf matter accumulation is typically highest during the fall (Gill et al., 2015). Accordingly, insect defoliators may, to a varying degree, decrease the terrestrial litter pool available for decomposition and subsequent export through aquatic systems (Carlisle et al., 1966). Conversely, McCaig et al. (2023) observed increased aromaticity (i.e., $SUVA_{254}$) in catchments that were recently affected by spruce budworm defoliation. The improvements to model explanatory power by 10- and 15-year insect infestation might by linked to the input of labile carbon into the soil ecosystem by insect frass (Lovett et al., 2002), or may be spurious. Legacy insect infestation (i.e., 20-year) also showed a significant positive correlation with mean [DOC]; however, this can be explained by the sharp increase in the spatial extent of disturbance to 100% catchment coverage in many sites as a result of the regional 2002 Spruce Budworm event. Therefore, group classification findings in this study agree with (a) Clow et al. (2011)'s observation of no significant changes in stream [DOC] after mountain pine beetle infestations in Colorado; and (b) McCaig et al. (2023)'s findings of no effect of spruce budworm defoliation on [DOC] in boreal and hemiboreal streams. Conversely, these conclusions contrast with the results from several other studies where stream [TOC] significantly increased after mountain pine beetle events, which may be a result of more immediate tree mortality (Brouillard et al., 2016; Mikkelson et al., 2013). Lewis and Likens (2007) also observed a short term (i.e., over the course of several weeks) increase in stream [DOC] following insect infestation; such an occurrence could not be captured by the sampling in this study. Ultimately, the results of this investigation suggest that the effect of insect infestation on water quality in boreal headwaters is complex and more work needs to be completed to generalise stream response patterns of this disturbance type.

No wildfire-dominated catchments were included in this study. Over the last 20 years, the study region had little wildfire impact despite wildfire serving as the leading cause of tree mortality by area in Canadian forests (Natural Resources Canada, 2022). The two mixed-disturbance catchments (M2 and M6), which had 25.3% and 20% of their respective catchment areas affected by wildfire 9 and 12 years ago, gave mixed insights as to how these catchments might be responding to this type of disturbance. This, in part, is due to these catchments experiencing significant harvesting over the same period. For instance, some of M2 and M6's water quality metrics (e.g., [DOC] and $SUVA_{254}$) were relatively similar to the ranges observed in other mixed-disturbance catchments. Conversely, M6 had the highest recorded [THM-FP] and [HAA-FP], and one of the highest and most variable DOC export estimates of the entire study. Although the effects of wildfire on the landscape and catchment functions are well documented (Bladon et al., 2014; Brandt et al., 2013), stream chemistry response is somewhat inconsistent as other boreal investigations have reported short term increases in stream [DOC] (Mertens et al, 2019; Emelko et al., 2011), and also decreases (Rodríguez-Cardona et al., 2020; Betts and Jones, 2009). Rodríguez-Cardona et al. (2020) suggest that several factors, such as fire extent, burn depth, and the type of organic matter consumed by blazes all affect watershed recovery timelines. Therefore, further investigation of wildfire-dominated catchments is needed to clarify the effects of this disturbance type on water quality in central Ontario.

4.3 DBP-FP

The formation potential of common DBPs, such as trihalomethanes and haloacetic acids, is a good indicator of the maximum amount of these compounds that may be formed from a given source water during water treatment (Rajamohan et al., 2012). Significant positive relationships between [DOC] and [THM-FP] and [HAA-FP] were observed which parallels results from other studies (Yang et al., 2015; Rajamohan et al., 2012; Engelage et al., 2009; Chow et al., 2007). UV_{254} also provided positive predictions of [THM-FP] and [HAA-FP] as found other forWater network studies (Monica Emelko, pers. communication). In addition, the ranges in [THM-FP] and [HAA-FP] observed in this study were consistent with numerous other investigations (Qadafi, 2020; Yang et al., 2015; Rajamohan et al., 2012; Engelage et al., 2009; Chow et al., 2007).

The influence of [DOC] on [THM-FP] and [HAA-FP] was most apparent over time as the temporal variation in [THM-FP] and [HAA-FP] closely resembled that of [DOC]. Yang et al. (2015) observed similar patterns when monitoring water quality during four storm events in South Korea. This, along with spatial heterogeneity in [THM-FP] and [HAA-FP], is likely tied to terrestrial DOC sourcing and the connectivity of source areas to the stream (Section 4.1; Yang et al., 2015); however, low site numbers (n = 8) limit the ability to explain differences in [THM-FP] and [HAA-FP] between catchment types. Nevertheless, this work highlights that [THM-FP] and [HAA-FP] are strongly coupled to the spatiotemporal variability in [DOC] at the regional scale.

4.4 Uncertainty and errors

This synoptic sampling campaign gave valuable insight into the hydrochemical behaviour of catchments with unique disturbance histories within the Boreal Shield Ecozone; however, the nature of the region and the timing of the study (i.e., COVID-19 pandemic) did contribute to some key limitations.

4.4.1 Study design

Resources and logistics meant that discharge estimates and concurrent water samples were limited to six times at 30 sites. More samples and sites would have provided a better understanding of how these water quality variables, particularly DOC, varied across space and over time. Most samples in this study were collected during baseflow conditions or on the receding limb of precipitation events. Although some receding limb samples in several catchments did indicate increases in [DOC] relative to baseflow (Appendix A), prominent short-term increases of DOC tend to occur during stormflow (Raymond et al., 2016; Hinton et al., 1997). Therefore, an absence of peak flow samples may lead to an underrepresentation of quantity and export of DOC (Kerr et al., 2016). In addition, sampling of small headwater streams can lead to larger export error when compared with the regularity in streamflow patterns of larger systems as missing event-based flows is common (Kerr et al., 2016). Export estimation can also be sensitive to the temporal duration it is calculated over, with lower sampling frequency and shorter sampling duration (i.e., seasonal timeframes) being shown to increase error in annual load (Kerr et al., 2016). Therefore, it is with good confidence that the DOC export estimates calculated in this study likely underrepresent true DOC export amounts flowing out of these catchments during the study period.

Capturing a wider range of flows would have increased rating curve reliability. In turn, better computation of continuous discharge estimates would have occurred, thereby leading to reduced uncertainty in the linear interpolation method used for the calculation of DOC export (Kerr et al., 2016). This would have resulted in an increased number of sites with reasonable DOC export estimates and a more accurate understanding of the quantity and spatial variability in export across the region.

Site accessibility and the type and extent of forest disturbance within the region during the last 20 years limited the availability of pristine and recently disturbed catchments. Ideally, pristine catchments (i.e., 0% forest disturbance in the last 20 years) would have been selected for every control site; however, no pristine catchments were accessible for examination in this study, such that catchments with as close to pristine status as possible had to be selected as controls. Unfortunately, it is impossible to know if the control catchments selected in this study exhibited similar hydrochemical behaviour. One crucial assumption for the control catchments monitored in this study was that they had all completely recovered from an intense Spruce Budworm infestation in 2002 that covered 100% of their catchment areas, respectively.

Only four harvest-dominated catchments were accessible in this study; however, investigating harvested catchments solely affected by clearcutting in this study avoids the potential for varying levels of impact that different harvesting methods may have on DOC quantity and quality. Nevertheless, examining sites affected by shelterwood and selection cut methods within the region would facilitate interesting comparison, specifically regarding stream [DOC] and DOC quality response, and DOC export estimates. Previous work suggests that partial cutting would likely impose less impact on stream solute concentrations than clearcutting (Webster et al., 2020; Kreutzweiser et al., 2008; Tetzlaff et al., 2007; Feller, 2005). Ultimately, low site numbers limit the understanding of spatiotemporal patterns of [DOC] in harvest-dominated catchments; therefore, these catchments may not be an adequate representation of how harvesting impacts water quality in the region. Moreover, the catchment areas of the harvest-dominated sites only ranged from 0.5 - 5.2 km^2 so the harvest-specific conclusions of this study should be limited to basin sizes within that range.

The nature of forest harvesting may vary from catchment to catchment. For instance, the number of roads and temporary bridges requiring construction and deconstruction, which can lead to increases in overland flow as a result of soil disturbance (Cambi et al., 2014), is likely to differ between areas of operation. These actions can result in perturbations in groundwater flow, particularly when roads are constructed on hillslopes (Cambi et al., 2014; Hubbart et al. 2007; Wemple et al. 1996). In addition, machinery can create ruts which vary in number and severity due to variations in topography, land cover, and the amount of catchment area affected by harvesting (Cambi et al., 2014). Ruts are particularly problematic on slopes where they can act as preferential runoff pathways (Cambi et al., 2014). The timing of operations is also important. Variability in soil wetness conditions influence the impact machinery usage has on the landscape, particularly with respect to soil compaction (Cambi et al., 2014). These factors can influence site cleanup, which varies in degree and can leave behind log and debris piles of various size that may act as significant leaching sources of carbon (Laudon et al., 2009; Kreutzweiser et al., 2008). Unfortunately, the spatial coverage of this study and the coarse nature of regional forest disturbance data used cannot account for these localised management effects.

Catchment area calculation and forest disturbance and land cover percentages relied on delineation, geospatial mapping techniques, and severity indexes that are prone to uncertainty. For instance, the choice of digital elevation model can impact catchment delineation accuracy (Keys and Baade, 2019). The Ontario Flow Assessment Tool, the delineation method used in this study, used a 30 m grid resolution; however, Zhang and Montgomery (1994) noted that a 10 m grid size markedly improved accuracy when compared to data of 30 m resolution. Additionally, dissolving forest disturbance polygons together to acquire total cumulative coverage (for each forest disturbance type) over the last 20 years did not account for areas of overlap within disturbance types (particularly insect infestation events). Therefore, disturbance intensity is likely underestimated in this study.

4.4.2 Field and data collection

Little was known about stream behaviour at low and peak flows prior to site selection. This proved particularly challenging for selecting locations to install long term water level loggers. As such, several installations had to be relocated due to low flows, which resulted in more uncertainty in streamflow and, in rare cases, large data gaps. Having a better understanding of water level variability at these sites would have likely resulted in better logger placements, and more extensive and accurate streamflow estimates.

Channel cross-sections selected for estimating discharge were confined to areas near highway crossings where terrain was traversable. Thus, the streambed of many channel sections selected in this study was less than ideal (e.g., large rocks, soft mud and/or vegetation), which increased the uncertainty of discharge estimates.

Several loggers measuring barometric pressure were exposed to extended periods of solar radiation during the study period which caused diurnal patterns to become superimposed on several streamflow regimes. Therefore, more distant surface loggers were used to calculate water pressure at the sites with affected loggers which may have affected water pressure accuracy.

4.4.3 Analyses

A shortcoming of the MLRA was that little explanatory power was observed for many SCs. In addition, there was variability in the explanatory power of the models across SCs which may have led to the inconclusive relationships (i.e., positive and negative coefficient estimates), such as coniferous forest cover % and instantaneous DOC flux. For instance, the base model adjusted r^2 values ranged from 0.21 - 0.71 for [DOC] across the seven SCs which indicates that predictor variable influence fluctuated in strength between SCs, as well as reflecting the large amount of noise in the dataset. Although, open water %, catchment area and legacy insect infestation tended to explain the most variability in mean [DOC], the poor explanatory power of several predictor variables, such as slope and wetland cover %, implies that some of the spatiotemporal patterns in [DOC] across this region are explained by environmental factors missing from this study.

There was a range in collinearity between catchment characteristics. For instance, it was difficult to disentangle the effects of catchment area and open water % on water quality due to their positive correlation, which has also challenged other researchers (Hudson et al. 2021). This was exemplified by mean [DOC]s significant negative correlations with both open water % and catchment area; however, some patterns in several catchments pointed to more lake-influence, such as dampened peak flow responses and consistent [DOC], which predictably led to lower within-catchment variability for several methods of DOC export estimation. In addition, open water % explained most of the variability in $SUVA_{254}$ whereas catchment area had noticeably less explanatory power but exhibited a stronger negative signal with instantaneous DOC flux.

Finally, many catchments had 0% coverage values for abiotic and wildfire disturbance which disproportionally influenced the correlations between these predictor variables and the water quality variables (Figure 3.8).

Chapter 5: Conclusion

5.1 Key findings

A synoptic sampling campaign was conducted from May 2021 to October 2021 in 30 catchments across the Boreal Shield Ecozone in central Ontario. The first research objective was to examine the spatial and temporal dynamics of DOC quantity and quality and DBP-FP quantity in catchments with unique disturbance histories. The second research objective was to assess the ability of landscape characteristics to explain observed patterns of DOC quantity and quality. The results from this study revealed that:

1. Streamflow regimes varied over space and time.
2. C - Q relationships for [DOC] primarily exhibited chemostatic and transport-limited behaviour.
3. DOC quantity and quality and DBP-FP quantity were variable over space and time.
4. Harvest-dominated catchments were associated with elevated [DOC] compared to all other catchment types.
5. DOC export estimates tended to be lower and less variable in catchments that: (1) did not experience recent harvest disturbance; (2) had catchment areas > 5 km^2; and (3) had upstream lakes in close proximity to sampling locations.
6. DOC composition was humified in nature and linked to terrestrial source areas.
7. [DBP-FP] was strongly coupled to the spatiotemporal patterns of [DOC].

8. Open water % and catchment area explained the most variability in mean [DOC] and mean $SUVA_{254}$; however, isolating their effects remains a challenge. Legacy insect infestation, and to a lesser degree legacy harvesting, also helped explain some variability in mean [DOC], while other predictor variables, such as slope, wetland cover % and recent forest disturbance, showed little explanatory power.

5.2 Implications for clean drinking water

DOC quantity and quality and DBP-FP quantity were spatiotemporally variable across a range of flow regimes within the Algoma region. Catchments that had experienced recent harvest events were associated with elevated [DOC], elevated [DBP-FP]s and tended to have higher variability in DOC export estimates. Since certain water treatment facility processes, such as direct/inline filtration and microfiltration, are designed to work best at consistently low DOC levels (<4 mg L^{-1}), variability in DOC quantity and quality across an important source water region could result in treatability concerns (Crittenden et al., 2012; Emelko et al., 2011). Additionally, stormflow responses to rainfall events in some catchments in this study lead to increases in [DOC] and DOC aromaticity (Raymond et al., 2016; Yang et al., 2015; Hinton et al., 1997), thereby leading to more treatability challenges (Health Canada, 2019; Emelko et al., 2011). Accordingly, understanding these spatial and temporal patterns in [DOC] and its fate across the landscape can help forestry and water professionals make informed management decisions such that water quality goals are met to ensure the highest safety for public consumption.

The aesthetic objective limit for [DOC] is 5 mg L^{-1} in Ontario (Government of Ontario, 2003); however, suggested treated water quality targets for [DOC], for DBP control specifically, are 2 mg L^{-1} (source with high specific DBP yield) and 4 mg L^{-1} (source with lower specific DBP yield) for other jurisdictions in Canada (Health Canada, 2019). These are further lowered to 1.8 mg L^{-1} for biological stability (Health Canada, 2019). In this study, every site exhibited higher mean [DOC] than the biological stability target and 90% of sites had higher mean [DOC] than the lower specific DBP yield target. The significant proportion (59%) of $SUVA_{254}$ values that exceeded 4 L mg^{-1} m^{-1} in this study is also concerning as NOM controls coagulant dosage above this threshold (Table 1.1). Nevertheless, the quantity and quality of DOC observed in boreal headwaters is likely to significantly differ from DOC at the intake point to water treatment facilities. This is due to large variability in the travel paths and residence times through terrestrial, fluvial, and lacustrine environments which can result in retention and mineralisation of organic matter (Mattsson et al., 2005; Algesten et al., 2003; Molot and Dillon, 1996), and a range of transformation and decomposition through microbial processing, chemical fixation, remobilisation, transport, and photodegradation (Creed et al., 2015; Aitkenhead-Peterson et al., 2003; Schiff et al., 1997; Aikens and Cotsaris, 1995). Moreover, hundreds of thousands of small headwater streams feed into larger rivers which have lower connectivity to terrestrial sources and show a tendency to homogenise DOC diversity downstream due to (a) lower terrestrial inputs; and (b) the increasing influence of in-stream production and processing of organic carbon (Creed et al., 2015; Tiwari et al., 2014; Freeman et al., 2007). Thus, movement of DOC from source to intake may reduce the variability in terrestrial organic matter composition downstream which may lessen the impact on water treatment operations (Government of Canada, 2019; Creed et al., 2015; Vannote et al., 1980). Conversely, increases in autochthonous DOC downstream, which is less amenable to coagulation during water treatment than terrestrially derived DOC, combined with (a) the terrestrial flushing of more reactive DOC during high flow events; and (b) the occasionally large and variable DOC export amounts in small, recently harvested catchments could impact water treatment costs and effectiveness under future climatic and anthropogenic stressors (Government of Canada, 2019; Raymond et al., 2016; Creed et al., 2015; Hinton et al., 1998).

5.3 Future work

Future work should clarify how factors such as catchment hydrology, land cover characteristics, and forest disturbance influence the quantity and quality of DOC over space and time, which may improve understanding on the implications to water treatment (such as DBP formation). Future experiments should capture more event-based flows with a focus on the rising limb of the hydrograph. Sampling event-based flows is critical since flow paths change relative to baseflow and hydrologically link different DOC source pools. Moreover, sampling event-based flows at a higher temporal resolution could be combined with hysteresis plots to better understand DOC mobilisation and sources. Longitudinal sampling of stream reaches could also provide more insight into the spatial variability of DOC in northern headwater systems. Future studies might consider the effect of beaver due to their: (a) prevalence in streams within the region; and (b) impact on streamflow regime, riparian environment dynamics, and water storage, which all influence water quality (Westbrook et al., 2020; Westbrook et al., 2006; Woo and Waddington, 1990).

Future MLRAs could include other important predictor variables such as dominant parent material, water travel time, or soil wetness conditions. Their inclusion may better explain the spatiotemporal variability in DOC. In addition, models should prioritise the inclusion of topographic and geological variables to better understand the influence of landscape characteristics on [DOC] during the summer months due to the strong control of these variables on stream solute concentrations during dry periods (Lintern et al., 2018). Finally, hierarchical partitioning (specifically through the ‘rdacca.hp’ R package) could be a useful supplement to multiple linear regression in the future (Lai et al., 2022; Chevan and Sutherland, 1991).

REFERENCES

Aaltonen, H., Tuukkanen, T., Palviainen, M., Laurén, A., Tattari, S., Piirainen, S., Mattsson, T., Ojala, A., Launiainen, S., Finér, L. (2021). Controls of organic carbon and nutrient export from unmanaged and managed boreal forest catchments. Water, 13(17), 2363.

Adler, T., Underwood, K.L., Rizzo, D.M., Harpold, A., Sterle, G., Li, L., Wen, H., Stinson, L., Bristol, C., Stewart, B., Lini, A., Perdrial, N., Perdrial, J.N. (2021). Drivers of dissolved organic carbon mobilization from forested headwater catchments: a multi scaled approach. Frontiers in Water, 3, 578-608.

Ågren, A., Buffam, I., Jansson, M., Laudon, H. (2007). Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. Journal of Geophysical Research: Biogeosciences, 112, G03003.

Aiken, G., and Cotsaris, E. (1995). Soil and hydrology: their effect on NOM. Journal - American Water Works Association, 87(1), 36-45.

Aitkenhead-Peterson, J.A., McDowell, W.H., Neff, J.C. (2003). Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters. Aquatic ecosystems: interactivity of dissolved organic matter, 25-70. Elsevier.

Amon, R.M.W. (2002). The biogeochemistry of dissolved organic matter in aquatic ecosystems – an overview. In Bright, M., P. C. Dworschak , and M. Stachowitsch. The Vienna School of Marine Biology—A tribute to Jörg Ott. Vienna Facultas Universitätsverlag. 1-18.

Andersson, J., and Nyberg, L. (2008). Spatial variation of wetlands and flux of dissolved organic carbon in headwater streams. Hydrological Processes, 22(12), 1965-1975.

Ates, N., Kitis, M., Yetis, U. (2007). Formation of chlorination by-products in waters with low SUVA—correlations with SUVA and differential UV spectroscopy. Water Research, 41(18), 4139-4148.

Battin, T.J., Kaplan, L.A., Findlay, S., Hopkinson, C.S., Martl, E., Packman, A.I., Newbold, J.D., Sabater, F. (2008). Biophysical controls on organic carbon fluxes in fluvial networks. Nature Geoscience, 1(2), 95-100.

Bieroza, M.Z., Heathwaite, A.L., Bechmann, M., Kylimar, K., Jordan, P. (2018). The concentration-discharge slope as a tool for water quality management. Science of The Total Environment, 630(2018), 738-749.

Bladon, K.D., Emelko, M.B., Silins, U., Stone, M. (2014). Wildfire and the future of water supply. Environmental Science & Technology, 48(16), 8936-8943.

Blöschl, G. (2005). Rainfall-runoff modeling of ungauged catchments. Encyclopedia of Hydrological Sciences. John Wiley & Sons, Inc.

Bond, T., Goslan, E., Parsons, S., Jefferson, B. (2012). A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. Environmental Technology Reviews, 1(1), 93-113.

Bosch, J.M., and Hewlett, J.D. (1982). A review of catchment experiments to determine the effect of vegetation changes on water yield and evapotranspiration. Journal of Hydrology, 55(1-4), 3-23.

Boulanger, Y., and Puigdevall, J.P. (2021). Boreal forests will be more severely affected by projected anthropogenic climate forcing than mixedwood and northern hardwood forests in eastern Canada. Landscape Ecology, 36, 1725-1740.

Boulanger, Y., Puigdevall, J.P, Bélisle, A.N., Bergeron, Y., Brice, M.H., Cyr, D., Grandpré, L.D., Fortin, D., Gauthier, S., Grondin, P., Labadie, G., Leblond, M., Marchand, M., Splawinski, T.B., St-Laurent, M.H., Thiffault, E., Tremblay, J.A., Yamasaki, S.H. (2023). A regional integrated assessment of the impact of climate change and of the potential adaptation avenues for Quebec's forests. Canadian Journal of Forest Research, 53(8), 556-578.

Brandt, J.P., Flannigan, M.D., Maynard, D.G., Thompson, I.D., Volney, W.J.A. (2013). An introduction to Canada's boreal zone: ecosystem processes, health, sustainability, and environmental issues. Environmental Reviews, 21(4), 207-226.

Brouillard, B.M., Dickenson, E.R.V., Mikkelson, K.M., Sharp, J.O. (2016). Water quality following extensive beetle-induced tree mortality: interplay of aromatic carbon loading, disinfection byproducts, and hydrologic drivers. Science of The Total Environment, 572, 649-659.

Buffam, I., Laudon, H., Seibert, J., Morth, C., Bishop, K. (2008). Spatial heterogeneity of the spring flood acid pulse in a boreal stream network. Science of the Total Environment, 407(1), 708-722.

Burd, K., Tank, S.E., Dion, N., Quinton, W.L., Spence, C., Tanentzap, A.J., Olefeldt, D. (2018). Seasonal shifts in export of DOC and nutrients from burned and unburned peatland-rich catchments, Northwest Territories, Canada. Hydrology and Earth System Sciences, 22(8), 4455-4472.

Cambi, M., Certini, G., Ner, F., Marchi, E. (2015). The impact of heavy traffic on forest soils: a review. Forest Ecology and Management, 338, 124-138.

Carignan, R., and Steedman, R.J. (2000). Impacts of major watershed perturbations on aquatic ecosystems. Canadian Journal of Fisheries and Aquatic Sciences, 57(Suppl. 2), 1-4.

Carlisle, A., Brown, A. H. F., White, E. J. (1966). Litter fall, leaf production and the effects of defoliation by tortrix viridana in a sessile Oak (quercus petraea) woodland. Journal of Ecology, 54, 65-85.

Chamberlin, T.C. (1890). The method of multiple working hypotheses. Science, 15(366), 92-96.

Chevan, A., and Sutherland, M. (1991). Hierarchical partitioning. The American Statistician, 45(2), 90-96.

Chow, A.T., Dahlgren, R.A., Harrison, J.A. (2007). Watershed sources of disinfection byproduct precursors in the Sacramento and San Joaquin rivers, California. Environmental Science & Technology, 41(22), 7645-7652.

Clow, D.W., Rhoades, C., Briggs, J., Caldwell, M., Lewis, W.M. (2011). Responses of soil and water chemistry to mountain pine beetle induced tree mortality in Grand County, Colorado, USA. Applied Geochemistry, 26, 5174-5178.

Coogan, S.C.P., Robinne, F., Jain, P., Flannigan, M.D. (2019). Scientists' warning on wildfire – a Canadian perspective. Canadian Journal of Forest Research. 49(9), 1015-1023.

Cortés, C. (2018). Genotoxicity of disinfection byproducts and disinfected waters: a review of recent literature. Mutation Research - Genetic Toxicology and Environmental Mutagenesis, 831, 1-12.

Creed, I. F., Sanford, S. E., Beall, F. D., Molot, L. A., Dillon, P. J. (2003). Cryptic wetlands: integrating hidden wetlands in regression models of the export of dissolved organic carbon from forested landscapes. Hydrological Processes, 17(18), 3629-3648.

Creed, I. F., Beall, F. D., Clair, T. A., Dillon, P.J., Hesslein, R.H. (2008). Predicting export of dissolved organic carbon from forested catchments in glaciated landscape with shallow soils. Global Biogeochemical Cycles, 22(4), GB4024.

Creed, I. F., McKnight, D.M., Pellerin, B.A., Green, M.B., Bergamaschi, B.A., Aiken, G.R., Burns, D.A., Findlay, S.E.G., Shanley, J.B., Striegl, R.G., Aulenbach, B.T., Clow, D.W., Laudon, H., McGlynn, B.L., McGuire, K.J., Smith, R.A., Stackpoole, S.M., Smith, R. (2015). The river as a chemostat: fresh perspectives on dissolved organic matter down the river continuum. Canadian Journal of Fisheries and Aquatic Sciences, 72(8), 1272-1285.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G. (2012). MWH's Water Treatment: principles and design. John Wiley & Sons Inc.

Dale, V.H., Joyce, L.A., McNulty, S., Neilson, R.P., Ayres, M.P., Flannigan, M.D., Hanson, P.J., Irland, L.C., Lugo, A.E., Peterson, C.J., Simberloff, D., Swanson, F.J., Stocks, B.J., Wotton, B. (2001). Climate change and forest disturbances: climate change can affect forests by altering the frequency, intensity, duration, and timing of fire, drought, introduced species, insect and pathogen outbreaks, hurricanes, windstorms, ice storms, or landslides. BioScience, 51(9), 723-734.

Davidson, S.J., Elmes, M.C., Rogers, H., Van Beest, C., Petrone, R., Price, J.S., Strack, M. (2019). Hydrogeologic setting overrides any influence of wildfire on pore water dissolved organic carbon concentration and quality at a boreal fen. Ecohydrology, 12(7), e2141.

Dawson, J.C., Tetzlaff, D., Speed, M., Hrachoqitz, M., Soulsby, C. (2011). Seasonal control on DOC dynamics in nested upland catchments in NE Scotland. Hydrological Processes, 25(10), 1647-1658.

DeAngelis, D.L. (2008). Boreal Forest. Encyclopedia of Ecology, 493-495. Elsevier.

Dillon, P.J., and Molot, L.A. (1997). Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. Water Resources Research, 33(11), 2591-2600.

Edzwald, J.K. (1993). Coagulation in drinking water treatment particles, organics and coagulants. Water Science and Technology, 27(11), 21-35.

Eimers, M.C., Buttle, J.M., Watmough, S.A. (2008). Influence of seasonal changes in runoff and extreme events on dissolved organic carbon trends in wetland- and upland-draining streams. Canadian Journal of Fisheries and Aquatic Sciences, 65(5), 796-808.

Emelko, M.B., Silins, U., Bladon, K.B., Stone, M. (2011). Implications of land disturbance on drinking water treatability in a changing climate: demonstrating the need for “source water supply and protection” strategies. Water Research, 45(2), 461-472.

Engelage, S.K., Stringfellow, W.T., Letain, T. (2009). Disinfection byproduct formation potentials of wetlands, agricultural drains, and rivers and the effect of biodegradation on trihalomethane precursors. Journal of Environmental Quality, 38(5), 1901-1908.

Erdozain, M., Emilson, C.E., Kreutzweiser, D.P., Kidd, K.A., Mykytczuk, N., Sibley, P.K. (2020). Forest management influences the effects of streamside wet areas on stream ecosystems. Ecological Applications, 30(4), e02077.

Fazekas, H.M., Wymore, A.S., McDowell, W.H. (2020). Dissolved organic carbon and nitrate concentration-discharge behavior across scales: land use, excursions, and misclassification. Water Resources Research, 56(8), e2019WR027028.

Feller, M.C. (2005). Forest harvesting and streamwater inorganic chemistry in western North America: a review. Journal of American Water Resources Assocociation, 41(4), 785-811.

Fogg, S.K., O'Daniel, S.J., Poole, G.C., Reinhold, A.M., Hyman, A.A., Pracheil, B. (2020). A simple, reliable method for long-term, in-stream data logger installation using rock-climbing hardware. Methods in Ecology and Evolution, 11(5), 684-689.

Freeman, E.C., Emilson, E.J.S., Webster, K., Dittmar, T., Tanentzap, A.J. (2023). Logging disrupts the ecology of molecules in headwater streams. Preprint. https://www.biorxiv.org/content/10.1101/2023.03.07.531469v1.abstract

Freeman, M.C., Pringle, C.M., Jackson, C.R. (2007). Hydrologic connectivity and the contribution of stream headwaters to ecological integrity at regional scales. Journal of the American Water Resources Association, 43(1), 5-14.

Gan, X., Karanfil, T., Kaplan Bekaroglu, S.S., Shan, J. (2013). The control of N-DBP and C-DBP precursors with MIEX®. Water Research, 47(3), 1344-1352.

Gill, A. L., Gallinat, A.S., Sanders-DeMott, R., Rigden, A. J., Short Gianotti, D.J., Mantooth, J.A., Templer, P.H. (2015). Changes in autumn senescence in northern hemisphere deciduous trees: a meta-analysis of autumn phenology studies. Annals of Botany, 116, 875-888.

Geological Survey of Canada. (1989). Quaternary geology of Canada and Greenland. Canadian government publishing centre.

Godsey, S.E., Kirchner, J.W., Clow, D.W. (2009). Concentration-discharge relationships reflect chemostatic characteristics of US catchments. Hydrological Processes, 23(13), 1844-1864.

Gough, R. (2014). Catchment influences on dissolved organic carbon concentration and character; implications for potable water treatment and trihalomethane control. Doctor of Philosophy Thesis, Bangor University.

Grabs, T., Bishop, K., Laudon, H., Lyon, S.W., Seibert, J. (2012). Riparian zone hydrology and soil water total organic carbon (TOC): implications for spatial variability and upscaling of lateral riparian TOC exports. Biogeosciences, 9(10), 3901-3916.

Hanley, K.W., Wollheim, W.M., Salisbury, J., Huntington, T., Aiken, G. (2013). Controls on dissolved organic carbon quantity and chemical character in temperate rivers of North America. Global Biogeochemical Cycles, 27(2), 492-504.

Health Canada. (2019). Guidance on natural organic matter in drinking water.

Health Canada. (2020). Guidelines for Canadian drinking water quality–summary table.

Hinton, M.J., Schiff, S.L., English, M.C. (1997). The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochemistry, 36, 67-88.

Hrachowitz, M., Benettin, P., Van Breukelen, B.M., Fovet, O., Howden, N.J.K., Ruiz, L., Van Der Velde, Y., Wade, A.J. (2016). Transit times-the link between hydrology and water quality at the catchment scale: Linking hydrology and transit times. Wiley Interdisciplinary Reviews: Water, 3(5), 629-657.

Hubbart, J.A., Link, T.E., Gravelle, J.A., Elliot, W.J. (2007). Timber harvest impacts on water yield in the continental/maritime hydroclimatic region of the United States. Forest Science, 53(2), 169-180.

Hudson, D.T., Leach, J.A., Webster, K., Houle, D. (2021). Streamflow regime of a lake-stream system based on long-term data from a high density hydrometric network. Hydrological Processes, 35(10), e14396.

Jantze, E.J., Laudon, H., Dahlke, H.E., Lyon, S.W. (2015). Spatial variability of dissolved Organic and inorganic carbon in subarctic headwater streams. Arctic, Antarctic, and Alpine Research, 47(3), 529-546.

Kerr, J.G., Eimers, M.C., Yao, H. (2016). Estimating stream solute loads from fixed frequency sampling regimes: the importance of considering multiple solutes and seasonal fluxes in the design of long-term stream monitoring networks: sampling frequency and stream solute load error. Hydrological Processes, 30(10), 1521-1535.

Keys, L., and Baade, J. (2019). Uncertainty in catchment delineations as a result of digital elevation model choice. Hydrology, 6(1), 13.

Kreutzweiser, D.P., Hazlett, P.W., Gunn, J.M. (2008). Logging impacts on the biogeochemistry of boreal forest soils and nutrient export to aquatic systems: a review. Environmental Reviews, 16, 157-179.

Lai, J., Zou, Yi., Zhang, J., Peres-Neto, P. (2022). Generalizing hierarchical and variation partitioning in multiple regression and canonical analyses using the rdacca.hp R package. Methods in Ecology and Evolution, 13(4), 782-788.

Larson, J.H., Frost, P.C., Zheng, Z., Johnston, C.A., Bridgham, S.D., Lodge, D.M., Lamberti, G.A. (2007). Effects of upstream lakes on dissolved organic matter in streams. Limnology and Oceanography, 52(1), 60-69.

Laudon, H., Köhler, S., Buffam, I. (2004). Seasonal TOC export from seven boreal catchments in northern Sweden. Aquatic Sciences - Research Across Boundaries, 66(2), 223-230.

Laudon, H., Hedtjärn, J., Schelker, J., Bishop, K., Sørensen, R., Ågren, A. (2009). Response of dissolved organic carbon following forest harvesting in a boreal forest. AMBIO: A Journal of the Human Environment, 38(7), 381-386.

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., Köhler, S.J. (2011). Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling. Ecosystems, 14(6), 880-893.

Laudon, H., Kuglerová, L., Sponseller, R.A., Futter, M., Nordin, A., Bishop, K., Lundmark, T., Egnell, G., Ågren, A. (2016). The role of biogeochemical hotspots, landscape heterogeneity, and hydrological connectivity for minimizing forestry effects on water quality. Ambio, 45(52), 152-162.

Leach, J.A., and Laudon, H. (2019). Headwater lakes and their influence on downstream discharge. Limnology and Oceanography Letters, 4(4), 105-112.

Ledesma, J.L.J., Grabs, T., Bishop, K.H., Schiff, S.L., Köhler, S.J. (2015). Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. Global Change Biology, 21(8), 2963-2979.

Leonard, L.T., Vanzin, G.F., Garayburu-Caruso, V.A., Lau, S.S., Beutler, C.A., Newman, A.W., Mitch, W.A., Stegen, J.C., Williams, K.H., Sharp, J.O. (2022). Disinfection byproducts formed during drinking water treatment reveal an export control point for dissolved organic matter in a subalpine headwater stream. Water Research X, 15, 100144.

Lintern, A., Webb, J.A., Ryu, D., Liu, S., Bende-Michl, U., Water, D., Leahy, P., Wilson, P., Western, A.W. (2018). Key factors influencing differences in stream water quality across space. WIREs Water, 5(1), e1260.

Lovett, G.M., Christenson, L.M., Groffman, P.M., Jones, C.G., Hart, J.F., Mitchell, M.J. (2002). Insect defoliation and nitrogen cycling in forests. BioScience, 52(4), 335-341.

Lupon, A., Ploum, S.W., Leach, J.A., Kuglerová, L., Laudon, H. (2023). Groundwater flow paths drive longitudinal patterns of stream dissolved organic carbon (DOC) concentrations in boreal landscapes. Hydrology and Earth System Sciences, 27(2), 613-625.

Mast, M.A. and Clow, D.W. (2008). Effects of 2003 wildfires on stream chemistry in Glacier National Park, Montana. Hydrological Processes, 22(26), 5013-5023.

Mattsson, T., Kortelainen, P., Räike, A. (2005). Export of DOM from boreal catchments: impacts of land use cover and climate. Biogeochemistry, 76(2), 373-394.

McCaig, M.L., Kidd, K.A., Smenderovac, E.E., Perrotta, B.G., Emilson, C.E., Stastny, M., Venier, L., Emilson, E.J.S. (2023). Influence of spruce budworm defoliation on stream habitat and microbiome structure and function. Manuscript submitted for publication.

McClain, M.E., Boyer, E.W., Dent, C.L., Gergei, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., Harvey, J.W., Johnston, C.A., Mayorga, E., McDowell, W.H., Pinay, G. (2003). Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems, 6(4), 301-312.

McDonald, T.A., and Komulainen, H. (2005). Carcinogenicity of the chlorination disinfection by-product MX. Journal of Environmental Science and Health, Part C, 23(2), 163-214.

McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, Kulbe, T., Andersen, D.T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnology and Oceanography, 46(1), 38-48.

McPhail, S., Buttle, J.M., Webster, K.L., Leach, J.A. (2023). Persistent chemostatic behaviour of stream solutes in a northern hardwood forest under climatic and atmospheric deposition changes. Hydrological Processes, 37(5), e14888.

Ministry of Natural Resources. (2009). Forest Information Manual: forest resources inventory technical specifications.

Minshall, G.W., Brock, J.T., Andrews, D.A., Robinson, C.T. (2001). Water quality, substratum and biotic responses of five central Idaho (USA) streams during the first year following the Mortar Creek fire. International Journal of Wildland Fire, 10(2), 185-199.

Mistick, E., and Johnson, M.S. (2020). High-frequency analysis of dissolved organic carbon storm responses in headwater streams of contrasting forest harvest history. Journal of Hydrology, 590, 125371.

Moatar, F., and Meybeck, M. (2005). Compared performances of different algorithms for estimating annual nutrient loads discharged by the eutrophic River Loire. Hydrological Processes, 19(2), 429-444.

Moatar, F., Abbott, B.W., Minaudo, C., Curie, F., Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. Water Resources Research, 53(2), 1270-1287.

Molot, L. A., and Dillon, P.J. (1996). Storage of terrestrial carbon in boreal lake sediments and evasion to the atmosphere. Global Biogeochemical Cycles, 10(3), 483-492.

Moola, F., and Roth, R. (2019). Moving beyond colonial conservation models: Indigenous protected and conserved areas offer hope for biodiversity and advancing reconciliation in the Canadian boreal forest. Environmental Reviews, 27(2), 200-201.

Moore, R.D., Spittlehouse, D.L., Story, A. (2005). Riparian microclimate and stream temperature response to forest harvesting: a review. Journal of the American Water Resources Association, 41(4), 813-834.

Moore, T.R. (2003). Dissolved organic carbon in a northern boreal landscape. Global Biogeochemical Cycles, 17(4), 1109.

Musolff, A., Schmidt, C., Selle, B., Fleckenstein, J.H. (2015). Catchment controls on solute export. Advances in Water Resources, 86(Part A), 133-146.

Musolff, A., Fleckenstein, J.H., Opitz, M., Büttner, O., Kumar, R., Tittel, J. (2018). Spatio-temporal controls of dissolved organic carbon stream water concentrations. Journal of Hydrology, 566, 205-215.

Naiman, R.J. (1982). Characteristics of sediment and organic carbon export from pristine boreal forest watersheds. Canadian Journal of Fisheries and Aquatic Sciences, 39(12), 1699-1718.

Natural Resources Canada. (2022). The state of Canada's forests: annual report 2022.

Natural Resources Canada. (2023). The boreal forest. https://natural-resources.canada.ca/our-natural-resources/forests/sustainable-forest-management/boreal-forest/13071

Nieminen, M. (2004). Export of dissolved organic carbon, nitrogen and phosphorus following clear-cutting of three Norway spruce forests growing on drained peatlands in southern Finland. Silva Fennica, 38(2), 123-132.

Nieminen, M., Koskinen, M., Sarkkola, S., Laurén, A., Kaila, A., Kiikkilä, O., Nieminen, T.M., Ukonmaanaho, L. (2015). Dissolved organic carbon export from harvested peatland forests with differing site characteristics. Water, Air, & Soil Pollution, 226(6), 181.

Nokes, C.J., Fenton, E., Randall, C.J. (1999). Modelling the formation of brominated trihalomethanes in chlorinated drinking waters. Water Research, 33(17), 3557-3568.

Ohno, T. (2002). Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. Environmental Science & Technology, 36(4), 742-746.

Olefeldt, D., Roulet, N., Giesler, R., Persson, A. (2013). Total waterborne carbon export and DOC composition from ten nested subarctic peatland catchments-importance of peatland cover, groundwater influence, and inter-annual variability of precipitation patterns: Waterbone Carbon Export From Subarctic Catchments. Hydrological Processes, 27(16), 2280-2294.

Oliver, C.D., and Larson, B.A. (1996). Forest stand dynamics: update edition. John Wiley & Sons Inc.

Oni, S.K., Futter, M.N., Bishop, K., Köhler, S.J., Ottosson-Löfvenius, M., Laudon, H. (2013). Long-term patterns in dissolved organic carbon, major elements and trace metals in boreal headwater catchments: trends, mechanisms and heterogeneity. Biogeosciences, 10(4), 2315-2330.

Palviainen, M., Peltomaa, E., Laurén, A., Kinnunen, N., Ojala, A., Berninger, F., Zhu, X., Pumpanen, J. (2022). Water quality and the biodegradability of dissolved organic carbon in drained boreal peatland under different forest harvesting intensities. Science of the Total Environment, 806, 150919.

Piirainen, S., Finer, L., Mannerkoski, H., Starr, M. (2002). Effects of forest clear-cutting on the carbon and nitrogen fluxes through podzolic soil horizons. Plant and Soil, 239(2), 301-311.

Ploum, S.W., Laudon, H., Peralta-Tapia, A., Kuglerová, L. (2020). Are dissolved organic carbon concentrations in riparian groundwater linked to hydrological pathways in the boreal forest?. Hydrology and Earth System Sciences, 24(4), 1709-1720.

Polderman, N.J., and Pryor, S.C. (2004). Linking synoptic-scale climate phenomena to lake-level variability in the Lake Michigan-Huron basin. Journal of Great Lakes Research, 30(3), 419-434.

Price, D.T., and Apps, M.J. (1995). The boreal forest transect case study: global change effects on ecosystem processes and carbon dynamics in boreal Canada. Water, Air, & Soil Pollution. 82, 203-214.

Price, D.T., Alfaro, R.I., Brown, K.J., Flannigan, M.D., Fleming, R.A., Hogg, E.H., Giradin, M.P., Lakusta, T., Johnston, M., McKenney, D.W., Pedlar, J.H., Stratton, T., Sturrock, R.N., Thompson, I.D., Trofymow, J.A., Venier, L.A. (2013). Anticipating the consequences of climate change for Canada’s boreal forest ecosystems. Environmental Reviews, 21(4), 322-365.

Qadafi, M. (2020). Trihalomethane and haloacetic acid formation potential of tropical peat water: effect of tidal and seasonal variations. International Journal of GEOMATE, 18(66), 111-117.

Rajamohan, R., Ebenezer, V., Rajesh, P., Venugopalan, V.P., Natesan, U., Murugesan, V., Narasimhan, S.V. (2012). Trihalomethane formation potential of drinking water sources in a rural location. Advances in Environmental Research, 1(3), 181-189.

Raymond, P.A., Saiers, J.E., Sobczak, W.V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse-shunt concept. Ecology, 97(1), 5-16.

Reckhow, D.A., Singer, P.C., Malcolm, R.L. (1990). Chlorination of humic materials: byproduct formation and chemical interpretations. Environmental Science & Technology, 24(11), 1655-1664.

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M. (2007). Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. Mutation Research, 636(1-3), 178-242.

Robinne, F., Hallema, D.W, Bladon, K.D., Buttle, J.M. (2020) Wildfire impacts on hydrologic ecosystem services in North American high-latitude forests: a scoping review. Journal of Hydrology, 581, 124360.

Roulet, N. and Moore, T.R. (2006). Browning the waters. Nature, 444(7117), 283-284.

Sanborn, P., Lamontagne, L., Hendershot, W. (2011). Podzolic soils of Canada: genesis, distribution, and classification. Canadian Journal of Soil Science, 91(5), 843-880.

Sánchez-Pinillos, M., Leduc, A., Ameztegui, A., Kneeshaw, D., Lloret, F., Coll, L. (2019). Resistance, resilience or change: post-disturbance dynamics of boreal forests after insect outbreaks. Ecosystems, 22(8), 1886-1901.

Selbes, M., Brown, J., Lauderdale, C., Karanfil, T. (2017). Removal of selected C- and N-DBP precursors in biologically active filters. American Water Works Association, 109(3), E73-E84.

Schiff, S.L., Aravena, R., Trumbore, S.E., Hinton, M.J., Elgood, R., Dillon, P.J. (1997). Export of DOC from forested catchments on the Precambrian Shield of central Ontario: clues from ^{13}C and ^{14}C. Biogeochemistry, 36(1), 43-65.

Shah, N.W., Baillie, B.R., Bishop, K., Ferraz, S., Högbom, L., Nettles, J. (2022). The effects of forest management on water quality. Forest Ecology and Management, 522, 120397.

Smith, H.G., Sheridan, G.J., Lane, P.N.J., Nyman, P., Haydon, S. (2011). Wildfire effects on water quality in forest catchments: a review with implications for water supply. Journal of Hydrology, 396(1-2), 170-192.

Smith, M.A. (2015). A reflection on first nations in their boreal homelands in Ontario: between a rock and a caribou. Conservation and Society, 13(1), 23-38.

Tabachnick, B.G., and Fidell, S.L. (1996). Using multivariate statistics third edition. Harper Collins College Publishers.

Tank, S.E., Frey, K.E., Striegl, R.G., Raymond, P.A., Holmes, R.M., McClelland, J.W., Peterson, B.J. (2012). Landscape‐level controls on dissolved carbon flux from diverse catchments of the circumboreal. Global Biogeochemical Cycles, 26(4), 2012GB004299.

Temnerud, J., and Bishop, K. (2005). Spatial variation of streamwater chemistry in two Swedish boreal catchments: implications for environmental assessment. Environmental Science & Technology, 39(6), 1463-1469.

Tetzlaff, D., Malcolm, I.A., Soulsby, C. (2007). Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments. Journal of Hydrology, 346(3-4), 93-111.

Thiffault, E. (2019). Boreal forests and soils. Developments in Soil Science, 36, 59-82.

Thurman, E.M. (1985). Organic geochemistry of natural waters. Springer.

Turnipseed, D.P., and Sauer, V.B. (2010). Discharge measurements at gaging stations: chapter 8 of book 3, section A. United States Geological Survey.

United States Geological Survey. (2006). Chapter A4: collection of water samples. In Book 9 handbooks for water-resources investigations: national field manual for the collection of water-quality data.

United States Geological Survey. (2023). Base flow in rivers. https://www.usgs.gov/special-topics/water-science-school/science/base-flow-rivers

United States Environmental Protection Agency. (1979). The analysis of trihalomethanes In drinking water by the purge and trap method (501.1).

United States Environmental Protection Agency. (2003). Determination of haloacetic acids and dalapon in drinking water by liquid-liquid microextraction, derivatization, and gas chromatography with electron capture detection, (552.3).

United States Environmental Protection Agency. (2006). National primary drinking water regulations: stage 2 disinfectants and disinfection byproducts rule; final rule. Federal Registrar, 71(2), 388-493.

Urban, N.R., Bayley, S.E., Eisenreich, S.J. (1989). Export of dissolved organic carbon and acidity from peatlands. Water Resources Research, 25(7), 1619-1628.

Uyanik, G.K., and Güler, N. (2013). A study on multiple linear regression analysis. Procedia – Social and Behavioural Sciences, 106, 234-240.

Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R., Cushing, C.E. (1980). The river continuum concept. Canadian Journal of Fisheries and Aquatic Sciences, 30(1), 130-37.

Vidon, P., Carleton, W., Mitchell, M.J. (2014). Spatial and temporal variability in stream dissolved organic carbon quantity and quality in an Adirondack forested catchment. Applied Geochemistry, 46, 10-18.

Watson, S.R. (2003). Cyanobacterial and eukaryotic algal odour compounds: signals or by-products? A review of their biological activity. Phycologia, 42(4), 332-350.

Webster, K.L., Beall, F.D., Creed, I.F., Kreutzweiser, D.P. (2015). Impacts and prognosis of natural resource development on water and wetlands in Canada's boreal zone. Environmental Reviews, 23(1), 78-131.

Webster, K.L., Leach, J.A., Hazlett, P.W., Buttle, J.M., Emilson, E.J.S., Creed, I.F. (2022). Long-term stream chemistry response to harvesting in a northern hardwood forest watershed experiencing environmental change. Forest Ecology and Management, 519, 120345.

Wei, X., Hou, Y., Zhang, M., Li, Q., Giles-Hansen, K., Liu, W. (2021). Re-examining forest disturbance thresholds for managing cumulative hydrological impacts. Ecohydrology, 14(8).

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science & Technology, 37(20), 4702-4708.

Wemple, B.C., Jones, J.A., Grant, G.E. (1996). Channel network extension by logging roads in two basins, Western Cascades, Oregon. Journal of the American Water Resources Association, 32(6), 1195-1207.

Westbrook, C.J., Cooper, D.J., Baker, B.W. (2006). Beaver dams and overbank floods influence groundwater-surface water interactions of a Rocky Mountain riparian area. Water Resources Research, 42, W06404.

Westbrook, C.J., Ronnquist, A., Bedard-Haugn, A. (2020). Hydrological functioning of a beaver dam sequence and regional dam persistence during an extreme rainstorm. Hydrological Processes, 34(18), 3726-3737.

Williams, C.A., Gu, H., MacLean, R., Masek, J.G., Collatz, G.J. (2016). Disturbance and the carbon balance of US forests: a quantitative review of impacts from harvests, fires, insects, and droughts. Global and Planetary Change, 143, 66-80.

Woo, M., and Waddington, J.M. (1990). Effects of beaver dams on subarctic wetland hydrology. ARCTIC, 43(3), 223-230.

Woodman, S.G., Khoury, S., Fournier, R.E., Emilson, E.J.S., Gunn, J.M, Rusak, J.A., Tanentzap, A.J. (2021). Forest defoliator outbreaks alter nutrient cycling in northern waters. Nature Communications, 12(1), 6355.

World Health Organization. (2004). Guidelines for Drinking-water Quality.

World Health Organization. (2005). Trihalomethanes in drinking water.

Wrzesiński, D., and Ptak, M. (2016). Water level changes in Polish lakes during 1976-2010. Journal of Geographical Sciences, 26(1), 83-101.

Yang, L., Hur, J., Lee, S., Chang, S., Shin, H. (2015). Dynamics of dissolved organic matter during four storm events in two forest streams: source, export, and implications for harmful disinfection byproduct formation. Environmental Science and Pollution, 22(12), 9173-9183.

Zarnetske, J.P., Bouda, M., Abbot, B.W., Saiers, J., Raymond, P.A. (2018). Generality of hydrologic transport limitation of watershed organic carbon flux across ecoregions of the United States. Geophysical Research Letter, 45(21), 11702-11711.

Zhang, W., and Montgomery, D.R. (1994). Digital elevation model grid size, landscape representation, and hydrologic simulations. Water Resources Research, 30(4), 1019-1028.

APPENDICES

Appendix A – Streamflow and rating curves

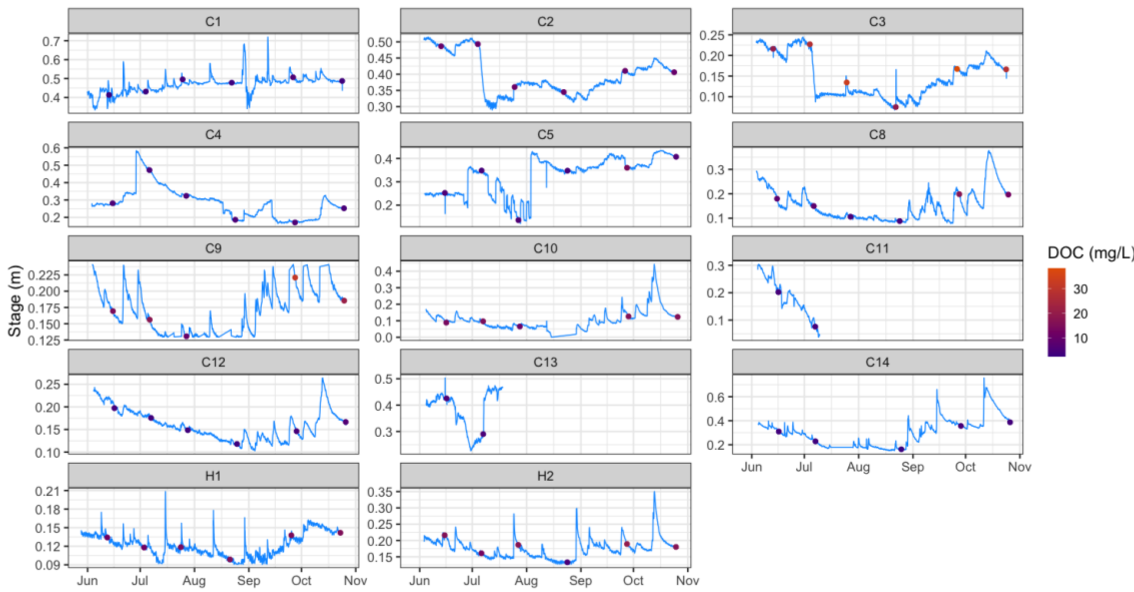

Figure A1 Stage and corresponding water samples for C1 through H2. Abrupt ends in water level (at C11 and C13) are due to streams drying up and unrecoverable data.

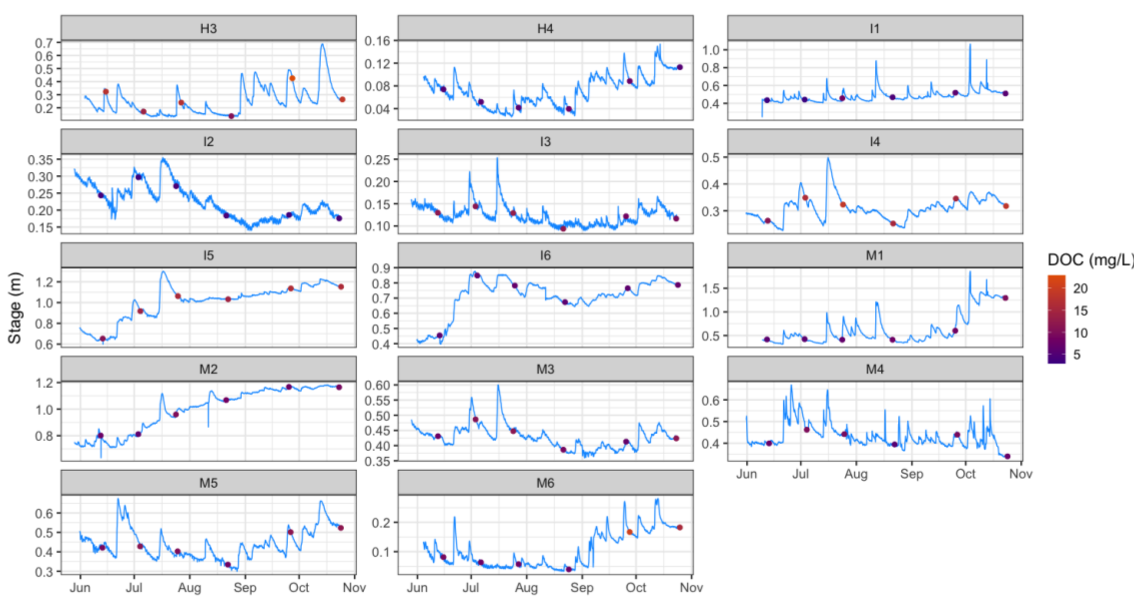

Figure A2 Stage and corresponding water samples for H3 through M6.

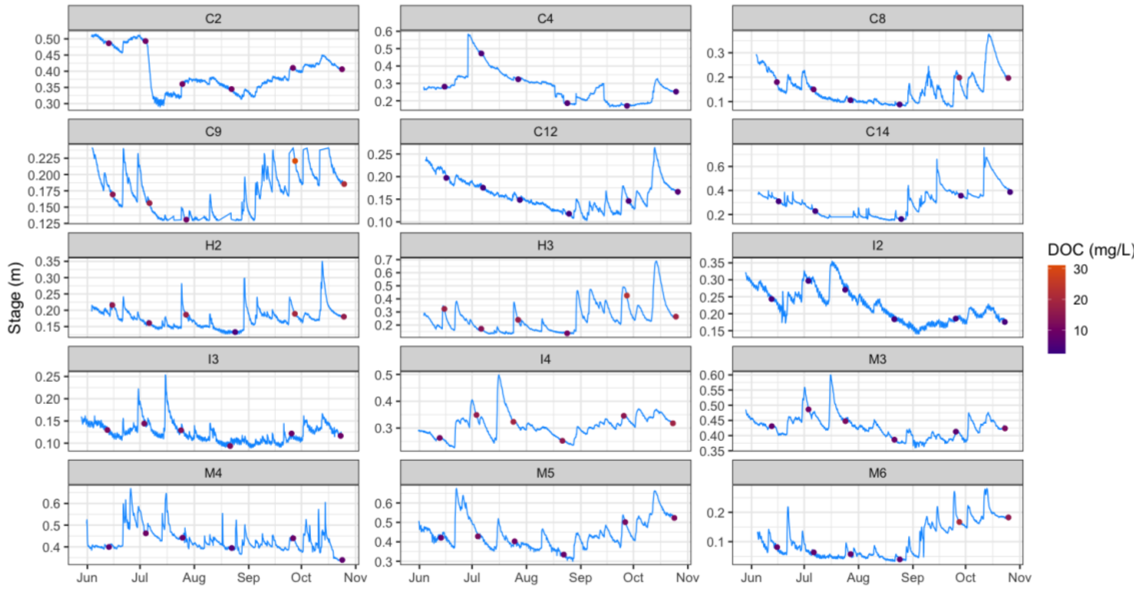

Figure A3 Stage and corresponding water samples for sites with high quality stage-discharge relationships (C2 through M6).

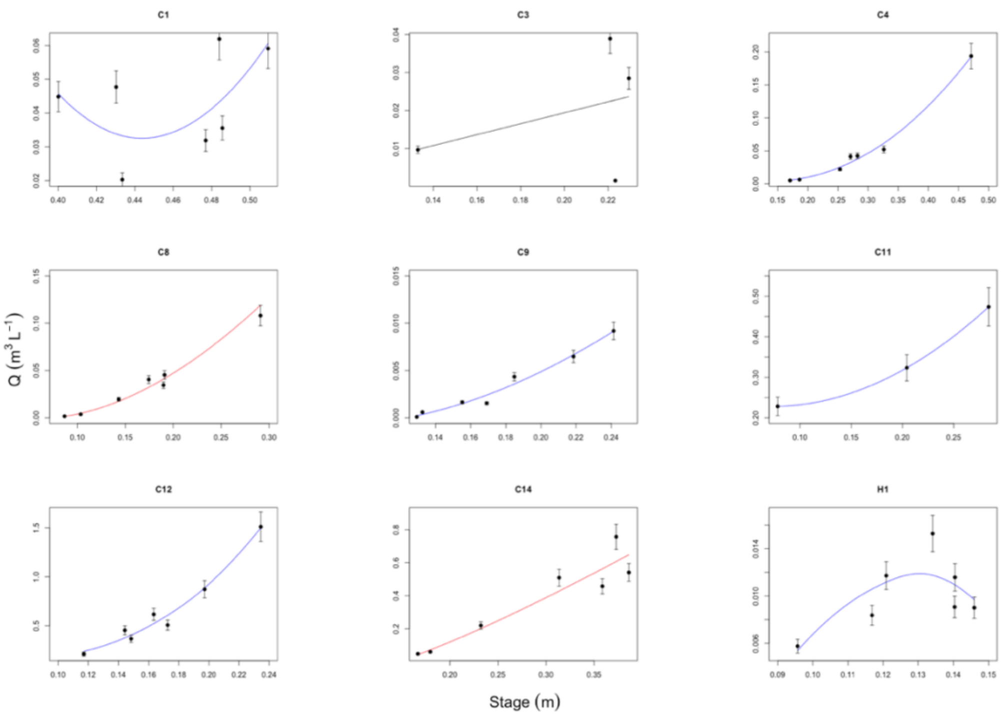

Figure A4 Rating curves for C1 through H1.

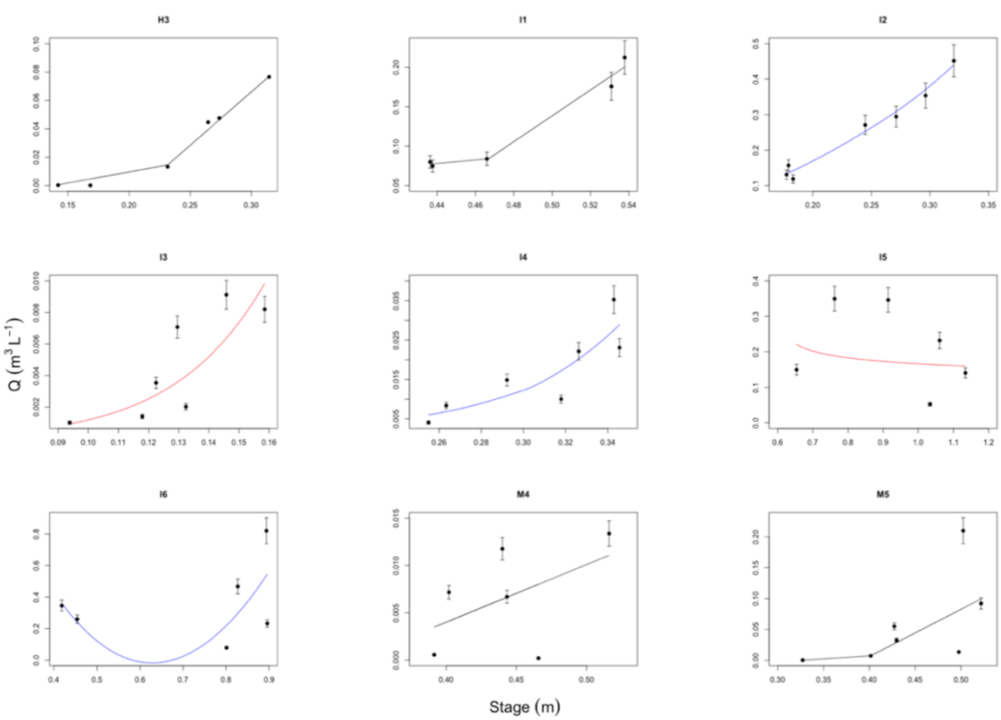

Figure A5 Ratings curves for H3 through M5.

Appendix B – Statistical analysis

Table B1 Spearman's correlation analysis values between catchment characteristic variables and water quality response variables. P-value reported in parentheses.

Variable	Mean [DOC] (mg L^{-1})	Mean instantaneous DOC flux (mg s^{-1} km^{-2})	DOC export (g C m^{-2})	Mean $SUVA_{254}$ (L mg^{-1} m^{-1})	Mean [THM-FP] (mg L^{-1})	Mean [HAA-FP] (mg L^{-1})
Coniferous forest %	0.14 (0.07)	-0.2 (0.02)	0.36 (0.19)	0.01 (0.89)	-0.29 (0.05)	-0.12 (0.42)
Deciduous forest %	-0.007 (0.9)	0.19 (0.03)	-0.28 (0.31)	-0.039 (0.6)	0.25 (0.089)	0.064 (0.68)
Catchment area (km^2)	-0.43 (0.0001)	-0.1 (0.22)	-0.39 (0.15)	-0.21 (0.005)	-0.52 (0.0001)	-0.6 (0.0001)
Elevation (m asl)	0.35 (0.0001)	0.018 (0.83)	-0.056 (0.84)	0.013 (0.87)	0.38 (0.008)	0.4 (0.006)
Latitude (DD)	-0.05 (0.5)	-0.16 (0.06)	0.13 (0.63)	-0.038 (0.82)	-0.28 (0.05)	-0.096 (0.53)
Longitude (DD)	0.32 (0.0001)	0.16 (0.06)	-0.008 (0.98)	-0.055 (0.46)	0.51 (0.0002)	0.48 (0.0008
Open water %	-0.45 (0.0001)	-0.036 (0.67)	-0.24 (0.4)	-0.51 (0.0001)	-0.42 (0.003)	-0.44 (0.003)
Slope (°)	-0.28 (0.0002)	-0.0046 (0.96)	-0.29 (0.29)	0.069 (0.36)	-0.00087 (1.0)	-0.15 (0.34)
Wetland cover %	0.12 (0.1)	0.046 (0.59)	0.26 (0.35)	0.06 (0.43)	-0.27 (0.06)	-0.24 (0.12)

Table B2 Spearman's correlation analysis values between forest disturbance variables and water quality response variables in disturbed catchments. P-value reported in parentheses.

Variable	Mean [DOC] (mg L^{-1})	Mean instantaneous DOC flux (mg s^{-1} km^{-2})	DOC export (g C m^{-2})	Mean $SUVA_{254}$ (L mg^{-1} m^{-1})	Mean [THM-FP] (mg L^{-1})	Mean [HAA-FP] (mg L^{-1})
5-year harvest (%)	0.2 (0.45)	0.2 (0.48)	0.63 (0.07)	0.12 (0.66)	-0.39 (0.44)	-0.21 (0.69)
5-year infestation (%)	-0.21 (0.43)	-0.036 (0.9)	-0.36 (0.35)	-0.58 (0.02)	-0.44 (0.38)	-0.44 (0.38)
5-year abiotic (%)	-0.04 (0.88)	-0.44 (0.1)	-0.51 (0.16)	-0.49 (0.05)	No data	No data
10-year wildfire (%)	0.14 (0.6)	-0.31 (0.26)	0.41 (0.27)	0.42 (0.11	0.39 (0.44)	0.65 (0.16)
10-year harvest (%)	0.21 (0.43)	0.26 (0.34)	0.63 (0.07)	0.36 (0.17)	-0.26 (0.66)	-0.14 (0.8)
10-year infestation (%)	0.38 (0.14)	0.59 (0.02)	0.27 (0.49)	-0.42 (0.1)	-0.39 (0.44)	-0.39 (0.44)
10-year abiotic (%)	-0.04 (0.88)	-0.44 (0.1)	-0.51 (0.16)	-0.49 (0.05)	No data	No data
15-year wildfire (%)	0.05 (0.85)	-0.37 (0.18)	0.41 (0.27)	0.46 (0.07)	0.39 (0.44)	0.65 (0.16)
15-year harvest (%)	0.16 (0.56)	0.19 (0.5)	0.54 (0.13)	0.35 (0.18)	-0.26 (0.66)	-0.14 (0.8)
15-year infestation (%)	0.38 (0.14)	0.59 (0.02)	0.27 (0.49)	-0.42 (0.1)	-0.39 (0.44)	-0.39 (0.44)
15-year abiotic (%)	-0.04 (0.88)	-0.44 (0.1)	-0.51 (0.16)	-0.49 (0.05)	No data	No data
20-year wildfire (%)	0.05 (0.85)	-0.37 (0.18)	0.41 (0.27)	0.46 (0.07)	0.39 (0.44)	0.65 (0.16)
20-year harvest (%)	0.24 (0.38)	0.53 (0.04)	0.82 (0.007)	0.41 (0.11)	-0.6 (0.24)	-0.49 (0.36)
20-year infestation (%)	0.51 (0.05)	0.13 (0.63)	-0.08 (0.76)	0.05 (0.87)	0.06 (0.91)	0.32 (0.54)
20-year abiotic (%)	-0.04 (0.88)	-0.44 (0.1)	-0.51 (0.16)	-0.49 (0.05)	No data	No data

Table B3 Multiple linear regression models and their corresponding codes.

Model	Variables
Base model	Open water + Catchment area + Slope + Wetland cover + Coniferous cover
5H	Base model + 5-year harvesting %
5I	Base model + 5-year insect infestation %
10H	Base model + 10-year harvesting %
10I	Base model + 10-year insect infestation %
15H	Base model + 15-year harvesting %
15I	Base model + 15-year insect infestation %
20H	Base model + 20-year harvesting %
5H + 5I	Base model + 5-year harvesting % + 5-year insect infestation %
10H + 10I	Base model + 10-year harvesting % + 10-year insect infestation %
15H + 15I	Base model + 15-year harvesting % + 15-year insect infestation %

Appendix C – DOC quality, DBP-FP and fluorescence indices

[THM-FP] and [HAA-FP] were positively correlated with $SUVA_{254}$ (Figure C1). $SUVA_{254}$ was also positively correlated with [DOC] (Figure C2).

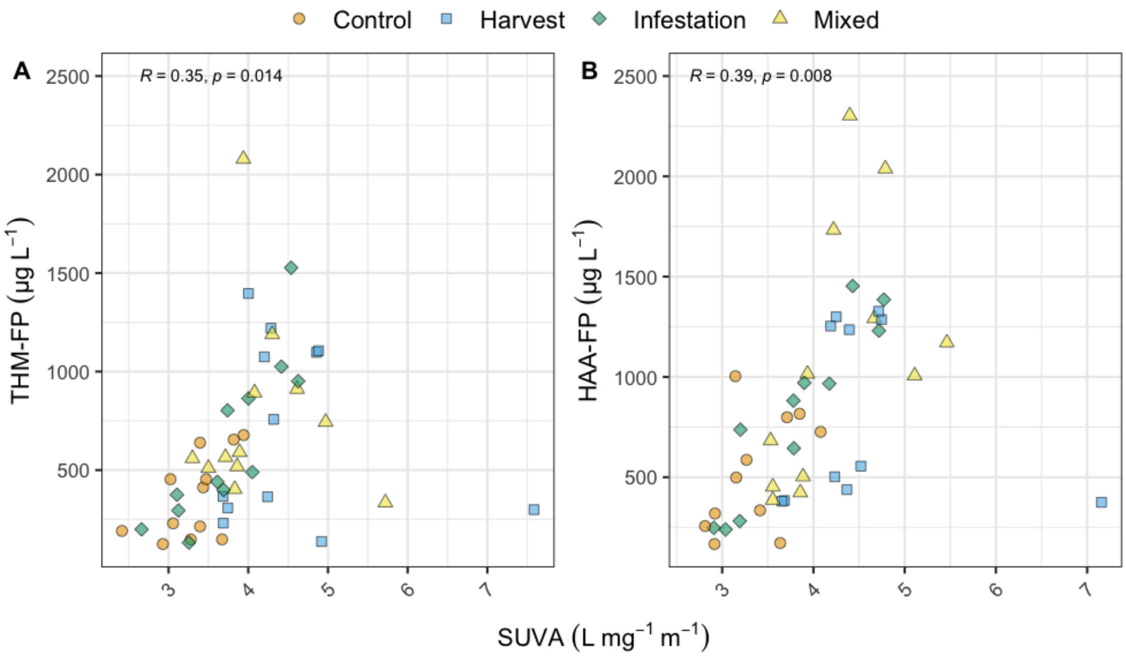

Figure C1 [THM-FP] (**A**) and [HAA-FP] (**B**) versus $SUVA_{254}$ at eight sites across the Algoma region.

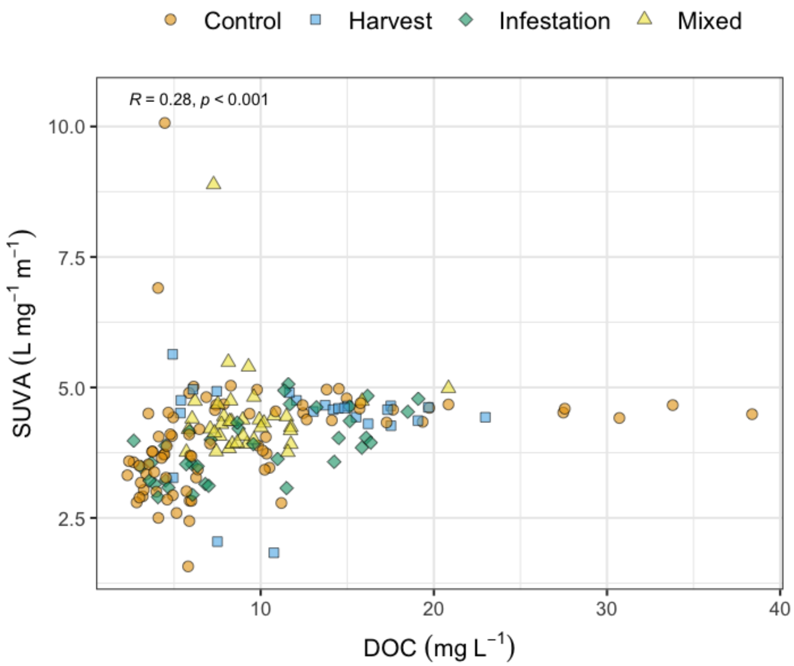

Figure C2 $SUVA_{254}$ versus [DOC] for 30 sites across the Algoma region.

FI and HIX values ranged from 1.1 - 1.55 and 0.77 - 0.98, respectively (Figure C3; Figure C4). These ranges indicated that DOC was predominantly sourced from terrestrial areas with little input from microbial sources, and was relatively humified (Ohno et al., 2002; McKnight et al., 2001) In general, large within- and between- group spatial variability was observed, except for HIX across mixed-disturbance catchments, where reduced variability was seen.

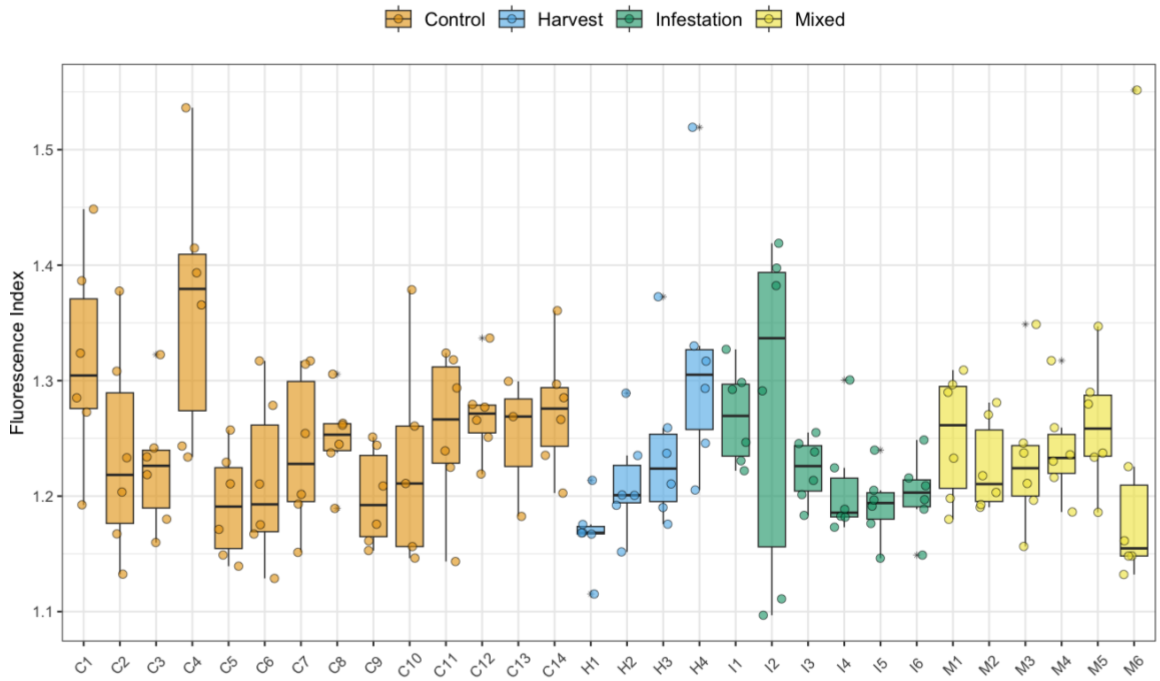

Figure C3 Variability in FI across study catchments within the Algoma region, central Ontario.

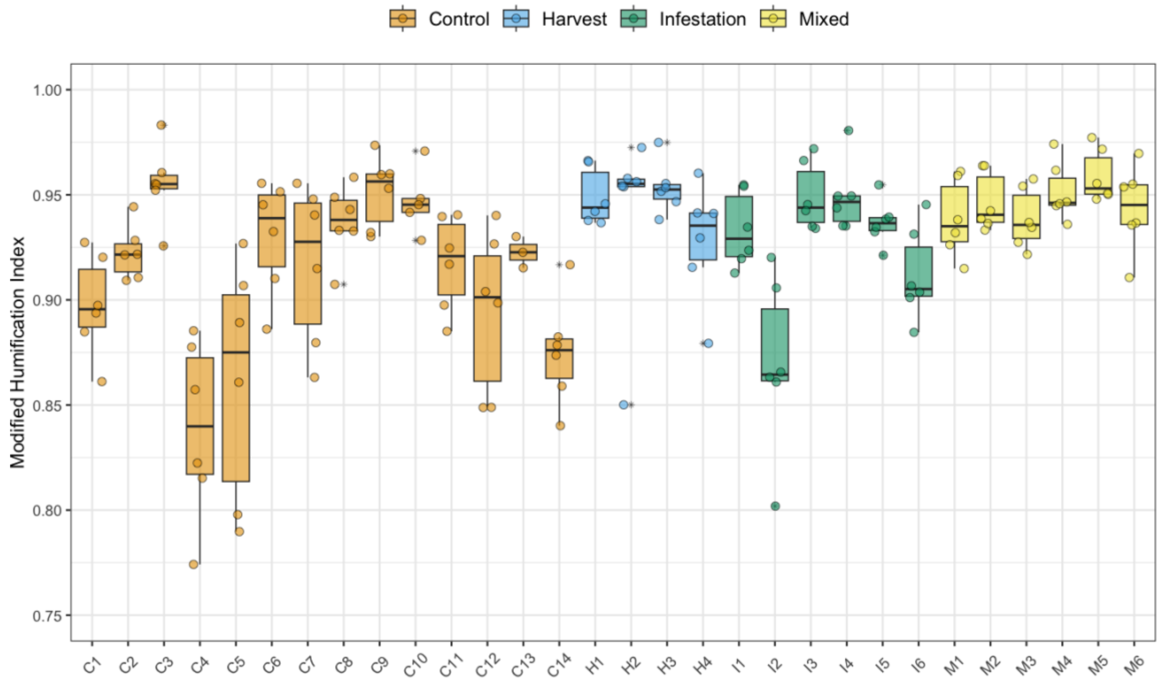

Figure C4 Variability in modified HIX, as per Ohno et al. (2002), across study catchments within the Algoma region, central Ontario.

Appendix D – Technology and instrument usage

All physical and digital instruments and devices used in the production of this thesis are summarised in Table E1. Notable R packages (and their respective outputs) used in the data analysis stage included:

- corrplot (correlation plot)
- dotwhisker (multiple linear regression coefficient plot)
- ggpubr (multiple linear regression coefficient plot)
- tidyverse (data cleaning; base figures)
- readxl (importation of Microsoft Excel data)

Table D1 Digital and physical technology used to complete this thesis project.

Device / Instrument	Software	Application
Computer	R	Data analysis
Computer	Rstudio	Integrated development environment
Computer	Github	Version control
Computer	Microsoft Excel	Data storage
Computer	ArcGIS	Geospatial mapping
SonTek FlowTracker 2 & Ott MF Pro	NA	Streamflow gauging
HOBO U20L water level data logger	HOBOware Pro	Water level and water and air temperature recording
Seal Analytical AA3 Autoanalyzer	AACE 6.07	DOC analysis
Cary 60 UV-Vis spectrophotometer	NA	Specific ultraviolet absorbance
Agilent Cary Eclipse	NA	3-D fluorescence scans
Shimadzu, TOC-V CPH Total Organic Carbon Analyzer	NA	DOC quantification
HP 6890 Series Gas Chromatograph	NA	THM-FP, HAA-FP quantification
TELEDYNE Tekmar Atomx 15-000-100	NA	THM-FP quantification

Appendix E – Ancillary climate data

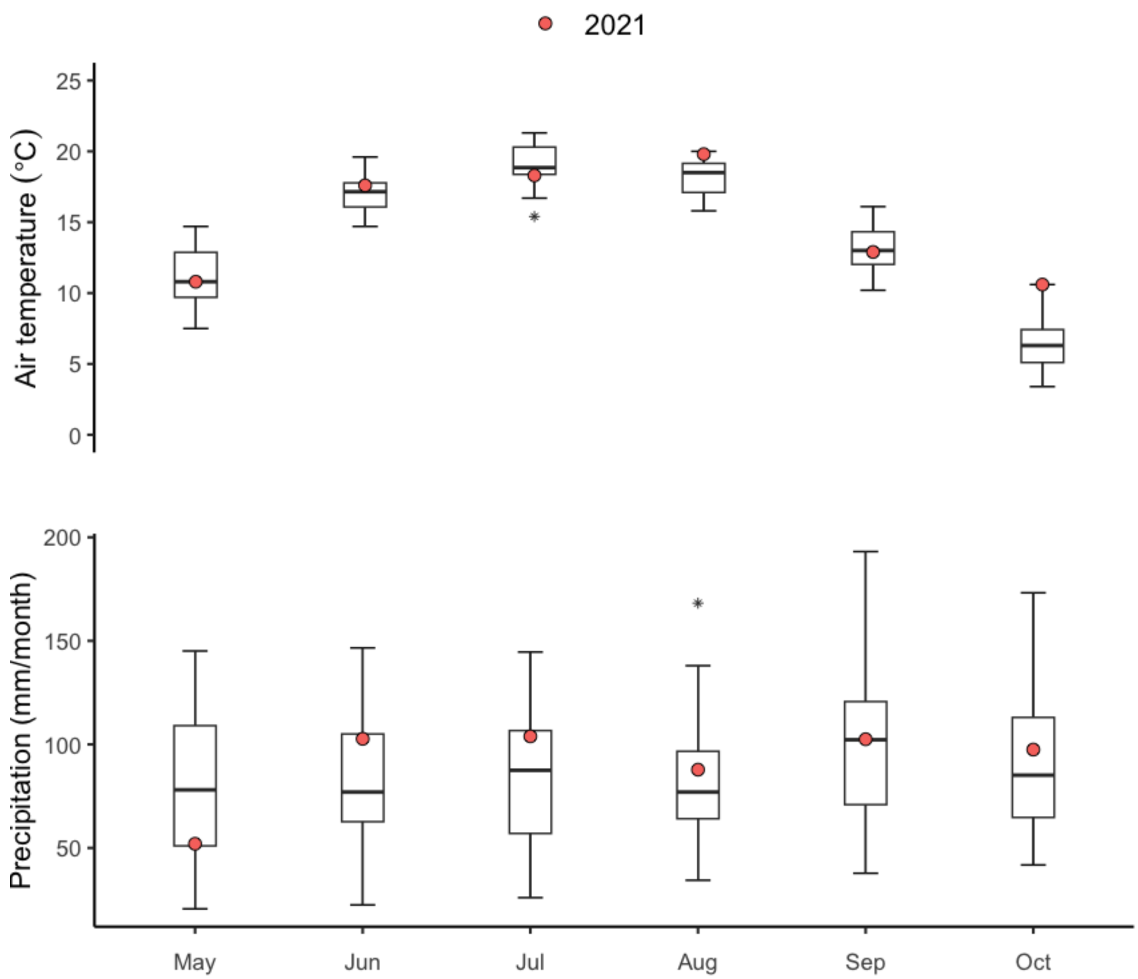

Figure E1 Boxplots of monthly (May to October) mean air temperature and monthly precipitation recorded at 'Sudbury A' climate station from 1990 to 2013 (monthly data was only available up to 2013). Red circles represent conditions during the 2021 late spring to fall period when the data in this investigation was collected.

Matthew Watkins personally thanks you for reading this master's thesis – a life-altering crucible he will never forget (Figure E2).

Figure E2 Extraction of installed streamflow equipment at I6 on the final fall sample run which occurred from October 23rd - 26th, 2021. Photo taken by Danielle Hudson.